Ceramifiable Polymer Composites for Fire Protection Application

A thesis Submitted in fulfilment of the requirement for
the degree of Doctor of Philosophy

Zynab Al-Hassany

B App Sci (Applied Chemistry) Honours

School of Applied Sciences
Science Engineering and Technology
RMIT University
November 2007
STATEMENT OF AUTHENTICITY

I, hereby declare that the work presented in this thesis, unless otherwise acknowledged, is that of the candidate alone and not has been submitted previously, in whole or in part, for any other academic award.

This work described in this research project carried out in the School of Applied Sciences, RMIT University since the official date of commencement of the program.

Zynab Al-Hassany
ACKNOWLEDGMENTS

I wish to thank my supervisor Professor Robert A. Shanks for his guidance, assistance, time and patient throughout my study.

I would like to thank my co-supervisor Dr Antonietta Genovese for her assistance and advice during the duration of this study.

I give my sincere thanks to Maggie Lu Guang Chen and Daniel Kaminski for their advice, patience, and emotional support during the duration of this project.

I give my special thanks for my husband, Amer Al-Sharefy for his encouragement and companionship. I am deeply indebted to my parents Ibrahim Al-Hassany and Ahlam Jabiry for all their tremendous support during my studies. Without their enormous support, I could not have reached such achievement. To my four sisters, Shyma, Zahra, Ala, and Maryam and my brother Haceeb, for the fun and enjoyable time that we always share together. Thanks for the help Ala and Maryam.

I gratefully acknowledge the financial support for my postgraduate studies provided by Co-operation Research Centre (CRC) in awarding me a CRC scholarship. In addition to the training and seminar, I have attended throughout the duration of my PhD.
JOURNAL PAPERS


Z. Al-Hassany, A, Genovese and R. A. Shanks. Structural and thermal interpretation of interactions between combination of binary or ternary fire retardant poly(vinyl acetate) composites; (in preparation).

Refereed conference paper

Advanced, Infrastructural, Natural, and Nanocomposites, UNSW, Sydney, Australia; 2006 (ACUN-5 Conference).
Z. Al-Hassany, A, Genovese and R. A. Shanks Thermal degradation of fire retardant poly(vinyl acetate) composites.

Conference paper

International Conference on Polymer Processing 2007 (ICPP), China.
Z. Al-Hassany, A. Genovese, W. Gunaratne and R. A. Shanks. Thermal degradation of fire retardant poly(vinyl acetate) composites.

Seminars

Thermal degradation of fire retardant poly(vinyl acetate) composites. Seminar, Department of Applied Chemistry, RMIT University, August 2005.

Thermal degradation of fire retardant poly(vinyl acetate) composites. Seminar, Monash University, September 2006
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
<td>CaCO₃ Calcium Carbonate</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscopy</td>
<td></td>
<td>CaO Calcium Oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
<td></td>
<td>Al Aluminum</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide Angle X-ray Diffraction</td>
<td></td>
<td>FB Firebrake</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
<td></td>
<td>ZB Zinc borate</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td></td>
<td>TBBPA tetrabromobisphenol-A</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetry Analysis</td>
<td></td>
<td>PBDEs Polybrominated</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative Thermogravimetry</td>
<td></td>
<td>di phenyl ethers</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermal Mechanical Analysis</td>
<td></td>
<td>HBCD Hexabromocyclododecane</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
<td></td>
<td>PA-6 Polyamide-6</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
<td></td>
<td>PA-6,6 Polyamide-6,6</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
<td></td>
<td>PA Polyamide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
<td></td>
<td>PSD Particle Size Distribution</td>
</tr>
<tr>
<td>Sf-TMA</td>
<td>Static Force Thermomechanical Analysis</td>
<td></td>
<td>HRR Heat Release Rate</td>
</tr>
<tr>
<td>PVAc</td>
<td>Poly(vinyl acetate)</td>
<td></td>
<td>TTI Time to Ignition</td>
</tr>
<tr>
<td>VA</td>
<td>Vinyl acetate</td>
<td></td>
<td>EHC Effective Heat Combustion</td>
</tr>
<tr>
<td>BAMMA</td>
<td>Poly(Butyl acrylate-co-</td>
<td></td>
<td>THRR Total Heat Release Rate</td>
</tr>
<tr>
<td></td>
<td>methyl methacrylate)</td>
<td></td>
<td>MLR Mass Loss Rate</td>
</tr>
<tr>
<td>EVA</td>
<td>(Ethylene-co-vinyl acetate)</td>
<td></td>
<td>SEA Smoke Extinction Area</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
<td></td>
<td>LOI Limiting Oxygen Index</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene Butadiene Rubber</td>
<td></td>
<td>JCPDS Joint Committee for Powder Diffraction Studies</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td></td>
<td>FWHM Full Width at</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td></td>
<td>Half-Maximum</td>
</tr>
<tr>
<td>mPE</td>
<td>metallocene Polyethylene</td>
<td></td>
<td>TBBA Tetrabromobisphenol-A</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
<td></td>
<td>PBBS Polybrominated</td>
</tr>
<tr>
<td>BMC</td>
<td>Bulk Molding Compounds</td>
<td></td>
<td>biphenyls</td>
</tr>
<tr>
<td>SMC</td>
<td>Sheet Molding Compounds</td>
<td></td>
<td>T₀ Onset temperature</td>
</tr>
<tr>
<td>UP</td>
<td>Unsaturated Polyester</td>
<td></td>
<td>Tc Crystallisation temperature</td>
</tr>
<tr>
<td>FR</td>
<td>Fire/Flame Retardant</td>
<td></td>
<td>ΔH Enthalpy</td>
</tr>
<tr>
<td>MH</td>
<td>Magnesium Hydroxide</td>
<td></td>
<td>T Temperature</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium Oxide</td>
<td></td>
<td>θ Angle</td>
</tr>
<tr>
<td>ATH</td>
<td>Aluminium Trihydroxide</td>
<td></td>
<td>α Stress</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium Oxide</td>
<td></td>
<td>λ Wavelength</td>
</tr>
<tr>
<td>Cl</td>
<td>Chlorine</td>
<td></td>
<td>d(hkl) distance between two adjacent parallel planes; interlayer spacing</td>
</tr>
<tr>
<td>K</td>
<td>Potassium</td>
<td></td>
<td>Lₜₜ(hkl) or Lₜₜ(c) perpendicular to reflection plane</td>
</tr>
<tr>
<td>Br</td>
<td>Bromine</td>
<td></td>
<td>β₀ shape of crystalline factor</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
<td></td>
<td>rpm rotation per minute</td>
</tr>
<tr>
<td>pH</td>
<td>percentage per minute</td>
<td></td>
<td>power of Hydrogen</td>
</tr>
<tr>
<td>°C</td>
<td>Degree</td>
<td></td>
<td>L Length</td>
</tr>
</tbody>
</table>

V
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>vol%</td>
<td>volume percent</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>μm</td>
<td>micrometer</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>°C•min⁻¹</td>
<td>Celsius degree per minute</td>
</tr>
<tr>
<td>J•g⁻¹</td>
<td>Joules per gram</td>
</tr>
<tr>
<td>mm•min⁻¹</td>
<td>millimeter per minute</td>
</tr>
<tr>
<td>m³•s⁻¹</td>
<td>meter cube per second</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>MPa</td>
<td>mega Pascal</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

STATEMENT OF AUTHENTICITY ................................................................. I

ACKNOWLEDGMENTS ........................................................................ II

Journal papers ...................................................................................... IV
Refereed conference paper ................................................................. IV
Conference paper ............................................................................... IV
Seminars ............................................................................................. IV

GENERAL ABBREVIATION AND NOMENCLATURE ............................. V

TABLE OF CONTENTS ........................................................................ VII

TABLE OF FIGURES ............................................................................. XI

LIST OF TABLES ................................................................................ XVI

SUMMARY .......................................................................................... XVII

CHAPTER 1: INTRODUCTION................................................................. 1

1.1 BACKGROUND INFORMATION .................................................. 1

1.2 AIM ............................................................................................. 5
1.2.1 Objectives: .............................................................................. 5
1.2.2 Research questions ............................................................... 5

1.3 THESIS STRUCTURE ................................................................... 6

CHAPTER 2: LITERATURE REVIEW ..................................................... 8

2.1 INTRODUCTION .......................................................................... 8

2.2 THE COMBUSTION PROCESS ..................................................... 9
2.2.1 Three classes of polymers can be defined on the basis on their thermal response: ...... 12

2.3 CERAMIFYING POLYMER SYSTEM ........................................... 13

2.4 FLAME OR FIRE RETARDANTS (FR) ........................................... 16
2.4.1 Mechanism of action of flame retardants .................................. 17

2.5 HYDROXIDES ............................................................................. 20
2.5.1 Magnesium hydroxide............................................................ 21
2.5.2 Aluminium hydroxide ............................................................ 25
2.6 FLAME RETARDANT SYNERGISTS ................................................................. 29

2.7 PHOSPHOROUS-CONTAINING FLAME RETARDANTS ..................................... 31
  2.7.1 Ammonium polyphosphate ................................................................. 31
  2.7.2 Intumescent systems ................................................................. 38
  2.7.3 APP:MH mixtures ........................................................................ 41
  2.7.4 APP:ATH mixture ................................................................. 43

2.8 BORON-CONTAINING FLAME RETARDANTS ............................................... 47
  2.8.1 Zinc borate ............................................................................... 47

2.9 DIFFERENT FORMS OF ZINC BORATES ...................................................... 48
  2.9.1 APP:zinc borate mixture .............................................................. 49
  2.9.2 The action of zinc borate in EVA:metal hydroxides systems ......... 51
  2.9.3 The action of zinc borate in PVC-based formulation .................. 53

2.10 MINERAL FOR ENHANCEMENT OF MECHANICAL PROPERTIES .............. 54
  2.10.1 Talc ......................................................................................... 55
  2.10.2 Kaolin ..................................................................................... 58
  2.10.3 Calcined kaolin ................................................................. 59
  2.10.4 Calcium carbonate .............................................................. 62
  2.10.5 Mica ..................................................................................... 67

CHAPTER 3: EXPERIMENTAL ............................................................................. 68

3.1 INTRODUCTION ............................................................................................. 68

3.2 MATERIALS AND METHODS ........................................................................ 68
  3.2.1 Polymers .................................................................................. 68
  3.2.2 Minerals and fire retardants ....................................................... 69
  3.2.3 Preparation of fire retardant polymer composites ...................... 70
  3.2.4 Thermogravimetric Analysis .................................................... 74
  3.2.5 Particle size distribution .......................................................... 76
  3.2.6 Wide angle X-Ray Diffraction ................................................ 76
  3.2.7 Fourier Transform Infrared Spectroscopy .................................... 79
  3.2.8 Mechanical testing ................................................................. 81
  3.2.9 Scanning Electron Microscopy .................................................. 83
  3.2.10 Cone Calorimetry ................................................................. 83

CHAPTER 4: THERMAL DEGRADATION AND STRUCTURAL CHANGES OF INORGANIC MINERALS ............................................................................. 86

4.1 INTRODUCTION ............................................................................................. 86

4.2 INDIVIDUAL FIRE RETARDANTS .............................................................. 87
  4.2.1 Thermal degradation of the hydrated fillers .............................. 87
  4.2.2 Thermal degradation of char forming fire retardants ............... 93

4.3 MINERAL FILLERS ...................................................................................... 96
  4.3.1 Decomposition of Talc .............................................................. 96
CHAPTER 5: THERMAL DEGRADATION OF POLY (VINYL ACETATE) COMPOSITES

5.1 INTRODUCTION .............................................................................................................. 116
5.2 RESULTS AND DISCUSSION ..................................................................................... 116
5.2.1 Thermal degradation of poly(vinyl acetate) ............................................................... 117
5.2.2 Degradation of PVAc composites ............................................................................ 122
5.3 INFRARED SPECTROSCOPY OF PVAc COMPOSITES OF KAOLIN SERIES .... 132
5.4 MECHANICAL PROPERTIES ..................................................................................... 134
5.5 CONCLUSION ............................................................................................................... 138

CHAPTER 6: THERMAL DEGRADATION AND FIRE PERFORMANCE OF FR BUTYL ACRYLATE METHYL METHACRYLATE CO-POLYMER COMPOSITES

6.1 INTRODUCTION .............................................................................................................. 140
6.2 RESULTS AND DISCUSSION ..................................................................................... 141
6.2.1 Characterization of co-polymer .............................................................................. 141
6.2.2 Thermal analyses ..................................................................................................... 141
6.2.3 Oxygen combustion calorimetry of fire retardant composites ............................... 155
6.2.4 Effect of fire retardant fillers on HRR of BAMMA composites ............................... 155
6.3 X-RAY DIFFRACTION PATTERN AFTER CONE CALORIMETRY ...................... 164
CHAPTER 7: STRUCTURAL AND THERMAL INTERPRETATION OF INTERACTIONS BETWEEN COMBINATION OF BINARY OR TERNARY FR IN PVAC COMPOSITES ...............................................................173

7.1 INTRODUCTION ..............................................................................................................173

7.2 RESULTS AND DISCUSSION ..........................................................................................174
7.2.1 Degradation of PVAc composites ..............................................................................174
7.2.2 Binary mixtures APP:ATH in the presence of PVAc ...................................................177
7.2.3 Binary mixture APP:CaCO3 in the presence of PVAc .................................................180
7.2.4 Ternary filler mixtures in the presence of PVAc ...........................................................183

7.3 MECHANICAL PROPERTIES ......................................................................................188

7.4 CONCLUSION ...............................................................................................................190

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK ...............................................................192

8.1 CONCLUSIONS .............................................................................................................192

8.2 RECOMMENDATIONS FOR FUTURE WORK .................................................................199

REFERENCES .................................................................................................................201
TABLE OF FIGURES

Figure 2.1: The combustion process ................................................................................. 10
Figure 2.2: Combustion of a polymer sample during cone calorimeter analysis.............. 12
Figure 2.3: Schematic of polymer FR systems ................................................................. 17
Figure 2.4: Portion of MH crystal viewed normal to the (110) plane and local
coordination of the Mg ion................................................................................................ 22
Figure 2.5: A schematic representation of the progressive evolution from the layered
structure of MH (part a), to that of MgO by progressive water elimination (parts b and
c)........................................................................................................................................ 22
Figure 2.6: TEM Images of particles of (a) MH and MgO heated at (b) 600 °C and
(C) 900 °C, electrograms are shown in the right upper corner ....................................... 23
Figure 2.7: X-ray diffraction patterns of (a) MH and (b) MgO ........................................ 24
Figure 2.8a: the structure of the two main polymorph and Figure 2.7b: the labelling of
ATH, (a) bayerite and (b) gibbsite, illustrating of the hydrogen/deuterium atoms
the difference in the stacking of the layers within the unit cell of (a) bayerite.............. 25
Figure 2.9a: X-ray diffraction patterns of ATH and Figure 2.9b: FTIR spectra of ATH
treated at various temperatures ............................................................................... 27
Figure 2.10: X-ray diffraction patterns of the three typical ATH samples ....................... 28
Figure 2.11: Reactions occurring during thermal degradation of APP............................ 33
Figure 2.12: TGA curves of both forms of APP ............................................................... 34
Figure 2.13: TGA curves of dried films............................................................................ 34
Figure 2.14: Curves of the weight difference for treated resin ......................................... 35
Figure 2.15: FTIR spectra of crystalline forms of APP I and APP II ............................... 36
Figure 2.16: X-ray diffraction patterns of crystalline forms of APP I and APP II ........... 38
Figure 2.17: schematic representation of intumescent process ........................................ 39
Figure 2.18: Intumescent compounds ............................................................................ 40
Figure 2.19: Calculated and experimental thermogravimetry curves for 50 % mixture
of APP and MH ................................................................................................................. 41
Figure 2.20: Lower part water (▲) and ammonia (o) evolution curves ......................... 42
Figure 2.21: Reactions occurring during thermal degradation of APP:MH 50% mixture. APP
and MH interact to form magnesium phosphate bonds .............................................. 42
Figure 2.22: a) Thermogravimetric mass loss and b) derivative curves of 50 wt%
mixture of APP:ATH ........................................................................................................ 44
Figure 2.23: Lower part water and ammonia evolution curves ...................................... 45
Figure 2.24: Reaction occurring between APP and ATH during heating to 800 °C a
50 wt% mixture of APP:ATH .......................................................................................... 45
Figure 2.25: X-ray diffraction pattern of a 50 wt% mixture of APP and ATH (a)
spectrum of the mixture at 25 °C; (b) spectrum of the mixture after heating to 800 °C
under N2 ............................................................................................................................ 46
Figure 2.26: A segment of the infinite polytriborate chains in (2ZnO·3B2O3·3.5H2O) ... 48
Figure 2.27: Proposed molecular structure of zinc borate ............................................. 49
Figure 2.28: SEM (6000X) of residues of air-pyrolysis of EVA containing zinc borate
(2ZnO•3B2O•3.5H2O) (33 %) and ATH (33 %)................................................................. 52

XI
Figure 2.29: SEM (6000X) of residues of EVA containing the zinc borate (2ZnO·3B2O·3.5H2O)........................................................................................................ 52
Figure 2.30: Structure of talc with silica tetrahedron and the magnesia octahedron positions ........................................................................................................................................................................ 55
Figure 2.31: Scanning electron micrographs of specimens sampled at different talc content: (a) S2, talc = 14.0 wt%; (b) S3, talc = 27.7 wt%; (c) S4, talc = 41.5 wt%; (d) S5, talc = 49.7 wt%; (e) S6, talc = 55.1 wt%; (f) S7, talc = 61.2 wt% ........................................................................................................ 57
Figure 2.32: Structure of kaolinite layer ........................................................................... 58
Figure 2.33: X-ray diffraction patterns of kaolinite at selected high temperature.......... 60
Figure 2.34: DTA graph of kaolinite pre-calcined to 1000 °C for 2 h and then pressed under packing condition-sample weight 85 mg with heating rate of 10 °C•min⁻¹ ............ 61
Figure 2.35 Scheme of transformation steps of kaolinite to mullite................................. 62
Figure 2.36: Crystal structures of carbonates: (a) calcite; (b) aragonite; and (c) nahcolite ........................................................................................................................................................................... 63
Figure 2.37: Effect of the filler loading on the tensile modulus of talc-, kaolin-, and CaCO₃- filled PP composites ............................................................................................ 66
Figure 2.38: Scheme of muscovite mica structure............................................................ 67

Figure 3.1: IKA-Werke stirrer Eurostar ............................................................................ 71
Figure 3.2: Perkin-Elmer TGA Series 7............................................................................ 74
Figure 3.3: Example of TGA curve of poly(vinyl acetate) ............................................... 75
Figure 3.4: Geometry construction of Bragg law.............................................................. 77
Figure 3.5: Broadening of a diffraction peak (FWHM) is related to the crystalline size according to the Scherrer equation ................................................................................ 78
Figure 3.6: Wide angle X-ray powder diffraction ........................................................................... 79
Figure 3.7: Schematic diagram of a generic Michelson Interferometer used in FTIR .... 80
Figure 3.8: FTIR spectroscopy in diffuse reflectance mode ............................................. 81
Figure 3.9: Instron Universal Testing Instrument, model 4465 ........................................ 82
Figure 3.10: Stress-strain diagram with tangent and secant modulus ................................ 83
Figure 3.11: Schematic diagram of a cone calorimeter..................................................... 84

Figure 4.1: Thermogravimetric mass loss and derivative curves for FRs, MH and ATH under inert atmosphere and heating rate of 10 °C •min⁻¹ ................................................................. 88
Figure 4.2: FTIR spectra of FR and their residues obtained after heating in the furnace to 800 °C ........................................................................................................................................ 90
Figure 4.3: Wide-angle X-ray diffraction patterns, structural evolution for MH residues obtained after heating to the temperatures as labelled ................................................. 91
Figure 4.4: Wide-angle X-ray diffraction patterns, structural evolution for ATH residues obtained after heating to 1050 °C .......................................................... 92
Figure 4.5: Thermogravimetric mass loss and derivative curves for FRs.......................... 93
Figure 4.6 Wide-angle X-ray diffraction patterns, structural evolution for zinc borate residues obtained after heating to the temperatures as labelled .................................. 94
Figure 4.7: Wide-angle X-ray diffraction patterns, structural evolution for APP residues obtained after heating to 1050 °C .............................................................. 96
Figure 4.8: Thermogravimetric mass loss and derivative curves for talc and mica under inert atmosphere and heating rate of 10 °C•min⁻¹ ...
Figure 4.9: Wide-angle X-ray diffraction patterns, structural evolution for talc residues obtained after heating to the temperatures as labelled in the spectra.

Figure 4.10: Wide-angle X-ray diffraction patterns, structural evolution for mica residues obtained after heating to 1050 °C.

Figure 4.11 Thermogravimetric mass loss and derivative curves for kaolin and CaCO₃ under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 4.12: Wide-angle X-ray diffraction patterns, structural evolution for kaolin residues obtained after heating to the temperatures as labelled in the spectra.

Figure 4.13: Wide-angle X-ray diffraction patterns, structural evolution for CaCO₃ residues obtained after heating to 1050 °C.

Figure 4.14: Particle size distribution of the pure individual fillers, MH, zinc borate and talc.

Figure 4.15: Thermogravimetric mass loss (a) and derivative curves (b) for various mixtures of APP:CaCO₃ and various ratios, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 4.16: Intumescences foam of APP:CaCO₃ mixture (1:1) after burning at 1050 °C.

Figure 4.17: Intumescences foam of APP:CaCO₃ mixture (2:3) after burning at 1050 °C.

Figure 4.18: Intumescences foam of APP:CaCO₃ mixture (1:4) after burning at 1050 °C.

Figure 4.19: Wide angle X-ray diffraction pattern and structural evaluation for APP:CaCO₃ mixtures obtained after heating to 1050 °C.

Figure 4.20: Thermogravimetric mass loss (a) and derivative curves (b) for FR filler mixtures, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 4.21: Wide angle X-ray diffraction pattern and structural evaluation for the FR filler mixtures obtained after heating to 1050 °C.

Figure 5.1: Free radical polymerisation.

Figure 5.2: Thermogravimetric mass loss (---) and derivative (- - -) for PVAc, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.3: FTIR spectra of PVAc residue degraded under inert atmosphere at different temperatures.

Figure 5.4: Thermogravimetric mass loss curves for kaolin composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.5: Derivative mass loss curves for kaolin composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.6: Thermogravimetric and derivative mass loss curves for kaolin-MH composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.7: Thermogravimetric and derivative mass loss curves for talc-MH composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.8: Thermogravimetric mass loss curves for talc composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.

Figure 5.9: Derivative mass loss curves for talc composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.
Figure 5.10: Thermogravimetric mass loss for FR kaolin composite (a) PVAcK0.3, (b) PVAcK0.4 (c) PVAcK0.5 and (c) PVAcK0.6, measured and (a', b', c' and d') theoretically calculated.......................................................... 132
Figure 5.11: FTIR spectra of PVAcK0.6 residue degraded under N2 at different temperatures. ........................................................................................................ 133
Figure 5.12: SEM observation of PVAcK0.6 burned at 400 °C (a and b)................... 137
Figure 5.13: SEM observation of PVAcK0.6 burned at 1050 °C (a and b)................... 137
Figure 5.14: SEM observation of PVAcT0.6 burned at 400 °C (a and b).................... 138
Figure 5.15: SEM observation of PVAcT0.6 burned at 1050 °C (a and b). ................... 138

Figure 6.1 FTIR spectra of BAMMA co-polymer.................................................. 141
Figure 6.2 Thermogravimetric mass loss (—) and derivative (- - -) curve for BAMMA co-polymer under inert atmosphere and heating rate of 10 °C·min⁻¹........ 142
Figure 6.3 a) Thermogravimetric mass loss and b) derivative curves for BAMMA composites (series 1), under inert atmosphere and heating rate of 10 °C·min⁻¹......... 144
Figure 6.4: Wide angle X-ray diffraction patterns for BAMMA composite residues (series 1) after heating in the furnace at 700 °C........................................... 145
Figure 6.5: Mass difference curves of BAMMA composites (series 1) (difference between experimental curves and calculated curves). ..................................... 146
Figure 6.6 a) Thermogravimetric mass loss and b) derivative curves for BAMMA composites (series 2), under inert atmosphere and heating rate of 10 °C·min⁻¹........... 148
Figure 6.7: Mass difference curves of BAMMA composites (series 2) (difference between experimental curves and calculated curves). ..................................... 149
Figure 6.8: Wide angle X-ray diffraction patterns for BAMMA composite residues (series 2) after heating in the furnace at 700 °C........................................... 150
Figure 6.9: Wide-angle X-ray patterns, structural evolution for BAMMA 011 composite obtained after heating to the temperatures as labelled in the spectra. ...... 153
Figure 6.10: Heat release rate curves for BAMMA co-polymer (BAMMA 01) and BAMMA 011 composite at 35 kW·m⁻² heat flux......................................................... 156
Figure 6.11: Heat release rate curves for BAMMA composites (series 1) at 35 kW·m⁻² heat flux........................................................................................................ 157
Figure 6.12 Photographs of the BAMMA composite residues (series 1) after cone calorimetry testing (incident heat flux 35 kW·m⁻²)............................................. 158
Figure 6.13 Heat release rate curves for BAMMA composites (series 2) at 35 kW·m⁻² heat flux........................................................................................................ 159
Figure 6.14: Photographs of the BAMMA composite residues (series 2) after cone calorimetry testing (incident heat flux 35 kW·m⁻²). ............................................. 160
Figure 6.15: Wide-angle X-ray spectra structural evolution of BAMMA composites (series 1) after calcinations regime by cone calorimeter................................. 164
Figure 6.16: Wide-angle X-ray spectra structural evolution of BAMMA composites (series 2) after calcinations regime by cone calorimeter................................. 165
Figure 6.17: Particle size distribution curves of BAMMA composites (series 1) ...... 166
Figure 6.18: Particle size distribution curves of BAMMA composites (series 2) ...... 167

Figure 7.1: a) Thermogravimetric mass loss and b) derivative curves for PVAc composites, under inert atmosphere and heating rate of 10 °C·min⁻¹............................. 175
Figure 7.2: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc composites obtained after heating to 1050 °C...................................................... 176

Figure 7.3: a) Thermogravimetric mass loss and b) derivative curves for PVAc:APP:ATH composites, under inert atmosphere and heating rate of 10 °C•min⁻¹. 178

Figure 7.4: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc:APP:ATH and PVAc:APP:mica composites obtained after heating to 1050 °C. 180

Figure 7.5: a) Thermogravimetric mass loss and b) derivative curves for PVAc:APP:CaCO₃ composites, under inert atmosphere and heating rate of 10 °C•min⁻¹...................................................................................................................... 182

Figure 7.6: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc:APP:CaCO₃ composites obtained after heating to 1050 °C...................................................... 183

Figure 7.7: a) Thermogravimetric mass loss and b) derivative curves for PVAc ternary composites, under inert atmosphere and heating rate of 10 °C•min⁻¹................. 185

Figure 7.8: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc ternary composites obtained after heating to 1050 °C. ................................. 186
LIST OF TABLES

Table 2.1: Textural characteristics of MH and MgO heated at 600 and 900 °C........... 24
Table 2.2: Crystal data and crystallite size information from X-ray diffraction patterns of MH and MgO.................................................................................................................. 25
Table 2.3: Physicochemical parameters for the ATH samples ................................ 28
Table 2.4: Examples of reported synergists for metal hydroxides.......................... 30
Table 2.5: The thermogravimetric analysis of APP samples.................................... 35
Table 2.6: X-ray diffraction patterns of (a) APP I and (b) APP II respectively .......... 38

Table 3.1: Property data of the minerals and fire retardants examined.................. 70
Table 3.2: Comparison of Properties of MH and ATH.......................................... 70
Table 3.3: Composition of the filled PVAc formulations using talc and kaolin minerals.......................................................................................................................... 72
Table 3.4: Composition of the filled BAMMA formulations................................. 72
Table 3.5: Composition of the filled PVAc formulations......................................... 73

Table 4.1: Thermogravimetric analysis of pure FR fillers..................................... 89
Table 4.2: Thermogravimetric analysis of the FR filler mixtures............................ 106

Table 5.1: Thermogravimetric analysis of PVAc and filled kaolin and talc composites series...................................................................................................................... 123
Table 5.2: Thermogravimetric analysis of filled kaolin and talc composites with no zinc borate (NZB)......................................................................................................... 129
Table 5.3: Mechanical properties for break strength of fire retardant PVAc composite residues............................................................................................................. 135

Table 6.1: The TGA analysis of filled BAMMA composites................................. 154
Table 6.2: Fire performance of BAMMA co-polymer and fire retardant BAMMA composites.................................................................................................................. 163
Table 6.3: Break stress of fire retardant BAMMA composites .............................. 168
Table 6.4: A summary table of BAMMA composites results............................... 169

Table 7.1: Thermogravimetric analysis of fire retardant PVAc composites.......... 187
Table 7.2: Mechanical properties for break strength of fire retardant PVAc composite .......................................................................................................................... 190
This thesis presents an investigation of a combination of several different mineral fillers in a polymeric matrix. Each mineral component imparted specific charring characteristics to the composite, and the combinations investigated formed residues ranging from soft and powdery to strong and dense. The decomposition mechanism and interactions of these compounds were studied.

The aim of this study was to investigate the inorganic components that have multifunctional ability for fire retardance and ceramic formation. One of the objectives was to develop composites with optimum selection of fillers where the thermal and oxidative removal of the polymer increased the ceramic strength. Several filler combinations offered fire retardance combined with ceramification and this was found to be enhanced by specific compound formation between the fillers.

Metal hydroxides (Magnesium hydroxide (MH) and aluminium hydroxide (ATH)) provided a fire retardant (FR) function through the release of water on degradation. When incorporated into the composites, the heat absorbed by the water release provided cooling of the substrate, by acting as a heat sink. MH was used with zinc
borate; ATH and/or calcium carbonate (CaCO₃) and mica, were used with ammonium polyphosphate (APP) to provide improved fire performance behaviour including the formation of a stronger char barrier. These FR fillers inhibited or suppressed the combustion process. They interfered with combustion during a particular stage of this process, i.e. during heating, decomposition, ignition or flame spread. They formed inert gases, which prevented oxygen from reaching the fire zone or scavenge the degradation radicals. There were many mechanisms involved in the action of FR used with polymers.

FR polymer composites were prepared by dispersion of filler particles in aqueous polymer emulsions. The resulting composites were analysed before and after furnace heating regimes to explore the filler interactions and strength development over the critical transitional stage.

The thermal degradation reaction mechanisms of individual FR fillers and inorganic minerals have been investigated using thermogravimetry (TGA). MH, ATH, talc and mica underwent dehydroxylation reactions that were initiated at different temperatures. The metal hydroxides formed thermally stable inorganic residues magnesium oxide (MgO) and aluminium oxide (Al₂O₃). The TGA results showed that ATH had lower thermal stability compared with MH. Talc, being a layered magnesium silicate, had a minor amount of water loss due to dehydroxylation, however it functioned by providing structure and platelet morphology for barrier performance through limiting gas diffusion and heat conduction. CaCO₃ decomposed at high temperature with the release of carbon dioxide (CO₂) and calcium oxide (CaO). Decomposition of mica formed mullite. Zinc borate and APP were used for their char enhancing properties. Zinc borate underwent several changes during decomposition; dehydroxylation leading to an amorphous structure before crystallising and further melting at elevated temperature. APP decomposition showed elimination of ammonia and water leading to the transformation of linear crystalline APP to crosslinked polyphosphoric acid (ultraphosphate). The structural changes of
the fillers were confirmed by X-ray diffraction. FR fillers combined with inorganic minerals such as kaolin, talc, and mica enhanced the mechanical properties.

The binary combination of the pure inorganic fillers, ATH and/or CaCO₃, had the potential to improve the FR action of APP. The combination showed interactions that had an impact on increasing the char yield and improving the insulation properties of the char. APP:ATH or CaCO₃ mixtures on heating led to the formation of thermally stable aluminium phosphate and/or calcium phosphate respectively. These new compounds showed good intumescence properties because of the gas released during conversion to the char product.

Ternary combinations of the pure inorganic fillers such as APP:ATH:CaCO₃ produced residues that were found to be tricalcium phosphate alumina (Al₂O₃•Ca₃(PO₄)₃). The presence of mica in the composite (APP:CaCO₃:mica) caused a shift in the mass loss steps to higher decomposition temperatures more than the other inorganic fillers due to the formation of calcium phosphate silicate (Ca₅(PO₄)₂•SiO₄).

The thermal decomposition of emulsion based poly(vinyl acetate) (PVAc) and butyl acrylate methyl methacrylate co-polymer (BAMMA) have been investigated using TGA. The degradation of PVAc led to the elimination of acetic acid, followed by a smaller mass loss from scission of the polymer back-bone. In addition, these unsaturated re-arranged and decomposed to aromatic and aliphatic hydrocarbons that was confirmed by FTIR analysis.

Introducing the binary (APP:ATH or CaCO₃, mica) and ternary (APP:CaCO₃:talc, mica or kaolin) filler combinations to PVAc significantly increased the thermal stability of the composites due to the formation of aluminium phosphate, calcium phosphate, calcium phosphate silicate, and tricalcium phosphate alumina. These new compounds led to the formation of a protective layer that provided increased thermal
stability by delaying the degradation of the composites. X-ray diffraction analysis confirmed the structural changes that occurred during the transformation.

The mechanical properties of the ceramic char formed after heating PVAc:binary/ternary, PVAc:MH:zinc borate:kaolin/talc and BAMMA composites at 1050 °C in the furnace were determined by tensile testing. This analysis showed an increase in the flexural strength of the ceramic char formed, higher residue strengths were achieved compared with composites with individual fillers such as PVAc:ATH, PVAc:APP and PVAc:CaCO₃. In addition, the flexural strength of the ceramic char residue of the burned composites that contained kaolin was higher than the composite residues that contained talc because kaolin had smaller particle size compared with talc. Furthermore, kaolin was already calcined; therefore, less water was released during decomposition.

The thermal decomposition of PVAc composites produced with kaolin or talc as filler with MH and zinc borate revealed that the first mass loss of PVAc (i.e. the elimination of acetic acid) overlapped with the decomposition of the fillers by dehydration. This indicated that the endothermic release of water from the hydrated fillers absorbed heat while water formed and vapourised, thereby cooling the substrate and causing polymer decomposition to shift to a high temperature due to volatiles being absorbed on the filler surfaces. A higher stabilisation of talc compared with kaolin composites observed.

The particle size distribution (PSD) of MH, zinc borate and talc revealed that talc had broad PSD, with a small proportion with large particle size. The PSD curve of MH showed a broad peak with the largest area compared with zinc borate and talc. Zinc borate showed one main distribution of particle size corresponding to the presence of large particles and two smaller distributions corresponding to small particle size. MH showed the smallest particle size compared with zinc borate and talc.
PSD of BAMMA-individual filler (MH or zinc borate or talc) composites showed results that were similar to the PSD of the pure fillers. MH loading increased the area of peak 1 (corresponds to small particle size) therefore the number of small particles that corresponded to diameter range from 0.26-1.67 μm increased. Introducing talc to the composites increased the area of peak 2 (corresponds to small particle size with small proportion of large particle size) (1.67-4.77 μm) and peak 3 (corresponds to large particle size) in the diameter range from 4.77-62.99 μm. The results revealed that introducing zinc borate to the composites caused peak 3 to shift to a range of larger diameters (4.77-62.99 μm).

The combined use of different filler mixtures such as MH:zinc borate showed the formation of a more thermally stable product magnesium orthoborate (3MgO•B2O3) that improved the high temperature surface protection when used with BAMMA and PVAc polymers.

The fire performance of BAMMA composites (BAMMA:MH:zinc borate or talc) was characterized by a decrease in heat release rate (HRR) due to the formation of a ceramic char that acted as an insulating barrier that slowed the gaseous emission produced by polymer combustion. Introducing MH to the BAMMA composites increased the time to ignition (TTI) due to the dehydration of MH to MgO. Zinc borate played the role of a binder (flux agent) in formation of the MgO-based ceramic. The synergies between combinations of one or a number of different fillers in a polymer were investigated. There was evidence of a synergism between MH and talc. This was confirmed with weight difference curves where the interactions between the fillers were observed. Ceramic chars were observed by scanning electron microscopy (SEM).
CHAPTER 1: INTRODUCTION

1.1 Background information

There has been considerable interest in the field of flame retardancy as the demand for improved safety in domestic, public, and industrial sectors increased. In recent years, fire retardant (FR) sealants have penetrated markets in building construction because of the requirement for sealing gaps in fire resisting construction applications [1]. Development of ceramic forming filler compounds, or combination of compounds, that form an effective thermal barrier under fire conditions could provide a significant improvement in the sealant performance.

The manner in which a coherent ceramic structure is formed is important. When the polymer decomposes and vaporises, loose filler particulates will be remaining and cause the material to disintegrate [2]. However de-vitrification of particular fillers must occur simultaneously with loss of polymer so that the ceramic maintains its shape by fusion of the inorganic particles. If the filler components are able to fuse into a ceramic structure with suitable properties, including no shrinkage, then the resulting ceramic can perform a protective barrier for a time to contain and protect people or equipment from a fire or smoke [3].
Sealants are required to adhere to substrate surfaces, although sealants are not relied on for structural support. Sealants act to complete fire and smoke barriers by separating adjacent areas from damage by spread of fire or smoke.

The continuous use and growth of FR sealants depend on finding materials with unique and dependable properties that can be used efficiently and produced economically. The main limitation of organic polymeric materials in many applications is their flammability. Therefore, the demand for FR polymer based materials has steadily increased as a consequence of the increased use of polymers in the home and environments mentioned previously. Studies for methods to improve the FR properties of polymer materials have been reported, with FR additives forming an increasingly significant part of the polymer industry [3, 4].

Additives used for ceramic formation, hereby termed ceramifying, sealant materials are substances that are dispersed in polymer materials in order to modify their behaviour in the course of processing and to improve the properties desired of final products. This is required to have minimal or no change in degradation of the polymer molecular structure. The behaviour of the sealant on exposure to fire depends greatly on the dispersed additives utilised and their particular function. Fire protection by sealants may proceed via intumescent behaviour where the sealant expands many times its original thickness. Alternatively, the sealant may provide a FR function by forming a ceramic like structural residue with little change in thickness but remain to provide an insulative barrier for the underlaying substrate.

Additives can be classified according to their effect on basic properties of polymeric materials and according to their functional and practical use. The most common approach to enhancing the fire performance is by the addition of FR additives that react chemically with the substrate and act in the condensed phase. Examples of such retardants are the hydrated fillers like magnesium hydroxide (MH), and aluminium trihydroxide (ATH). They decompose to give the respective metal oxides and water. Char forming materials provide an inert or slow burning phase on the surface of the polymer. When an intumescent material is used, a foamed char is formed. The char
insulates the polymer from radiant heat, does not rapidly decompose to gases, obstructs gases from escaping from the polymer mass and keeps oxygen away from the polymer. Suitable materials used are ammonium polyphosphates (APP) and zinc borate [5, 6].

On heating, these FR act by diluting the fuel source and increasing the pathway for the pyrolysis gases to reach the combustion zone. Furthermore they change the decomposition path of the material so that less volatile combustible products and more intumescent char is formed. The intumescent char offers heat and flame resistance until it reaches a temperature above 400 °C where the polymer burns. MH has attracted attention as a halogen free FR, because of its smoke suppression property, flame retardancy and good thermal stability that allows higher processing temperature than ATH [5, 7].

However the hydrated fillers are not very effective, especially in hydrocarbon polymers that require addition level of up to 60 % in order to achieve an acceptable combustion resistance, such high additions in turn lead to deteriorated toughness of the sealant materials. In order to minimize the negative effect of the hydrated fillers, inorganic materials such as kaolin, talc and CaCO₃ have been used as a third phase [8]. These inorganic materials provide mechanical enhancement that improve the toughness and strength of the hydrated fillers contained polymer, and reduce the cost of the material, depending on the composition. The mechanical characteristics of these materials are significantly influenced by the interfacial interactions that depend on the size of the interface and the strength of the interaction, additive volume fraction, particle size, additive geometry, and compatibility with polymer [8].

Emulsion polymers such as poly(vinyl acetate) (PVAc), poly(butyl acrylate-co-methyl methacrylate) (BAMMA), poly(vinyl alcohol), polyacrylonitrile, poly(styrene-co-butadiene) and various other co-polymers are suited for the addition of fillers to enhance their thermal stability and fire performance behaviour [2]. Each polymer has inherent properties when solvent has been removed in the drying process, for instance flexibility, durability and chemical resistance. The flammability of these polymers is particularly severe when they undergo depolymerisation to form
flammable monomers or active products. The decomposition of these polymers and some mineral components during pyrolysis was found to create porosity and foaming in many compounds due to the rapid escape of gaseous degradation products. This could be minimised by restricting the escape of degradation gases, such as hydrocarbons fractions, carbon dioxides and water [9]. Two polymers were utilised as a carrier for the filler system that could act as sealant type base materials. The polyacrelate (BAMMA) is a flexible polymer and fillers incorporated to produce flexible composites. PVAc was investigated since it exhibits two mass losses, the first overlapping with the decomposition of the hydrated fillers.

The key to superior formation of the ceramic char residue is in the inorganic additive systems, and on the filler particles and their state of dispersion in the host polymer. The polymer response to heat or fire rate of decomposition also plays a significant role. In this study, the composites were prepared by dispersion of filler particles in aqueous emulsion and dried. The resulting composites were analysed before and after furnace heating regimes to explore the filler interactions and strength development over the critical transitional stage. The formation of the FR sealant via this process depends upon the thermodynamic interaction between the polymer and the filler. The fillers can inhibit the flow of the polymer by providing structure to the material, and they can partake in the formation of a ceramic to provide structural integrity and maintain a barrier against the spread of fire [9].

The mechanisms of burning are studied to invent additives that will retard particular pathways so that burning rate will be reduced and protective barrier properties will be retained. Burning begins with an external source of heat; the polymer will soften, melt or char and eventually decompose forming volatile gases. The decomposition gases will diffuse from the polymer and ignite with oxygen in the gas phase. Radicals formed will be present in the gas phase to continue and accelerate chain reactions that support combustion process.
Each of the steps involved in burning can be modified to interrupt or interfere with their mechanism to retard the combustion process. Various additives function by preferential absorption of heat, formation of inert gases to dilute fuel, reducing the diffusion rate of pyrolysis gases to the combustion zone and formation of a char or barrier at the surface. FRs incorporated into the ceramic forming composites will be discussed with particular reference to their interaction and action in the systems.

1.2 Aim

The aim of the work is to investigate inorganic components that have multifunctional ability for FR and ceramic formation and to develop FR composites with the optimum selection of fillers, where the thermal and oxidative removal of the polymer increases the ceramic strength with temperature treatment.

1.2.1 Objectives:
- To correlate the composition, mixing and particle size requirements for ceramic forming materials and the time-temperature conditions needed for ceramic formation.
- To investigate the synergies between combinations of one or a number of different fillers in the emulsion polymer.
- To investigate inorganic composites where FR fillers combine to provide properties and time-temperature behaviour that form useful ceramics.
- To investigate the thermal stability and mechanical properties of FR polymer composites.
- Comparison of the effect using binary and ternary filler combinations on thermal stability and mechanical properties of polymer composites.
- Interpretation of the structural changes occurring during transformation of FR fillers.

1.2.2 Research questions

This proposed research raises some questions that are important for meeting the objectives.

The questions that need to be addressed are:
• What are suitable FR that have multifunctional ability to assist in the fire performance and fusion to promote the formation of a ceramic like material of adequate strength while the polymer undergoes decomposition and combustion?
• What are the effects of particle size on the ceramic strength?
• What is the choice of suitable combination and concentration of FR fillers?
• What are the effects of varying the filler contents on the polymer composites?
• How does the FR control or delay the burning pathway mechanism in the condensed phase or gaseous phase while the polymer is subjected to heat or fire?

1.3 Thesis Structure
A literature review presented in Chapter 2 covers the aspects of polymer applications where fire retardants (FR) are needed, mechanism of polymer burning, mechanism of FR and synergism of FR.

The general materials and experimental methods used for Poly(vinyl acetate) (PVAc) composites, and butyl acrylate methyl methacrylate co-polymer (BAMMA) composites that contain FR additives are outlined in Chapter 3.

The thermal properties and the structural changes of FR and minerals of calcined kaolin, talc, mica and CaCO₃ mineral that enhance the FR properties, magnesium hydroxide (MH) and aluminium hydroxide (ATH) for dehydration through endothermic reaction, zinc borate for formation of char barrier ammonium polyphosphate (APP) for the development of intumescent char are studied in Chapter 4.

The thermal behaviour of the original PVAc and PVAc composites in the presence of kaolin, talc, MH and zinc borate are detailed in Chapter 5.
The advantages in the use of a combination of zinc borate and MH in BAMMA composites are investigated in Chapter 6.

The interpretations of the thermogravimetry in terms of interaction between combinations of binary or ternary FR systems in PVAc composites is discussed in Chapter 7.

Finally, conclusions of the thesis and further recommendations are given in Chapter 8.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The human and financial costs of fire have made flammability of materials an important issue. Fire is a significant cause of loss of life and property. A fire requires fuel and many materials used in construction, coating, furnishings and decorations are combustible [10]. Demands for a lowering of the fire hazard posed by combustible materials, such as wood, polymers, textiles and sealants are made for all the important living and working spaces, and this lowering may be achieved by the use of suitable FR treatments [11]. Such FR treatments can prevent the start of a fire or delay it to such an extent that people at risk from fire will have sufficient time to make their escape. FRs do not prevent or stop fire, but retard its progress. In order to develop effective FR the mechanism of burning must be understood so that specific retardants can be added for each particular step in the mechanism.

The mechanisms of burning can be considered as separate steps that can be retarded by slowing the rate of the process, reducing a reactive product or inhibiting diffusion of oxygen to the combustion zone. Suitable design and composition of FR involves quantifying these steps, comparing materials and evaluating the effectiveness of additives. Polymers form a major part of the built environment, of the materials around us. Fire safety thus, in part, depends upon
these materials [10]. There are many diverse approaches for enhancing the fire stability of polymers. The most common approach has involved the addition of additives. Halogen compounds are widely used for FR polymers but the corrosiveness and toxicity of their combustion products and the smoke production have caused concern [12]. Therefore there was a strong emphasis on non-halogenated FR as it provided safer degradation products.

The mechanism of burning is complex; it mainly involves a rapid oxidation and heat, although many steps are involved in the mechanisms. A flame can be described as an auto-accelerating reaction cycle, so any substance that can retard one step in the cycle will slow the whole cycle.

Ceramifying polymer materials have been developed by incorporating ceramic forming pre-cursors into thermoplastics. In a fire situation, the polymer component is pyrolysed. Sometimes, a porous, coherent ceramic begins to form at sufficiently low temperatures to maintain the structural integrity of the material through to temperatures of over 1000 °C. The ceramic forming systems can be adjusted to minimize dimensional changes, or to provide a degree of intumescence through entrapment of volatile gases from the polymer [13].

### 2.2 The Combustion Process

Fire is known as a gas phase reaction. Thus, in order for a substance to burn, it must become a gas. Natural and synthetic polymers can ignite on exposure to heat. Ignition occurs either spontaneously or results from an external source such as a spark or flame [14]. If the heat evolved by the flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the evolved combustibles within the flammability limits, then a self-sustaining combustion cycle will be established (Figure 2.1). This self-sustaining combustion cycle occurs across both the gas and condensed phases.
FRs act to break this cycle by affecting the chemical and/or physical processes occurring in one or both of the phases. There are a number of ways in which the self-sustaining combustion cycle can be interrupted, causing a reduction in the rate of heat transfer to the polymer and thus remove the fuel supply. Fundamentally, four processes are involved in polymer flammability: preheating, decomposition, ignition and combustion/propagation. Preheating involved heating of the material by means of an external source, which raised the temperature of the material at a rate dependent upon the thermal intensity of the ignition source, the thermal conductivity of the material, the specific heat of the material, and the latent heat of fusion and vaporization of the material [15].

When sufficiently heated, the material begins to degrade, i.e., it loses its original properties as the weakest bonds begin to break. Gaseous combustion products are formed, the rate being dependent upon such factors as intensity of external heat, temperature required for decomposition, and rate of decomposition. The concentration of flammable gases increases until it reaches a level that allows sustained oxidation in the presence of the ignition source. The ignition characteristics of the gas and the availability of oxygen are two important variables in any ignition process [15].

After ignition and removal of the ignition source, combustion becomes self-propagating if sufficient heat is generated and is radiated back to the material to continue the decomposition process. The combustion process is governed by such variables as rate of heat generation, rate of heat transfer to the surface, and rates of
decomposition. Flame retardancy, therefore, can be achieved by eliminating any one of these variables. A FR should inhibit or even suppress the combustion process. Depending on their nature, FR could act chemically and/or physically in the solid, liquid or gas phase [15].

Researchers studied the overall burning process that has been achieved by isolating the individual steps (pyrolysis, product formation, oxidation reaction etc.) the approach assisted the understanding of a complex mechanisms of the burning and the identification of the precursors supporting flammability, smoke, toxicity, etc. so that these problems could be controlled within the burning process, for example by promoting char formation rather that the release of flammable species at elevated temperatures [16].

The most common techniques for characterizing fire tests and the combustion process are:

*Underwriter’s Laboratory standard 94 (UL94) (26):*
In Underwriter’s Laboratory standard 94 (UL94) test a thin sample of the polymer is ignited and one measures the ease of extinction of the flame. The standard, which is normally required to offer a commercial FR, is the V-0 rating which means each sample self-extinguishes within 10 s [17].

*Limiting oxygen index (LOI):*
The limiting oxygen index (LOI) is used to provide a single value for flammability. LOI is the minimum oxygen content required in an oxygen/nitrogen atmosphere for material to burn, for a pre-specified time and specimen length [18].

*Cone calorimeter:*
The cone calorimeter complements the suit of furnace tests and is used as a special research technique to understand the burning characteristics and decomposition/combustion of polymers under the range of conditions permitted in the cone [19]. Cone calorimeter technique has become the established small-scale standard for measuring the heat release rate (HRR) from a burning polymer under a controlled radiant heat source; radiant heat is the major cause of fire spread, and
the timing and magnitude of the peak of heat release rate (PHRR) is the single most important factor in predicting fire growth rate (Figure 2.2 shows the cone calorimeter in operation) [19]. Other measurements of temperatures, evolved gases and mass changes are provided (this will be described in details in Chapter 3).

Figure 2.2: Combustion of a polymer sample during cone calorimeter analysis

The cone calorimeter is an instrument that duplicates fire conditions and provides quantitative data on many aspects of burning. Chemistry is the science behind the combustion process and knowledge of the mechanisms has led to the development of effective FR. The rapid pace of research into fire and FR is providing many new products, an increasing knowledge and new ways of measuring the chemistry of burning [18].

2.2.1 Three classes of polymers can be defined on the basis on their thermal response:

- Those that degrade completely with breaking of the main chain (melting or thermoplastic polymers)
- Those that undergo rupture of side fragments with the formation of both volatiles (aromatics) and char.
- Crosslinked polymers, whose main degradation product is char.
2.3 Ceramifying Polymer System

Traditional passive fire protection materials rely on hydrated inorganic intumescent substances such as sodium silicates and expandable graphite that form a thermally insulating char. High expansion factors of over 30 can be achieved, providing high thermal resistance. However, these chars have some limitations in fires where they must have sufficient mechanical strength to resist falling away from the protected substrate in the presence of turbulent airflows and mechanical stresses. One approach to improve the fire protective coatings is through the use of ceramifying polymer systems [20]. These materials contain inorganic fillers that form a coherent ceramic at intermediate to high temperatures, bridging structure over critical phase changes of the polymer and filler systems. Ceramifying polymers generally consist of polymer matrix with refractory silicate minerals that form the ceramic framework in combination with a flux system. This can allow a coherent ceramic structure to form at a relatively low temperature, providing a suitable combination of minerals, flux and polymer are tailored to perform this function [20]. Other functional additives may be added including FR and stabilizers or glass stiffeners that contain a third category of oxides to strengthen, increase the viscosity and widen the melting range of the material. The resulting hardened polymer composite crystalline product may have a phase (mineral) composition quite different from that of the initial mixture, as a consequence of high-temperature reactions. The crystalline phases in ceramics exhibit strength, chemical resistance and stability at elevated temperatures. The total ceramifying additive level may be required to be quite high, although the materials can still be processed like conventional polymers. A wide range of ceramifying polymers can be produced, including thermoplastics, thermosets and polymer emulsions suitable for coatings [20]. Ceramification can be combined with intumescence through a mechanism that traps volatiles from the polymer decomposition as the ceramic structure is formed. This can produce a strong, cellular coating layer with good thermal resistance for fire protection applications [20]. Ceramifying polymers are not normally FR. However, they can be modified with organic or inorganic FR systems to achieve low flammability ratings [21].
Ceramification can assist fire performance by producing a stable surface layer that insulates the underlying layers and may inhibit volatile emissions from the polymer. This can delay ignition and reduce heat release rates (HRR) from the material. A key characteristic of ceramifying polymers is their ability to form a self-supporting structure throughout the temperature range from ambient service temperature to over 1000 °C. Reactions in the inorganic ceramic forming systems can commence from temperatures as low as 350 °C and continue to 800 °C or higher. This is achieved with fluxes which produce a controlled, low level of liquid phase at these temperatures. Liquid phases exist when the original polymer material melt or liquefy during burning [20].

The degradation reactions are usually endothermic, though self-sustaining through radical chain reactions. The products of degradation are small molecules that become gases after absorbing latent heat of vaporisation. A study by Parwez et al. [22] showed that the property profile of ceramic fibre insulated laminated boards made them suitable for numerous applications such as decorative laminates, building and construction materials and low temperature insulation. The author determined the FR behaviour of ceramic fibre laminates through the burning rate of commercial decorative laminates [22]. Laminates developed with ceramic fibres without any FR agent showed burning rate of 9 cm$\cdot$min$^{-1}$. Incorporation of 0.25 phr of FR agent reduced burning rate to 8.2 cm$\cdot$min$^{-1}$, while further increasing it to 0.5 phr reduced burning rate to 7 cm$\cdot$min$^{-1}$. Increasing the FR in the composition to 0.75 phr resulted in a nominal reduction of burning rate [22]. Ceramic fibre reinforced samples without any FR agents showed markedly lowered burning rates.

The most important properties of ceramic fibres particularly, alumina silica fibres are low thermal conductivity, resistance to thermal physical degradation at high temperature, high tensile strength and elastic modulus. It is due to these attributes that these fibres are used as thermal insulating materials.

Cartier et al. [23] discussed the FR properties of two EVA (8 and 19) copolymer-based formulations. The two formulations were based on both concept of intumescences and the concept of ceramification. The author found that EVA-8 exhibited poor heat resistance; its limiting oxygen index (LOI = 17 vol%) was low and was not classed (NC) by the UL 94 test. Thus, the polymer required the
incorporation of additives to achieve FR properties. The intumescences formulations EVA-8 (60 wt%)/APP (33 wt%)/PA-6 (7 wt%) exhibited good FR properties after processing at 250 °C using the twin-screw extruder at 59 rpm. It showed LOI = 30 vol% and a V0 UL 94 rating, i.e. self-extinction and no dripping. The FR properties (of the ceramic-like formulations) of EVA-19 (LOI=22 vol% and NC by the UL 94 test) were significantly improved at 65 wt% total loading of Al(OH)₃ (LOI 44 vol% and V1 UL94 rating). These properties were reinforced by substituting a small amount of Al(OH)₃ with zinc borate. This effect was optimum at 5 wt% of zinc borate.

Duquesne et al. [24] investigated the role of the binder in an intumescent paint. The protection of metallic materials against fire had become an important issue in the construction industry. In fire, such materials distort leading to the collapse of building structures, and as a consequence, to dramatic human and economical losses. Intumescent paints were a way to achieve such protection. FR coatings, acting by the phenomena of intumescences, form on heating an expanded multicellular layer, which acted as a thermal barrier that prevented heat from penetrating and flames from spreading.

Almeras et al. [25] studied the effects of fillers (talc and CaCO₃) on (polypropylene/ ammonium polyphosphate/ polyamide-6 (PP/APP/PA-6). It was shown that talc induced an increase in the Young’s modulus and a decrease in the elongation at break. CaCO₃ led to a decrease in the elongation at break, but there was no improvement in the Young’s modulus. Talc increased the fire protective performance due to formation a ceramic-like protective shield at the surface, whereas CaCO₃ decreased it because of a reaction with APP. In addition, the reference compound, prepared without filler (PP/APP/PA-6) had typical HRR curve with two peaks, separated by a plateau, in which the first peak may be assigned to the development of intumescent protective structure and the second to the degradation of this protective layer. The incorporation of CaCO₃ increased the first HRR peak from 200 to 350 kW.m² and decreased the time needed for the complete degradation compared with the reference compound. The addition of talc in a separate step decreased the first peak of HRR but no significant
differences could be observed in the value of the second HRR peak and in the time of combustion [25].

Sergei et al. [26] studied the FR action of phosphorus-containing compounds in aliphatic PA. The author found that APP could be incorporated in PA-6, PA-6,10 and even into high melting PA-6,6 in spite of relatively low thermal stability of APP. APP produced a continuous intumescent char on the surface which efficiently decreased the heat transfer to the polymer surface and slowed the decomposition of PA.

2.4 Flame or Fire Retardants (FR)

There are four main categories of FR chemicals (Figure 2.3) that consist of [10]:

- **Inorganic FR**: typically includes non-halogenated based materials such as aluminium trihydroxide (ATH), magnesium hydroxide (MH), ammonium polyphosphate (APP), and red phosphorus. This group represents about 50 vol% of the global FR production.

- **Halogenated FR**: most prominent are based on chlorine and bromine, but may contain other halogens. The brominated FR such as aromatic, including tetrabromobisphenol-A (TBBPA), polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) Aliphatics that are in general used in relatively small quantities. Cycloaliphatics including hexabromocyclododecane (HBCD) are included in this group. This group represents about 25 vol% of the global production.

- **Organo-phosphorus FR**: mainly comprise of phosphate esters and represent about 20 vol% of the global production. Organo-phosphorus FR may contain bromine or chloride.

- **Nitrogen-based organic FR**: such as melamine and melamine derivatives act by intumescence. The FRs are most often used in combination with other FRs. Gasses released from the compounds cause the material to swell forming an insulating char on the surface.
2.4.1 Mechanism of action of flame retardants

FRs are used for their function in reducing the flammability of materials. This action can be conducted by blocking the flame physically or initiating a chemical reaction that stops the flame or flame propagation. They act by removing the heat from the solid polymer [27]. Heat is required to melt or decompose the polymer, so selection of an appropriate polymer type will be the basis of selection of a FR. Flame retardancy is improved by FR that cause the formation of a surface film of low thermal conductivity or high reflectivity, which reduces the rate of heating [15]. It is improved by FRs that serve as a heat sink by being preferentially decomposed at low temperature. Char-forming materials provide an inert or slow burning phase on the surface of the polymer. The char insulates the polymer from heat, does not readily decompose to gases, and obstructs gases from escaping from the polymer mass and keeps oxygen from the polymer [15].
Suitable materials are APP, zinc borate, organoclays and melamine derivative. Filled polymers are inherently more stable because when there is more filler there is less polymer to burn, the filler may play an active role in the char formation [28]. The char will bind any liquid phase of the polymer and decrease the rate of further decomposition into gases [29]. Aromatic polymers, particularly when crosslinked such as phenol-formaldehyde (PF) resins, are efficient char-forming polymers without the addition of other materials. PF resins contain significant amounts of covalently bound oxygen. This can affect a reduction in flammability because less heat is released during burning if the polymer has already been partially oxidized [29].

Decomposition of the solid and liquid phase can be restricted by antioxidants. Antioxidants are compounds that effectively retard the onset of polymer oxidation without changing the sensory qualities of the decomposition product. In addition it improves the polymer performance and enhance its stability [30]. These additives react with radicals and hydroperoxides that initiate and propagate the degradation reactions. Free radical inhibition involves the reduction of gaseous fuels generated by burning materials. Heating of combustible materials, results in the generation of hydrogen, oxygen, hydroxide and peroxide radicals that are subsequently oxidized with flame. Antioxidants act to trap these radicals and thereby prevent their oxidation [15].

The various ways in which FR can act physically or chemically are described in the following subsection [2, 27].

### 2.4.1.1 Physical Action

There are several ways in which the combustion process can be retarded by physical action:

- **By cooling:** the degradation reactions of the additive can play a part in the energy balance of combustion. The endothermic processes triggered by additives such as the hydrated fillers MH and ATH cool the substrate to a temperature below that required to sustain the combustion process, by forming a protective layer that protects the remaining material [15].
• *By formation of a protective layer (coating):* Under external heat flux the additives form a condensed combustible layer (charring or altering thermal degradation processes) that can be shielded from the gaseous phase with a solid or gaseous protective layer that causes a reduction of the heat transfer from the heat source to the material. The condensed phase is thus cooled, smaller quantities of pyrolysis gases are evolved, and the oxygen necessary for the combustion process is excluded and heat transfer is impeded [15]. Phosphorus additives act primarily in the condensed phase by promoting charring, through the formation of phosphoric acid that decrease release of flammable volatiles. The same mechanism was observed using boron containing compounds [31].

• *By dilution:* The incorporation of inert substances (e.g. mineral fillers such as talc) and additives that evolve inert gases on decomposition dilute the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded [15].

2.4.1.2 Chemical Action

The most significant chemical reactions interfering with the combustion process take place in the solid and gas phases [32]:

• *Reaction in the gas phase:* The free radical mechanism of the combustion process that takes place in the gas phase is interrupted by the FR or its degradation products. The exothermic processes are thus stopped, the system cools, and the supply of flammable gases is reduced and eventually suppressed. In particular metallic oxides can act as flame inhibitors. The active HO• radicals are absorbed on the surface of oxide particles [15].

• *Reaction in the solid phase:* Two types of reaction can take place. Firstly, breakdown of the polymer can be accelerated by the FR, causing pronounced flow of the polymer and, hence, its withdrawal from the sphere of influence of the flame, which breaks away. Secondly, the FR can cause a layer of carbon (charring) to form on the polymer surface. This can occur, for example, through the dehydrating action of the FR
generating double bonds in the polymer. These form a carbonaceous layer by cyclising and crosslinking [33].

Structural modification of the plastic, or use of an additive FR, might induce decomposition or melting upon exposure to a heat source so that the material shrinks or drips away from the heat source. It is possible to significantly retard the decomposition process through selection of chemically stable structural components or structural modifications of a polymer. In general, anything that will prevent the formation of a combustible mixture of gases will prevent ignition. However, this distinguishes the cases in which the FR or the modified polymer unit, upon exposure to a heat source, will form gas mixtures that will react chemically in the gas phase to inhibit ignition. The goal of FR in the combustion and propagation stages is to decrease the rate of heat generated or radiated back to the substrate.

2.5 Hydroxides

Hydroxides are commonly used in composite materials due to their ability to undergo endothermic dehydration in fire conditions, as well as acting as a precursor for the preparation of metal oxide. Hydrated fillers, MH and ATH, are in widespread use as FR fillers for polymers, as environmentally acceptable alternatives to halogen compounds [34]. In addition to reducing ignition and HRR during combustion, they are effective smoke suppressants, due to catalytic activity of the high oxide surface area produced on thermal decomposition of the hydroxide. MH and ATH have been used in polyolefins for their fire performance behaviour. These are often used with zinc borate to provide improved fire performance behaviour including the formation of a stronger char barrier. Additionally, specific interactions may exist between certain polymers and fillers, which influence their mechanism of action. The FR effect was found to come from three sources; the dehydration endotherm, the heat capacity of the oxide residue and the heat capacity of the involved gases. Several comparisons exist on the relative efficiency of MH and ATH in the same polymer type. Study by Rychly et al. [23] showed that using MH and ATH in (ethylene-co-vinyl acetate) (EVA) with 30 % vinyl acetate (VA) revealed that MH yielded an oxygen index of 46 %, whereas using ATH it was only 37 %. Results from thermogravimetry
(TGA), suggested that water release was delayed from ATH yet accelerated from MH, possibly arising from the reaction with acetic acid, generated during polymer decomposition.

In a cone calorimetry study [35], compositions of polypropylene (PP) that contain the same mass of either glass beads or MH have been examined. In both cases the HRR were significantly reduced, but the reduction was far greater for MH. The degradation of MH filled polyamide-6 (PA-6) and polyamide-6,6 (PA-6,6) has been studied and it was found that the presence of MH enhanced the degradation of the polyamide [36]. This was attributed to the release of water from the decomposition of MH and its subsequent attack on the polyamide (PA). With PA-6,6, polymer degradation occurred before MH decomposition, while with PA-6 there was better overlap between MH and PA-6 degradations, resulting in enhanced flame retardancy [25, 26].

2.5.1 Magnesium hydroxide

MH has a high decomposition temperature (325 °C), making it more suitable for use in thermoplastic applications compared with other hydrated fillers. The decomposition is an endothermic reaction proceeding to form magnesium oxide (MgO) as described in the equation shown below [37]:

\[
\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \quad \Delta H = 380 \text{kJ} \cdot \text{mol}^{-1}
\]

MH is a symmetric layered structure with a relatively small (five atoms per cell) unit cell. The cations are 6-fold-coordinated (Figure 2.4). The OH groups are vertical, with the shortest H-H interlayer and interlayer distance at 1.97 and 3.15 Å, respectively. The interaction, among the OH group is weak; therefore MH is a model of a crystal structure with OH groups free from any H-bonding interactions [38].
MH layered structure consists of single sheets of charge-neutral Mg(OH)$_6$ octahedra that are stacked parallel to (001). The (001) surface expose only the OH sites that are oriented perpendicular to (001) in the crystal on average. Figure 2.5 shows the decomposition steps involved in the conversion of MH (step a) and elimination of water and formation of MgO (steps b and c) [39].
Transmission electron microscopy (TEM) and atomic force microscopy (AFM) methods were applied to image the evolution of the morphology of crystalline MgO formed from MH on sintering procedures and compared with more regular MgO samples. The resulting aggregate formed by topotactic MH to MgO transformation, maintained the shape of the original MH microcrystals. The effect of successive annealing at higher temperature caused an increase of the MgO terraces from 2-3 to 10 nm [40]. The average edge length of the MgO cubes corresponded to approximately 7 nm and a high value of surface area of 200 m²g⁻¹. The increased dimension and roughness as compared with MH shows transition to a new crystalline habit, caused by the topotactic transformation of MH to MgO with release of H₂O [39]. Annealing at 800 °C resulted in a further enlargement of MgO aggregates with a decreased mean height and in lower values of surface average roughness. Textural and acid-base properties of MgO depend, to a great extent, on the synthesis conditions, such as pH, sequence of the addition of reagents, and calcination temperature [28]. Figure 2.6 shows the morphology of the materials using a JEM-100CXII electron microscope (accelerating voltage 100 kV and resolution 0.204 nm) [40].

![TEM Images](image.png)

Figure 2.6: TEM Images of particles of (a) MH and MgO heated at (b) 600 °C and (C) 900 °C, electrograms are shown in the right upper corner [40]
The textural characteristics of MH and MgO heated at 600 and 900 °C are shown in Table 2.1.

**Table 2.1: Textural characteristics of MH and MgO heated at 600 and 900 °C [40]**

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>S_{HET} (m²/g)</th>
<th>S_{mes} (m²/g)</th>
<th>S_{mac} (m²/g)</th>
<th>V_{mic} (cm³/g)</th>
<th>V_{mes} (cm³/g)</th>
<th>V_{mac} (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂</td>
<td>200</td>
<td>73</td>
<td>0</td>
<td>41</td>
<td>32</td>
<td>0</td>
<td>0.218</td>
</tr>
<tr>
<td>MgO</td>
<td>600</td>
<td>80</td>
<td>2</td>
<td>37</td>
<td>42</td>
<td>0.001</td>
<td>0.199</td>
</tr>
<tr>
<td>MgO</td>
<td>900</td>
<td>51</td>
<td>0</td>
<td>17</td>
<td>34</td>
<td>0</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Note: Micropores correspond to R < 1 nm, mesopores to 1 < R < 25 nm and macropores to R > 25 nm and T is the calcination temperature.

The X-ray diffraction pattern given in Figure 2.7 shows the diffraction peaks indexed as the hexagonal structure MH (joint committee for powder diffraction studies (JCPDS) file number 07-0239). The significant peak broadening indicates that the MH has a very small particle size [41]. It was noted that the crystallite size, estimated by means of the Debye-Scherrer formula based on the full width at half-maximum (fwhm) of different diffraction peaks, has different values (Table 2.2), for example, 6.86 nm (001), 9.66 nm (101), and 18.8 nm (110), which indicated that the particles have a thin plate morphology with layers in the (001) direction [41].

![X-ray diffraction patterns of (a) MH and (b) MgO [41]](image)
Table 2.2: crystal data and crystallite size information from X-ray diffraction patterns of MH and MgO [41]

<table>
<thead>
<tr>
<th></th>
<th>peak position (d) value, Å</th>
<th>Miller indices ((hkl))</th>
<th>fwhm (deg)</th>
<th>crystallite size (nm) (estimated by Scher. equation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg(OH)}_2) hexa.</td>
<td>4.765</td>
<td>001</td>
<td>1.16</td>
<td>6.86</td>
</tr>
<tr>
<td></td>
<td>2.362</td>
<td>101</td>
<td>0.86</td>
<td>9.66</td>
</tr>
<tr>
<td></td>
<td>1.791</td>
<td>102</td>
<td>1.24</td>
<td>7.02</td>
</tr>
<tr>
<td></td>
<td>1.568</td>
<td>110</td>
<td>0.48</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>1.492</td>
<td>111</td>
<td>0.70</td>
<td>13.1</td>
</tr>
<tr>
<td>(\text{MgO}) cubic</td>
<td>2.112</td>
<td>200</td>
<td>0.88</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>1.492</td>
<td>220</td>
<td>0.68</td>
<td>13.5</td>
</tr>
</tbody>
</table>

2.5.2 Aluminium hydroxide

There are three typical ATH with different crystal structure, i.e., gibbsite \((\text{Al(OH)}_3)\), \(\gamma\)-alumina, and \(\alpha\)-alumina. The two most important polymorphs of ATH are gibbsite and bayerite (Figure 2.8a and 2.8b) [42].

![Figure 2.8a: the structure of the two main polymorphs ATH, (a) bayerite and (b) gibbsite, illustrating the difference in the stacking of the layers [42]](image)

![Figure 2.8b: the labelling of of the hydrogen/deuterium atoms within the unit cell of (a) bayerite and (b) gibbsite [42]](image)

All of the polymorphs of ATH are composed of layers of aluminium (Al) octahedra with hydroxyl groups on either side that hydrogen bond the layers together. The difference between the polymorphs is the stacking sequence of the
layers. Gibbsite and bayerite represented the two stacking series, with nordstrandite and doyleite being intermediated structure [43]. Al ions are coordinated with six hydroxyls and each hydroxyl is shared with two Al ions.

Gibbsite model has a layered-type structure, where the AlO$_6$ octahedra are linked with one shared edge along the a-b plane. Each oxygen atom is linked to a hydrogen atom. The O$_1$H$_1$ bonds are located in the layers, forming the interlayer hydrogen bonds. The O$_3$H$_3$ bonds are located between layers and form interlayer hydrogen bonds and the O$_2$H$_2$ form tilting interlayer hydrogen bonds. This resulted in the presence of different types of coordinated hydroxyls with different proton affinities and site densities [44].

The dehydration of ATH produces crystalline aluminium oxide (Al$_2$O$_3$). ATH decompose endothermically when heated according to the following reaction:

$$2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \Delta H = 298 \text{kJ} \cdot \text{mol}^{-1}$$

The combustion process is retarded by physical action; this reaction triggers various processes affecting the combustion zone. As a result of the endothermic decomposition of ATH, the polymer is cooled, and thus fewer pyrolysis products are formed. Together with the charring products, the Al$_2$O$_3$, formed on the surface of the substrate acts as an insulating protective layer. The water vapour formed has a diluting effect in the gas phase and forms an oxygen-displacing shield gas over the condensed phase [45].

Chemical reactions such as the interruption of the radical chain mechanism of the combustion processes in the gas phase could not be detected.

Figures 2.9a and 2.9b shows the X-ray diffraction pattern and the Fourier Transform Infrared (FTIR) spectroscopy of ATH residues calcined at various temperatures, respectively. ATH calcined at 300 °C exhibited reflections characteristic of aluminium monohydroxide (boehmite) that were confirmed by the FTIR at the same temperature with characteristic bands at 475, 625, and 750 cm$^{-1}$ [46]. With the increase in the calcination temperature, boehmite dehydrated to form transition ATH with bands characteristic of a mixture of c, d, and h, ATH nanometric phases. At 500 °C, X-ray diffraction pattern and FTIR
revealed a minor amount of the h-phase, which increased with the thermal treatment at 1200 °C [46].

Figure 2.9a: X-ray diffraction patterns of ATH heated at various temperatures [46]

Figure 2.9b: FTIR spectra of ATH heated at various temperatures [46]

Figure 2.10 shows the results of the X-ray diffraction pattern measurements that indicate that the three samples represented the three different common ATH structures. In sample A, the predominant phase was found to be gibbsite with a little bayerite phase. Sample B was transition of alumina, mainly semicrystalline γ-alumina phase [47]. Sample C was well crystallized α-alumina structure (Table 2.3) [47].
2.5.2.1 Use of aluminium hydroxide in thermoplastics

ATH decomposition commenced at 200 °C, so difficulties were experienced with molding compounds that have to be preoccupied above this temperature. Mineral fillers usually result in an increased stiffness of the polymer composite, a compromise to the tensile and impact strength. As a result of the lamellar structure, the good flow properties of ATH enable outstanding surfaces to be
obtained. Of importance to its application in the electrical industry was an improvement in electrical properties such as dielectric strength and tracking resistance [15].

\textbf{2.6 Flame Retardant Synergists}

Many FR synergists do not have significant FR properties by themselves; their use increases the overall effectiveness of the FR system. While char formation in the condensed phase and halogen interference in the vapour phase take place when FRs are used alone, the presence of a synergist can increase the FR’s effectiveness, lowering the quantity of the FR needed to meet the required standard. Since high levels of FRs often affect product quality, a synergist is often used to reduce the amount of FR. Additionally, the cost of FRs can be significant; therefore, any method to decrease the quantity of FR needed is beneficial [48]. As an example of synergistic mechanisms, some synergists retard fire via two processes. In the condensed phase, a char layer is formed during the reaction with the synergistic compound, the FR and the polymer. This char acts as a shield as it reduces the rate of decomposition of the polymer; therefore, less fuel is available for the flame. In the vapour phase, the chemical reaction is slowed. This adds to the FR’s inhibitory effects on combustion by allowing it to react more completely with free radicals of oxygen and hydrogen, which are necessary for combustion to occur [48].

The high filler levels used in FR composites might cause problems with processing and mechanical properties. It is of scientific and industrial significance to include processing synergists to improve dispersion and permit high filler contents required for FR such as in organophosphorous FRs, when used alone, organophosphorous FR concentrations may need to be extremely high. These concentrations of the FR often affect the properties of the product. Testing has shown that adding inorganic synergists can dramatically increase the FR efficiency. Therefore, a significantly smaller quantity of the FR is required [8, 49].

One of the most important synergistic effects in FR chemistry is that between halogen and antimony, where antimony reacts in the form of antimony trioxide with the formation of radicals, forming antimony tribromide and antimony
oxybromide or their chlorinated equivalents. These FR react in the gaseous phase and usually contain halogens of the chlorine or bromine type. The other halogens, iodine and fluorine, do not function as FR because the organic iodine compounds are too unstable, while organofluorine compounds are too stable for the reactions that take place in the gaseous phase in combustion [8].

Table 2.4 gives an overview of synergists reported or patented for use in combination with hydrated fillers, such as MH and ATH, in various polymer matrices. An indication of observed effects and possible modes of action is also given [8].

### Table 2.4: Examples of reported synergists for metal hydroxides [8]

<table>
<thead>
<tr>
<th>Co-additives</th>
<th>Hydrated Fillers</th>
<th>Polymers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony trioxide</td>
<td>ATH</td>
<td>PVC (flexible)</td>
<td>• Reduced overall filler level</td>
</tr>
<tr>
<td>Antimony trioxide:zinc borate</td>
<td>ATH</td>
<td>PVC (flexible)</td>
<td>• Reduced overall filler level</td>
</tr>
<tr>
<td>Borate compounds (zinc borate:calcium borate)</td>
<td>ATH</td>
<td>EVA</td>
<td>• Enhanced flammability,</td>
</tr>
<tr>
<td>MH:ATH combinations</td>
<td>ATH:MH</td>
<td>PVC</td>
<td>• Reduced flammability,</td>
</tr>
<tr>
<td>Molybdenum compounds (molybdenum oxide:molybdate salts)</td>
<td>ATH:MH</td>
<td>PVC</td>
<td>• Reduced flammability</td>
</tr>
<tr>
<td>Red phosphorus</td>
<td>ATH:MH</td>
<td>• Reduced overall filler levels</td>
<td>• Suppression of phosphine formation by metal hydroxide</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Coloured formulations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Low co-additive addition</td>
</tr>
</tbody>
</table>
2.7 Phosphorous-Containing Flame Retardants

Phosphorous containing FRs are active in the condensed phase and influence pyrolysis and char formation. In the condensed phase they then form phosphoric and related acids that act as a heat sink as they undergo endothermic reaction [40]. The remainder partakes in the formation of a glassy char residue in the condensed phase that has multifunctional purpose to form a barrier protecting underlying polymer and lowering the evolution of combustible gases in the gas phase, and limiting the diffusion of oxygen and the heat transfer. In the gas phase they stop the free radical oxidation process of the carbon at the carbon monoxide stage, preventing the highly exothermic reaction of carbon dioxide formation [10, 50].

2.7.1 Ammonium polyphosphate

APP is a stable, non-volatile compound and the ammonium salt of polyphosphoric acid. The chain length (n) of this polymeric compound is both variable and branched, and can be greater than 1000 (Crystal phase II APP (APP II)). Short and linear chain APP (n < 100) (Crystal phase I APP (APP I)) are more water sensitive (hydrolysis) and less thermally stable than longer chain APP (n >1000), which show a very low water solubility (< 0.1 g / 100 mL) [51]. The structure is [NH₄PO₃]ₙ and shown below. It is recognised as efficient and multipurpose FR, which is already used in many applications such as epoxy resins, polyurethane, unsaturated polyester phenolic resins and others. APP is slowly hydrolysed to monoammonium phosphate (orthophosphate) in the presence of water, which is accelerated by higher temperatures. The structure of APP with regards to chain length has an impact on the crystalline structure, thermal stability and its decomposition temperature.

Chemical formula and structure of APP is:

![Chemical structure of APP](image_url)
2.7.1.1 Crystal phase I APP

APP I was characterised by a variable linear chain length, showing a lower decomposition temperature and higher water solubility than crystal phase II APP. Short chain low molecular weight APP I begin to decompose at temperatures greater than 150 °C, where it ultimately degrades to produce polyphosphoric acid and ammonia [52].

The general structure of APP I is given below. In APP I n (number of phosphate units) is generally lower than 100 [52].

\[ \text{NH}_4^+ \text{P(O)}_n \text{O}_- \text{NH}_4^+ \]

\[ n < 100 \]

2.7.1.2 Crystal phase II APP (APP II)

APP II structure is crosslinked/branched as shown below. However when the substance contains branching phosphate groups called ultraphosphate [53]. Ultraphosphates undergo rapid decomposition upon dissolution. The molecular weight is much higher than APP I with n value higher than 1000. APP II has a higher thermal stability and lower water solubility than APP I it initiates decomposition at temperatures above 300 °C. The crosslinked phosphoric acid forms condensed species which undergo fragmentation volatile P_2O_5 like moieties during the second step of decomposition that occurs at about 550 °C the evaporation of phosphoric acid and the dehydration of the acid to P_4O_{10} which undergoes sublimation.

Moreover, the final residual weight differs for APP II which has a bigger residual weight than APP I [52].
According to Drevelle et al. [54], the thermal degradation of APP I and APP II occurred in two steps, (Figure 2.12 and Table 2.5). The first step corresponded to a weight loss of 15 % for APP II and of 20 % for APP I. The second step presented the maximum weight loss at 590 and 620 °C for APP I and APP II, respectively. Figure 2.11 shows the chemical reaction occurring during the thermal degradation of APP [7].

Figure 2.11: Reactions occurring during thermal degradation of APP [7]
When APP was added to the acrylic binder resin, the thermal stability of the binder was strongly modified (Figure 2.13 and Table 2.5). Both crystalline forms of APP stabilized the structure from 380 to 800 °C. The major degradation step presented a maximum rate of degradation at 365–370 °C (with a 50 % weight loss versus a 78 % weight loss for the pure resin). Then, the material degraded slowly between 380 and 680 °C. Finally, a second step of degradation was observed at a higher temperature (25 % weight loss at the maximum rate of degradation) and led to the formation of a stable residue (10 %) [54].
As a result, the degradation mechanism of the binder resin was modified by the addition of APP. Chemical reactions between the APP and resin occurred and led to a thermally stable structure. This was shown by the curves of the weight difference, which show eventual interactions between the APP and binder resin (Figure 2.14). First, these curves demonstrated that there was no difference between the crystalline forms of APP. The temperature range in which the interactions of the additives and binder led to the stabilization of the material was 380-800 °C. A destabilization of the material was observed between 270 and 370 °C. This could be attributed to a catalytic action of degradation of H₃PO₄ (formed during the degradation of APP) on the binder resin [54].

![Figure 2.14: Curves of the weight difference for treated resin [54]](image)

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature</th>
<th>Resin</th>
<th>APP I</th>
<th>APP II</th>
<th>Resin + APP I</th>
<th>Resin + APP II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Onset (°C)</td>
<td>285</td>
<td>270</td>
<td>300</td>
<td>245</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>Maximum (°C)</td>
<td>370</td>
<td>335</td>
<td>335</td>
<td>365</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>End (°C)</td>
<td>440</td>
<td>450</td>
<td>460</td>
<td>430</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>Residual weight (%)</td>
<td>22</td>
<td>80</td>
<td>85</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Onset (°C)</td>
<td>440</td>
<td>480</td>
<td>460</td>
<td>430</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>Maximum (°C)</td>
<td>590</td>
<td>590</td>
<td>620</td>
<td>730</td>
<td>730</td>
</tr>
<tr>
<td></td>
<td>End (°C)</td>
<td>590</td>
<td>890</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Residual weight (%)</td>
<td>7</td>
<td>12</td>
<td>18</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Onset (°C)</td>
<td>580</td>
<td></td>
<td></td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Maximum (°C)</td>
<td></td>
<td></td>
<td></td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>End (°C)</td>
<td>590</td>
<td></td>
<td></td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Residual weight (%)</td>
<td>2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2.5: The thermogravimetric analysis of APP samples [54]
Figure 2.15 shows the FTIR spectra of both forms of APP. The figure illustrated the presence of peaks corresponding to phosphates and ammonium: at about 1250 cm\(^{-1}\) for P=O bonds and at 1010 and 1060 cm\(^{-1}\) for P-O bonds. The band at 800 cm\(^{-1}\) characterized the bond P-O-P. The characteristic peaks of APP I at 760, 680, and 602 cm\(^{-1}\) were absent in the spectrum of APP II [54].

Figure 2.15: FTIR spectra of crystalline forms of APP I and APP II [55]

Phosphorous-containing FR such APP is particularly effective in materials having high oxygen content, such as cellulose. This is explained by the reaction shown below to describe their FR action. The APP is converted by thermal decomposition to phosphoric acid, which in the condensed phase extracts water from the pyrolysing substrate; thereby causing it to char. Lyons et al. [56] has described the individual reaction stages as follows:

According to equation 2.1 and 2.2, the thermal decomposition led to the formation of phosphoric acid. The mechanisms were assumed to hold true for all oxygen containing polymers (such as polyurethane and polyester).

\[
\text{R-CH}_2-\text{CH}_2-\text{O-P} \xrightarrow{\Delta} \text{R-CH=CH}_2 + \text{HOP}^{-}.
\]

Equation 2.1
The phosphoric acid formed according to equation 2.2 esterifies and dehydrates the cellulose and led to charring as shown in equations 2.3 and 2.4:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH} + \frac{\text{PO}_3\text{O}}{} & \rightarrow \text{CH}_2\text{CH}_2\text{O} - \frac{\text{PO}}{} + \frac{\text{POH}}{} \quad \text{Equation 2.3} \\
\text{CH}_2\text{CH}_2\text{OP} & \rightarrow \text{CH} = \text{CH} + \frac{\text{POH}}{} + \text{charring} \quad \text{Equation 2.4}
\end{align*}
\]

A second possibility of forming unsaturated compounds with subsequent charring was the acid-catalysed elimination of water from the cellulose (equation 2.5):

\[
\text{R} - \text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{R} - \text{CH}_2\text{CH}_2\text{OH}_2 \rightarrow \text{R} - \text{CH}=\text{CH}_2 + \text{H}_2\text{O} + \text{H}^+. \quad \text{Equation 2.5}
\]

### 2.7.1.3 X-ray diffraction of APP I and APP II

X-ray diffraction patterns of APP I and APP II are given in Table 2.6a and 2.6b respectively. The only crystalline impurities which were identified by X-ray patterns were APP II, cyanuric acid, and melamine cyanurate. Figure 2.16 showed that crystalline form APP I contained some impurities, unlike crystalline form APP II [55]. The impurities were ammonium carbonate and ammonium hydrogen phosphate. Crystalline form II had an orthorhombic structure with a_4.256 Å, b_6.475 Å, and c_12.04 Å. Form APP I had an orthorhombic structure with a_14.50 Å, b_21.59 Å, and c_4.85 Å [57].
2.7.2 Intumescent systems

Intumescents are substances that expand as a result of heat exposure thus increasing in volume and decreasing in density. Intumescent are endothermic to varying degrees, as they can contain chemically bound water [58]. An intumescent system is composed of three active agents: an acid agent, a carbon
source and a blowing agent (Table 2.7). Several reactions between these agents occur during the thermal degradation of the system which leads to the formation of an expanded carbonaceous char.

Table 2.7: Typical composition of an intumescent flame protection system

<table>
<thead>
<tr>
<th>Carbon supplier</th>
<th>Polyols as starch, pentaerythritol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid source</td>
<td>Ammonium polyphosphate</td>
</tr>
<tr>
<td>Expanding agent</td>
<td>Melamine</td>
</tr>
</tbody>
</table>

The carbonaceous char provides protection to the material or its support and limits the heat and mass transfers between the material and the flame and as a consequence insulates the material from the flame which results in fire proofing of the materials. The efficiency of the carbonaceous char is related to its ability to expand and form a multicellular structure and consequently to its physical properties during the intumescent process. One of the main aspects of intumescent char physical structure its uniformity and porosity [58]. The char can be dense or porous. The type of char depends on the way the intumescence develops, which is closely linked to its chemical transformation during heating. The expansion of an intumescent coating is due to the slow diffusion of the evolved degradation gases released into the degraded matrix as presented in Figure 2.17 [59].

![Figure 2.17: schematic representation of intumescent process [59]](image-url)
Typical intumescent process

1. Softening of the binding agent/polymer
2. Release of an inorganic acid
3. Carbonization of polyols
4. Gas production through expanding agent (melamine)
5. Swelling out of the mixture
6. Solidification through crosslinking reactions

There are some self-intumescent compounds that contain all three required functions in a single molecule (Figure 2.18). Such intumescent coatings can satisfy environmental and toxicity issues as the coatings are halogen-free and the decomposition gases are water and ammonia [60].

![Figure 2.18: Intumescent compounds [60]](image)

In an ideal situation, the volume of a char can be increased to 100 times the original in an intumescence process. During burning the substrate is thermally softened, that leads to the reaction medium.
2.7.3 APP:MH mixtures

The chemical reactions between APP and MH were studied by Castrovinci [5] to observe the thermally stable structure between the two fillers. This was shown by the curves of the weight difference, which put forward eventual interactions between APP and MH fillers.

The curves of the weight differences between the experimental and expected TGA curves were determined as follows [27]:

\[
\Delta[M(T)] = M_{\text{exp}}(T) - M_{\text{theo}}(T)
\]

Where \(\Delta[M(T)]\) is the curve of the weight difference, \(M_{\text{exp}}(T)\) is the TGA curve of the FR mixture (APP:MH), and \(M_{\text{theo}}(T)\) is the TGA curve calculated by a linear combination of the TGA curves of the pure APP and MH:ATH heated separately.

The \(\Delta[M(T)]\) curve enabled the observation of an ultimate increase or decrease in the thermal stability of the polymer related to the presence of the additive. Synergistic effects were represented by a positive \(\Delta[M(T)]\) value and a negative \(\Delta[M(T)]\) value represents antagonistic effects [27].

The TGA curve of 50 % mixture of APP:MH carried out was expected to show ammonia from APP and water from MH to evolve in the same range of temperature (300-500 °C) with a maximum rate at 396 °C, but instead three steps of weight loss were observed with maximum rates at 346, 431, and 455 °C (Figure 2.19).

![Figure 2.19: Calculated and experimental thermogravimetry curves for 50 % mixture of APP and MH [7]](image_url)
The first experimental weight loss step shown in Figure 2.17 (DTG, T\text{max} 346 °C) was due to ammonia and water evolution, whereas the other two steps (T\text{max} 431 and 455 °C) were overlapping with water evolution involved in the reaction. Figure 2.120 illustrates the evolution curves of ammonia and water which shows that the evolution of ammonia occurred at a low temperature, which was lower than expected (341 °C instead of 410 °C) due to the release of water from MH, causing the ammonia evolution equilibrium to shift to a lower temperature at which ammonia overcame electrostatic attraction by the proton of polyphosphoric acid in pure APP [7].

Figure 2.20: Lower part water (Δ) and ammonia (○) evolution curves [7]

The chemical reaction of MH hydroxyl groups with protons of polyphosphoric acid freed ammonia from the ammonium salt with formation of magnesium phosphate bonds, as shown in Figure 2.21 [7].

Figure 2.21: Reactions during thermal degradation of APP:MH 50% mixture. APP and MH interact to form magnesium phosphate bonds [7]
The thermal dehydration of MH (430 °C) was partially replaced by a chemical reaction with APP that led to elimination of water at 320 °C. The weight loss step at $T_{\text{max}}$ 431 °C involving the release of water showed a shoulder in the water evolution curve, which was due to the dehydration of unreacted MH occurring in the same temperature range as on heating the pure MH. Large water evolution was observed at 462 °C, which was explained as the water elimination from the basic magnesium phosphate moieties formed by the partial neutralization of MH by APP (Figure 2.20). This interpretation in the agreement with decreasing significance of water elimination from unreacted MH at 385 °C and 431 °C with increasing content of APP (40, 50 and 70 % respectively) [7].

At 650 °C the experimental weight loss was higher than expected and above 650 °C the weight loss was lower than expected because of the presence of MH that led to the formation of magnesium phosphate, which prevented the volatilisation of phosphorus moieties derived from highly crosslinked phosphoric acid (ultraphosphate) thermal decomposition above 650 °C [7, 61].

### 2.7.4 APP:ATH mixture

The thermal degradation of ATH occurred in a lower temperature range than the ammonia and water elimination in pure APP. During the thermal degradation of APP:ATH mixture, a competitive reaction mechanism occurred between the thermal and chemical degradation of ATH, which in the case of MH was shifted to the higher temperature of MH thermal degradation compared with ATH. The acceleration of ammonia evolution from APP was less effective with ATH because the dehydration to Al$_2$O$_3$ led to the loss of ATH basic properties on heating [5, 61].

$T_{\text{max}}$ for ammonia evolution from APP decreased when APP:ATH ratio was increased (>1) causing a shift in the competitive reaction mechanisms in favour of chemical reaction between APP and ATH in comparison with ATH thermal dehydration. The $T_{\text{max}}$ of APP:ATH mixture with 70:30 ratio was found to be 400 °C compared with the pure APP which was 450 °C [5, 61].

ATH water evolution occurred at 336 °C, which was not affected in the presence of 50 % APP whereas when APP was increased to 70 % two steps were obtained with $T_{\text{max}}$ of 315 and 490 °C. In the stage at lower temperature, water was
eliminated by chemical reaction between APP and ATH at temperatures similar to those observed in APP:MH mixture. Dehydration at high temperature involved thermal degradation of the basic aluminium polyphosphate that occurred with a mechanism similar to that of MH [5].

Experimental and calculated curves (Figure 2.22) of the APP:ATH mixture with 50 wt% showed a different behaviour. The TGA curve showed a weight loss higher than the calculated curve on the basis of the behaviour of APP and ATH heated separately between 300 and 570 °C. Whereas a lower weight loss was observed in the experimental TGA above 570 °C than in the calculated curve. It was found that in ATH a reaction developed between thermal dehydration and chemical elimination of water by reaction with APP which depended on ATH:APP ratio [5].

![Figure 2.22: a) Thermogravimetric mass loss and b) derivative curves of 50 wt% mixture of APP:ATH [5]](image)

Figure 2.23, shows the evolution of ammonia that occurred at a lower temperature than expected (338 °C instead of 400 °C). As described earlier (APP:MH mixture) this was due to the basicity of ATH, that shifted ammonia evolution equilibrium at a temperature lower than that at which ammonia overcame electrostatic attraction by the protonation of polyphosphoric acid in pure APP.
The chemical reaction of ATH hydroxyl groups with protons of polyphosphoric acid freed ammonia from the ammonium salt with formation of APP bonds (Figure 2.24) [5].

Figure 2.23: Lower part water and ammonia evolution curves [48]

Figure 2.24: Reaction occurring between APP and ATH during heating to 800 °C a 50 wt% mixture of APP:ATH [5]
During the thermal degradation of APP:ATH compound a mixture of thermally stable aluminium orthophosphate (AlPO₄) and aluminium metaphosphate ([Al-(PO₃)₃]ₙ), a trivalent cation long chain polyphosphate, was obtained at 800 °C as shown by X-ray diffraction pattern of Figure 2.25 [5].

Reactions shown in Figure 2.24 illustrate the formation of the APP that suppressed volatilisation of phosphorous, which might explain the thermal behaviour of the APP:ATH mixture above 570 °C as compared with the calculated curve. The interaction between ATH and APP led to a larger elimination of ammonia and acidic OH from APP than when it was heated alone. Furthermore, water elimination was hindered from OH groups isolated in the crosslinked ultraphosphate structure. Moreover, water and ammonium diffusion in the glassy ultraphosphate might be hindered, whereas direct APP:ATH reaction resulted in a more complete ammonia and water elimination than that calculated between 270 and 570 °C. The formation of crystalline Al-P-O compounds, disrupting the continuity of ultraphosphate, allowed gases to leave easily from the solid phase [5].

The effect of ATH on a surface protection from fire for a styrene butadiene rubber (SBR) provided by APP showed that the presence of a suitable amount of APP
(10 wt% or 12 wt%) led to the formation of an inorganic continuous shielding structure based on the viscous crosslinked structure of ultraphosphate [5]. At low loading (3-5 wt%) APP had negligible effect on SBR combustion behaviour, while increasing the amount of APP over 15 wt% an apparent combustion promoting effect on SBR that took over ultraphosphate protection, was observed. The presence of as little as 1 wt% of ATH led to the formation of ceramic, crystalline and thermally stable particles of APP dispersed on the surface of the polymer matrix [5].

2.8 Boron-Containing Flame Retardants

Boron-containing compounds can become active in the condensed phase, and, in several cases, in the gas phase as well. A major application of borates was the use of mixtures of boric acids and borax as FR for cellulose. Boron-containing compounds acted by endothermic, controlled release of water and formation of a glassy coating protecting the substrate [62].

2.8.1 Zinc borate

Several crystalline structures of zinc borate are known but few find industrial uses in significant amounts. Zinc borates are multifunctional FR, they can provide many of benefits in FR polymer systems, such as synergist of most halogen sources, and they are synergists of both chlorine and bromine-containing FR. Their efficiency depends on the type of halogen source (aliphatic versus aromatic) and the base polymer used. In certain polymers and in the presence of halogen source, zinc borates can display synergistic effects with antimony oxide in fire retardancy [52].

In comparison with antimony oxide, zinc borates are predominately a condensed phase FR and can function as smoke suppressants. In addition they can act as after glow suppressants due to the presence of B$_2$O$_3$ moiety in zinc borate. Zinc oxide moiety in zinc borate promotes the char formation with halogen sources; and B$_2$O$_3$ moiety stabilises the char [8].
2.9 Different Forms of Zinc Borates

The performance of different synthetically made zinc borate commercialised under the brand name Firebrake: FBZB (2ZnO•3B₂O₃•3.5H₂O), FB415 (4ZnO•B₂O₃•H₂O) and FB500 (2ZnO•3B₂O₃) were studied. Each of these compounds could be prepared selectively by reactions of zinc oxide with boric acid in water. The specific product was obtained by adjusting the ratio of B₂O₃:ZnO and temperature [6].

Zinc borate can be divided into two categories, anhydrous (2ZnO•3B₂O₃) and hydrated. Hydrated borates account for most boron-containing minerals and synthetic borates consumed by industry have structures containing B-OH groups (hydroxyl-hydrated borates) and may contain interstitial water. It was reported [6] that there are at least eight crystalline forms of the hydrated zinc borates, these had compositions 4ZnO•B₂O₃•H₂O, ZnO•B₂O₃•~1.12H₂O, ZnO•B₂O₃•2H₂O, 6ZnO•5B₂O₃•3H₂O, 2ZnO•3B₂O₃•7H₂O, ZnO•3B₂O₃•3H₂O, 3ZnO•5B₂O₃•14H₂O and ZnO•5B₂O₃•4.5H₂O. The anhydrous zinc borate is recommended for use in engineering polymers processed at above 300 °C which is the upper limit of the zinc borate (2ZnO•3B₂O₃•3.5H₂O) [6].

Hydrated zinc borate (2ZnO•3B₂O₃•3.5H₂O) (same as 2ZnO•3B₂O₃•3H₂O) [63] undergoes 3 molar equivalents water loss, forms an amorphous zinc borate and boron oxide that improves the strength of residue, softening over a broad temperature range. 2ZnO•3B₂O₃•3.5H₂O consists of a network of infinite polytriborate chains co-ordinated with zinc centres, with hydrogen bonding existing between hydroxyl groups is shown in Figure 2.26.

Figure 2.26: A segment of the infinite polytriborate chains in (2ZnO•3B₂O₃•3.5H₂O) [63]
2ZnO•3B₂O₃•3.5H₂O shown in Figure 2.27 is the most widely used among all of the known zinc borates; it has been used extensively in PVC, polyamides, epoxy resins, polyolefin, and elastomers [64].

![Proposed molecular structure of zinc borate](image)

Figure 2.27: Proposed molecular structure of zinc borate [64]

Borate compounds exhibit considerable structural variability, having spatial arrangements directed by the demands of interstitial cations. Hydrogen bonding plays an additional important role in integrating and stabilising the structures. Borates differ from other oxide materials, such as aluminates and silicates, in which the main group element oxide components play a role in directing the structure.

### 2.9.1 APP:zinc borate mixture

The thermal behaviour of a mixture containing APP and zinc borate (2ZnO•3B₂O₃•3.5H₂O) was investigated by Samyn [52] and the interactions between the two fillers were examined by TGA. The thermal degradation of APP:zinc borate mixture of different ratios showed that the addition of zinc borate in APP enhanced the thermal stability as a function of the zinc borate content. The
author described the mechanism of the degradation of the APP:zinc borate mixture as follows: at 260 °C, the two components did not react. The mixture appeared as a slightly brown powder that indicated the degradation of APP had just began as shown in Equations 2.6 and 2.7; zinc borate did not show any changes occurred.

\[
\text{[NH}_4\text{PO}_3\text{]}_n \to [\text{HPO}_3\text{]}_n + n\text{NH}_3 \quad \text{Equation 2.6}
\]

\[
[\text{HPO}_3\text{]}_n + \text{Carbon source} \to \text{[BPO}_4\text{]} + \text{H}_3\text{PO}_4 \quad \text{Equation 2.7}
\]

From 290 °C the degradation of zinc borate started as described in Equation 2.8 leading to an amorphous product [52].

\[
2\text{ZnO}, 3\text{B}_2\text{O}_3, 3\text{H}_2\text{O} \to 2\text{ZnO}, 3\text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \text{Equation 2.8}
\]

Then the different TGA analysis measured proved that the reaction between the degradation products of APP and zinc borate occurred between 300 and 415 °C leading to the formation of boronphosphate (BPO₄) species (Equations 2.9 and 2.10) [52].

\[
10[\text{HPO}_3\text{]}_n + 2\text{ZnO}, 3\text{B}_2\text{O}_3
\]
\[
\quad \to 6\text{BPO}_4 + (n - 6)/4\text{P}_4\text{O}_{10} + 2\text{ZnO} + n/2\text{H}_2\text{O} \quad \text{Equation 2.9}
\]

\[
10\text{H}_3\text{PO}_4 + 2\text{ZnO}, 3\text{B}_2\text{O}_3
\]
\[
\quad \to 6\text{BPO}_4 + \text{P}_4\text{O}_{10} + 2\text{ZnO} + 15\text{H}_2\text{O} \quad \text{Equation 2.10}
\]

At 580 °C zinc phosphates was formed from a reaction between zinc oxide and P₄O₁₀ as shown in Equation 2.11 [52].

\[
3\text{ZnO} + 0.5\text{P}_4\text{O}_{10} \to \text{Zn}_3(\text{PO}_4)_2 \quad \text{Equation 2.11}
\]
2.9.2 The action of zinc borate in EVA: metal hydroxides systems

Zinc borate act as synergists when substituting partially metal hydroxides in thermopolymers. Poly(ethylene-co-vinyl acetate) (EVA) filled by 60% of different ratios of MH:zinc borate (2ZnO•3B2O•3.5H2O/ 4ZnO•B2O•H2O) was studied by cone calorimetry [6, 65]. HRR results of different EVA19-based formulations (with 19% vinyl acetate (VA) content) showed that the peak of HRR in time and intensity (HRR peak = 185 kW•m⁻² at 80 s) is not modified upon incorporating zinc borate. Time to ignition (TTI) was unchanged [66]. Bourbigot [6] has reported that the effect of zinc borate (4ZnO•B2O•H2O) was revealed at longer times, when the second peak of HRR appeared, whereas for zinc borate (2ZnO•3B2O•3.5H2O) the second HRR peak was slightly decreased in which it spread over time similar to the formulations with out zinc borate that could be due to the low dehydration temperature of 2ZnO•3B2O•3.5H2O (290 °C) compared with that of 4ZnO•B2O•H2O (415 °C).

A study of a halogen-free system [67] showed that partial replacement of ATH with zinc borate (2ZnO•3B2O•3.5H2O) in EVA can favourably alter the oxidative-pyrolysis of the base polymer, as was shown by a decrease in the exothermicity in the oxidative pyrolysis range and a delay of the peak oxidative-pyrolysis weight loss rate. The combination of ATH and zinc borate formed a porous and ceramic-like residue at temperature above 550 °C. This residue was an important thermal insulator for the unburned, underlying polymer (Figure 2.28).

Clerc and Zhang studied the fire performances by cone calorimetry that showed the partial substitution of ATH with zinc borate led to a decrease in the HRR, increase in TTI, and a delay in the degradation of a protective surface structure. The use of zinc borate in conjunction with red phosphorous and ATH in polyolefin showed a synergy for this combination as was evidenced by limiting oxygen index (LOI) test results [62, 68].
Shen et al. [64], has found that the use of zinc borate alone in EVA resulted in the formation of a glassy residue as shown in the scanning electron microscopy (SEM) (Figure 2.29).

Figure 2.28: SEM (6000X) of residues of air-pyrolysis of EVA containing zinc borate (2ZnO•3B2O•3.5H2O) (33 %) and ATH (33 %) [64]

Figure 2.29: SEM (6000X) of residues of EVA containing the zinc borate (2ZnO•3B2O•3.5H2O) [64]
Co-polymer EVA:MH formulation study [6, 64] revealed that zinc borate can form a synergistic mixture where both fillers (MH and zinc borate) enhance the effect of the other. The transformation of MH to MgO led in the first step of degradation to a decrease in the temperature of the substrate, causing an increase in TTI of the material. In addition the second degradation step resulted in the formation of a protective MgO-based ceramic [66]. Zinc borate played the role of a flux agent in the formation of the MgO-based ceramic, this material formed at the surface of the substrate which then functioned as a physical/thermal barrier that caused a slow degradation of the polymeric matrix and reduce the flow of the flammable molecules.

### 2.9.3 The action of zinc borate in PVC-based formulation

Zinc borate in halogen-containing systems, such as poly(vinyl chloride) (PVC) led to an increase in the amount of the char formed during the polymer combustion. Zinc borate can react with hydrogen halide, released from the thermal degradation of a halogen source, to form zinc chloride, zinc hydroxychloride, boric oxide, water and a small amount of boron trichloride. The zinc species remaining in the condensed phase can alter the pyrolysis by catalysing dehydro-halogenation and promoting crosslinking between polymer chains, resulting in increased char formation and decrease in both smoke production and flaming combustion. The release of boric oxide, a low melting glass, can stabilize the char and inhibit afterglow through glass formation. The water release between 290-450 °C (accompanied by an endothermicity of 500 J·g⁻¹) can promote the formation of a foamy char [69].

Other boron compounds, such as barium metaborate or calcium borate, show negligible FR activity. Boron compounds are likely to be active in the solid phase by forming a glassy coating and in oxygen-containing substrates by simultaneous, pronounced charring [70].

Antimony trioxide-metal borates (barium, calcium, and zinc borate) were found to be good smoke reducers. Zinc borate showed the best effect with regards to flame retardancy and reduced smoke development of PVC [71]. These additives are used as fillers and therefore added in larger quantities; this resulted in dilution of the PVC, and further reduction of PVC smoke density [71].
Ning [72] studied the effect of zinc borate \((2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O})\), ATH and their mixture on the FR and smoke suppressant properties of PVC through the LOI. The results showed that LOI of PVC increased and the smoke density decreased with increasing zinc borate, ATH, and zinc borate:ATH content. The LOI of PVC:zinc borate:ATH was much higher than that of PVC:zinc borate and PVC:ATH. The smoke density of PVC:zinc borate:ATH was much lower than that of PVC:zinc borate and PVC:ATH, which indicated that zinc borate and ATH had a good synergistic effect on the FR and smoke density of PVC.

In addition the thermal decomposition temperature of PVC was reduced in the first step with the addition of a small amount of zinc borate and zinc borate:ATH whereas it increased the thermal decomposition temperature in the second step. According to investigation performed by Kroushi [73], the partial replacement of antimony oxide with the zinc borate can reduce the HRR, as well as carbon monoxide production at a heat flux of 35 kW\(\cdot\)m\(^{-2}\).

### 2.10 Mineral for Enhancement of Mechanical Properties

The mineral fillers used in polymers can be beneficial for several reasons associated with production; storage, processability, of polymer compounds and as means for enhancing the mechanical properties of polymer composites. The addition of hydrated fillers to the polymers may cause an increase in elastic modulus that is accompanied by a decline in the strength of the material. The magnitude of these effects may be significant, especially when filler levels are high, potentially limiting the application of the material. The degree of interfacial adhesion at the boundary between the polymer and the filler has critical bearing on the ability of a particulate composite to resist crack propagation.

Mineral fillers such as talc, kaolin, calcium carbonate (CaCO\(_3\)) and mica are often used to enhance the FR properties with subtle changes in stability of composites. The minerals act by forming a diffusion barrier that is able to limit the transfer of degradation products from the solid phase [68].
2.10.1 Talc

Talc is a natural, hydrated silicate with the formula $[\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}]$. Talc occurs in four particle shapes: fibrous, lamellar, needle shaped and modular (steatitic); however, only the lamellar form is used in commercial applications (Figure 2.30). The basic constituent of talc, the oxide and hydroxides of magnesium, exist as a sandwich between two silicon oxide layers. This imparts to each lamella a certain degree of water repellence and high chemical inertness.

![Figure 2.30: Structure of talc with silica tetrahedron and the magnesia octahedron positions](image)

Talc is an important industrial mineral used for reinforcement and improved mechanical performance. The mechanical properties e.g. tensile or elongation properties are dependent on talc content and compatibility between the polymer and talc. Improvement in interfacial adhesion between talc and the polymer can be achieved with compatibilising components enabling improved dispersion [74]. There are several advantages in the use of talc in polymer composites to improve their properties such as increase in stiffness, flexural modulus and torsion modulus, increase in flexural strength, reduction in creep and at elevated temperatures talc provides improvement in the bend-creep modulus, improvement in the heat deflection temperature and in dimensional stability, improvement in shrinkage warpage, combined at the same time with a lower coefficient of thermal expansion, improvement in the thermal conductivity, and finally increase in the surface hardness of molded parts [75].
2.10.1.1 Use of talc in thermoplastics

The structure and properties of polypropylene:talc (PP:talc) composites, the dependence of tensile strength, initial modulus and elongation at break of various specimens were investigated by Wu [75]. The investigation showed that PP gave mechanical properties, i.e. a tensile strength of about 24 MPa, a Young’s modulus of 380 MPa and an elongation at break of about 1300 %, with introducing high amount of talc the elongation value exhibited a monotonic decrease, which was consistent with the general observation found in polymer–inorganic filler composite systems [76].

Adding a small amount of talc had a positive effect in improving the mechanical properties of the whole composite. When talc content was lower than 14 %, both the tensile strength and the Young’s modulus increased. This indicated that the composite was reinforced and toughened. For composites with talc contents from 14 to 50 %, the Young’s modulus increased from 420 to 1250 MPa [76]. A dramatic change in the Young’s modulus was observed where the weight fraction of talc was about 50 %. The Young’s modulus decreased and may be attributed to high filler loading. A high content of talc resulted in a poor dispersion and a discontinuous PP phase as observed from changing morphology from low to high content (Figure 2.31) [75].
Talc had been incorporated into EVA containing mineral FR formulations with the aim of finding synergies in the flammability properties [4]. The results showed that the first step in the thermal degradation of EVA was delayed in the presence of talc and it was assumed that this behaviour was due to the talc lamellar character, which could build a layer acting as a mass diffusion barrier for volatile combustible compounds issuing from the degraded polymer [77].

Talc was combined with brominated FR:antimony trioxide blends in a polypropylene:polyethylene (PP:PE) copolymer at constant total loading...
(40 wt%). It was observed that 50 % of the brominated blend could be replaced by talc without significant loss of FR properties and with an improvement in the stiffness and maximal tensile stress of the filled copolymer [4].

2.10.2 Kaolin

Kaolin is hydrated aluminium silicates $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ possessing a determinable crystal lattice with a plate-like, hexagonal structure [15]. Each sheet within the kaolin structure is comprised of a layer of silica tetrahedra (silicon, each of which is surrounded by four oxygen ions), and a layer of aluminium octahedra (aluminium ions, each of which is surrounded by 6 oxygen or hydroxyl ions) (Figure 2.32). Kaolin generally possesses a high degree of whiteness, non-conductor of electricity, high resistance to chemicals and has good resistance towards strong acids [27].

![Figure 2.32: Structure of kaolinite layer [27]](image)

2.10.2.1 Use of kaolin in thermoplastics

Kaolin is frequently used in thermosetting compounds, such as unsaturated polyester premix (UP premix), bulk molding compounds (BMC) and sheet molding compounds (SMC) [15]. In thermoplastics, kaolin was used, as filler for wire insulating materials, since it improved the electrical properties. Kaolin contributed to an improvement in chemical resistance as well as to a reduction in
water absorption. It lowered the crack propagation tendency in the end product and improved shock resistance and surface quality. The lamellar structure additionally resulted in an improvement in the surface hardness of the finished products. Fellahi [78] has reported that the modulus and strength of a kaolin-filled epoxy resin increased with increasing filler loading but the elongation at break and impact properties were decreased. Kaolin has a platelet structure and a high aspect ratio, the particle size and distribution are very important in determining the mechanical properties of the polymer composites. Abu Bakar [79] used surface treated kaolin to improve the mechanical properties of polypropylene:metallocene polyethylene (PP:mPE) blend. The results showed that surface treated kaolin-filled PP could enhance low temperature impact toughness in comparison with an unfilled blend. This revealed that the surface-treated kaolin had a significant filler-polymer interfacial adhesion, and kaolin particles were dispersed in a lamellar form in the kaolin-filled PP:mPE matrix. This was may a reason that the kaolin-filled PP:mPE blend exhibited better impact performance at a low temperature [79].

2.10.3 Calcined kaolin
Calcined kaolin is harder than natural kaolin, but improves the electrical properties in polymers (e.g. high dielectric PVC). Kaolin is obtainable with various silane coatings that facilitate dispersion of the filler in the polymers. The behaviour of kaolin on heating depends on their structure, crystal size and degree of crystallinity. After the removal of absorbed water at just over 100 °C, kaolin decomposed above 500 °C, losing its hydroxyl groups as water. At higher temperatures (>900 °C), the kaolin (metakaolin) underwent further reactions to form crystalline compounds, the end products being free silica and mullite (Figure 2.33) [80].
The transformation of kaolin to metakaolinite resulted in the loss of structural hydroxyl groups. Differential thermal analysis (DTA) study of kaolinite has been performed by varying packing density and rate of heating [80]. Both these two parameters influence the intensities of both endothermic and exothermic peaks related to the dehydration, dehydroxylation and crystallisations of Al-Si spinel, mullite and cristobalite phases [80]. The DTA curve in Figure 2.34 shows the endotherm of the conversion to the new crystalline phase of metakaolinite. Transmission electron microscopic (TEM) evidence indicated that it was not an amorphous oxide mixture, but retained a crystalline order from the original kaolin [81].
Mullite formation in kaolin showed two high temperature exotherms. It was concluded that there were two simultaneous ways of mullitization instead of a single solid-state reaction process as shown below [74, 81]:

\[
\text{Metakaolinite} \xrightarrow{\text{980 °C}} \text{first exotherm} \quad \begin{array}{l}
\text{i) Al-Si sinel phase (20-30 wt\%)} \\
\text{ii) Mullite (weakly crystalline, trace)} \\
\text{iii) Aluminosilicate phase (amorphous, 30-40 wt\%)} \\
\text{iv) SiO}_2 \text{ (amorphous, \sim 36 wt\%)}
\end{array}
\]

Kaolin changes to mullite ultimately by three separate transformation steps. The sequence of transformation is shown schematically in Figure 2.35. The amorphous silica phase formed from decomposition of metakaolinite at the first exothermic peak temperature finally crystallized beyond 1400 °C [81].
2.10.3.1 Kaolin ion exchange
Ion-exchange is one of the important processes which control the distribution of elements between solution and particulate phases. Although kaolin exhibits the least exchangeability among clay minerals, several studies have confirmed the potential of natural kaolin for the adsorption of metal ions from solution. O’Day et al. [82] observed that Co(II) was bound to the kaolin as co-complexes (both inner and outer sphere complexes) using X-ray diffraction pattern.

2.10.4 Calcium carbonate
CaCO₃ has three polymorphs: calcite, aragonite, and nahcolite (Figure 2.36). Calcite is thermodynamically the most stable form at room temperature and pressure, with promising industrial (plastic, rubbers, papers, and paints), implants, and bio-optoelectronics applications. Aragonite is metastable, transforming to calcite at 300-400 °C in biogenic samples, and at 660-751 °C as fast transformation in natural crystals [83].
2.10.4.1 Use of calcium carbonate in thermoplastics

CaCO$_3$ is one of the most commonly used inorganic fillers in thermoplastics, such as PVC and PP [84]. The enhancement of strength in CaCO$_3$-filled composites is minimal. This might be due to the lack of surface interactions between the filler and the polymer. Various attempts have been made to improve the surface interactions of CaCO$_3$ such as the use of stearic acid, titanate, and silane coupling agent. Leong [85] has pointed out several requirements needed to be met to enhance the toughness mechanism:

- The dispersion of the filler particles must be sufficiently good to prevent the creation of stress concentration points caused by agglomerated particles,
- Polymer-filler de-bonding must occur to allow unhindered plastic deformation around the particles, thereby increasing the ductility of composites.

CaCO$_3$ frequently used in thermoplastics leading to improvements in their properties: such as increasing the impact strength, high surface gloss in the finished product, good elongation at break, tear propagation resistance and tensile
strength, high modulus of elasticity, good weathering resistance, reduced shrinkage, improved stability and aging resistance, and non-toxic with heat resistance up to 600 °C [76].

The properties of low density polyethylene (LDPE) were modified by addition of CaCO3 [76, 86]. Low specific heat and high thermal conductivity of the filled LDPE resulted in higher throughput during extrusion and injection molding. Hardness, stiffness, heat deflection temperature, slip resistance and resistance to stress cracking increased; weldability, printability and anti-blocking properties were improved. Melt index, shrinkage and elongation, as well as water vapour and oxygen permeability decreased. CaCO3 had no adverse influence on the photooxidation of films and enabled reduction to be made in the titanium dioxide content [86].

Studies showed that CaCO3 as fillers in PP are in many respects distinguished by the same advantages as talc [85]. Although the same high stiffness was not obtained at the same degree of filling, impact strength was appreciably higher. However CaCO3 possessed the following advantages over talc: easier dispersibility, higher melt index, completely free from asbestos, better surface of finished parts, suitable for contact with food, lower abrasion in processing machines. In injection molding, the use of CaCO3 resulted in products with higher stiffness and dimensional stability at shorter cycle times (higher thermal conductivity). In PP films, the filler improved the deep drawing properties [87].

PA-6 filled with CaCO3 lowered the raw material price and was used in applications in the electrical, household appliance, washing machine and automobile sectors where good dimensional stability without shrinkage problems were desired. Molding compounds filled with CaCO3 were distinguished by a good surface quality, high heat deflection temperatures, good stiffness and toughness, as well as resistance to many solvents, fuels, oil, and fats [79].

2.10.4.1.1 The mechanical properties and interfacial interactions in talc, kaolin, and CaCO3 filled polymer

The three types of mineral fillers, talc, kaolin and CaCO3 (10-40 wt% filled loading) were compounded with polypropylene (PP) using a twin screw extruder were investigated by Leong [85]. The results showed that in most cases, the strength and the stiffness of the talc-filled PP composites was significantly higher
than those of the CaCO$_3$ and kaolin-filled PP composites. However, CaCO$_3$ being a non reactive filler, increased the toughness of PP. The kaolin-filled PP composites also showed some improvement in terms of strength and stiffness, although the increase in these properties were not as significant as those of the talc-filled PP composites [85]. The effects of the interfacial reaction between the filler and the PP on the mechanical properties were evaluated with semiempirical equations. The nucleating ability of all three fillers was studied with differential scanning calorimetry (DSC), and the strongest nucleating agent of the three was talc, followed by CaCO$_3$ and kaolin [85]. This research evaluated the exothermic crystallisation peaks of unfilled PP and filled PP composites at 30 wt% filler (talc, kaolin, and CaCO$_3$) loadings using DSC. They found that on the basis of the decreasing height of the peaks for filled PP with respect to unfilled PP, it appeared that the incorporation of the fillers reduced the crystallinity of PP [85].

As the filler content increased, the PP mass fraction decreased proportionately, and only the PP component contributed to the crystallisation peak. The study showed that both the onset temperature ($T_o$) and the crystallisation temperature ($T_c$) increased with incorporation of fillers into the PP matrix [85]. The increase in these temperatures could be attributed to the formation of nuclei at an earlier stage and at a higher temperature during the cooling process.

Researchers [76, 85], concluded that all the fillers used have nucleating effects on the PP matrix, the strongest nucleating agent was talc and the weakest was kaolin. Strong nucleation would modify and change the crystalline structure of PP from $\beta$ spherulites, which were weaker, into the stronger $\alpha$ form. The composite obtained a higher modulus, better dimensional stability, and increased strength with an increase in the polymer matrix crystallinity. Therefore, the larger increase in strength for the talc-filled PP composite was partly due to increased crystallinity of the polymer matrix. The effect of crystallinity on the mechanical properties of CaCO$_3$- and kaolin-filled PP composites, however, was minimal, as both these fillers showed only weak nucleating abilities in comparison with talc. Therefore, the mechanical properties of these composites must be affected by other factors [85].

In addition the study showed a significant and almost linear improvement in the modulus of PP observed, especially for talc-filled PP [79, 85]. Figure 2.37 shows the tensile modulus of talc-, CaCO$_3$-, and kaolin-filled PP composites, which
indicated that the tensile modulus had only a very weak dependence on the specific surface area and particle shape of the fillers. This was due to the fact that the modulus was measured before any significant plastic deformation took place and so this did not take into consideration the interaction between the fillers and the polymer matrix. The increase in the modulus of PP could only be caused by [85]:

1. The substitution of PP by the largely more rigid filler and
2. The filler restricting the mobility and deformability of the matrix by introduction of a mechanical restraint.

Figure 2.37: Effect of the filler loading on the tensile modulus of talc-, kaolin-, and CaCO₃-filled PP composites [85]

CaCO₃-filled PP, showed a reduction in strength was observed with increasing filler loading. The initial increase in strength for talc- and kaolin-filled PP composites was mainly due to good filler-matrix interactions, largely due to the platy nature of the fillers. Platy fillers have high aspect ratios, and this increased the wettability of the fillers by the matrix, thus creating fewer microvoids between the fillers and matrix. Increased filler–matrix interactions enabled more stress to be transferred from the matrix to the fillers during external loading. The results suggest that the filler–matrix interactions were strongest for talc-filled PP, followed by those for kaolin-filled PP composites and CaCO₃-filled PP composites [79].
2.10.5 Mica

The lamellar reinforcement mica is obtained from the minerals muscovite (\(K_2\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_4\)) or phlogopite (\(K_2(\text{MgFe}^{2+})_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH,F})_4\)). Mica has a density of 2.8 g cm\(^{-3}\). The structure of muscovite mica (Figure 2.38) is composed of layers of octahedrally coordinated Al ions between inward facing (Si, Al)-O sheets; the later being made up of linked 6-membered rings of (Si, Al)-O tetrahedral [88].

![Figure 2.38: Scheme of muscovite mica structure [88]](image)

Mica used in thermoplastics showed the following improvements: high stiffness, high dimensional stability, good electrical properties, and good dimensional stability under heat [89].

Mica was used in the automobile industry as an inexpensive substitute for glass fibres in polypropylene parts. Mica addition increased stiffness, ductility, and high-heat dimensional stability in polymers, and improved resiliency in rubber. A limiting factor for its utility is the ability of mica flakes delaminating from nonpolar materials under shear. Poor adhesion of mica to nonpolar substrates was due to its hydrophilicity. The interaction with hydrophobic matrices might be significantly improved by changing the polarity of the surface of the mica sheets, for example by exchange of the natural alkali ions against alkylammonium ions of a certain length. Then the mica surface is rendered nonpolar and the interfacial free energy with the adjoining organic polymeric material is strongly reduced [89].
CHAPTER 3: EXPERIMENTAL

3.1 Introduction

In this chapter, the various materials and preparations of FR polymer composites based on PVAc and acrylic emulsion systems are described. The investigation of materials was conducted by thermogravimetry (TGA), Fourier transform infrared (FTIR) spectrometry, X-ray diffraction, cone calorimeter fire test, scanning electron microscopy (SEM) and mechanical property testing.

3.2 Materials and Methods

3.2.1 Polymers

Poly(vinyl acetate)

The raw material poly(vinyl acetate) (PVAc) (Acropol 63-075) was obtained from Nuplex Industries (Aust.) Pty Ltd in the form of an emulsion of the polymer with 55 % homopolymer and 0.5 % vinyl acetate content. The specific gravity was 1.00 (water = 1).
Butyl acrylate methyl methacrylate co-polymer

Butyl acrylate methyl methacrylate co-polymer (BAMMA) (Texicryl 17-0246) was obtained from Nuplex Industries (Aust) Pty Ltd in the form of an emulsion polymer. The acrylic co-polymer contained 70 % homopolymer with 0.5-2 % ammonia content.

3.2.2 Minerals and fire retardants

The properties of the mineral fillers and the FR used in this project are listed in Table 3.1. The calcined kaolin was obtained from Burgess Pigment Company, Sandersville, GA, USA. The talc was obtained from Unimin Australia Ltd. The magnesium hydroxide (Magnifin 10HA) (MH) was obtained from Magnesiaprodukte GmbH and Co KG, Germany. Aluminium trihydroxide (Hydral 710) (ATH) was obtained from Almatis, Inc, USA, is has a reflective index of 1.57, and Mohs hardness of 2.5-3.5. Ammonium polyphosphate (FR CROS 484) (APP) was obtained from Budenheim Iberica, Spain; it is a crystalline phase II ammonium polyphosphate, it is nearly insoluble in water and completely insoluble in organic solvents. The P<sub>2</sub>O<sub>5</sub> content is approximately 72 % and N content is approximately 14 %. Calcium carbonate (CaCO<sub>3</sub>) was obtained from Omya-Southern Pty Ltd.

The zinc borate (Firebrake FB) was obtained from US Borax. Mica (MT60C) is muscovite mica manufactured by MinTech International, Bloomington, IN, USA. The MT60C grade is coarse and greater than 90 % is retained on a 100 mesh (150 μm) screen, 99 % is retained on a 240 mesh (63 μm) screen. A high softening temperature (Tg = 800 °C) glass frit (Glass #8 KMP4103) was obtained from Ferro Corporation, Australia. The softening temperature of the glass frit is defined as the temperature at which it has a viscosity of 10<sup>7.6</sup> dPa.s.
Table 3.1: Property data of the minerals and fire retardants examined.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density g•cm⁻³</th>
<th>Mean particle diameter (µm)</th>
<th>Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>2.79</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Kaolin</td>
<td>2.59</td>
<td>3.0</td>
<td>95</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>2.7</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>2.8</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>ATH</td>
<td>2.42</td>
<td>3.0-12.00</td>
<td>100</td>
</tr>
<tr>
<td>MH</td>
<td>2.4</td>
<td>1.4-1.8</td>
<td>99.8</td>
</tr>
<tr>
<td>Zinc borate</td>
<td>4.0-5.0</td>
<td>8-20</td>
<td></td>
</tr>
<tr>
<td>APP</td>
<td>1.95</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

The Comparison of properties of MH and ATH, and their physical and chemical properties are shown in Table 3.2. MH has a 100 °C higher decomposition temperature than ATH, allowing a higher processing temperature in compounding. MH adsorbs more energy than ATH during the decomposition process [90].

Table 3.2: Comparison of Properties of MH and ATH [90]

<table>
<thead>
<tr>
<th>Properties</th>
<th>MH</th>
<th>ATH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bound Water, %</td>
<td>31.0</td>
<td>34.6</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.36</td>
<td>2.42</td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.56 - 1.58</td>
<td>1.57</td>
</tr>
<tr>
<td>Initial Decomposition Temperature</td>
<td>330 °C</td>
<td>230 °C</td>
</tr>
<tr>
<td>Enthalpy of Decomposition</td>
<td>1377 J•g⁻¹</td>
<td>1171 J•g⁻¹</td>
</tr>
</tbody>
</table>

3.2.3 Preparation of fire retardant polymer composites

FR fillers were dispersed in the desired polymer matrix on a laboratory scale using the IKA-Werke stirrer Eurostar power control-viscosity model P4 with dissolver blade operating at ~290 rpm as shown in Figure 3.1. The maximum speed rate capability of the disperser is 530 rpm. The blade was immersed in the emulsion polymer matrix to prepare the FR polymer composites. The FR fillers were then added gradually in different weight fractions (Tables 3.3, 3.4 and 3.5)
to the polymer solution and dispersed for 8 to 10 min to obtain a uniform mix. When mixing was completed, the FR polymer mixtures were spread into Teflon based mould (3 mm) and dried at room temperature overnight followed by further drying under vacuum at 60 °C for 48 h.

Figure 3.1: IKA-Werke stirrer Eurostar
Table 3.3: Composition of the filled PVAc formulations using talc and kaolin minerals

<table>
<thead>
<tr>
<th>Composition</th>
<th>Polymer (wt%)</th>
<th>Talc (wt%)</th>
<th>Kaolin (wt%)</th>
<th>MH (wt%)</th>
<th>Zinc borate (wt%)</th>
<th>Glass frit (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PVAcK0.6</td>
<td>60</td>
<td>-</td>
<td>57</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcK0.5</td>
<td>50</td>
<td>-</td>
<td>57</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcK0.4</td>
<td>40</td>
<td>-</td>
<td>57</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcK0.3</td>
<td>30</td>
<td>-</td>
<td>57</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.6</td>
<td>60</td>
<td>57</td>
<td>-</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.5</td>
<td>50</td>
<td>57</td>
<td>-</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.4</td>
<td>40</td>
<td>57</td>
<td>-</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.3</td>
<td>30</td>
<td>57</td>
<td>-</td>
<td>24</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>PVAcK0.6NZB</td>
<td>60</td>
<td>-</td>
<td>57</td>
<td>34</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>PVAcK0.3NZB</td>
<td>30</td>
<td>-</td>
<td>57</td>
<td>34</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.6NZB</td>
<td>60</td>
<td>57</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>PVAcT0.3NZB</td>
<td>30</td>
<td>57</td>
<td>-</td>
<td>34</td>
<td>-</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 3.4: Composition of the filled BAMMA formulations

<table>
<thead>
<tr>
<th>Composition</th>
<th>BAMMA (wt%)</th>
<th>MH (wt%)</th>
<th>Zinc borate (wt%)</th>
<th>Talc (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAMMA 01</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BAMMA 02</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BAMMA 03</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>BAMMA 04</td>
<td>50</td>
<td>37.5</td>
<td>0</td>
<td>12.5</td>
</tr>
<tr>
<td>BAMMA 05</td>
<td>50</td>
<td>12.5</td>
<td>0</td>
<td>37.5</td>
</tr>
<tr>
<td>BAMMA 06</td>
<td>50</td>
<td>0</td>
<td>12.5</td>
<td>37.5</td>
</tr>
<tr>
<td>BAMMA 07</td>
<td>50</td>
<td>25</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>BAMMA 08</td>
<td>45</td>
<td>33</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>BAMMA 09</td>
<td>50</td>
<td>16.7</td>
<td>8.3</td>
<td>25</td>
</tr>
<tr>
<td>BAMMA 010</td>
<td>50</td>
<td>20</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>BAMMA 011</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3.5: Composition of the filled PVAc formulations

<table>
<thead>
<tr>
<th>Composition</th>
<th>Polymer (wt%)</th>
<th>CaCO₃ (wt%)</th>
<th>Talc (wt%)</th>
<th>APP (wt%)</th>
<th>ATH (wt%)</th>
<th>Kaolin (wt%)</th>
<th>Mica (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:CaCO₃</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:talc</td>
<td>50</td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:ATH</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:kaolin</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>PVAc:mica</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>50</td>
<td>37.5</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>50</td>
<td>12.5</td>
<td>37.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>50</td>
<td>20</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>50</td>
<td>37.5</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>50</td>
<td>12.5</td>
<td>37.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>50</td>
<td>20</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:Mica</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:ATH:CaCO₃</td>
<td>50</td>
<td>16.7</td>
<td>16.7</td>
<td>16.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Mica</td>
<td>50</td>
<td>18</td>
<td>12</td>
<td></td>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Kaolin</td>
<td>50</td>
<td>18</td>
<td>12</td>
<td>12</td>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Talc</td>
<td>50</td>
<td>18</td>
<td>20</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:ATH</td>
<td>50</td>
<td>18</td>
<td>12</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to measure change in the weight of a material as a function of temperature, or time whilst being subjected to a constant temperature. TGA consists of two major components: a sensitive ultramicrobalance and a furnace element (Figure 3.2). The microbalance used is sensitive, with mass detection to 0.1 μg, and a maximum capacity of 1300 mg. TGA operates on a null balance principle that is designed to use a servo-controlled torque motor to automatically compensate for weight changes in the material under investigation.

When a sample is placed in the sample pan, the beam that supports the sample pan deflects. A beam position detector measures the deflection with an optical sensor and uses a current to return the beam to its original position. The amount of current necessary to restore the beam is a direct measure of the weight on the beam. The current is amplified and filtered. The mass of a sample is continuously monitored as a function of temperature and time by balancing the force it exerts in the gravity of the earth. The measurement always relies on calibration by direct comparison with standard masses.

The sample pan is hanging from a wire that is attached to a microbalance. The pan is surrounded by a furnace whose temperature is accurately controlled. The microbalance covers a temperature range from 10 to 1000 °C and features a standard furnace sealing mechanism.

Figure 3.2: Perkin-Elmer TGA Series 7
TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite compositions. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample (as shown in Figure 3.3). The gases used to purge a material before or after analysis are usually N₂ or air.

3.2.4.1 Thermal stability

The thermal stability behaviour of the composites was measured using a Perkin-Elmer TGA7. Materials weighing 7-15 mg were placed in an open platinum pan that was hanging from the micro-balance inside the furnace. Analysis was performed from 30 to 800 °C at a heating rate of 10-20 °C·min⁻¹. A N₂ purge through the material chamber was implemented instead of oxygen to obtain a stable thermal environment because, during fire the oxygen will be used by the flame. The onset of degradation temperature, maximum degradation rate temperatures, and maximum rate of weight loss under N₂ atmosphere was determined. The maximum degradation rate temperature was found from the peak maxima in the derivative weight loss curve (DTG). Figure 3.3 is an example of a common TGA curve; it shows the thermal degradation of PVAc where it illustrate the steps of water release, acetic acid release, and the polyene residue degradation.

![Figure 3.3: Example of TGA curve of poly(vinyl acetate)](image)

Figure 3.3: Example of TGA curve of poly(vinyl acetate)
3.2.5 Particle size distribution

The particle size distributions (PSD) were measured using the laser beam scattering apparatus (Mastersizer X, Model MSX025A, Malvern Instruments Ltd., Malvern, U.K.). The laser beam was focused into a small volume (10-20 mg) of a dilute solution, which contains colloidal particles, and the scattering light under a particulate angle (90°) was collected. The phase and polarization of the light scattered by any individual particle is determined by its size, shape and composition. The mixture was stirred continuously; it gave rapid results on products having a wide range of particle size. The instrument generated particle size distribution data enabling it to compare different varieties of polymer compositions.

3.2.6 Wide angle X-Ray Diffraction

Wide angle X-ray diffraction is an analysis technique, which has been used for the determination of the crystalline phases in multiphase powdered materials and the atomic and molecular structures of single crystals. Wide angle X-ray diffraction is a suitable technique for identification of the fillers and transformations of crystalline phases. X-ray diffraction causes a beam of x-radiation to penetrate through the specimen and measuring the angle at which a specific characteristic X-ray wavelength $\lambda$ is diffracted. The diffraction angle $\theta$ can be related to the interplanar spacing (d distance) [91].

Part of the X-ray is diffracted by the layer of atoms on the material surface. The undiffracted X-ray beam penetrates to the second layer of atoms where further diffraction occurs. The remainder of the X-ray beam passes through to the next layer. Diffraction occurs when the wavelength of radiation is comparable with the characteristic spacing between layers of the atoms and the diffracting centres are distributed in a regular configuration. Analysis of the angle positions, peak intensities, and shapes in the X-ray diffractograms is used to give information on crystal structure and physical state. The fundamental relation governing the wide-angle X-ray diffraction process is the Bragg law which states [91]:

$$n\lambda = 2d_{(hk0)} \sin \theta$$

Equation 3.1
The Bragg law as shown in Equation 3.1 relates to the spacing between crystal planes, \( d_{(hkl)} \), in a material in relation to the particular Bragg angle, \( \theta \), at which reflections from these planes are observed, as shown in Figure 3.4. Where \( n \) is the order of reflection and is any integer such that \( \sin \theta \leq 1 \), \( \lambda \) is the wavelength of incident radiation in nanometre, \( d_{(hkl)} \) is the distance between two adjacent parallel planes, \( \theta \) is the incident angle of the X-ray beam to the plane of atoms.

\[
\text{Equation 3.2}
\]

\[
L_{(hkl)} = \frac{K \lambda}{\beta_0 \cos \theta}
\]

\( \beta_0 \) is the half-height width of the diffraction peak (full width at half maxima FWHM) in radian, \( K \) is the shape factor of the average crystalline thickness, related to the shape of crystalline thickness and definition of \( \beta_0 \) \( L_{(hkl)} \); 0.9. Figure 3.5 shows an individual diffraction peak.
The crystalline thickness can be estimated from the shape of the peak, and peak broadening. The broadening of a particular peak in a diffractogram is related to particular reflection plane from within the crystal unit cell. It is inversely proportional to $\beta_0$ of an individual peak, hence the narrower the peak the larger the crystalline size.

Crystalline information of the materials were determined using the wide angle X-ray diffraction on a Bruker D8 Advance diffractometer (Figure 3.6) using Cu-K\(\alpha\) radiation ($\lambda = 0.154$ nm) with the operation voltage and current maintained at 40 kV and 35 mA respectively. The diffraction intensities were recorded every 0.1 from 20 scans over the rage of 5-45°, and 40 s of collecting time.
Figure 3.6: Wide angle X-ray powder diffraction

Powdered materials were prepared by packing a small amount of the material into shallow cups then subjected to X-rays. The resultant diffractograms can yield specific identity of constituent components, both quantitative and qualitative. Sample’s X-ray patterns were matched to JCPDS standard data when available.

3.2.7 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is at present the most important method for identification of additives and processing aids since it requires only small quantities of substances and allows the identification of solid, liquid and gaseous substances. FTIR spectroscopy reveals information about molecular vibrations that cause a change in the dipole of moment of bonds [93]. It offers a fingerprint of the chemical bonds present within materials. FTIR spectroscopy is a powerful analytical tool for examining both inorganic and organic materials. FTIR spectrometry illustrated in Figure 3.6 shows a beam of radiation from the source is focused on a beam splitter, where half the beam is reflected to a fixed mirror and the other half of the beam is transmitted to a moving mirror that reflects the beam back to the beam splitter from where it travels, recombined with the original half beam, to the
detector. The FTIR intensity variation with optical path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. The FTIR absorption spectrum can be obtained by measuring an interferogram with and without a sample in the beam and transforming the interferograms into spectra.

FTIR spectra were recorded in the range of 4000-400 cm\(^{-1}\), using a Perkin-Elmer FTIR spectrometer 1725X. KBr disks were prepared by mixing a 1.2 mg sample with 200 mg of KBr.

![Schematic diagram of a generic Michelson Interferometer used in FTIR](image)

**Figure 3.7: Schematic diagram of a generic Michelson Interferometer used in FTIR**

In addition the Perkin-Elmer 1725 FTIR spectrometer (Figure 3.7) was used in diffuse reflectance mode where the IR beam penetrates the polymer sample supported on the reflecting metallic surface (aluminium pan) as shown in Figure 3.8.
3.2.8 Mechanical testing

3.2.8.1 Thermal mechanical analysis
Thermal mechanical analysis (TMA) is a technique used to study and characterize materials as a function of temperature or time. The static force-thermomechanical analysis (sf-TMA) of the polymer composite and residues were measured. The flexural properties of the polymer composites were measured using a Perkin-Elmer DMA7e with Pyris software version 3.81. The polymer composite was placed on the three point bend clamp and a static force scan was applied from 25 to 8000 mN at 150 mN·min$^{-1}$. The linear region was considered for Young’s modulus and modulus at 0.2 % strain. Measurements were conducted in at least triplicate.

3.2.8.2 Flexural test
The breaking strength of the chars were measured after subjecting the composite to various temperatures in an electric muffle furnace using an Instron Universal Testing Instrument, model 4465 (Instron corporation, series IX Automated Materials Testing system Australia) with a 5 kN load cell attached (Figure 3.9).
Instron software (Version 1.0, 1999) maintained control and recorded the test measurements.

A three-point bend configuration was used with a maximum static load of 100 N and crosshead speed of 0.2 mm min\(^{-1}\). The rectangular specimen length was 30 mm and the width was 13 mm. Ultimate stress was selected when fracture occurred as indicated by a rapid reduction of the load. It was calculated using the following formula (for rectangular specimens):

\[
S = \left( \frac{3PL}{2bd^2} \right) \tag{Equation 3.3}
\]

Where \(S\) is the maximum stress; \(P\) the load; \(L\) the span; \(b\) the width of the specimen; and \(d\) is the depth of the specimen.
The three point bend test shows the rate of change of strain as a function of stress, and the tangent modulus of elasticity that is the slope of the stress-strain curve.

![Stress-strain diagram with tangent and secant modulus](image)

Figure 3.10: Stress-strain diagram with tangent and secant modulus

Depending on the type of loading represented by the stress-strain diagram (Figure 3.10), modulus of elasticity may be reported as a compressive modulus of elasticity; flexural modulus of elasticity; shear modulus of elasticity; tensile modulus of elasticity or torsional modulus of elasticity.

### 3.2.9 Scanning Electron Microscopy

#### 3.2.9.1 Surface structure

The changes in morphology of the sample with temperature were observed using a Philips FEI Quanta 200 environmental scanning electron microscope (ESEM) scanning electron microscope under vacuum (0.5 Torr). The electron beam power was set at 30 kV, electron beam spot size 4, and images captured by a secondary electron detector. The powder was placed on an aluminium stub with double sided adhesive carbon tape.

### 3.2.10 Cone Calorimetry

The cone calorimeter is a small-scale fire test apparatus. The cone calorimetry instrument is based on the principle of oxygen consumption calorimetry. This empirical principle is based on the observation that, generally, the net heat of combustion of any organic material is directly related to the amount of oxygen required for combustion. Approximately 13.1 MJ of heat are released per
kilogram of oxygen consumed. Cone calorimetry is the most generally accepted and powerful instrument in this field and is the subject of three standard test methods ASTM E1354, AS/NZS 3837:1998 and ISO 5660.

Figure 3.11 shows the layout of the specific cone calorimeter used for investigation of FR composites [94]. The measurement of heat release rate (HRR), mass loss rate (MLR), time to ignition (TTI), smoke density and gas species production rate are monitored over time.

At the core of the instrument is a radiant electrical heater in the shape of a truncated cone. This heating element irradiates a flat horizontal sample, 88 x 88 mm and up to 10 mm thick, placed beneath it, at a preset heating flux of $35 \text{ kW/m}^2$. The sample is placed on a load cell for continuous monitoring of its mass as it burns. Ignition is provided by an intermittent spark igniter located above the sample.

The gas stream containing the combined combustion products is captured through an exhaust duct system, consisting of a high temperature centrifugal fan, a hood, and an orifice plate flowmeter. The typical air flow rate is $0.024 \text{ m}^3\text{s}^{-1}$. Oxygen concentration in the exhaust stream was measured with an oxygen analyser.

---

**Figure 3.11: Schematic diagram of a cone calorimeter [94]**

---

84
capable of an accuracy of 50 ppm, and the HRR was determined by comparing the oxygen concentration with the value obtained when no sample is burning.
Chapter 4: Thermal Degradation and Structural Changes of Inorganic Minerals

4.1 Introduction

In this chapter the thermal stability and the structural changes of FR mineral fillers were investigated using TGA, X-ray diffraction and FTIR respectively. The FR function is to control or delay the burning pathway mechanism in the condensed phase or gaseous phases while the polymer composite is subjected to heat or fire.

Metal hydroxides such as MH and ATH were used to provide function through the release of water on degradation. When incorporated into a composite, the heat absorbed by the water release acts as a heat sink and therefore cools the substrate. MH was combined with zinc borate and ATH was combined with APP to provide improved fire performance behaviour with physical action of promotion to achieve a stronger char barrier in composite materials. In addition inorganic mineral fillers such as kaolin, talc, CaCO$_3$, and mica were introduced to the filler mixtures (MH:zinc borate and ATH:APP) to provide mechanical enhancement to the material.
4.2 Individual Fire Retardants

4.2.1 Thermal degradation of the hydrated fillers

The thermogravimetric data from thermal dehydration MH and ATH are summarised in Table 4.1. These hydrated fillers function principally in the condensed phase, through endothermic decomposition and water release, which inhibits the thermal feedback. The metal hydroxides form thermally stable inorganic residues of magnesium oxide (MgO) and aluminium oxide (Al$_2$O$_3$) respectively.

4.2.1.1 Decomposition of magnesium hydroxide

Thermogravimetric mass loss and the derivative curves for MH are shown in Figure 4.1. The decomposition of MH commenced at 325 °C and the maximum temperature was at 407 °C (0.78 %•min$^{-1}$) corresponding to completion of the main step of the dehydration, (elimination of 28.4 wt% of water) and transition to MgO. A change in the crystal structure results in a high surface area oxide due to structural water loss. A slower rate of degradation was noted in the range of 400 and 600 °C. Additionally, the MgO residue functioned as a barrier at the surface, suppressing the fuel support rate. This effect was observed by the changes in HRR curves that will be discussed in detail in Chapter 6.

A study into the mechanism of MH dehydration was conducted by Yoshida [95] using Mg K-edge XANES (X-ray absorption near-edge fine structure). The results showed that dehydration started from the outer surface edges, and once MgO has formed, this nucleated the reaction and conversion to MgO into the bulk of the MH [96].
Figure 4.1: Thermogravimetric mass loss and derivative curves for FRs, MH and ATH under inert atmosphere and heating rate of 10 °C·min⁻¹

The FTIR spectra of MH, at ambient and after dehydration at 800 °C are shown in Figure 4.2. At ambient the spectrum reveals the absorption band of OH that appeared at 3698 cm⁻¹. The elimination of water and the formation of MgO is observed at 800 °C and indicated by the broad bands developed in the range of 3698 and 2750 cm⁻¹, and the appearance of 1650 and 1450 cm⁻¹ band.
Table 4.1: Thermogravimetric analysis of pure FR fillers

<table>
<thead>
<tr>
<th>Fillers</th>
<th>Derivative peak (°C)</th>
<th>Mass loss at each step (%)</th>
<th>Overall Mass loss at 800 °C (%)</th>
<th>Overall Mass remaining at 800 °C (%)</th>
<th>Onset T of the 1st step of degradation (°C)</th>
<th>Rate %•min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MH</td>
<td>407 (1)</td>
<td>29 (1)</td>
<td>31</td>
<td>68</td>
<td>374</td>
<td>0.78</td>
</tr>
<tr>
<td>ATH</td>
<td>277 (1)</td>
<td>32 (1)</td>
<td>35</td>
<td>64</td>
<td>239</td>
<td>5.50</td>
</tr>
<tr>
<td>APP</td>
<td>333 (1) 550 (2)</td>
<td>18 (1)</td>
<td>90</td>
<td>9</td>
<td>281</td>
<td>11.95</td>
</tr>
<tr>
<td>Zinc borate</td>
<td>378 (1) 411 (2) 425 (3)</td>
<td>14 (1)</td>
<td>14</td>
<td>85</td>
<td>357</td>
<td>0.67</td>
</tr>
<tr>
<td>Talc</td>
<td>653 (1) 1.63 (1)</td>
<td>2</td>
<td>98</td>
<td>569</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>797 (1) 4 (1)</td>
<td>4</td>
<td>95</td>
<td>740</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Kaolin</td>
<td>202 (1) 0.73 (1)</td>
<td>0.73</td>
<td>0.73</td>
<td>99</td>
<td>100</td>
<td>3.44</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>740 (1)</td>
<td>43 (1)</td>
<td>43</td>
<td>56</td>
<td>673</td>
<td>4.21</td>
</tr>
</tbody>
</table>
The structural changes occurring during the transformation were determined by X-ray diffraction with the patterns obtained for MH at specific heat treatment temperatures (HHT: 200, 400, 600, 800, 1000 °C). The patterns are shown in Figure 4.3. The MH was heated in the furnace to the target temperatures and residues collected as set in relation to various transitions observed by thermogravimetry.

At ambient temperature, MH presented a crystalline diffraction pattern consistent with JCPDS (brucite 44-1482). The three characteristic peaks are indexed at $\theta = 18.8^\circ$ (001), $33.0^\circ$ (100) and $38.1^\circ$ (101). At 200 °C, the X-ray pattern showed no visible change for the hexagonal structure. At 400 °C the decomposition reaction prevailed and water was eliminated on conversion to the crystalline phase MgO
(periclase 45-09460). New peaks appeared as indicated in the diffraction pattern. In particular, the peak at $2\theta = 42.9^\circ$ was observed to be initially broad at 400 °C, although with increasing temperature, the peak became sharper and more intense. Full development of the crystalline structure for MgO was obtained by 1000 °C. The unit cell structure of MgO observed is a face centred cubic lattice [97], the structure indexed at $2\theta = 42.9^\circ$ (200) and 36.9° (111).

![Wide-angle X-ray diffraction patterns, structural evolution for MH residues obtained after heating in the furnace to the temperatures as labelled](image)

**Figure 4.3:** Wide-angle X-ray diffraction patterns, structural evolution for MH residues obtained after heating in the furnace to the temperatures as labelled

### 4.2.1.2 Decomposition of aluminium trihydroxide

ATH is a commonly used hydrated metal oxide, and used for its action in providing water release, as does MH. The conversion to water and the aluminium oxide is an endothermic process. ATH is used for its ability to form a foamed like char layer that had inherent low thermal conductivity. This property has been observed to be favourable in FR composites [98].

The thermogravimetric mass loss of ATH as shown in Figure 4.1, exhibits a single mass loss the maximum rate of loss occurring at 290 °C. On comparison with MH, the ATH has a lower thermal activation temperature (onset temperature of ATH was 239 °C, and MH was 374 °C), while the mass loss rate for ATH was higher than for MH.
CHAPTER 4  FIRE RETARDANT FILLERS

Reaction for decompositions:

\[ \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \quad \Delta H = 380 \text{ kJ} \cdot \text{mol}^{-1} \]
\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad \Delta H = 298 \text{ kJ} \cdot \text{mol}^{-1} \]

The structural changes that the hydrated ATH underwent are revealed in the X-ray diffraction pattern shown in Figure 4.4. At ambient temperature; ATH shows an X-ray diffraction pattern consistent with JCPDS (Gibbsite 12-04600). The peaks are indexed in order of intensity (hkl in parenthesis) at \( \theta = 18.4 \) (002), 20.4 (110), 20.6 (200), 26.6 (202), 26.9 (112), 28.1 (211), 28.9 (202), 36.8 (120), 37.1 (004), 37.9 (121), 39.5 (104), 40.4 (213), 41.9 (221), 44.6° (402).

At 1050 °C the disappearance of some diffraction peaks was noted due to the endothermic water release that lead to the formation of alumina (29-0063) [5, 7], the main diffraction peaks are indexed at \( \theta = 19.6 \) (111), 31.9 (220), 37.6 (311) and 39.5° (222).

Figure 4.4: Wide-angle X-ray diffraction patterns, structural evolution for ATH residues obtained after heating to 1050 °C
4.2.2 Thermal degradation of char forming fire retardants

4.2.2.1 Decomposition of zinc borate

The thermogravimetric mass loss curve of zinc borate is shown in Figure 4.5. Zinc borate underwent a dehydration reaction that commenced over the temperature range of ~ 300 to 378 °C. Two main peaks appearing at ~ 411 and 425 °C, have mass loss rates of 0.67 and 0.56 %•min\(^{-1}\) respectively. A third broader peak began at lower temperature, but was overlaid by the two main degradation peaks. These three peaks are due to the three molar equivalents of water loss through the condensation of B-OH groups, leading to the formation of anhydrous forms of zinc borate [63] as identified through X-ray diffraction analysis that revealed there was no change observed in the original zinc borate as the temperature rose to 200 °C.

A loss in the X-ray reflection peaks was observed on heating as the structurally bound water escaped causing a collapse in the original crystalline structure. The diffraction pattern peak relative intensities decreased and almost disappeared at 400 °C as shown in Figure 4.6. Further heating resulted in crystallisation evident by the appearance of new peaks at 600 °C. The structure is ascribed to the low melting zinc borate phase 3ZnO•B\(_2\)O\(_3\) [21]. The more thermally stable zinc borate
Chapter 4  Fire Retardant Fillers

Phase is assumed to be $4\text{ZnO} \cdot 3\text{B}_2\text{O}_3$ (JCPDS = 72-0435). At 800 °C the disappearance of some diffraction peaks was noted as a result of melting of a less thermally stable zinc borate phase [21]. The main peaks of the $4\text{ZnO} \cdot 3\text{B}_2\text{O}_3$ structure are indexes as $2\theta = 29.4^\circ$ (211) and $38.2^\circ$ (310). No sign of crystalline zinc oxide (ZnO) was found by X-ray diffraction.

![Figure 4.6 Wide-angle X-ray diffraction patterns, structural evolution for zinc borate residues obtained after heating in the furnace to the temperatures as labelled](image)

The FTIR spectra of zinc borate at ambient and after degradation at 800 °C are shown in Figure 4.2. At ambient zinc borate spectrum reveals three main absorption bands that appeared at 3490, 3250 and 2500 cm$^{-1}$ respectively that are ascribed to the hydroxyl or water groups. The absorption band at 3421 cm$^{-1}$ is attributed to symmetric OH stretching mode. Other bands of interest involve the boron-oxygen linkages and their arrangement in the structure, which appear strongly absorbing and relatively broad. The vibrational modes of the borate network can be divided in three particular regions. The 1200–1600 cm$^{-1}$ band is the first region, which is due to asymmetric stretching relaxation of the B-O bond of trigonal BO$_3$ units. The second region is located between 800 and 1200 cm$^{-1}$, and is due to the B-O bond stretching of tetrahedral BO$_4$ units and the last band around 700 cm$^{-1}$ is due to the bending of B-O-B linkages in the borate network. Thus, the band around 1283 cm$^{-1}$ is due to B-O stretching vibrations of (BO$_3$)$_3$.
units in the metaborate chain and of the orthoborate arrangements. The peak observed at 935 cm\(^{-1}\) is attributed to the B-O bond stretching of BO\(_4\) units [99]. The peaks due to the hydroxyl groups and loss of water have diminished following the collapse of the hydrated zinc borate. The remaining zinc borate structure showed the broad peaks due to the B-O network as described.

### 4.2.2.2 Decomposition of ammonium polyphosphate

The thermogravimetric mass loss and corresponding derivative curves for APP are shown in Figure 4.5. The decomposition of APP reveals two mass loss steps, the first step, commenced at around 333 °C, consists essentially of elimination of ammonia and water, leading the transformation of linear crystalline APP to a highly crosslinked polyphosphoric acid (ultraphosphate), whereas the second step, at a temperature higher than 550 °C, corresponded to polyphosphoric acid evaporation and dehydration of the acid to P\(_4\)O\(_{10}\) that sublimes [27, 54].

Ammonia evolution from APP is acidic and this promotes the charring of the organic polymer (dehydrogenation). In an intumescent process, the first step consists of a reaction of the acidic species released by the acid source with the carbonisation agent with formation of a mixture of esters. However, it has been reported that the polymer can contribute to the intumescence process [100].

X-ray diffraction patterns of APP at selected temperatures are shown in Figure 4.7. At ambient APP shows a diffraction pattern consistent with JCPDS (Ammonium polyphosphate 44-0739). The peak are indexed at 2\(\theta\) = 14.4, 15.9, 16.4, 22.4, 23.3, 24.9, 25.5, 26.1, 26.9, 27.6, 28.7, 31.0, 31.7, 33.9, 35.4, 36.6, 38.3, 39.3, 43.6°. A change in the structure was evidenced at 200 °C following partial decomposition. New peaks appeared at 2\(\theta\) = 16.9 and 29.9° signifying the conversion to phosphorus pentoxide.

APP sample was melted at higher temperature (300 °C) therefore at 200 °C the changes may not be due to phosphorus oxide species, but a structural loss in crystalline lattice observed.
4.3 Mineral Fillers

4.3.1 Decomposition of Talc

The thermogravimetric mass loss and derivative curve for talc (Mg$_3$[(OH)$_2$•Si$_4$O$_{10}$]) is shown in Figure 4.8. Talc underwent almost no mass loss (1.63 %) until 600 °C, and a small loss in the temperature range of 600-800 °C. The mass loss is attributed to the collapse of the magnesium silicate structural water, an endothermic process creating the formation of a dehydrated magnesium silicate.

The FTIR spectra of talc (Figure 4.2) is characterised by the vibration frequencies that are mainly found at 3677 cm$^{-1}$ due to OH stretching band, 1052 and 1020 cm$^{-1}$ are due to the stretching vibration of $v_3$ and $v_1$ Si-O-Si bonds respectively, 669 cm$^{-1}$ due to OH bending, 543 cm$^{-1}$, 452 cm$^{-1}$ are due to the Si-O-Mg bond and 533 cm$^{-1}$ is due to the $\nu$(Mg-OH) bond [101].
The structural changes that hydrated talc underwent were determined in the X-ray diffraction pattern shown in Figure 4.9. No changes in the original talc X-ray patterns occurred as the temperature was raised from 200-600 °C, complementary to the thermogravimetry observations. At ambient temperature talc showed diffraction pattern consistent with JCPDS (Monoclinic talc 19-0770). The peaks are indexed at $2\theta = 9.5$ (002), 18.9 (002), 19.0 (020), and 28.7° (006). The X-ray pattern of talc reveals the presence of traces of dolomite at $2\theta = 31.9°$ (104), chlorite at $2\theta = 12.2°$ (002) and it could contain some magnesite at $2\theta = 26.5°$ (004) [98]. Decomposition occurred at 800 °C and the water expelled resulted in the conversion of the monoclinic talc ($\text{Mg}_3[(\text{OH})_2\cdot\text{Si}_4\text{O}_{10}]$ talc 2M JCPDS =19-0770) to enstatite ($\text{Mg}_7\text{Si}_3\text{O}_6$ JCPDS = 73-1937) and amorphous silica ($\text{SiO}_2$ JCPDS = 33-1161), the peaks of enstatite are indexed at $2\theta = 9.7$ (200), 13.9 (210), 20.4 (111), 21.9 (410), 26.9 (121), 28.2 (420), 31.6 (511), 35.7 (611), 40.5 (122) and 42.8 (630). Amorphous silica was detected at $2\theta = 20.8$ (100), 26.6 (101), 36.5 (110), 39.4 (102), 40.3 (111) and 42.5° (200).

This was described by Wesolowski [102] as illustrated in the following equation:

$$[\text{Mg}_3(\text{OH})_2\cdot\text{Si}_4\text{O}_{10}] \xrightarrow{800^\circ\text{C}} 3\text{Mg} \cdot \text{SiO}_3 + \text{SiO}_2 + H_2O$$  \hspace{1cm} \text{Equation 4.1}
At 1000 °C most of the diffraction peaks corresponding to talc have disappeared and all the remaining peaks confirms the presence of protoenstatite (Mg\textsubscript{3}Si\textsubscript{2}O\textsubscript{6} JCPDS = 03-0523). When talc is hydroxylated, two hydroxyl groups produced a molecule of water, but the remaining O\textsuperscript{2-} ion displaces within the crystal lattice to form Si-O-Si bridges. This causes the silicon oxide tetrahedra, [SiO\textsubscript{4}]\textsuperscript{4-}, to form a chain thus transforming the layer structure of talc into the chain structure of protoenstatite. According to Wesolowski [102] Up to 1450 °C protoenstatite converts to clinoenstatite whereas silica crystallizes as cristobalite.

Talc formation and the common mineral impurities can be described as follows [103]:

\[
\text{2Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 \rightarrow \text{Mg}_3\text{Si}_4\text{O}_9(\text{OH})_2 + 3\text{MgCO}_3 + \text{H}_2\text{O} \\
\text{Serpentine} \quad \text{Talc} \quad \text{Magnesite}
\]

\[
\text{4SiO}_3 + 3\text{CaMg(CO)}_3 \rightarrow \text{Mg}_3\text{Si}_4\text{O}_9(\text{OH})_2 + 3\text{CaCO}_3 + \text{CO}_2 + \text{Calcite} \\
\text{Quartz} \quad \text{Dolomite} \quad \text{Talc}
\]

\[
\text{Equation 4.2}
\]

\[
\text{Equation 4.3}
\]

Figure 4.9: Wide-angle X-ray diffraction patterns, structural evolution for talc residues obtained after heating in the furnace to the temperatures as labelled

### 4.3.2 Decomposition of Mica

The thermogravimetric mass loss and the corresponding derivative for mica, a potassium aluminium silicate (K\textsubscript{2}Al\textsubscript{4}(Al\textsubscript{2}Si\textsubscript{6}O\textsubscript{20})(OH)\textsubscript{4}) are shown in Figure 4.8.
The TGA curve of mica showed one major step that occurred at 797 °C with a mass loss of 4 %, although further mass loss would have occurred on further heating. The structural changes of mica during the decomposition are shown in Figure 4.10. At ambient mica diffraction pattern is consistent with JCPDS (Muscovite 01-1098) the peaks are indexed at $2\theta = 8.9$ (002), 17.7 (004), 26.7 (006), 27.9 (114), 29.8 (025), 31.2 (115), 32.0 (116), 35.0 (131), 36.3° (133), the X-ray pattern for mica at room temperature shows all peaks for muscovite together with possible impurities such as quartz (peaks at $2\theta = 20.9$, 26.8, and 39.5°) and kaolin (peaks at $2\theta = 12.4°$).

At 1050 °C the decomposition reaction of mica is completed and resulted in conversion of mica to mullite phase ($3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$ 01-0613) due to the loss of structural water [104]. This is represented by the appearance of new peaks in the diffraction pattern at $2\theta = 16.4$, 26.0, 30.9, 33.3, 35.2, 39.1, 40.8, and 42.6° The appearance of a broad peak $2\theta = 10-33^\circ$ is assigned to a polycrystalline silica [27-1402] which is due to an amorphous structure that seems to be retained even on heating to 1050 °C. Most mullite peaks overlapped with those of mica, but the characteristic peaks at 35.7° and that at 41.3°.

![Figure 4.10: Wide-angle X-ray diffraction patterns, structural evolution for mica residues obtained after heating in the furnace to 1050 °C](image-url)
4.3.3 Decomposition of Kaolin

The thermogravimetric mass loss and the corresponding derivative for kaolin are shown in Figure 4.11. The kaolin showed <1 % mass loss, with this being due to the fact that the particular grade had already been calcined. The calcination process would have removed organic matter and structural water that would have otherwise been lost. The FTIR of kaolin shown in Figure 4.2 reveals bands at 460, 1080 and 1150 cm\(^{-1}\), corresponding to Si-O vibrations from SiO\(_4\). At 800 cm\(^{-1}\), a band appears corresponding to Al-O bending of tetrahedral Al.

![Figure 4.11 Thermogravimetric mass loss and derivative curves for kaolin and CaCO\(_3\) under inert atmosphere and heating rate of 10 °C\(\cdot\)min\(^{-1}\)](image)

There is a little change in the original kaolin X-ray patterns as the temperature raised from 200-600 °C similar to the thermogravimetry changes. The X-ray diffraction pattern of kaolin (Figure 4.12) is consistent with JCPDS (kaolinite 81-0886). The peaks are indexed at \(2\theta = 24.9\) (002), 26.0 (111), 26.4 (111), 27.1 (012), 28.3 (112), 29.9 (030), 31.2 (121), 32.2 (031), 33.1 (122), 34.4 (102), 35.2 (130), 36.0 (200), 37.5 (210), 38.3 (202), 39.1 (113), 40.1 (132), 41.1 (132), 42.2 (211), 43.3 (222), 44.3 (140), and 44.6° (141). Kaolin does not crystallise well, as it has poor crystalline structure. At 400 and 600 °C the crystal structure of kaolin seems to be disrupted which can be seen from the broad peak in the diffraction patterns. At 800 to 1000 °C the peaks became broader as kaolin is converted to...
mullite, that is aluminium silicate consistent with JCPDS (01-0613) and the peaks are indexed at \(2\theta = 16.4, 26.0, 26.3, 30.9, 33.3, 35.2, 39.1, 40.9,\) and \(42.6^\circ\).

Figure 4.12: Wide-angle X-ray diffraction patterns, structural evolution for kaolin residues obtained after heating in the furnace to the temperatures as labelled

4.3.4 Decomposition of calcium carbonate

Thermogravimetric mass loss of CaCO\(_3\) (Figure 4.11) shows a mass loss of 43 % at 740 °C. This mass loss is associated with the removal of CO\(_2\) to form CaO, according to the following reaction:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \text{Equation 4.4}
\]

This is observed in the X-ray diffraction pattern shown in Figure 4.13. At ambient temperature CaCO\(_3\) diffraction pattern is consistent with JCPDS (calcite 72-1650). The peaks are indexed at \(2\theta = 23.1\) (012), 29.5 (104), 31.7 (006), 35.9 (110), 39.4 (113), and \(43.1^\circ\) (202). At 1050 °C the X-ray diffraction pattern reveals the conversion of CaCO\(_3\) to CaO. This is shown by the reflection peaks at \(2\theta = 32.2\) (111) and \(37.4^\circ\) (200).
4.4 Particle Size Distribution of FR fillers

The particle size distribution (PSD) curves of MH, zinc borate and talc are shown in Figure 4.14. The MH PSD curve reveals two distinct size distributions. The first corresponds to very small particle size with diameter range from 0.27-1.67 µm. The second designated peak corresponds to larger particle [105] with diameter range of 1.67-29.35 µm. This indicates that there is a higher proportion of lower particle size MH, confirming the technical data for the material.

Figure 4.13: Wide-angle X-ray diffraction patterns, structural evolution for CaCO₃ residues obtained after heating in the furnace to 1050 °C

Figure 4.14: Particle size distribution of the pure individual fillers, MH, zinc borate and talc
The PSD of zinc borate curve shows one main distribution of particle size, and two smaller distributions. The first peak that corresponds to small particle sizes range from 0.27 to 1.67 µm. A very small peak appeared in the diameter range of 1.67 to 3.14 µm. The third peak of zinc borate that corresponds to large particle size and is the dominant size with diameter range of 3.14 to 62.99 µm.

The PSD curve of talc shows broad particle size distribution, with a small proportion with particle size of 0.27 to 1.67 µm. The major proportion has diameter range of 1.67 to 62.99 µm, the curve very broad peak with the largest area compared with the other two fillers.

4.5 Binary Mixtures

4.5.1 Decomposition of APP:CaCO₃ mixture

To observe the interaction between APP and CaCO₃ a series of mixtures of varying ratios were analysed by thermogravimetry to determine if any changes occurred in comparison with the individual components. The resultant mass loss curves are shown in Figure 4.15, with the ratio composition indicated. The APP component formed primarily the minor phase of the mixtures. Some changes in the mass loss curves were observed, indicating the possible reaction between the two components. All curves show three degradation steps. While pure APP had decomposed to form ammonia in its first step of conversion, the second step was not as drastic in rate of mass loss (Table 4.2). We can observe that a slower second step of decomposition occurs at temperatures greater than that of the sublimation or evaporation of phosphorus pentoxide derived from APP. At this step, the last main degradation step would be partially attributed to the decomposition of CaCO₃ in which CO₂ is eliminated. The derivative mass loss curves show that there are changes and potential reactions that occur between particular species. The derivative curve shows new broad peaks in the range of 400-600 °C that exhibit relatively low rate of mass loss, but that is then followed by a more rapid decomposition at 600-800 °C. For APP:CaCO₃ 1:4, the high temperature decomposition would primarily be due to the unchanged CaCO₃. For the 1:1 and 2:3, the change is less rapid, indicating added complexity in the decomposition of the compound/s that have formed during the heating.
A favourable reaction can occur between phosphoric acid in combination with basic calcium carbonate in order to produce salts and other volatiles. The species likely to form at high temperature are calcium phosphates, as indicated by Levchik [106]. The decomposition of these two mixtures commenced at similar temperatures (150 °C) with a maximum mass loss of 36 % at 313 °C (2.19 %•min⁻¹) for 1:1 mixture and 219 °C (2.28 %•min⁻¹) for 2:3 mixture. The onset temperature was found to be 266 °C for 1:1 mixture and 269 °C for 2:3 mixture. Whereas the decomposition of APP:CaCO₃ (1:4) mixture commenced at higher temperature (~218 °C) with a maximum mass loss of 40 % at 301 °C (1.44 %•min⁻¹).

The reaction between APP:CaCO₃ can be explained as follow [107]:

\[
3\text{CaCO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O} + 3\text{CO}_2
\]

Equation 4.5

\[ a) \]
This demonstrates that increasing CaCO₃ loading leads to the highest mass loss and the lowest mass loss rate because pure CaCO₃ had a lower rate (4.21 %•min⁻¹) than pure APP (11.95 %•min⁻¹).

The thermogravimetry results show that APP:CaCO₃ decomposed more slowly compared with the individual components. This proved the FR action of the intumescent char and confirmed a synergistic FR action between the two components due to gas evolution that is shown in Figures 4.16, 4.17, and 4.18 with change in composition. APP alone might reduce the flammability of the material, but the burning rate of the pure APP was high, however the addition of CaCO₃ resulted in a reduction in the flammability of the composites as well as the burning rate.

Photographs of APP:CaCO₃ mixtures reveal that as temperature was raised the APP decomposed releasing ammonia and the molten suspension of carbonised material swells forming a thick dense foam [108]. Figures 4.16, 4.17 and 4.18 (of 1:1 (2.49 cm), 2:3 (1.82 cm) and 1:4 (0.55 cm) ratios respectively) show a strong white layer formed by metallic salts of polyphosphoric acid. In addition CaCO₃ decomposes at ~ 600 °C therefore the residue of APP and CaCO₃ interacted to give the final product of calcium phosphate. Comparison of the three Figures
(4.16, 4.17 and 4.18) reveals that upon increasing the content of APP the volume of the intumescent char increase.

Table 4.2: Thermogravimetric analysis of the FR filler mixtures

<table>
<thead>
<tr>
<th>Fillers</th>
<th>Derivative peak (°C)</th>
<th>Mass loss at each step (%)</th>
<th>Overall Mass loss at 800 °C (%)</th>
<th>Overall Mass remaining at 800 °C (%)</th>
<th>Onset T of the 1st step of degradation (°C)</th>
<th>Rate %•min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>APP:CaCO₃ 50:50</td>
<td>313 (1) 338 (2) 441 (3) 736 (4) 767 (5)</td>
<td>18 (1) 4 (2) 14 (3)</td>
<td>36 63</td>
<td>266</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>APP:CaCO₃ 20:80</td>
<td>301 (1) 540 (2) 739 (3)</td>
<td>8 (1) 3 (2) 30 (3)</td>
<td>40 59</td>
<td>272</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>APP:CaCO₃ 40:60</td>
<td>293 (1) 351 (2) 450 (3) 750 (4) 787 (5)</td>
<td>15 (1) 4 (2) 17 (3)</td>
<td>36 63</td>
<td>269</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>APP:ATH 1:1</td>
<td>269 (1) 597 (2)</td>
<td>30 (1) 6 (2)</td>
<td>36 64</td>
<td>237</td>
<td>4.51</td>
<td></td>
</tr>
<tr>
<td>CaCO₃:ATH 1:1</td>
<td>259 (1) 704 (2)</td>
<td>16.46 (1) 23.73 (2)</td>
<td>40 59</td>
<td>234</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>APP:mica</td>
<td>301 (1) 535 (2) 727 (3)</td>
<td>12 (1) 5 (2) 4 (3)</td>
<td>21 79</td>
<td>269</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>APP:CaCO₃:mica 1:1:1</td>
<td>320 (1) 800 (2)</td>
<td>13(1) 9 (2)</td>
<td>22 78</td>
<td>281</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>APP:ATH:CaCO₃ 1:1:1</td>
<td>264(1) 301 (2) 729 (3)</td>
<td>8 (1) 9 (2) 20 (3)</td>
<td>37 62</td>
<td>232</td>
<td>1.81</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4  Fire Retardant Fillers

Figure 4.16: Intumescences foam of APP:CaCO₃ mixture (1:1) after burning at 1050 °C

Figure 4.17: Intumescences foam of APP:CaCO₃ mixture (2:3) after burning at 1050 °C

Figure 4.18: Intumescences foam of APP:CaCO₃ mixture (1:4) after burning at 1050 °C

The structural changes of APP:CaCO₃ mixture determined by the X-ray diffraction patterns are shown in Figure 4.19. The X-ray pattern of APP:CaCO₃ 1:1 and 2:3 shows several peaks arising from the presence of calcium phosphate this is in agreement with thermogravimetry results. The peaks for calcium phosphate oxide (Ca₃(PO₄)₂ 02-0786 and 01-0941) are indexed at 2θ = 13.4, 17.0, 21.6, 25.6, 27.7, 30.9, 32.2, 34.2, 35.3, 37.1, 39.7, 40.9, 43.2 and 44.8°. In addition there are several peaks revealing the presence of calcium phosphate (Ca₃P₂O₇ 02-0647), the peaks are indexed at 2θ = 14.8, 18.9, 20.4, 21.9, 24.2, 26.9, 27.8, 29.1, 29.7, 30.3, 31.0, 32.2, 32.9, 33.7, 35.2, 35.4, 36.5, 37.6, 38.7, 40.0, 40.6, 42.4, 43.5 and 44.6°.
Figure 4.19: Wide angle X-ray diffraction pattern and structural evaluation for APP:CaCO₃ mixtures obtained after heating to 1050 °C

The APP:CaCO₃ (1:4) mixture showed several peaks arising from APP (44-0739 and 01-0817) the peaks are indexed at 2θ = 14.7, 16.4, 22.4, 23.3, 26.1, 26.9°. Several peaks arising from CaO (04-0777) was observed that indexed at 2θ = 32.2, 37.4, 28.7, and 34.1°. In addition there were a few weak peaks that appeared corresponding to calcium phosphate indexed at 2θ = 18.9, 24.2, 26.9, 29.7, 32.2, 32.9, 33.7, 35.4, 36.5, 38.7, 40.0, 40.6, 42.4, 43.5 and 44.6°.

4.5.2 Decomposition of APP:ATH mixture

Replacing CaCO₃ with ATH (APP:ATH mixture) showed the highest decomposition temperature (269 °C) with the highest mass loss of 30 % and rate of 4.51 % min⁻¹ compared with the other mixtures. The onset temperature was found to be 237 °C. In addition the thermogravimetric mass loss of this mixture (Figure 4.20) showed only one major step of degradation, the peak due to the degradation of APP at 550 °C is not present, this gives evidence of interaction or consumption of a part of the APP and ATH that occurred on heating; as reported by Castrovinci [5].
Since ATH is basic and APP gives acidic groups on thermal degradation [100], this suggests that APP:ATH (1:1 ratio) mixture reacted during the thermal dehydration and elimination of water from ATH promoting APP decomposition through liberation of ammonia. The basicity of ATH and therefore respective oxide Al$_2$O$_3$ surfaces shifted the temperature of APP degradation to a lower temperature (269 °C) with elimination of ammonia and water. This was almost 65 °C lower compared with the pure APP (333 °C). The chemical reaction of
ATH hydroxyl group with protons of polyphosphoric acid freed ammonia from the ammonium salt with formation of aluminium phosphate. The chemical reaction between APP and ATH is discussed in detail in Chapter 2. The structural change occurring during the transformation of aluminium phosphate was determined by X-ray diffraction patterns as shown in Figure 4.21. The X-ray pattern reveals a mixture of thermally stable aluminium orthophosphate (AlPO₄) and aluminium metaphosphate ([Al(PO₃)₃]ₙ), a trivalent cation long chain polyphosphate was found to be present on heating the APP:ATH mixture. The diffraction pattern is consistent with JCPDS (13-0430 for [Al(PO₃)₃]ₙ; 11-0500 and 03-0446 for AlPO₄). The peaks are indexed at $2\theta = 15.8$ (211), 18.2 (220), 20.4 (310), 24.2 (321), 25.9 (400), 29.1 (420), 30.5 (332), 31.9 (422), 33.2 (510), 35.8 (521), 38.2 (530), 40.5 (611) and 41.56° (620) for [Al(PO₃)₃]ₙ and $2\theta = 17.7$ (110), 21.8 (111), 25.0 (020), 25.1 (200), 25.5 (002), 28.2 (021), 31.2 (112), 35.8 (220), 36.0 (022), 42.3 (311) and 44.4° (222) for AlPO₄.

4.5.3 Decomposition of APP:mica mixture
Replacing ATH with mica (APP:mica) showed one major step and two minor steps of degradation, the first step started at 301 °C with 12 % of mass loss. The rate was found to be 1.33 %•min⁻¹. Introducing mica seemed to shift the mass loss steps to higher temperature and increased the onset of decomposition temperature (269 °C) compared with the other composites (Figure 4.20). In addition this mixture shows the highest mass remaining at 800 °C (79 %). This may be due to heat shielding effect of mica flakes that is attributed to its chemical structure. At 1050 °C the X-ray pattern of APP:mica (Figure 4.21) reveals the appearance of mullite (3Al₂O₃·2SiO₂ 01-0613) at $2\theta = 16.4$, 26.0, 30.9, 33.3, 35.2, 39.1, 40.8, and 42.6°, muscovite (02-0058) at $2\theta = 16.4$, 26.0, 26.3, 30.9, 33.3, 35.2, 39, 40.8 and 42.6°, potassium aluminium silicate (microcline KAlSi₃O₈ 01-0705) at $2\theta = 20.7$, 22.1, 23.1, 24.1, 25.5, 26.6, 27.4, 29.4, 30.4, 31.0, 32.4, 34.3, 35.6, 36.9, 38.6, 41.8, 43.0 and 44.8, and ammonium aluminium silicate (NH₄•AlSi₂O₆ 40-0474) was detected at $2\theta = 9.3$, 13.4, 16.0, 18.7, 24.06, 25.1, 25.9, 26.9, 28.6, 29.3, 30.2, 31.3, 31.5, 32.9, 33.7, 34.1, 36.0, 37.8, 38.5, 39.3, 40.6, 41.0, 41.9, 43.3 and 44.3°. In addition the presence of aluminium phosphate was detected
(AlPO₄ 03-0445), by the appearance of new main diffraction peaks that emerged at 2θ = 20.8° (100), 22.4° (101), 26.8° (102), 36.5° (110), 39.1° (104), 40.0° (112), and 42.2° (200).

### 4.5.4 Decomposition of CaCO₃:ATH mixture

The thermogravimetry mass loss of CaCO₃:ATH mixture (Figure 4.20) shows two degradation steps. The first step started at 259 °C that was found to be the lowest compared with the other mixtures with a rate of 3.71 %·min⁻¹ and onset temperature of 237 °C. In addition, this mixture revealed the lowest mass remaining at 800 °C (59 %).

The X-ray diffraction pattern of CaCO₃:ATH (Figure 4.21) reveals that this mixture approached a complete conversion to oxide structures (CaO and Al₂O₃) at 1050 °C, this is represented by the appearance of new peaks that are due to the presence of calcium aluminium oxide (equivalent to C₃A₅ in the phase diagram) [109]. The reaction between the two oxides can be explained as follow:

\[
CaO + Al₂O₃ \rightarrow Ca(AlO₂)_2
\]

Equation 4.6

The peaks of calcium aluminium oxide are indexed at 2θ = 19.9, 25.4, 26.9, 28.8, 30.2, 31.1, 32.8, 34.5, 35.7, 36.8, 38.9, 41.4 and 44.1°. There was evidence of CaO (04-0777 lime) and Al₂O₃ (42-1468 corundum) available at 1050 °C that were detected at 2θ = 32.196 and 37.360° and at 2θ = 37.784 and 41.683° respectively.
4.6 Ternary Mixtures

4.6.1 Decomposition of APP:CaCO₃:ATH mixture

The thermogravimetric mass loss of APP:CaCO₃:ATH (1:1:1) mixture (Figure 4.20) shows three degradation steps, the results reveal that introducing ATH to APP:CaCO₃ mixture led to an early thermal decomposition with a mass loss of 8 % at 264 °C (1.81 % min⁻¹) and an onset of 232 °C. In addition, the presence of ATH lowered the rate of decomposition compared with APP:CaCO₃ mixture without ATH this is due to the water release from ATH.

The X-ray diffraction pattern of the APP:CaCO₃:ATH ternary mixture reveals the presence of tricalcium phosphate represented by the diffraction peaks that are consistent with JCPDS (01-0941 Ca₃(PO₄)₂) at 2θ = 13.0, 17.0, 21.6, 25.6, 27.7, 30.9, 32.2, 34.2, 35.3, 37.1, 39.7, and 40.9°. In addition the diffraction pattern shows the presence of peaks that are due to alumina and are consistent with JCPDS (04-0878 Al₂O₃) at 2θ = 14.3, 19.7, 21.1, 32.0, 33.1, 34.9, 37.3, 38.8, 39.8, 41.8, 42.8 and 43.9°. Therefore the combination of the three fillers gives residues of tricalcium phosphate alumina (Al₂O₃·Ca₃(PO₄)₃) according to the ternary phase diagram [110]. There was an evidence of CaO that was not reacted at 2θ = 32.429 and 37.620°.
4.6.2 Decomposition of APP:CaCO$_3$:mica mixture

APP:CaCO$_3$:mica mixture shows a similar thermogravimetry mass loss curve compared with APP:mica mixture (Figure 4.20). The derivative curve reveals two major steps of degradation, with a slight shift of the first degradation step to a higher temperature (320 °C and rate of 1.41 %•min$^{-1}$). This indicated that introducing CaCO$_3$ to the mixture (APP:mica) led to the presence of calcium phosphate which is clearly shown by the second major degradation step at 800 °C with 9 % mass loss.

The X-ray diffraction pattern shown in Figure 4.21 reveals that at 1050 °C muscovite was detected, and this is represented by the peaks at 20 = 8.9, 17.7, 21.5, 22.0, 23.3, 26.7, 27.9, 29.8, 31.2, 32.0, 35.0 and 36.3°, while main changes were observed from a reaction between APP and CaCO$_3$. Calcium phosphate and calcium phosphate silicate were detected at elevated temperature, and they were likely to have formed when the liquid phase of APP (polyp phosphoric acid) mediating the reaction with CaCO$_3$. Normally CaCO$_3$ thermally degrades at much higher temperatures (740 °C), however the condition that was present caused the acid-base reaction to liberate the CO$_2$.

The X-ray pattern confirms the presence of calcium phosphate and this is shown by the appearance of new peaks at 20 = 30.3, 31.0, 32.2, 32.9, 33.7, 35.2, 35.4, 36.5, 37.6, 38.7, 40.0, 42.4, 43.5 and 44.6° and calcium phosphate silicate (Ca$_5$(PO$_4$)$_2$SiO$_4$ 21.0157) at 20 = 10.4 (110), 11.4 (200), 15.8 (011), 16.8 (111), 19.6 (211), 22.0 (021), 22.8 (121), 23.0 (400), 23.4 (311), 24.8 (221), 27.2 (102), 28.0 (411), 28.9 (202), 29.6 (031), 30.3 (212), 31.7 (330), 31.9 (022), 33.0 (511), 34.4 (331), 34.8 (600), 35.4 (402), 36.5 (322), 37.8 (032), 38.4 (611), 39.2 (620), 39.5 (530), 39.7 (422), 40.6 (512), 41.6 (113), 42.7 (440), 42.9 (213), 43.6 (522) and 44.6° (123).

4.7 Conclusion

The key thermal degradation reaction mechanisms of individual minerals for structure and FR functionality have been discussed. Each system was studied with reference to thermal stability and structural changes initiated by temperature and the presence of other components in binary and ternary systems. The reactions
were studied in ratios of 1:1 or 1:1:1 in binary or ternary mixtures to maximise the potential interactions that could be found in combustion when binary and ternary filler systems are applied to polymer composites. The ratios were chosen to limit the number of compositions although it is known that changes in ratio will shift reactions and modify potential products formed. This chapter has provided a basis for explaining filler interactions in polymer composites that is developed in further chapters in this thesis.

The individual fillers have been discussed. The simplest compounds are those of MH, ATH and talc. These undergo dehydroxylation reactions that are initiated at different temperatures. ATH has lower thermal stability compared with MH, although both are used in FR composites for their water release and residual oxide. Talc, being a layered magnesium silicate, has a minor amount of water loss due to dehydroxylation, but has function for providing structure and platelet morphology for barrier performance for gas and heat transfer. CaCO₃ provides a low cost bulk filler in FR composites, but decomposes at high temperatures with release of CO₂ forming its residual oxide.

Reaction mechanisms become significantly more complex for APP and zinc borate. Both these components are used for their char enhancing function, although on their own decomposition lead to different final products. APP is a linear crystalline polyphosphate that undergoes transformation to a highly crosslinked polyphosphoric acid (ultraphosphate) with the release of ammonia and water, converts to a polyphosphoric acid and with increasing temperature sublimes. In composites, the type of polymer and interactions modifies the behaviour; APP promotes charring and bubbling and may result in the entrapment of acid. Zinc borate is used for char enhancing properties and undergoes several changes; dehydroxylation leading to an amorphous structure before crystallising and furthermore melting at elevated temperature.

The thermogravimetric mass loss curves of the individual fillers reveal water loss due to the dehydration of MH, ATH, mica, and talc. In addition they showed the release of CO₂ from CaCO₃ leading to CaO and the dehydration reaction of zinc borate that led to the formation of anhydrous form of zinc borate. APP decomposition showed elimination of ammonia and water leading to the transformation of linear crystalline APP to highly crosslinked polyphosphoric acid.
(ultraphosphate). The structural changes of the inorganic fillers were confirmed by the X-ray diffraction patterns.

The binary combination of inorganic powders ATH and/or CaCO$_3$ have the potential to improve the FR action of APP. The combination showed interactions that had an impact by increasing the char yield and improving the insulation properties of the char. APP:ATH/or CaCO$_3$ mixture on heating led to the formation of more thermally stable aluminium phosphate and/or calcium phosphate respectively. These new compounds showed the best intumescence properties.

The ternary combination of inorganic powders increased the thermal stability according to thermogravimetric mass loss curves and in addition the combination of three fillers showed less amorphous materials after calcinations. APP:ATH:CaCO$_3$ mixture residues were found to be tricalcium phosphate alumina.

Furthermore from the results observed the presence of mica in the composite caused a shift to the mass loss steps to higher decomposition temperatures and increased in the thermal stability of the material more than the other inorganic fillers.
CHAPTER 5: THERMAL DEGRADATION OF POLY 
(VINYL ACETATE) COMPOSITES

5.1 Introduction

An investigation of the thermal degradation of PVAc and PVAc composites is presented in this chapter. The PVAc degradation residues formed under inert atmosphere were analysed by FTIR spectroscopy. The fire resistance of filled PVAc with MH, zinc borate and either talc or kaolin mineral were studied. This chapter focuses on the affect of mineral filler (talc or kaolin) in composites containing the FRs, MH and zinc borate. Mechanical testing and TGA analysis of the FR composites characterized the changes with the FR content, the synergism between FR components in the composites and improvement of the thermal stability of the composite.

5.2 Results and Discussion

Poly(vinyl acetate)

Poly(vinyl acetate) (PVAc) is a thermoplastic produced by polymerizing vinyl acetate (VA) monomer dissolved in acetic acid (Figure 5.1).
CHAPTER 5                                     DEGRADATION OF PVAc COMPOSITES

Figure 5.1: Free radical polymerisation

PVAc, has the advantage that it is available in the form of an emulsion that is readily diluted with water, making it easy to apply. It has advantage of being aqueous based and therefore safe to use since it does not contain flammable solvents. PVAc is soft and flexible with glass transition temperature (T_g) of 29 °C, allowing it to be used in cold climates. PVAc adhesive's mechanical resistance decreases with increasing temperature.

5.2.1 Thermal degradation of poly(vinyl acetate)

The mechanism of thermal degradation of PVAc is a complex process. PVAc degradation reaction involves chain scission, hydrogen abstraction, mild chain and end-chain scission, radical addition, hydrogen transfer and disproportionate, conjugated double bonds formation, crystallisation, aromatization, fusion of aromatic ring, char formation and graphitization. These reactions are presented in Scheme 5.1 [111]. Reaction 1 shows the free radical reaction of the elimination of acetic acid, which starts at a low temperature and gives unsaturation within the macromolecular chain. Reaction 2 shows the chain scission that occurs at high temperature, causing more acetic groups to be eliminated (reaction 3) and end chain unsaturation builds up.

As internal unsaturation increases, crosslinking increases through macroradical attack on internal unsaturation, and through aromatic rings that was created by the Diels-Alder condensation of double bonds belonging to different chains as shown
in reaction 4. In addition, reaction 4 illustrated the formation of the remaining ester groups experience scission of the ester link and α,β-unsaturation ketones.

Scheme 5.1: Mechanism of PVAc degradation [111]

Holland [112] studied the elimination process which occurs during the thermal degradation of PVAc using thermal analysis–Fourier transform infrared spectroscopy was found that elimination of acetate groups initially began slowly, but increased as degradation proceeded due to an additional process. The additional process of elimination was considered to be due to a four-membered transition state, activated by double bonds adjacent to the acetate unit. In addition the results indicated that quantitative yields of acetic acid were produced by the elimination reaction that led to polyene residue. The double
bonds produced by the elimination of acetic acid could activate the elimination of adjacent acetic acid groups leading to the increase in the rate of degradation. TGA curve for PVAc treated under an inert atmosphere at heating rate of 10 °C•min⁻¹ is shown in Figure 5.2. The majority of mass loss took place at 354 °C, due to acetic acid elimination from the polymer side-chains. This was followed by a smaller mass loss from the breakdown of the polymer backbone at the higher temperature of 450 °C. The derivative curve shows the peaks that indicate increases mass loss rate, clearly indicating the decomposition steps with temperature. These unsaturated sequences re-arrange and decompose to aromatic and aliphatic hydrocarbons as will be confirmed by FTIR. The first step of degradation was almost exclusively elimination of side groups, and the second step was due to the thermal degradation of polyenic structure produced by the elimination reaction. The complex array of free radical reactions, rearrangements and chain scissions led to the decomposition of the main chain as observed by the second slower mass loss (~ 8 %•min⁻¹) in the mass loss curve.

A gradual mass loss below 200 °C is observed (Figure 5.2), that is attributed to the presence of tightly bound water or traces of unreacted monomer in the emulsion polymer that were not volatilised during the drying stage. The remaining mass loss at higher temperature greater than 450 °C is ascribed to the slower pyrolysis of the char that had formed through the main decomposition. A small residual amount (4 % for PVAc) still remained at 800 °C. The amount of acetic acid content of PVAc was determined theoretically to be 72 %. This means that the complete elimination of all acetate side-groups would lead to a char of ~ 28 % confirming that elimination of acetic acid was the predominant degradation process.
Figure 5.2: Thermogravimetric mass loss (—) and derivative (- - -) for PVAc, under inert atmosphere and heating rate of 10 °C•min⁻¹

An indication of the degradation steps, temperature ranges and the nature of the reactions in each step of PVAc were determined by FTIR. The FTIR spectra of PVAc residues are shown in Figure 5.3, at the temperatures indicated. The spectra show broad peaks arising from the presence of various trace amounts of additives or unreacted monomer. The PVAc however, was transparent when completely dry. Nonetheless, the peaks of interest are still present in the spectrum, although at slightly higher wavenumber. This has been summarised in the literature previously, our spectrum is compared with reference material [111, 113]. Both PVAc show the asymmetric aliphatic CH₃ and CH₂ bands (νₘ: 3000, 2951 cm⁻¹, respectively) and their symmetric bands (νₛ: 2898, 2849 cm⁻¹, respectively) are present [111, 113, 114]. The aliphatic CH₃ has a band at 1422 and 1375 cm⁻¹ corresponding to an asymmetric and a bending vibration. The ester carbonyl (C=O) of the functional group symmetric band appeared at 1753 cm⁻¹ and the C-O-C asymmetric and symmetric vibrations appeared at 1271 and 1115 cm⁻¹, respectively [111].
The FTIR spectra of PVAc residues obtained at 360 °C show that ester groups are still present at 1753 cm\(^{-1}\); therefore the elimination of acetic acid at the end of the first step is not fully complete. This effect can be due to the chain reaction of acetic acid elimination leaving some isolated ester groups between two double bonds in the polymeric structure of the residue; the 2921 and 1691 cm\(^{-1}\) bands characteristic of the internal unsaturation are fully developed. Simultaneously, there are signs of aromatization bands that appeared at 1570, 797 and 633 cm\(^{-1}\), and the 1382 band moves to 1453 cm\(^{-1}\).

At 445 °C the FTIR spectra of PVAc residues obtained are the same as there was an increase in the degree of aromatization in the residue as shown by the decrease in the absorption of conjugated double bonds (942 cm\(^{-1}\)) and by the increased absorptions at 2921 and 1437 cm\(^{-1}\) also the presence of 760 cm\(^{-1}\) is attributed to the aromatic C-H bending.
A new C=O band appeared at 1706 cm$^{-1}$. Hydroxyl and carbonyl groups are evident in the spectra obtained at high temperatures; this may arise from aromatization of the aliphatic structures, as observed in the spectra of PVAc heated at 500 °C, which revealed a complete loss of aliphatic hydrocarbon groups (2921 cm$^{-1}$) and a partial loss of carbonyl species. A high content of aromatic rings is fully developed as seen from the C-H vibration of substituted polycondensed aromatic ring (870, 820, 760 and 700 cm$^{-1}$).

5.2.2 Degradation of PVAc composites

The thermal decomposition of filled PVAc composites containing kaolin or talc were investigated by incorporation of increasing amount of a particulate filler composition from 0.4 to 0.7 wt fraction, although we will refer to composites in regards to polymer content as detailed in Table 5.1.
Table 5.1: Thermogravimetric analysis of PVAc and filled kaolin and talc composites series

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mineral</th>
<th>Composite ratio</th>
<th>Onset T (°C)</th>
<th>Derivative peak (°C)</th>
<th>Mass remaining at 800 °C (%)</th>
<th>Rate %·min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>_</td>
<td>100:0</td>
<td>347</td>
<td>354 (1)</td>
<td>4</td>
<td>5.53</td>
</tr>
<tr>
<td>PVAcK0.6</td>
<td>Kaolin</td>
<td>60:40</td>
<td>276 344 460 573</td>
<td>278 (1) 389 (2) 487 (3) 643 (4)</td>
<td>36</td>
<td>1.71</td>
</tr>
<tr>
<td>PVAcK0.5</td>
<td>Kaolin</td>
<td>50:50</td>
<td>275 322 439</td>
<td>286 (1) 349 (2) 472 (3)</td>
<td>51</td>
<td>2.45</td>
</tr>
<tr>
<td>PVAcK0.4</td>
<td>Kaolin</td>
<td>40:60</td>
<td>323 332 444</td>
<td>342 (1) 474 (2)</td>
<td>59</td>
<td>3.05</td>
</tr>
<tr>
<td>PVAcK0.3</td>
<td>Kaolin</td>
<td>30:70</td>
<td>284 350 460</td>
<td>280 (1) 390 (2) 489 (3)</td>
<td>70</td>
<td>3.23</td>
</tr>
<tr>
<td>PVAcT0.6</td>
<td>Talc</td>
<td>60:40</td>
<td>273 345 463</td>
<td>276 (1) 382 (2) 487 (3)</td>
<td>48</td>
<td>1.81</td>
</tr>
<tr>
<td>PVAcT0.5</td>
<td>Talc</td>
<td>50:50</td>
<td>255 341 390 462</td>
<td>269 (1) 356 (2) 413 (3) 490 (4)</td>
<td>55</td>
<td>2.77</td>
</tr>
<tr>
<td>PVAcT0.4</td>
<td>Talc</td>
<td>40:60</td>
<td>268 301 390</td>
<td>258 (1) 320 (2) 440 (3)</td>
<td>68</td>
<td>3.27</td>
</tr>
</tbody>
</table>

The thermogravimetric decomposition mass loss curves for the kaolin series are displayed in Figure 5.4. The degradation of PVAcK0.6, containing 0.6 wt fraction polymer shows several steps in the decomposition profile with the onsets of each step at 276, 344, 450 and 573 °C.
Figure 5.4: Thermogravimetric mass loss curves for kaolin composites, under inert atmosphere and heating rate of 10 °C•min⁻¹

The derivative curve in Figure 5.5 shows the steps more clearly by the presence of the peaks as the mass loss rate changes. As previously observed, PVAc exhibited a small mass loss at temperature below 200 °C. In this range the fillers themselves loose negligible mass. A small mass loss at higher temperature was observed at 278 °C, as indicated by the small peak in the curve. The peak is attributed to the formation of water arising from MH and the early steps of dehydration of zinc borate.

Figure 5.5: Derivative mass loss curves for kaolin composites, under inert atmosphere and heating rate of 10 °C•min⁻¹.
Both these FR fillers begin to decompose at similar temperatures (> 250 °C). The maximum rate of mass loss occurs at 414 °C (1.1 %•min^{-1}) for MH while zinc borate has two overlapping mass losses at 378 and 416 °C (~ 0.7 %•min^{-1}). Meanwhile, in the same temperature region, the deacetylation of PVAc also occurs followed by the structural disintegration of the polyolefin species, formation of aromatic species, isomerisation and formation of volatile compounds. The main decomposition temperature region encompassing these mass losses of various volatiles has resulted in a shift towards higher temperature. The degradation of PVAcK0.5 is similar to the degradation of PVAcK0.6 composite, only it showed three steps of degradation, as the decomposition of fillers retard the polymer decomposition. These two composites decomposed at higher temperature compared with the original PVAc. This was due to the presence of FR MH and zinc borate in the PVAc composites which caused the deacetylation reaction to shift to higher temperature. The endothermic release of water from both FRs absorbs heat the vapourisation will cause a further cooling effect on the substrate. Since MH has a relatively high endothermic enthalpy of 1450 J•g^{-1} this will provide the most effective contribution to the heat absorption process. The water loss results in a decrease in the onset of the decomposition as listed in Table 5.1. In addition, the shift in main polymer decomposition to higher temperature may be due to the volatiles being absorbed on the filler surfaces, hence reducing mass loss until higher temperature is reached. This has been suggested to occur with MH for it forms a high surface area inorganic MgO after decomposition, as described Chapter 2. The total amount of water eliminated on thermal dehydration of the MH corresponding to 30.87 wt% is in agreement with theoretical value [115].

The high filler content and less polymer content in the composite (e.g. PVAcK0.4 and PVAcK0.3) can increase tortuosity pathway for the volatiles to be required to migrate from to reach the surface and escape. PVAcK0.4 and PVAcK0.3 composites show two main steps of degradation with onset at 322 ± 10 °C and the maximum rate of mass loss at 349 °C. This indicates that the FRs enhance the thermal stability as the material degrades more slowly at 439 °C with a maximum mass loss at 472 ± 5 °C. A 7 to 10 % residue is formed at 500 °C that is stable to 800 °C. The decomposition for high filler content, degradation starts at comparatively lower temperature, but the material is more stable at a higher
temperature range, i.e. up to 500 °C, for reasons explained earlier. Whereas high polymer content \( \text{PVAcK0.6 and PVAcK0.5} \), degradation starts at higher temperature and the material is stable at 800 °C, this is due to the release of water that will attack the polymer chains leading to hydrolysis of PVAc resulting in a splitting of the molecular chain. Decomposition products continue to degrade by random chain scission to form the final product that contains polyene residue, MgO and boron oxide with a lower molecular mass.

According to Silvalingam [116] the PVAc is mildly affected by the metal oxide in this case (MgO). The degradation of PVAc starts with the release of acetic acid and this can react with the metal oxide (MgO) to form metal acetate. Therefore MgO may have induced the decrease in the decomposition temperature. From 300 - 400 °C, the degradation of the polymer composites was high due to anticipated degradation of MH. In the 400 - 530 °C temperature range the degradation of polymer composites was lower than the expected this may be due to the reaction of the additives with the products of degradation of PVAc.

The action of zinc borate comes into account primarily for its fluxing and purpose of binding the inorganic fillers in the composite. Zinc borate is able to undergo dehydration, although the endothermic process is less effective than MH. A small proportion of zinc borate, particular \( 2\text{ZnO}\cdot3\text{B}_2\text{O}_3\cdot3\text{H}_2\text{O} \), acts as a synergistic agent in polyolefins as has been cited in literature [64, 117] and hence this is extended to our PVAc-based formulations. Zinc borate released about 11 wt% of water in the temperature range of 290–450 °C. The dehydration of zinc borate gives an amorphous structure with boric oxide, which is beneficial for the purpose of improving the char properties.

Composites containing talc or kaolin and MH as FR component with no zinc borate (NZB) (Figure 5.6 and 5.7), were prepared for comparison with the zinc borate composite systems. Several decomposition stages still occurred due to water released from MH, the elimination of acetic acid and decomposition of polyene residue. The polymer decomposition rate for PVAcK0.6 was 12.72 and 2.12 %•min\(^{-1}\) with and without zinc borate, respectively indicating that the presence of zinc borate was important in the composites, as it acts as a synergists agent when it is introduced with MH. The mechanism of action of MH is to form a protective MgO-ceramic and zinc borate reinforces its efficiency by acting as a binder (formation of \( \text{B}_2\text{O}_3/\text{ZnO} \) glass). This MgO-ceramic residue combines with
the degraded polymeric material, leading to a more protective surface layer during decomposition.

However, for PVAcT0.6, the rate was 14.05 and 13.73 % min\(^{-1}\) with and without zinc borate, respectively, these results shows that the presence of zinc borate increases the rate of polymer decomposition for the composites that contain kaolin, and decreases the rate of polymer decomposition for the composites that contain talc. This might be due to the increase of conductivity caused by the lamellar particles of talc and the lack of water issued from MH limits the resistance of the material.

![Figure 5.6: Thermogravimetric and derivative mass loss curves for kaolin-MH composites, under inert atmosphere and heating rate of 10 °C min\(^{-1}\)](image)

The first decomposition step is indicated by a small peak due to the formation of water arising from MH. The second step shows overlapping peaks that is due to the acetic acid elimination and continuing decomposition of MH as it converts to MgO. The third step is attributed to the structural degradation of the polyene backbone in the PVAc. The mass loss of the minerals (kaolin (0.73 %) and talc (1.63 %) are relatively low; hence the mass losses are mainly attributed to the polymer and water evolved from the FRs.

The onset of each stage was at 264, 358 and 455 °C for PVAcK0.6NZB, 260, 354 and 459 °C for PVAcT0.6NZB, 269, 327, 381 and 484 °C for PVAcK0.3NZB, and lastly 259, 357, 375, 394 and 479 °C for PVAcT0.3NZB. This suggested that
excluding zinc borate decreased the onset temperature in comparison with PVAcK0.6, PVAcT0.6, PVAcK0.3 and PVAcT0.3 that contain zinc borate. Table 5.2 lists the stages showing that without zinc borate present in the composite, the degradation stages start at lower temperature. Consequently this indicates that having MH by itself in the composites to an early decomposition for all of the four composites because of the release of water from MH which effectively cools the substrate through the endothermic reactions that act in relation to fire resistance. Eliminating zinc borate leads to the disappearance of the amorphous phase, since zinc borate effect is due to the softening and retaining/trapping volatiles.

![Figure 5.7: Thermogravimetric and derivative mass loss curves for talc-MH composites, under inert atmosphere and heating rate of 10 °C·min⁻¹](image)

The TGA curves of the PVAc composites revealed some form of interaction between zinc borate and MH that takes place during MH decomposition. Zinc borate degrades well above 380 °C (Chapter 4). The heat treatment of MH and zinc borate in the polymer leads to the formation of boron oxide, this behaviour has been shown to occur with different zinc borates (FB415) [118]. This affirms that the presence of MgO contributes to the degradation of zinc borate. Boron oxide is said to form an amorphous glassy layer, it being a low temperature-
fluxing component. This enables function to bind particles and inhibit the oxygen mass transfer to the polymer fuel system and further oxidise of the char.

Table 5.2: Thermogravimetric analysis of filled kaolin and talc composites with no zinc borate (NZB)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mineral</th>
<th>Composite ratio PVAc: Filler</th>
<th>Onset T (°C)</th>
<th>Derivative peak (°C)</th>
<th>Mass remaining at 800 °C (%)</th>
<th>Rate %•min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAcK0.6NZB</td>
<td>Kaolin</td>
<td>60:40</td>
<td>264 (1)</td>
<td>276 (1)</td>
<td>39</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>358 (2)</td>
<td>374 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>455 (3)</td>
<td>382 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>479 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAcK0.3NZB</td>
<td>Kaolin</td>
<td>30:70</td>
<td>251 (1)</td>
<td>269 (1)</td>
<td>68</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>353 (2)</td>
<td>327 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>450 (3)</td>
<td>381 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>484 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAcT0.6NZB</td>
<td>Talc</td>
<td>60:40</td>
<td>260 (1)</td>
<td>272 (1)</td>
<td>40</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>354 (2)</td>
<td>359 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>459 (3)</td>
<td>380 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>408 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>476 (5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAcT0.3NZB</td>
<td>Talc</td>
<td>30:70</td>
<td>249 (1)</td>
<td>259 (1)</td>
<td>68</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>344 (2)</td>
<td>357 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>451 (3)</td>
<td>375 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>394 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>479 (5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mass remaining at 800 °C for the kaolin composites shown in Table 5.1 increases with increasing the filler content which is very close to the filler amount in the composites before burning, with minor differences. The residues appeared grey which indicates that some inorganic components have not completely pyrolysed and therefore are retained although water/other volatiles evolved.

The substitution of kaolin by talc leads to significant changes in the thermal stability, where the mass loss onset occurred at lower temperatures and improved thermal stability of the polymer composite decomposition. The deacetylation of the PVAc was shifted toward higher temperatures. The platelet structure of talc (2:1 layer structure, octahedral sheet sandwiched by two tetrahedral sheets) is compared with the structure of kaolin (1:1 layer structure, tetrahedral and
octahedral sheets). Talc having small particle size and better wettability by polymers enables a better dispersion and barrier properties to be formed [68]. The TGA mass loss and derivative curves of PVAcT0.6, PVAcT0.5 PVAcT0.4 and PVAcT0.3 shown in Figure 5.8 and 5.9, revealed four stages of degradation.

![Thermogravimetric mass loss curves for talc composites, under inert atmosphere and heating rate of 10 °C min⁻¹](image)

The first small peak at ~ 270 °C is attributed to the formation of water arising from MH and zinc borate. The PVAcT0.4 and PVAcT0.3 show that this first peak is shifted to high temperature the increased filler content, therefore a higher mass loss is observed than in the PVAcT0.5 and PVAcT0.6 where the maximum mass loss occurred at ~350 °C. The derivative curves for all talc composites show two overlapping peaks (350 and 390 °C) due to the water loss from MH and zinc borate in the same temperature region where the deacetylation of PVAc occurred. This was followed by a small mass loss due to the polymer backbone at ~460 °C. The third peak that occurred at 390 °C was more pronounced for the composites with high filler content, perhaps because the filler absorbed some degradation products that decomposed at higher temperature and were retarded by the filler. Table 5.1 showed that the rate of mass loss of the polymer component in the talc series decreased with increased filler content.
TGA curves shown in Figure 5.8 indicate that talc has both a strong catalytic effect on deacetylation reaction (first mass loss) and a charring effect [68]. The talc seems to promote the formation of a polymer-filler char that was comparatively more thermally stable. Effectively the derivative peak showed a small shift to higher temperatures (from 347 °C for pure PVAc to 350 °C for PVAcT0.6). PVAcT0.3 degradation started at lower temperature as shown in Figure 5.8 since it consists of the highest talc content. According to Durin-France et al. [4], synergy was found to occur when in systems containing talc, zinc borate (FB415) and MH this is because talc tends to increase the thermal conductivity of the polymer that is caused by the lamellar particles of talc. The kaolin itself is calcined with <1 % mass loss is present, since organic matter and water would have been removed in the treatment, therefore the calcination process (dehydroxylation) might have effected the catalytic activity of kaolin compared with talc.

To observe the influence of the fillers on the decomposition of the polymer, theoretical curves were constructed from the individual component in their relative proportion. Figure 5.10 illustrates the enhanced thermal stability of the filled PVAc composites with the experimental and theoretical mass loss curves for kaolin system. The effect on the PVAc degradation of adding the filler in comparison with the calculated weight loss curves for respective amounts of each
individual component, assumes that they are not influenced by each other. The measured mass loss indicate otherwise, with composites containing a high relative proportion of MH and zinc borate filler (PVAcK0.3 (a and a’) and PVAcK0.4 (b and b’)) exhibiting decomposition at similar lower temperatures for the first mass loss stage, but as temperature increased to about 400 °C, the mass loss rate measured was more gradual than that calculated.

Composites containing a lower amount of filler (PVAcK0.5 and PVAcK0.6) show a higher temperature mass loss compared with the theoretical curve, indicating that a degree of mutual interactions exist between the phases present. The stages of decomposition for the acetic acid formation and pyrolysis of the polyene is more pronounced as the behaviour of the polymer degradation was the dominant process. These results show that although MH and zinc borate filler decreased the initial thermal stability of the composite, the rate of degradation of PVAc can be reduced through the various mechanisms described above.

![Figure 5.10: Thermogravimetric mass loss for FR kaolin composite (a) PVAcK0.3, (b) PVAcK0.4 (c) PVAcK0.5 and (c) PVAcK0.6, measured and (a’, b’, c’ and d’) theoretically calculated](image)

5.3 Infrared Spectroscopy of PVAc Composites of Kaolin Series

The FTIR spectra of PVAcK0.6 degraded under nitrogen in the TGA furnace at increasing heat treatment temperatures (25, 325, 377, 427, 476 and 500 °C)
throughout the decomposition are shown in Figure 5.11. This composition was selected as it provides a high temperature residue with a low decrease in the onset temperature of degradation.

![FTIR spectra of PVAcK0.6 residue degraded under inert atmosphere at different temperatures](image)

Figure 5.11: FTIR spectra of PVAcK0.6 residue degraded under inert atmosphere at different temperatures

The FTIR spectrum of the original composite at ambient showed typical absorption bands that are due to the polymer and fillers. Identified peaks strongly evident can be observed for MH, while other peaks are due to the zinc borate and kaolin. The MH peaks are at 3696, 2923, 2363, 1638 and 1423 cm\(^{-1}\) respectively. The asymmetric aliphatic CH\(_3\) and CH\(_2\) bands from PVAc (\(\nu_a\): 3000, 2951 cm\(^{-1}\), respectively) are shifted to 3415 and 2934 cm\(^{-1}\) respectively due to the overlap of kaolin and MH bands. The aliphatic CH\(_3\) also has band at 1422 and 1375 cm\(^{-1}\) corresponding to an asymmetric and a bending vibration are shifted to 1435 and 1379, respectively due to the presence of kaolin and zinc borate [119, 120]. The ester carbonyl (C=O) of the functional group symmetric band appeared at
1753 cm$^{-1}$ is shifted to 1733 cm$^{-1}$ due to MH and kaolin and the C-O-C asymmetric and symmetric vibrations appeared at 1271 and 1115 cm$^{-1}$, are shifted to 1261 and 1107 cm$^{-1}$ respectively [37].

At 325 ºC, the spectrum shows the 3698, 3455 and 2925 cm$^{-1}$ bands that characterise the presence of MH, kaolin and zinc borate, a large band appeared at 1740 and 1630 cm$^{-1}$ due to overlapping of kaolin and PVAc residue. [118]. At 377 ºC the spectrum shows a broad band at 3415 cm$^{-1}$ that illustrates the bands at 3698 and 3455 cm$^{-1}$ are developed due to the dehydration of zinc borate and the presence of MgO and aromatics (bands overlapping in the frequency range). Simultaneously, there are signs of aromatisation bands that are detected at 1581, 801 and 621 cm$^{-1}$ exhibited by the polymer. Heat treatment at temperatures of 427, 476 and 500ºC showed a similar spectrum to the previous temperature of 377 ºC. The spectrum shows the residue of the polymer and the fillers after the second stage of degradation that demonstrate the bands are overlapped and the main peaks presence are 3430, 2926 (symmetric aliphatic CH$_3$ and CH$_2$ bands), 2360 (CH$_3$), 1592 (aromatic ring), 1417 (CH$_2$ of the vinyl group), 1093 (CH$_2$ of the vinyl group) and 812 cm$^{-1}$ (aromatic ring) respectively. Peaks were observed for the formation of MgO at 3500, 1700 and 1500 cm$^{-1}$.

5.4 Mechanical Properties

The flexural properties of the PVAc composites were measured to observe the influence of filler composition. From stress-strain data, the modulus at 0.2 % strain, Young modulus and ceramic residue strength after heating to 400 and 1050 ºC were determined and listed in Table 3. The modulus increased from 27 to 370 MPa for the kaolin mineral based systems and from 7 to 470 MPa for the talc mineral as expected for increasing filler content. Both systems increase significantly with kaolin or talc showing a more linear trend with increasing filler content.

The results show that decreasing the polymer content significantly increased the flexural strength, modulus and toughness. Addition of filler significantly enhanced the mechanical performance of the PVAc. The increase in the flexural modulus, expressing the initial stiffness of the material, and its strength, were attributed to the inclusion of rigid filler in the PVAc composites.
It has been frequently demonstrated that the strength of a material is influenced by the nature of the interactions between the polymer and the filler. The elasticity of a composite is usually reduced by incorporation of any rigid inorganic content [121]. MH and zinc borate are the most promising inorganic fillers for the polymer composites that show improvement in the mechanical properties and the toughness. After burning the composites at 400 and 1050 °C zinc borate underwent a transformation that led to a char barrier made of a boron-based glassy phase. Compositions PVAcK0.4 and PVAcK0.3 from the kaolin series, (modulus 249 and 370 MPa respectively) and PVAcT0.4 and PVAcT0.3 from the talc series (modulus 180 and 470 MPa respectively) (Table 5.3) that contain less polymer reveal high Youngs modulus indicating that these compositions were hard or stiff, whereas PVAcK0.6, PVAcK0.5 (modulus 27 and 179 MPa respectively), PVAcT0.6 and PVAcT0.5 (modulus 7 and 19 MPa respectively) with high polymer content exhibit lower Young modulus. There was a large difference between the modulus of the kaolin and talc series as the kaolin series modulus were greater than those of the talc series, this could be due to the low adhesion between the PVAc and the talc than between kaolin and PVAc [122, 123].

![Table 5.3: Mechanical properties for break strength of fire retardant PVAc composite residues](image)

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Modulus at 0.2% strain (MPa)</th>
<th>Young Modulus (MPa)</th>
<th>Ceramic residue strength (MPa)</th>
<th>After heating to 400 °C</th>
<th>1050 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAcK0.6</td>
<td>27</td>
<td>106</td>
<td>0.12</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>PVAcK0.5</td>
<td>179</td>
<td>1090</td>
<td>0.36</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>PVAcK0.4</td>
<td>249</td>
<td>1660</td>
<td>0.58</td>
<td>6.67</td>
<td></td>
</tr>
<tr>
<td>PVAcK0.3</td>
<td>370</td>
<td>1980</td>
<td>1.01</td>
<td>16.9</td>
<td></td>
</tr>
<tr>
<td>PVAcT0.6</td>
<td>7</td>
<td>3</td>
<td>0.07</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>PVAcT0.5</td>
<td>19</td>
<td>30</td>
<td>0.81</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>PVAcT0.4</td>
<td>180</td>
<td>277</td>
<td>0.98</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>PVAcT0.3</td>
<td>470</td>
<td>708</td>
<td>1.49</td>
<td>5.12</td>
<td></td>
</tr>
</tbody>
</table>

Flexural mechanical properties of the PVAc composites after burning in a furnace at 1050 and 400 °C illustrate that both kaolin and talc composites show an
increase in the ceramic residue strength with increasing filler content, after burning the composites at 1050 °C the ceramic residue strength of the kaolin series (1.68, 2.95, 6.67 and 16.9 respectively from the least filled to the most filler composites) was higher than that at 400 °C where they show a lower ceramic residue strength (0.12, 0.36, 0.58, 1.01 respectively). Talc series burned at 1050 °C were similar to the kaolin series that showed an increase in the residue strength with increasing filler content (0.15, 0.36, 1.33 and 11.12 respectively). In addition, these residues were stronger than those obtained at 400 °C (0.07, 0.81, 0.98 and 1.49 respectively). The increase in the strength for kaolin filled PVAc composites was mainly due to the good polymer-filler interaction.

In addition studies revealed that the specific surface area is one of the most important characteristics of the filler, which determines the amount of the surface contact between the polymer and the filler [124, 125]. Fillers with high surface area will contribute to more surface contact between the filler and the polymer, increasing the mechanical properties of the composites. Fillers with fine or small particles have higher surface area than fillers with large particle size. However the finer the particles, the greater their tendency is to agglomerate and this can cause an adverse effect on the mechanical properties as shown in the SEM (Figure 5.12). Figure 5.12a and 5.12b illustrates the SEM of PVAcK0.6 composite burned at 400 °C. Large voids can be seen between the particles due to the disappearance of the polymer and the presence of ceramic residue this is shown in Figure 5.12b (high magnification of Figure 5.12a). Figure 5.12a reveals the continuous sheet structure of kaolin that produced thin particles, which are often found in nature as overlapping sheets, these sheets are bound via hydrogen bonding of the octahedral-layer hydroxyl face of one flake to the tetrahedral-layer oxygen face of the adjacent sheet. Therefore the kaolin layers known as aggregates consist of particles.
Figure 5.12: SEM observation of PVAcK0.6 burned at 400 °C (a and b)

At higher temperature (1050 °C) Figure 5.13a and 5.13b show better fusion and reveal a high stacking density of the fillers with the distance between the particles is small.

Figure 5.13: SEM observation of PVAcK0.6 burned at 1050 °C (a and b)

The talc composite PVAcT0.6 burned at 400 °C is shown in Figure 5.14a and 5.14b. Many microvoids are present compared with the kaolin composite and this is due to the platy nature of talc, as mentioned before this increases the wettability of the filler by polymer therefore after burning, while the polymer volatilised many microvoids will be present.
Figure 5.14: SEM observation of PVAcT0.6 burned at 400 °C (a and b)

Figure 5.15a and 5.15b show the PVAcT0.6 burned at 1050 °C revealing better fusion, but more cracks are present than at 400 °C. Figure 5.15b shows the large particle size of talc that caused the residue strength of this material to be lower than that of the material that contained kaolin.

Figure 5.15: SEM observation of PVAcT0.6 burned at 1050 °C (a and b)

5.5 Conclusion

The thermal degradation of PVAc was investigated. It was observed that PVAc degraded below 330 °C leading to the elimination of acetic acid, and production of double bonds in the polymer chain. The rate of loss of acetate side-groups was
found to increase as degradation proceeded. It was found that non-volatile residue formed by degradation of PVAc consisted of polymeric backbone.

PVAc composites produced with kaolin or talc as filler with FR MH and zinc borate show that increasing the filler content increases the thermal stability of the polymer. It is concluded that when compounded with magnesium hydroxide and zinc borate, the thermal stability of the composites will be significantly increased by filler that releases water on decomposition, resulting in rapid hydrolysis of the polymer chain. Therefore the degradation steps became less pronounced as diffusion of char pyrolysis gases were influenced by filler content. A higher stabilisation of talc compared with kaolin composites was observed.

Various tests have been performed on the polymer composites with kaolin and talc to compare their mechanical properties. Generally kaolin improved the flexural and the ceramic strength of the composites. However talc composites showed lower strength due to the larger talc particle size that increased the wettability by PVAc causing more microvoids after pyrolysing polymer. This made the talc composites weak. SEM micrographs show the stacking density of the filler is relatively high for the kaolin composites whereas talc composites showed more cracks and microvoids.
CHAPTER 6: THERMAL DEGRADATION AND FIRE PERFORMANCE OF FR BUTYL ACRYLATE METHYL METHACRYLATE CO-POLYMER COMPOSITES

6.1 Introduction

The degradation of the emulsion based butyl acrylate methyl methacrylate (BAMMA) copolymer was investigated by thermogravimetry and X-ray diffraction. The BAMMA residues during the degradation transition were analysed by Fourier transform infrared (FTIR) spectroscopy.

The principle of using talc mineral in conjunction with FR was to determine the changes in the thermal stability of the composites. MH is used as the FR filler in the composite as it forms a class of water releasing compounds that on exposure to elevated temperature evolve water to effectively cool the substrate through an endothermic reaction. Hydrated zinc borate was incorporated to improve the char properties by providing a glassy residue. Furthermore, zinc borate has been selected to investigate the advantages in the combination of zinc borate and MH.


6.2 Results and Discussion

6.2.1 Characterization of co-polymer

The FTIR spectrum of the acrylic co-polymer BAMMA is shown in Figure 6.1. The FTIR spectrum showed characteristic absorption peaks at 2955 and 2875 cm\(^{-1}\) are due to C-H stretching mode of alkyl group. The C-H stretching vibration of the aromatic ring assigned to a peak around 3263 cm\(^{-1}\). The absorptions at 1384 and 1446 cm\(^{-1}\) is due to the presence of methyl and methylene groups. In the co-polymer C=O stretching vibrations is observed at 1730 cm\(^{-1}\), this stretching vibration is due to ester group. The absorption band in the range of 1270 and 1240 cm\(^{-1}\) may have contribution from C to O stretching vibrations of ester group. The band at 757 cm\(^{-1}\) is due to the CH\(_2\) rocking mode of methylene chain [87].

![Figure 6.1 FTIR spectra of BAMMA co-polymer](image)

6.2.2 Thermal analyses

Figure 6.2 shows the thermal degradation of BAMMA which shows only one major step of degradation with a maximum weight loss of 96 % at about 423 °C and onset decomposition of 384 °C. The degradation has completed by ~500 °C attributed to main chain and side chain decomposition. A minor amount of residue (0.15 %) remained at high temperature (800 °C).
Figures 6.3, 6.4 and 6.5 show the thermogravimetric mass loss, X-ray diffraction patterns and weight difference curves for series 1 respectively, and Figures 6.6, 6.7 and 6.8 show the thermogravimetric mass loss, weight difference curves, and X-ray diffraction patterns for series 2 respectively.

The thermogravimetric mass loss and derivative curves of BAMMA composites series 1 (composites without zinc borate) and series 2 (composites with zinc borate) are shown in Figures 6.3 and 6.6, respectively. The X-ray analysis pattern of series 1 and 2 heated in the furnace from ambient to 700 °C are shown in Figure 6.4 and 6.8 respectively.

When MH is introduced (BAMMA 02, Figure 6.3) to the polymer, the degradation shifted to a lower temperature (411 °C) compared with the pure polymer (BAMMA 01), and is accompanied by the endothermic release of water and conversion of MH to MgO, this is clearly shown in the derivative curve. Furthermore the curve shows a small second step of degradation that appeared at 475 °C due to the char degradation. The MgO has a relatively large surface area and is known to retain degradation products that later volatiles at the higher temperature than otherwise would for the pure polymer [8].

X-ray diffraction analysis of BAMMA 02 confirms the presence of MgO, the diffraction pattern consistence with JCPDS (periclase 87-0653). The peaks are indexed in order of intensity ($hkl$ in parenthesis) at $\theta = 37.04^\circ$ (111) and $\theta =$
43.037° (200) which is equivalent to the pure MH powder having heat treatment at 800 °C. The weight difference curve as shown in Figure 6.5 is the difference between the theoretical and measured mass losses, where the theoretical curve is the additive summation of the mass fraction for each component of the composite. This curve has been useful in observing interactions between components, giving indication of improvement or reduction in thermal property; in this case the mass loss over temperature. The curve for BAMMA02 containing MH (50 %) shows no change up to 330 °C indicating no difference in mass change as per individual components. In the 330 to 400 °C temperature range (negative difference weight loss curve) the degradation of the composites is slightly higher than expected due to the anticipated decomposition of MH. In addition, the figure shows that in the range of 400-800 °C the loss of weight is lower than expected (positive difference weight loss curve) revealing that the stabilization of the material is occurring in this temperature range [59]. This is because the MH and MgO provide heat sink function, absorbing preferentially the heat during its endothermic transformation. On exhaustion of water source, the polymer decomposition will occur and therefore the mass difference appears to increase significantly in magnitude.

Replacing MH by talc (BAMMA 03) showed one major step of degradation that occurred at 416 °C, with onset occurring at marginally higher than the BAMMA 02 composite. There was no evidence of char degradation as was observed for with MH. The slight increase in onset is due to no structural water loss at this temperature and the platelet morphology of talc. Talc platelets provide a mass transfer barrier (for volatile gases and oxygen) at the polymer surface and by reducing the mobility of polymer chains even after they break during the degradation [68]. The talc does not retain the higher molecular weight volatile species compared with the MgO, as observed for reasons previously described. X-ray diffraction pattern analysis of BAMMA 03 reveals the structural changes of talc at 700 °C due to the water release on heating. As described in Chapter 4 the decomposition of talc is accompanied by the formation of enstatite (Mg•SiO₃) and amorphous silica (SiO₂) at 800 °C. There are some traces of dolomite (JCPDS = 36-0426) and magnesite (JCPDS = 86-0175) traces still present at 700 °C as temperature is not sufficiently high enough to initiate its decomposition.
The weight difference curve (Figure 6.5) of BAMMA 03 reveals that no interaction occurred up to 340 °C. From 340 to 450 °C temperature range talc clay particle heat shielding has assisted in delaying the thermal degradation of the polymer, as we have observed by the increased onset of degradation. However, once that threshold has been reached for polymer decomposition, the rate of has increased and rapidly decomposed, leading to the weight difference curve to reach
back to about 0 at 450 °C. From 450 to 800 °C temperature range the degradation of the composite remains constant and no interaction is noticed.

The partial substitution of talc by MH with different ratios of the mixture BAMMA:talc:MH (BAMMA 04: MH is the major component and BAMMA 05: talc is the major component) leads to significant changes on the degradation steps. The degradation of BAMMA 04 and BAMMA 05 occurs in two steps (Figure 6.3 and Table 6.1); the first step corresponds to a weight loss of 37 % for BAMMA 04 and 46 % for BAMMA 05. The second step represents the maximum weight loss at 464 and 471 °C for BAMMA 04 and BAMMA 05 respectively.

The first step which starts at about 402 ± 10 °C corresponds to the decomposition of the polymer and the release of water from MH and at the same time the process will absorb a great amount of heat to lessen the temperature on the surface of materials, retard the decomposition of polymer, and reduce the formation of potential combustible compounds [126].

TGA curves shown in Figure 6.3 demonstrates that increasing MH content (BAMMA 04) leads to a shift in the first and second mass loss to a lower temperature (402 and 464 °C respectively) and it seems to bring a better thermal stability of sample mass compared with BAMMA 05. Whereas having talc as a
major component, the first and second steps of degradation to shift to higher temperatures (412 and 471 °C, respectively).

The X-ray diffraction pattern of BAMMA 04 is shown in Figure 6.4. As described in Chapter 4 the large number of reflection of the individual components were observed at 200 and 400 °C whereas in BAMMA 04 composite, the mixture of the two components (furnaced at 700 °C) shows the appearance of new broad peaks in the range of $2\theta = 20-40^\circ$ indicating a reaction is occurring and formation of a new crystalline phase exist, due to the dehydration reaction of talc and MH where the water is expelled resulting to the appearance of the major oxides MgO and SiO$_2$.

These observations are in agreement with a study of FR EVA composites by Durin-Frances et al. [4], such systems containing binary and ternary filler components (MH:zinc borate:talc). Evidenced was a synergism between MH and talc (57:3 wt%) for the presence of high content of the hydrated filler in the composite. In addition this is confirmed with the weight difference curve where BAMMA 04 showed the interaction started at ~ 250 °C. Therefore this suggests that the presence of high content of MH with less content of talc in the composite shows interaction at low temperature [4].
Figure 6.5 illustrates that the degradation of this composite in the temperature range of 250-420 °C is higher than expected due to the expected decomposition of MH in this range. Furthermore in the range of 420-800 °C the loss of weight was lower than expected showing that the interaction of the fillers and the polymer lead to the stabilization of the material at this temperature range. The results can be explained by the protective effect of the endothermic decomposition of MH and the reaction of the additives with the products of degradation of the BAMMA co-polymer.

The X-ray pattern of BAMMA 05 shows that the peaks become sharper and more defined with the relative intensity increasing with increasing talc content. The weight difference curve shows that up to 370 °C no interaction appears between the fillers and the polymer. This can be explained by the reactivity of the polymer with the filler leads to a thermal destabilization, moreover it might be due to a catalytic action of degradation that formed during the degradation of the fillers. Having a major amount of talc in the composite does not lead to equivalent FR properties compared with BAMMA 04, since the resistance to ignition is slightly reduced and the self-extinguishability of talc is increased compared with BAMMA 04 [68, 75]. In the range of 370-600 °C the weight of loss is lower than expected, revealing the existence of interaction between the filler and the polymer leading to stabilisation of the material in this temperature range.

In the case of formulation containing only zinc borate and talc (BAMMA 06), significant changes were not observed in the derivative curve. A single sharp decomposition peak at 417 °C (24.11 %·min⁻¹) was exhibited, and this was similar behaviour compared with and without zinc borate. A minor decrease in the rate compared with BAMMA 03 (19.66 %·min⁻¹) this suggest that there is a slight interaction between talc and zinc borate. In addition, the X-ray pattern of BAMMA 06 seem to be a combination of pure talc and zinc borate although the (211) reflection of zinc borate and the (003) reflection of talc overlap in the vicinity of 2θ = 28.7-29.4°. This is an evident indication of the co-existence of the two components and lack of reaction between them. The weight difference curve of BAMMA 06 shows a decrease in the thermal stability between 400 and 500 °C while a slight increase in the thermal stability is observed from 500 to 800 °C.
Figure 6.6 a) Thermogravimetric mass loss and b) derivative curves for BAMMA composites (series 2), under inert atmosphere and heating rate of $10 \degree C \text{ min}^{-1}$

The action of zinc borate in BAMMA formulations (series 2) shows that zinc borate acts as a synergistic agent. BAMMA 07, BAMMA 08, BAMMA 09 and BAMMA 010 are composites that containing zinc borate (Figure 6.6) with different ratios of the mixture BAMMA:talc:MH:zinc borate. All of these composites show two steps of degradation the first step is due to the degradation of the polymer, zinc borate and transformation of MH to MgO. Then the
protective MgO-based ceramic is formed which is shown by the second step. The X-ray patterns of series 2 (Figure 6.8) reveals that zinc borate plays the role of a binder (formation of boron oxide) in the formation of the MgO-based ceramic, this material at the surface of the substrate act then as a physical/thermal barrier [127].

BAMMA 07 where it contains a major amount of MH and an equal amount of zinc borate and talc shows two degradation steps that occurred at 412 and 469 °C respectively, the composite degraded at a high temperature with the onset of degradation at 381 °C. The X-ray diffraction patterns shows the structural changes occurring during the transformation in BAMMA 07 which reveals that with the addition of MH a new peak appeared at $2\theta = 17.9^\circ$. In addition the figure reveals the appearance of new diffraction peaks compared with BAMMA 06 in the vicinity range of $2\theta = 20-45^\circ$. Meanwhile the formation of MgO is revealed by the diffractions (111) and (200) at $2\theta = 35.3^\circ$ and $42.9^\circ$ respectively.

Zinc borate is capable of flow at high temperature, because it has a softening temperature over the range of 300-700 °C, therefore it can react with the basic and highly catalytic MgO surfaces [128, 129]. The weight difference curve of BAMMA 07 shows that no interaction observed up to 390 °C. There is however interaction observed in the temperature range of 390-600 °C, a large increase in thermal stability indicated by the higher positive mass difference.

![Figure 6.7: Mass difference curves of BAMMA composites (series 2) (difference between experimental curves and calculated curves)](image)
BAMMA 08 contains a major amount of MH (36 wt%), low zinc borate (9 wt%) and talc (15 wt%). The thermal degradation revealed a shift in the first and second mass loss to a lower temperature (410 and 464 °C respectively) compared with BAMMA 07. The weight difference curve of BAMMA 08 shows an interaction that started at 250 °C with a decrease at about 10 wt% in the thermal stability between 250 and 410 °C. This thermal destabilisation suggests a reaction between filler and the polymer leading to the formation of volatiles. Figure 6.7 shows that the degradation of BAMMA 08 composite in the temperature range of 410-600 °C is lower than expected showing that the interaction between the fillers and the polymer lead to the stabilization of the material at this temperature range. The protective effect of the endothermic decomposition of water, barrier layering provided by talc and zinc borate present, all interact to stabilise the polymer to higher temperature, in addition to limiting degradation products from leaving the substrate.

The X-ray diffraction pattern of BAMMA 08 shows that increasing MH content resulted in an increase in the relative intensity compared to BAMMA 07. The intense reflections observed indicates a stable crystalline structure which has been assigned to magnesium borate, 3MgO•B₂O₃ (JCPDS 75-1807) [130, 131], having an orthorhombic unit cell structure and is indexed at 2θ = 33.5 (121), 36.4 (130), 40.4 (211), 41.4 (131), 38.8 (201), 25.8 (101), 22.4 (011), 27.9 (111) and 21.2° (020).
On the other hand BAMMA 09 has substantial amount of talc (25 wt%) and 16.7 wt% of MH and 8.3 wt% of zinc borate shows that the composite decomposed at higher temperature (416 °C) compared with BAMMA 08 with onset of degradation at 386 °C. The X-ray pattern of BAMMA 09 reveals that with increasing talc content the peaks become sharper, in addition it resulted to the appearance of new weak diffraction peaks indicating a new crystalline structure of enstatite (Mg\textsubscript{2}SiO\textsubscript{3}) and amorphous silica (SiO\textsubscript{2}). Whereas BAMMA 010 contains a high amount of MH (25 wt%) and talc (20 wt%) and a minor amount of zinc borate (5 wt%) and it reveals an early decomposition of the first and the second step (410 and 453 °C respectively) compared with BAMMA 09. This might suggest the formation of boron oxide. Carpentier [118] have indicated that the decomposition of zinc borate (FB 415) is caused in the presence of MH. Similar behaviour may be expected for this particular zinc borate as it has been shown to occur for (FB 415 structure) in the presence of MH.

The weight difference curve reveals that the degradation of BAMMA 010 shows a decrease in the thermal stability between 245 and 415 °C, due to the volatise formation from the reaction between the filler and the polymer. Figure 6.7 illustrates that the degradation of BAMMA 010 in the temperature range of 415-
600 °C is lower than expected suggesting that the interaction of the fillers and the polymer lead to the stabilization of the material at this temperature range. From the X-ray results it can be concluded that the partial substitution of MH with zinc borate (BAMMA 07, BAMMA 08, BAMMA 09, and BAMMA 010) leads to the presence of magnesium borate and zinc oxide. In addition the evolution of a crystalline boron oxide was revealed amongst the X-ray peaks of very low intensity. The formation of zinc oxide by the reaction between the dehydrated zinc borate and magnesium oxide can be described by the following reaction [132]:

$$2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 + 3\text{MgO} \rightarrow 3\text{MgO} \cdot \text{B}_2\text{O}_3 + 2\text{ZnO}$$  \hspace{1cm} \text{Equation 6.1}$$

A new composite was made without talc, a mixture of BAMMA:MH:zinc borate (2:1:1 ratio) (BAMMA 011) in order to observe the interactions between MH and zinc borate. It was heated from 300 °C to a target temperature set in relation to various transitions that occurred during decomposition, as observed by thermogravimetry where it shows two degradation steps. The first major step occurred at 415 °C (8.99 %•min⁻¹) with onset decomposition of 383 °C. The second step of decomposition occurred at 470 °C (0.99 %•min⁻¹). The target temperatures were 400, 700 and 900 °C. The X-ray patterns of BAMMA 011 after calcinations in the furnace are shown in Figure 6.9. The results reveal that the peaks become narrower and better defined compared with the composites that contain talc. In addition the broad amorphous peak in the range of 2θ = 5-20° has been disappeared and peaks appeared at 300 °C for MgO. Moreover at 300 °C some relatively weak reflections were observed for zinc borate in the range of 2θ = 20-39°. This is because water was still retained in the structure.
Figure 6.9: Wide-angle X-ray patterns, structural evolution for BAMMA 011 composite obtained after heating to the temperatures as labelled in the patterns.

At 400 °C the loss of hydrated zinc borate crystalline structure is evidenced, meanwhile the formation of MgO is revealed by weak reflections at $2\theta = 42.9$, 62.3 and 78.7°. At 700 °C intense reflections are observed and are retained at 900 °C.
Table 6.1: The TGA analysis of filled BAMMA composites

<table>
<thead>
<tr>
<th>BAMMA composites</th>
<th>Polymer Content</th>
<th>Derivative peak (°C)</th>
<th>Mass loss at each stage (%)</th>
<th>Overall Mass loss at 800 °C (%)</th>
<th>Overall Mass remaining at 800 °C (%)</th>
<th>Onset $T$ of the 1st step of degradation (°C)</th>
<th>Rate %•min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAMMA 01</td>
<td>100</td>
<td>424 (1)</td>
<td>99 (1)</td>
<td>99</td>
<td>0.2</td>
<td>384</td>
<td>38.92</td>
</tr>
<tr>
<td>BAMMA 02</td>
<td>50</td>
<td>412 (1)</td>
<td>45 (1)</td>
<td>62</td>
<td>37</td>
<td>374</td>
<td>11.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>476 (2)</td>
<td>14 (2)</td>
<td></td>
<td></td>
<td></td>
<td>4.95</td>
</tr>
<tr>
<td>BAMMA 03</td>
<td>50</td>
<td>416 (1)</td>
<td>49 (1)</td>
<td>50</td>
<td>50</td>
<td>381</td>
<td>19.66</td>
</tr>
<tr>
<td>BAMMA 04</td>
<td>50</td>
<td>402 (1)</td>
<td>45 (1)</td>
<td>62</td>
<td>37</td>
<td>363</td>
<td>11.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>464 (2)</td>
<td>16 (2)</td>
<td></td>
<td></td>
<td></td>
<td>6.91</td>
</tr>
<tr>
<td>BAMMA 05</td>
<td>50</td>
<td>412 (1)</td>
<td>38 (1)</td>
<td>53</td>
<td>46</td>
<td>378</td>
<td>13.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>471 (2)</td>
<td>15 (2)</td>
<td></td>
<td></td>
<td></td>
<td>5.65</td>
</tr>
<tr>
<td>BAMMA 06</td>
<td>50</td>
<td>417 (1)</td>
<td>50 (1)</td>
<td>51</td>
<td>48</td>
<td>389</td>
<td>24.11</td>
</tr>
<tr>
<td>BAMMA 07</td>
<td>50</td>
<td>412 (1)</td>
<td>42 (1)</td>
<td>60</td>
<td>39</td>
<td>381</td>
<td>15.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>469 (2)</td>
<td>17 (2)</td>
<td></td>
<td></td>
<td></td>
<td>6.12</td>
</tr>
<tr>
<td>BAMMA 08</td>
<td>50</td>
<td>410 (1)</td>
<td>39 (1)</td>
<td>55</td>
<td>44</td>
<td>369</td>
<td>14.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>464 (2)</td>
<td>16 (2)</td>
<td></td>
<td></td>
<td></td>
<td>4.00</td>
</tr>
<tr>
<td>BAMMA 09</td>
<td>50</td>
<td>416 (1)</td>
<td>37 (1)</td>
<td>55</td>
<td>43</td>
<td>386</td>
<td>15.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>473 (2)</td>
<td>18 (2)</td>
<td></td>
<td></td>
<td></td>
<td>6.22</td>
</tr>
<tr>
<td>BAMMA 010</td>
<td>50</td>
<td>410 (1)</td>
<td>42 (1)</td>
<td>57</td>
<td>42</td>
<td>346</td>
<td>11.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>453 (2)</td>
<td>16 (2)</td>
<td></td>
<td></td>
<td></td>
<td>8.01</td>
</tr>
<tr>
<td>BAMMA 011</td>
<td>50</td>
<td>415 (1)</td>
<td>48 (1)</td>
<td>58</td>
<td>39</td>
<td>383</td>
<td>8.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470 (2)</td>
<td>10 (2)</td>
<td></td>
<td></td>
<td></td>
<td>0.99</td>
</tr>
</tbody>
</table>
6.2.3 Oxygen combustion calorimetry of fire retardant composites

The combustion behaviour of BAMMA composites was investigated using the cone calorimetry. Several parameters are obtained from a cone calorimeter test. The heat release rate per unit area is measured (HRR, kW·m⁻²), an important parameter that expresses the intensity of the fire, which determines other parameters, such as time to ignition (TTI, s), effective heat of combustion (EHC, Δhₑ, MJ·kg⁻¹), total heat release (THR) and mass loss rate (MLR), specific extinction area (SEA, m²·kg⁻¹), carbon monoxide (CO) and carbon dioxide (CO₂).

6.2.4 Effect of fire retardant fillers on HRR of BAMMA composites

The cone calorimetric results for BAMMA co-polymer and composites are shown in Table 6.2. Figure 6.11 shows the HRR curves obtained as a function of time, for each BAMMA composite compared with BAMMA 01. The figure shows that the FR causes a reduction in HRR and an increase in the total burn time and in TTI, as compared with BAMMA 01.

The changes of HRR as a function of burning time for BAMMA 01 and BAMMA 011 are shown in Figure 6.10 BAMMA 01 burned readily once ignited which was at the shortest time (20 s) and this was accompanied by a rapid increase in the heat release rate (619 kW·m⁻²) with a very broad peak that appeared in the range of 80-335 s, with the time at PHRR was found to be 235 s (Table 6.2).

BAMMA 011 (Figure 6.10) shows that excluding talc from the formulation lead to HRR with different shape compared with the other composites. The first peak appeared at ~ 200 kW·m⁻² and the second peak appeared to have the highest HRR (391 kW·m⁻²) compared with the other composites suggesting that excluding talc increased the HRR, MLR and the time at PHRR, it lead to the lowest EHC value. This behavior is ascribed to the disruption of the composite structure. The loss of water from the composite during heating caused the composite residue to lose there flexibility therefore it became rigid as shown in Figure 6.14.
BAMMA 02, containing only MH, shows two separate HRR peaks (Figure 6.11). The first peak occurred at 145 s with HRR 178 kW·m⁻² and the second peak occurred at 665 s with HRR 185 kW·m⁻². Introducing MH to the composite reveals a large decrease in the HRR value (178 kW·m⁻²) compared to BAMMA 01 (985 kW·m⁻²). This is due to the reduction of the available fuel for combustion by dilution effect, resulting in a gray crumbled powder residue, was mainly inorganic that contained MgO and volatiles (Figure 6.12) [21, 133]. In addition the TTI of BAMMA 02 (~40 s) increased compared with that of BAMMA 01 (20 s) due to the water (from MH) evolved in cooling substrate.

The TTI was most increased by replacing MH with talc (BAMMA 03), due to talc platelet morphology, that likely to retain the polymer protected from the heat, as previously noted for increased thermal stability due to water formation on decomposition. BAMMA 03 shows the highest HRR (peak 1) this is because there was no water to cool.

The specimen thickness is observed to be twice its original thickness this is because of the platelet structure of talc that caused the composite to expand as shown in the photographs presented in Figure 6.12.
The fire retardation efficiency can be increased by the addition of other FR components. The effect of the partial substitution of talc with MH with varying filler content (BAMMA 04 and BAMMA 05) significantly changed the burning behaviour of the composites with HRR halved and the HRR curves of both composites exhibiting two peaks with maxima occurring at 140 and 570 s for BAMMA 04 and at 150 s and 570 s for BAMMA 05. The TTI was increased to 40 s for BAMMA 04 and 42.33 s for BAMMA 05 compared with BAMMA 01. This is attributed to the dehydroxylation of MH, as heat was absorbed to eliminate water. The water vapour contributed to the effect by diluting the volatile compounds in the gaseous phase. The MgO remained in the condensed phase acting as an insulating barrier on the underlying polymer and protecting it from the heat source, as well as limiting the diffusion of gases to the combustion zone [134]. As water evolved from the FR is exhausted, the pyrolysis gases involved from the BAMMA 01 increased in concentration in the combustion zone [127, 133]. In addition the substrate structure is disrupted (Figure 6.12 BAMMA 04 and BAMMA 05 photographs) this contributes to the HRR increasing to the second maxima before decreasing as fuel becomes exhausted.
Figure 6.12 Photographs of the BAMMA composite residues (series 1) after cone calorimetry testing (incident heat flux 35 kW·m⁻²).

Figure 6.13 show BAMMA 06 composite (replacing MH with zinc borate) HRR curve increasing once ignited (275 kW·m⁻²), then remaining between 200 and 238 kW·m⁻² for the duration of combustion. In addition BAMMA 06 appeared to have the lowest time at PHRR for the first peak. The photograph of BAMMA 06 composite (Figure 6.14) reveals dark gray residue suggesting that more carbon char is trapped in the residue; this explains the presence of a carbonaceous char. The addition of a third component zinc borate by the partial substitution of MH (BAMMA 07) resulted in a TTI of 40.3 s, which is slightly longer compared with BAMMA 04 due to an increased endothermic response from the FR system.
BAMMA 08 shows a HRR curve similar to that of BAMMA 07 but it appeared to have the lowest HRR for the first peak compared with the other composites. In addition it showed a decrease in the TTI and time at PHRR of the first peak. This because BAMMA 08 has 33 % MH higher than BAMMA 07, therefore more cooling occurred that reduced the HRR values. On visual observation, the char residue of BAMMA 07 after testing had comparatively stronger char than BAMMA 08. This is because BAMMA 08 has more MgO and talc compared with zinc borate content. Whereas in BAMMA 07 there is relatively higher zinc borate content causing the char residue to be strong.

Figure 6.13 Heat release rate curves for BAMMA composites (series 2) at 35 kW·m⁻² heat flux
Figure 6.14: Photographs of the BAMMA composite residues (series 2) after cone calorimetry testing (incident heat flux 35 kW·m⁻²).
The TTI was most decreased for BAMMA 09, with an increase in the first HRR peak (247 kW•m⁻²) and a decrease in the second HRR peak (212 kW•m⁻²), due to loss of water and volatiles, in addition it may arise from glassy char formation in the condensed phase reducing the rate of diffusion of pyrolysis gases. BAMMA 09 contains half the amount of talc compared with BAMMA 03 but with the presence of MH in BAMMA 09 the residues became more porous to allow the heat to transfer and polymer combustion.

BAMMA 010 had the same filler combination with high talc loading as in BAMMA 09 and showed an increase in the second HRR. This behavior was due to disruption of the composite structure. TTI was slightly increased compared with BAMMA 09, as previously noted for the increased thermal stability due to water formation on decomposition.

We can conclude from these results that the longer the combustion progressed, the lower the mass loss rate. The longer the combustion time, the larger the amount of char formed at the end of the combustion. FR reduced the HRR of BAMMA and increased the total burn time and char yield compared with the pure polymer. In addition the results showed that talc has best effect in delaying the TTI.

Photographs of the BAMMA composites of series 2 are shown in Figure 6.14 where the foaming behaviour is observed to be different with the addition of zinc borate, the photographs show more rigid residues with crack formation compared with the composites of series 1 due to the escape of gasses during heat treatment causing the formation of cracks in the composites. Intumescence was noted for all of these composites.

The cone calorimeter test (Table 6.2) showed that increasing talc loading or having talc as the major phase increased the HRR and TTI due to the absorbed heat and elimination of water. Increasing zinc borate loading decreased HRR, EHC, and MLR due to the formation of a strong and coherent char at the exposed surface derived from the fluxing (binding) action of zinc borate. Increasing MH or having it as the major phase decreased the intensity of fire resulting in a lower HRR, This is due to the water release from MH that decomposed to form an inorganic MgO. Excluding MH as shown in BAMMA 06 did produce a second maximum and remained constant for a period of time for the duration of combustion.
It can be found from Table 6.2 that BAMMA 08 composite with 8 wt% zinc borate has the best synergist effect with MH and talc in the BAMMA composition. However the data in Table 6.2 indicate that the FR performances of BAMMA:talc:MH composites was enhanced by partly substituting MH with zinc borate. The mechanism of the reduction in HRR was mainly due to the physical process instead of chemical process as reported in the literature [115]. Zinc borate consequently formed a char layer by fusing with MH, which acts as a heat insulation barrier. This charred layer prevented heat transfer and transportation of degraded products between melting polymer and surface, thus reducing the HRR and related parameter.
Table 6.2: Fire performance of BAMMA co-polymer and fire retardant BAMMA composites

| Sample  | TTI (s) | Peak HRR (kW m\(^{-2}\)) (1) | Peak HRR (kW m\(^{-2}\)) (2) | Time at PHRR (s) (1) | Time at PHRR (s) (2) | Mean HRR\(_{180}\) (kW m\(^{-2}\)) | Ave EHC (Dhc) (MJ kg\(^{-1}\)) | THR (MJ m\(^{-2}\)) | Ave SEA (m\(^{2}\) kg\(^{-1}\)) | Ave CO (kg kg\(^{-1}\)) | Ave CO\(_{2}\) (kg kg\(^{-1}\)) | MLR Period 10\%-90% of mass loss (PM) |
|---------|---------|-------------------------------|-------------------------------|----------------------|----------------------|-------------------------------|------------------------|----------------|----------------|----------------|----------------|----------------|-------------------------------|
| BAMMA 01 | 20      | 985                           | 619                           | 235                  | 335                  | 636                           | 23.4                   | 199.8         | 282.7         | 0.0153         | 1.73           | 29.80          |
| BAMMA 02 | 39.3    | 178                           | 185                           | 145                  | 665                  | 159                           | 18.8                   | 156.2         | 241.1         | 0.0100         | 1.36           | 7.67           |
| BAMMA 03 | 51      | 302                           | 303                           | 140                  | 455                  | 250                           | 22.2                   | 151           | 430.3         | 0.0213         | 1.57           | 11.27          |
| BAMMA 04 | 39      | 275                           | 238                           | 85                   | 270                  | 229                           | 21.7                   | 88.6          | 456.3         | 0.0203         | 150            | 9.67           |
| BAMMA 05 | 40      | 167                           | 197                           | 140                  | 570                  | 146                           | 19.6                   | 149.6         | 283.6         | 0.0107         | 1.39           | 7.66           |
| BAMMA 06 | 40.3    | 161                           | 178                           | 155                  | 695                  | 143                           | 20.1                   | 163.6         | 283.1         | 0.0103         | 1.46           | 7.13           |
| BAMMA 07 | 38      | 159                           | 181                           | 90                   | 670                  | 135                           | 19.8                   | 158.7         | 328.9         | 0.0133         | 1.49           | 6.83           |
| BAMMA 08 | 42.3    | 199                           | 215                           | 150                  | 570                  | 180                           | 21.2                   | 147.1         | 340.9         | 0.0167         | 1.55           | 8.20           |
| BAMMA 09 | 35.3    | 247                           | 212                           | 190                  | 580                  | 204                           | 21.2                   | 173           | 378.3         | 0.0180         | 1.53           | 9.10           |
| BAMMA 010| 40.7    | 179                           | 200                           | 170                  | 595                  | 157                           | 20.5                   | 149           | 300.1         | 0.0140         | 1.46           | 7.70           |
| BAMMA 011| 37.7    | 196                           | 390                           | 70                   | 215                  | 262                           | 15.6                   | 91.3          | 245.6         | 0.0180         | 1.28           | 14.87          |
6.3 X-ray diffraction pattern after cone calorimetry

The structural changes of the BAMMA composites of series 1 and 2 after completing cone calorimetry were analysed by X-ray diffraction as shown in Figures 6.15 and 6.16 respectively. The X-ray patterns show similar behaviour compared with the composites burned in the furnace, except the broad peak in the range of $2\theta = 5-20^\circ$ is not present. Sharp peaks appeared for the composites that contained talc at $2\theta = 9.5$ (011), 19.0 (002), 19.9 (020) and 28.7$^\circ$ (003). The X-ray patterns after cone calorimetry calcination regime showed sharp peaks, due to the BAMMA co-polymer burning readily once ignited.

![Figure 6.15: Wide-angle X-ray spectra structural evolution of BAMMA composites (series 1) after calcinations regime by cone calorimeter](image)

Figure 6.15: Wide-angle X-ray spectra structural evolution of BAMMA composites (series 1) after calcinations regime by cone calorimeter
6.4 Particle size distribution of BAMMA composites

One of the most important properties of a polymer composite dispersion is the PSD. This property is important not only during the synthesis of the polymer composites, where it strongly influences entry and exit mechanisms of radicals and the stability of the dispersion but also in the chemical, physical and mechanical properties of the final product [135]. It was found that there is a relationship between the degradation rate of polymer composites and particle size. Table 6.1 shows that the rate of pyrolysis decreased for composites with fine particles such as MH (BAMMA 02), whereas gradually increased in case of composites containing larger particle size such as talc (BAMMA 03) and zinc borate.

In finer particles, degradation products formed within the particle can diffuse easily to the surface while in larger particles degradation products have a longer path to the surface of the particle during which autocatalytic degradation of the remaining polymer material can occur [135].

PSD were affected by MH loading as shown in Figure 6.17 for BAMMA 02 and BAMMA 04 and in Figure 6.18 for BAMMA 07 and BAMMA 08. It can be seen
in these figures the affect of MH on peak 1. As MH loading increased the area of peak 1 increased, therefore the number of fine particles that correspond to diameter from 0.26-1.67 μm increased.

Peak 2 corresponds to larger particles with diameter that range between 1.67-4.77 μm. The area of peak 2 appeared to decrease as the MH loading increased, and the peak shifted to a range of smaller diameters.

![Particle size distribution curves of BAMMA composites](image)

**Figure 6.17: Particle size distribution curves of BAMMA composites (series 1)**

Series 1 and 2 (Figure 6.17 and 6.18 respectively) reveal that introducing talc to the composites show broad particle size distribution with a small proportion with particle size of 0.27 to 1.67 μm. In addition the presence of talc in the composites decreased the area of peak 1 and increased the area of peak 2 (1.67-4.77 μm) and peak 3 (4.77-62.99 μm). The effect of peak 3 is mainly influenced by the addition of talc, this can be seen in all of the composites that contain high talc loading such as (BAMMA 03, BAMMA 05, BAMMA 06, BAMMA 07, BAMMA 08, BAMMA 09 and BAMMA 010). This peak became broader with increasing talc loading causing the appearance of large particle size distribution with diameters that range between 4.77-62.99 μm.
Series 2 (Figure 6.18) reveals the effect of the addition of zinc borate on peak 1, 2 and 3. As shown in BAMMA 06 (BAMMA:talc:zinc borate) introducing zinc borate increased the area of peak 1 and 2 and decreased the area of peak 3 compared with BAMMA 03 (BAMMA:talc) composite. Series 2 revealed that introducing zinc borate to the composites causes peak 3 to shift to a range of larger diameters.

6.5 Mechanical properties

The flexural properties of the BAMMA composites were measured to observe the changes with filler composition. Flexural mechanical properties of the BAMMA ceramic-like residue after burning in the furnace at 1050 °C are shown in Table 6.3. The table illustrates that the composites of series 1 where they contain only talc and/or MH reveal low ceramic residue strength. BAMMA 02 shows that having only MH in the composite leads to very low residue strength (0.03 MPa) and having only talc in the composites (BAMMA 03) significantly doubles the residue strength (0.06 MPa) compared with BAMMA 02. The combination of the two fillers (talc and MH) shows an improvement in the residue strength as shown in BAMMA 04 and BAMMA 05 (0.05 and 0.09 MPa respectively). From the results of series 1 illustrated in Table 6.3 it is concluded that increasing talc
content increased the residue strength as clearly shown in BAMMA 05 due to the platelet structure of talc.

An increase in the residue strength was observed after the addition of zinc borate to the composites (series 2). This was due to some fusion domains that present during the calcinations of zinc borate, which lead to a ten-fold increase in the rigidity of the residues.

Table 6.3: Break stress of fire retardant BAMMA composites

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Sealant residue stress burned at 1050 °C (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series 1</strong></td>
<td></td>
</tr>
<tr>
<td>BAMMA 02</td>
<td>0.03</td>
</tr>
<tr>
<td>BAMMA 03</td>
<td>0.06</td>
</tr>
<tr>
<td>BAMMA 04</td>
<td>0.05</td>
</tr>
<tr>
<td>BAMMA 05</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>Series 2</strong></td>
<td></td>
</tr>
<tr>
<td>BAMMA 06</td>
<td>0.21</td>
</tr>
<tr>
<td>BAMMA 07</td>
<td>0.20</td>
</tr>
<tr>
<td>BAMMA 08</td>
<td>0.19</td>
</tr>
<tr>
<td>BAMMA 09</td>
<td>0.23</td>
</tr>
<tr>
<td>BAMMA 010</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The results are affected by the specific surface area of the fillers that determined the amount of the surface contact between the polymer and the filler. As previously described in Chapter 5, fillers with high surface area and small particle size contributed to more surface contact between the filler and the polymer, leading to an increase in the mechanical properties of the composites. However, fillers with fine particles such as MH, causes a greater tendency to agglomerate and this can be determined to the mechanical properties as shown in BAMMA 02.
### Table 6.4: A summary table of BAMMA composites results

<table>
<thead>
<tr>
<th>BAMMA composites</th>
<th>Polymer:Fillers (wt%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAMMA 01</td>
<td>BAMMA</td>
<td>- Reduced overall filler level&lt;br&gt;- Increased smoke</td>
</tr>
<tr>
<td>BAMMA 02</td>
<td>BAMMA:MH 50:50</td>
<td>- Shifted degradation step to lower temperature&lt;br&gt;- Evidence of char degradation&lt;br&gt;- Water release&lt;br&gt;- MgO formed&lt;br&gt;- Decreased HRR value&lt;br&gt;- Decreased smoke&lt;br&gt;- Showed the smallest particle size&lt;br&gt;- Very low residue strength</td>
</tr>
<tr>
<td>BAMMA 03</td>
<td>BAMMA:talc 50:50</td>
<td>- Enhanced flammability,&lt;br&gt;- No evidence of char degradation&lt;br&gt;- Structural water loss&lt;br&gt;- Enstatite formed&lt;br&gt;- Mass transfer barrier&lt;br&gt;- Showed the highest HRR peak&lt;br&gt;- Expanded char residue observed&lt;br&gt;- Showed the largest particle size&lt;br&gt;- Doubled residue strength</td>
</tr>
<tr>
<td>BAMMA 04/ BAMMA 05</td>
<td>BAMMA:MH:talc 50:37.5:12.5/ BAMMA:MH:talc 50:12.5:37.5</td>
<td>- Significant changes on degradation steps&lt;br&gt;- Retarded the decomposition of the polymer&lt;br&gt;- Reduced the formation of potential combustible compounds&lt;br&gt;- Water release&lt;br&gt;- BAMMA 04 better thermal stability than BAMMA 05&lt;br&gt;- MgO and SiO₂ formed&lt;br&gt;- Synergism between MH and talc evidenced&lt;br&gt;- BAMMA 04 small particle size with small proportion of large particle size</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>Degradation of BAMMA Composites</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>BAMMA 05</strong></td>
<td><strong>BAMMA 05</strong> large particle size with small proportion of small particle size</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• HRR halved</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Residue strength increased</td>
<td></td>
</tr>
<tr>
<td><strong>BAMMA 06</strong></td>
<td>BAMMA: zinc borate:talc 50:12.5:37.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No significant changes observed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Decreased thermal stability at low temperature, while increased thermal stability at high temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• HRR increased once ignited then remained constant</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Lowest time at PHRR observed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Carbonaceous char evidenced</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• PSD: area of peak 1, 2 increased and area of peak 3 decreased</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Rigid residue</td>
<td></td>
</tr>
<tr>
<td><strong>BAMMA 07</strong></td>
<td>BAMMA: MH: zinc borate:talc 50:25:12.5:12.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Zinc borate acted as a synergistic agent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Protective MgO-based ceramic formed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Interaction observed at high temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Strong char residue</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Peak 3 shifted to a higher range of particle size</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Rigid residue</td>
<td></td>
</tr>
<tr>
<td><strong>BAMMA 08</strong></td>
<td>BAMMA: MH: zinc borate:talc 50:33:8:14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Thermal destabilisation observed due to the formation of volatiles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• 8 wt% zinc borate showed the best synergy effect with MH and talc in BAMMA composition.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Relative intensity increased</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Magnesium borate and zinc oxide formed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Protective MgO-based ceramic formed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Lowest HRR for the first peak observed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Peak 3 shifted to a higher range of particle size</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Rigid residue</td>
<td></td>
</tr>
<tr>
<td><strong>BAMMA 09</strong></td>
<td>BAMMA: MH: zinc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Decomposed at high temperature</td>
<td></td>
</tr>
</tbody>
</table>
bend: talc
50:6.7:8.3:25

- Sharper X-ray diffraction peaks observed
- Porous residue formed
- Enstatite, amorphous silica, magnesium borate and zinc oxide formed
- TTI most decreased
- First HRR increased whereas second HRR decreased
- Peak 3 shifted to a higher range of particle size
- Rigid residue

BAMMA 010  BAMMA:MH:Zinc borate: talc
50:20:5:25

- Early decomposition observed due to the formation of boron oxide
- Interaction observed at higher temperature
- Magnesium borate and zinc oxide formed
- Protective MgO-based ceramic formed
- Second HRR peak increased due to disruption of composite structure
- Peak 3 shifted to a higher range of particle size
- Rigid residue

BAMMA 011  BAMMA:MH:zinc borate
50:25:25

- Sharper and better defined x-ray peaks
- Loss of hydrated zinc borate structure evidenced
- MgO observed
- Increased HRR, MLR and the time at PHRR
- Lowest EHC value observed
- Rigid residue obtained

6.6 Conclusion

The endothermic properties of MH and zinc borate FR have important features in their function. FR fillers function principally in the condensed phase, through endothermic decomposition, water release, and oxide residue formation, which inhibits thermal feedback. Other characteristics physio-chemical properties are
important, such as the structural changes that occur on exposure to a radiant heat source or fire.

This study has shown that the BAMMA composites undergo structural changes with temperature. The interaction between the FR fillers MH and zinc borate were found to change their thermal degradation process. Zinc borate was found to react with MgO to form of a different crystalline phase, magnesium orthoborate (3MgO•B₂O₃) with crystalline ZnO a by-product of the reaction.

In this study, high zinc borate content leads to a significant improvement of flame retardance during cone calorimetry experiments. The results showed that zinc borate reinforces magnesium oxide structure, changing it from a powdery structure to an expanded rigid structure. In comparison with the pure BAMMA co-polymer, the FR performances in BAMMA composites are characterized by decrease of HRR peak due to retention of volatiles by the ceramifying filler. During combustion, the presence of FR in the polymer leads to the formation of a surface protective layer. This protective layer acted as a barrier, limiting the mass and heat transfers between the flame and the polymer and slows down the toxic gases emission produced by polymer combustion.

Combination of FR with mineral filler synergists significantly reduced the overall filler level and an acceptable level of performance was achieved. Talc was observed to increase the thermal stability and encourage ceramic formation, attributed to the catalytic surface properties that appear during the degradation mechanism. In addition talc enhanced the mechanical properties of the BAMMA composites.
CHAPTER 7: STRUCTURAL AND THERMAL INTERPRETATION OF INTERACTIONS BETWEEN COMBINATION OF BINARY OR TERNARY FR IN PVAc COMPOSITES

7.1 Introduction

The properties of PVAc in the presence of various types of FR are discussed in this chapter. Fillers such as talc, kaolin, CaCO₃ and mica that can undergo endothermic changes at elevated temperatures are used to reduce the flammability and improve the mechanical properties of the composites.

ATH that functions through degradation to Al₂O₃ is used for its decomposition that is accompanied by release of water into the vapour phase diluting the volatile species obtained from polymer degradation. The use of binary and ternary filler combinations in PVAc is studied in this chapter aiming at the formation of thermally stable materials such as aluminium phosphate and calcium phosphate improve high temperature surface protection of the polymer.

The effect on the thermal stability of PVAc composites were investigated using TGA to provide information describing the nature of the filler-filler interactions, together with their relative decomposition temperatures. The structural changes of PVAc composites were determined by wide angle X-ray diffraction technique.
7.2 Results and Discussion

7.2.1 Degradation of PVAc composites

Thermogravimetric mass loss and the corresponding derivative mass loss for PVAc:CaCO₃, PVAc:talc, PVAc:APP, PVAc:ATH, PVAc:kaolin and PVAc:mica are shown in Figure 7.1a and b respectively. The TGA curve of PVAc:CaCO₃ shows three steps of degradation with onset at 326 °C. The majority mass loss (34 %) took place at 353 °C (7.69 %•min⁻¹), due to acetic acid elimination from the polymer side chains, followed by a smaller mass loss from the breakdown of the polymer backbone at the higher temperature of 469 °C, this step took place at 20 °C higher than that of the pure PVAc (450 °C Chapter 5, Figure 5.2) due to the presence of CaCO₃ in the composites. The third step of degradation occurred at 780 °C (2.44 %•min⁻¹) due to the release of CO₂. This step took place at about 40 °C higher than that of the pure CaCO₃ (740 °C, 4.21 %•min⁻¹ Chapter 4, Table 4.1).

The X-ray diffraction pattern of PVAc:CaCO₃ after calcination at 1050 °C is shown in Figure 7.2. The diffraction pattern shown the transformation of CaCO₃ to CaO, this is shown by reflection peaks at 2θ = 28.7 and 34.1°. The peaks appear broad as the diffraction pattern domains converts from CaCO₃ to CaO to which the crystalline structure transforms [110]. In addition there are other sharp peaks appeared in the diffraction pattern that are consistent with JCPDS (calcite 72-1650), this shows that CaCO₃ still present and not all have been converted to CaO. The thermogravimetric mass loss of the three composites PVAc:talc, PVAc:kaolin and PVAc:mica reveal two steps of degradation, the first step is due to the elimination of acetic acid and the second step is due to the breakdown of the polymer backbone, the comparison of the three composites shows that talc brought better thermal stability to the composite than kaolin and mica. The majority mass loss of PVAc:talc occurred at 357 °C with a rate of 8.15 %•min⁻¹. Whereas the majority mass losses of PVAc:kaolin and PVAc:mica were found to be almost equal (362 and 363 °C respectively) because both fillers (kaolin and mica) transform to mullite after calcination. From the thermogravimetric mass loss observed it is concluded that introducing talc, kaolin and mica to PVAc led to an increase in the rate of the reaction compared with the pure polymer (5.53 %•min⁻¹). The X-ray diffraction pattern of PVAc:Kaolin shows no changes.
compared with the pure kaolin. The X-ray patterns of PVAc:Talc is consistent with JCPDS (3MgO·4SiO$_2$·H$_2$O Monoclinic talc 19-0770). The peaks are indexed at $2\theta = 9.5$ (002), 18.9 (002), 19.0 (020), and 28.7° (006). In addition there were indications of enstatite (Mg$_2$SiO$_3$) and amorphous silica (SiO$_2$) as described in Chapter 4.

Figure 7.1: a) Thermogravimetric mass loss and b) derivative curves for PVAc composites, under inert atmosphere and heating rate of 10 °C·min$^{-1}$
The X-ray diffraction pattern of PVAc:Mica reveal no changes in comparison with the pure mica, it reveals the conversion of mica to mullite phase (01-0613) [104]. This is represented by the reflection peaks at 2θ = 16.4, 26.0, 30.9, 33.3, 35.2, 39.1 40.8 and 42.6°.

The thermogravimetric mass loss of PVAc:ATH revealed two steps of degradation. Figures 7.1 show a gradual mass loss commencing below 250 °C. The majority mass loss occurred at 372 °C with the lowest rate of 1.58 %·min⁻¹ compared with the other composites, due to the release of water from ATH which effectively cooled the substrate through the endothermic reaction and hence decreased the rate of decomposition. The second mass loss step occurred at 475 °C due to breakdown of the polymer backbone. ATH shows that above 700 and 800 °C, 37 % char remained, which is expected to be residual alumina.

Figure 7.2: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc composites obtained after heating to 1050 °C

The X-ray diffraction pattern (Figure 7.2) of PVAc:ATH residue shows sharper and better defined peaks with relative intensity increasing compared to the pure ATH (Chapter 4 Figure 4.3). The main reflection peaks that appeared in the diffraction pattern are indexed at 2θ = 19.6 (111), 31.9 (220), 37.6 (311) and 39.5° (222) that are due to γ–Al₂O₃ (alumina 29-0063).
The thermal degradation of PVAc:APP was achieved in three steps of degradation. The first step occurred at lower temperature (345 °C) compared with the other composites in Figure 7.1; this is because PVAc degraded at lower temperature with APP present, therefore PVAc degradation was enhanced by the acidity of APP. The first step of degradation was due to acetic acid elimination as well as elimination of ammonia and water from APP. However above 400 °C the FR enhanced the residual level and hence thermal stability due to the transformation of the linear crystalline APP to a crosslinked ultraphosphate which undergoes fragmentation to volatiles P₄O₁₀ like moieties at 617 °C.

7.2.2 Binary mixtures APP:ATH in the presence of PVAc

The thermogravimetric mass loss and corresponding derivative of PVAc:APP:ATH composites with varying filler ratios are shown in Figure 7.3. All of the four composites show two steps of degradation. The first degradation step is due to the acetic acid elimination from PVAc and water release from ATH as well as the elimination of ammonia, this lead to the formation of aluminium phosphate (as confirmed by the X-ray diffraction pattern in Chapter 4, Figure 4.21). The second step of degradation is due to the breakdown of the polymer backbone.

PVAc:APP:ATH 1:4 and 2:3 show almost an equivalent behaviour. The first and second degradation steps of both composites occurred at 347 and 476 °C respectively. The only difference observed is that PVAc:APP:ATH (1:4) shows that increasing the ATH content gave a rate of 8.95 %•min⁻¹ that was lower than that of PVAc:APP:ATH (2:3) (10.08 %•min⁻¹). The comparison of both composites suggests that increasing APP content accelerated the rate of the reaction. About 50 % mass loss was observed in the first degradation steps for both composites.
Figure 7.3: a) Thermogravimetric mass loss and b) derivative curves for PVAc:APP:ATH composites, under inert atmosphere and heating rate of 10 °C min⁻¹

The thermogravimetric mass loss of PVAc:APP:ATH (4:1 and 1:1) shows that the first degradation steps occurred at 348 (11.05 % min⁻¹) and 351 °C (10.08 % min⁻¹) respectively. The second degradation steps occurred at 469 and 476 °C, respectively. The rate of decomposition of the four composites was decreased between 400 and 600 °C. A high temperature residue of ~ 64 % was still remained at 800 °C for all of the four composites.
The comparison of PVAc:APP:ATH and APP:ATH mixture (Chapter 4, Figure 4.20) shows that introducing PVAc to the composite shifted the first degradation step to higher temperature (349 °C, ~ 8.90 %•min\(^{-1}\)) with onset of ~320 °C compared with APP:ATH (without PVAc Chapter 4, Figure 4.20 and Table 4.2) which degraded at 269 °C (4.51 %•min\(^{-1}\)) with onset of 237 °C. In addition PVAc:APP:ATH (1:1, 2:3, 1:4, and 4:1) showed about 48-59 % mass loss in the first step of degradation where the APP:ATH mixture showed only 30 % mass loss. This result indicated that introducing APP:ATH to PVAc had increased the thermal stability of the polymer.

In addition, the thermogravimetric mass loss of APP:ATH filler mixture showed two separate peaks for the individual fillers, there were new peaks that overlapped with the major individual peaks due to the formation of aluminium phosphate, whereas with the presence of PVAc in the composites (Figure 7.3a), the thermogravimetric mass loss did not show separate peaks for the individual fillers as the polymer acts as a binder to allow reaction within, this is seen in the derivative curve (Figure 7.3b) where it shows two major peaks of the polymer degradation.

This was confirmed with X-ray diffraction pattern shown in Figure 7.4. The X-ray diffraction pattern of PVAc:APP:ATH (1:4, 4:1, 2:3 and 1:1) set show a broad peak that appeared in the range of 2θ = 5-16° in the presence of PVAc in the composites. Whereas the APP:ATH mixture (Chapter 4) did not show this broad peak which is due to partially amorphous structure.

All of the PVAc:APP:ATH composites reveal the transformation of APP:ATH to aluminium phosphate in the composites and this is shown by the appearance of new peaks at 2θ = 15.8 (211), 18.2 (220), 20.4 (310), 24.2 (321), 25.9 (400), 29.1 (420), 30.5 (332), 31.9 (422), 33.2 (510), 35.8 (521), 38.2 (530), 40.5 (611) and 41.56° (620) that are consistent with JCPDS (13-0430 \([\text{Al}(\text{PO}_3)_{3}]_n\)). There are other peaks that present in the X-ray diffraction pattern due to Al\(_2\)O\(_3\) and CaO.

In addition composition with high APP content (PVAc:APP:ATH 4:1) shows evidence of potentially more conversion of the phase formation. This is indicated by the intense peaks.
The thermogravimetric mass loss of PVAc:APP:mica and the corresponding derivative curve is shown in Figure 7.3 a and b. As described earlier in Chapter 4, (Figure 4.20) APP:Mica mixture’s first degradation step occurred at 301 °C (1.33 %•min\(^{-1}\)) and with introduction of PVAc to the filler mixture the degradation step shifted to a higher temperature (351 °C and mass loss of 54 %) with a high rate of 9.79 %•min\(^{-1}\) hence increased the thermal stability of the polymer.

The X-ray diffraction pattern of PVAc:APP:mica (Figure 7.4) reveals the conversion of mica to mullite phase (3Al\(_2\)O\(_3\)•2SiO\(_2\) 01-0613) due to the loss of water [104]. This is represented by peaks in the diffraction pattern at \(2\theta = 16.4, 26.0, 30.9, 33.3, 35.2, 39.1, 40.8, \) and 42.6°.

### 7.2.3 Binary mixture APP:CaCO\(_3\) in the presence of PVAc

As described earlier in Chapter 4 APP:CaCO\(_3\) filler mixture (Figure 4.19) showed 3-4 steps of degradation that were clearly seen in the derivative curves, the first major step showed two overlapping peaks that occurred at \(\sim 300\) and 330 °C (\(\sim 2.19\) %•min\(^{-1}\)) with mass losses of 3-4 % and onset of 270 °C. In the range of 400-600 °C the derivative curves of APP:CaCO\(_3\) filler mixtures showed a small
peak that appeared with a rate of 0.38 %•min⁻¹. In addition the second major steps occurred at 730-770 °C. These two major degradation steps were due to the elimination of ammonia from APP and CO₂ from CaCO₃, and the overlapping peaks were due to the formation of calcium phosphate during calcinations. Whereas after introducing PVAc to the composites with verifying the filler ratios PVAc:APP:CaCO₃ (1:1, 2:3, and 1:4) (Figure 7.5 a and b) only two major steps were observed. The first degradation step occurred at 350-370 °C with a rate of 8.98 %•min⁻¹ and an onset of ~320 °C that is due to acetic acid and ammonia eliminations. The second step of degradation occurred at ~ 470 °C that is due to the breakdown of the polymer backbone and formation of calcium phosphate. At 800 °C a minor step of degradation occurred with a rate of ~ 0.65 %•min⁻¹ which shows that CaCO₃ still existed.

The comparisons of APP:CaCO₃ filler mixture and PVAc:APP:CaCO₃ composite shows that introducing filler mixture to the polymer increased the thermal stability of the polymer. The presence of polymer in the composites accelerated the rate of the reaction compared with the filler mixtures with no polymer (Chapter 4, Figure 4.19 and Table 4.2); this is because polymer and fillers degraded in the same temperature range. In addition polymer acts as a binder holding the filler particles together therefore only the major steps of the polymer were clearly seen in TGA. At higher temperature (400-600 °C) the formation of calcium phosphate was noted from the overlapping peaks (breakdown of polymer backbone and formation of calcium phosphate in the same temperature range) in the derivative curves as CO₂ evolved from decomposition of CaCO₃.
The structural changes occurring during the transformation were determined in the X-ray diffraction patterns (Figure 7.6) PVAc:APP:CaCO₃ composite residues show similar behaviour to those of the APP:CaCO₃ filler mixtures described earlier in Chapter 4 (Figure 4.19). The X-ray pattern showed a broad peak in the
range of $2 \theta = 5-20^\circ$ due to partially amorphous structure. New peaks appeared due to the formation of calcium phosphate that are consistent with $(\text{Ca}_3(\text{PO}_4)_2$ 02-0786 and 01-0941) are indexed at $2 \theta = 13.4, 17.0, 21.6, 25.6, 27.7, 30.9, 32.2, 34.2, 35.3, 37.1, 39.7, 40.9, 43.2$ and $44.8^\circ$. PVAc:APP:CaCO$_3$ (1:4) shows an indication of the presence of CaO in the composite residue.

Figure 7.6: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc:APP:CaCO$_3$ composites obtained after heating to 1050 °C

7.2.4 Ternary filler mixtures in the presence of PVAc

The thermogravimetric mass loss of PVAc ternary composites and the corresponding derivative curves are shown in Figure 7.7 a and b. PVAc:APP:ATH:CaCO$_3$ (1:1:1 and 1.2:1.8:2.0) composites degraded at the same temperature (349 °C) with onset of 321 and 318 °C respectively. This suggests that varying the filler content did not provide any effect on the first degradation step. There was a slight decrease in the decomposition temperature of PVAc:APP:CaCO$_3$:ATH (1:1:1) (475 °C) compared with PVAc:APP:CaCO$_3$:ATH (1.2:1.8:2.0, 480 °C). The first degradation step was due to the filler decomposition that overlapped with the polymer decomposition. The second step of degradation was due to the polyene residue from the polymer and
from the filler residues which are possibly Ca/Al phosphates. There is a small degradation step that occurred at ~ 800 °C that was due to the CaCO₃ degradation.

X-ray diffraction patterns of PVAc ternary composites are shown in Figure 7.8. PVAc:APP:CaCO₃:ATH (1:1:1 and 1.2:1.8:2.0) ternary composites reveal the presence of tricalcium phosphate (JCPDS 01-0941 Ca₃(PO₄)₂) and alumina were seen in the Figure 7.8. Comparison of the two composites revealed that the presence of the polymer in the composites lead to sharper and more intense peaks, whereas the X-ray diffraction pattern of the ternary filler mixture without PVAc (APP:CaCO₃:ATH) (Chapter 4, Figure 4.21) showed broader and less intense peaks. In addition the X-ray pattern shows that the combination of the three fillers led to the of tricalcium phosphate alumina (Al₂O₃•Ca₃(PO₄)₃) according to the ternary phase diagram [110].

The degradation of PVAc:APP:CaCO₃:mica/or kaolin composites are similar in that they both showed two steps of degradation that occurred at 346 and ~473 °C respectively. These two composites degraded at higher temperature compared with the other ternary composites this was due to the presence of FR fillers in the PVAc composites which caused the deacetylation reaction to shift to higher temperature.

The X-ray diffraction pattern of PVAc:APP:CaCO₃:mica shows the presence of muscovite at 2θ = 8.9, 17.7, 21.5, 22.0, 23.3, 26.7, 27.9, 29.8, 31.2, 32.0, 35.0 and 36.3°, calcium phosphate at 2θ = 30.3, 31.0, 32.2, 32.9, 33.7, 35.2, 35.4, 36.5, 37.6, 38.7, 40.0, 42.4, 43.5 and 44.6° and calcium phosphate silicate (Ca₅(PO₄)₂SiO₄ 21.0157) at 2θ = 10.4 (110), 11.4 (200), 15.8 (011), 16.8 (111), 19.6 (211), 22.0 (021), 22.8 (121), 23.0 (400), 23.4 (311), 24.8 (221), 27.2 (102), 28.0 (411), 28.9 (202), 29.6 (031), 30.3 (212), 31.7 (330), 31.9 (022), 33.0 (511), 34.4 (331), 34.8 (600), 35.4 (402), 36.5 (322), 37.8 (032), 38.4 (611), 39.2 (620), 39.5 (530), 39.7 (422), 40.6 (512), 41.6 (113), 42.7 (440), 42.9 (213), 43.6 (522) and 44.6° (123). The thermal degradation of PVAc:APP:CaCO₃:talc showed two degradation steps that occurred at 348 and 473 °C respectively with ~ 63 % overall mass loss at 800 °C, which was the highest mass loss compared with the other composites. This suggests that this composite contains a large amount of water compared with the other ternary composites. The X-ray diffraction pattern of PVAc:APP:CaCO₃:kaolin/talc show similar behaviour, both composites
revealed the presence of calcium phosphate. New reflection peaks appeared from PVAc:APP:CaCO₃:kaolin composite residue due to mullite, from the kaolin, and new peaks appeared in the X-ray pattern of PVAc:APP:CaCO₃:talc composite due to the transformation of talc to enstatite (Mg·SiO₃).

Figure 7.7: a) Thermogravimetric mass loss and b) derivative curves for PVAc ternary composites, under inert atmosphere and heating rate of 10 °C·min⁻¹.
Figure 7.8: Wide angle X-ray diffraction pattern and structural evaluation for the PVAc ternary composites obtained after heating to 1050 °C
### Table 7.1: Thermogravimetric analysis of fire retardant PVAc composites

<table>
<thead>
<tr>
<th>PVAc composites</th>
<th>Polymer Content</th>
<th>Derivative peak (°C)</th>
<th>Mass loss at each stage (%)</th>
<th>Overall Mass loss at 800 °C (%)</th>
<th>Overall Mass remaining at 800 °C (%)</th>
<th>Onset T (°C) of the 1st step of degradation</th>
<th>Rate %•min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>100</td>
<td>354</td>
<td>71</td>
<td>95</td>
<td>4</td>
<td>347</td>
<td>5.53</td>
</tr>
<tr>
<td>PVAc:CaCO₃</td>
<td>50</td>
<td>353</td>
<td>34</td>
<td>70</td>
<td>30</td>
<td>326</td>
<td>7.69</td>
</tr>
<tr>
<td>PVAc:Talc</td>
<td>50</td>
<td>359</td>
<td>33</td>
<td>45</td>
<td>54</td>
<td>334</td>
<td>2.44</td>
</tr>
<tr>
<td>PVAc:APP</td>
<td>50</td>
<td>345</td>
<td>44</td>
<td>89</td>
<td>10</td>
<td>315</td>
<td>1.64</td>
</tr>
<tr>
<td>PVAc:ATH</td>
<td>50</td>
<td>372</td>
<td>47</td>
<td>62</td>
<td>37</td>
<td>338</td>
<td>2.10</td>
</tr>
<tr>
<td>PVAc:Kaolin</td>
<td>50</td>
<td>362</td>
<td>36</td>
<td>48</td>
<td>51</td>
<td>334</td>
<td>1.58</td>
</tr>
<tr>
<td>PVAc:Mica</td>
<td>50</td>
<td>363</td>
<td>35</td>
<td>49</td>
<td>51</td>
<td>338</td>
<td>1.82</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃ 1:1</td>
<td>50</td>
<td>348</td>
<td>43</td>
<td>60</td>
<td>39</td>
<td>320</td>
<td>8.98</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃ 1:4</td>
<td>50</td>
<td>377</td>
<td>41</td>
<td>57</td>
<td>42</td>
<td>344</td>
<td>1.25</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃ 4:1</td>
<td>50</td>
<td>355</td>
<td>45</td>
<td>62</td>
<td>38</td>
<td>318</td>
<td>0.59</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃ 2:3</td>
<td>50</td>
<td>349</td>
<td>43</td>
<td>61</td>
<td>38</td>
<td>320</td>
<td>2.05</td>
</tr>
<tr>
<td>PVAc:APP:ATH 4:1</td>
<td>50</td>
<td>348</td>
<td>48</td>
<td>64</td>
<td>36</td>
<td>326</td>
<td>11.05</td>
</tr>
<tr>
<td>PVAc:APP:ATH 1:4</td>
<td>50</td>
<td>347</td>
<td>50</td>
<td>65</td>
<td>34</td>
<td>318</td>
<td>1.75</td>
</tr>
<tr>
<td>PVAc:APP:ATH 2:3</td>
<td>50</td>
<td>351</td>
<td>48</td>
<td>63</td>
<td>37</td>
<td>322</td>
<td>1.75</td>
</tr>
<tr>
<td>PVAc:APP:ATH 1:1</td>
<td>50</td>
<td>349</td>
<td>50</td>
<td>65</td>
<td>34</td>
<td>323</td>
<td>1.56</td>
</tr>
<tr>
<td>PVAc:APP:Mica 1:1</td>
<td>50</td>
<td>351</td>
<td>42</td>
<td>54</td>
<td>45</td>
<td>323</td>
<td>9.79</td>
</tr>
<tr>
<td>PVAc:APP:ATH:CaCO₃ 1:1:1</td>
<td>50</td>
<td>349</td>
<td>45</td>
<td>60</td>
<td>39</td>
<td>317</td>
<td>1.66</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Mica 1:2:1.8:2.0</td>
<td>50</td>
<td>346</td>
<td>39</td>
<td>56</td>
<td>43</td>
<td>321</td>
<td>9.24</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Kaolin 1:2:1.8:2.0</td>
<td>50</td>
<td>346</td>
<td>40</td>
<td>54</td>
<td>47</td>
<td>319</td>
<td>1.39</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Talc 1:2:1.8:2.0</td>
<td>50</td>
<td>348</td>
<td>48</td>
<td>63</td>
<td>37</td>
<td>213</td>
<td>0.72</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:ATH 1:2:1.8:2.0</td>
<td>50</td>
<td>349</td>
<td>50</td>
<td>56</td>
<td>34</td>
<td>318</td>
<td>8.80</td>
</tr>
</tbody>
</table>
7.3 Mechanical properties

The flexural properties of the PVAc composites were measured to observe the changes with composition and if any improvement in strength was gained by formation of species during the polymer to ceramic transformation. Flexural mechanical properties of the PVAc composites residue after furnace heat treatments to at 400 and 1050 °C, results are shown in Table 7.2. The results illustrate that the PVAc composites had low residue strength after calcination at 400 °C and higher residue strength after calcination at 1050 °C, because some fillers like CaCO₃, mica and talc undergo structure changes at temperatures greater than 400 °C.

PVAc:kaolin, composite showed the highest residue strength after calcination at 1050 °C (0.95 ± 0.29 MPa) this is due to kaolin's fine particle size. Whereas PVAc:mica and PVAc:talc show low residue strength (0.56 ± 0.30 and 0.67 ± 0.40 MPa respectively) due to their platelet structure and large particle size. PVAc:ATH showed very weak residue strength (0.30 ± 0.07 MPa); because ATH was used as a FR agent and it did not increase the strength of the composite. A higher quantity of ATH in the composite improves the residue strength, although limited as the alumina does not fuse.

The results in Table 7.2 shows that having CaCO₃ as a major content in the composite gave powdery residues, this is seen in PVAc:CaCO₃ and PVAc:APP:CaCO₃ (1:4) composites. Whereas having APP as a major content in the composites gave a liquid residue as expected for pure APP leaving no residue for flexural or X-ray tests, in addition this behaviour was observed in PVAc:APP (calcined at 400 and 1050 °C). PVAc:APP:CaCO₃ (1:1 and 2:3) composites show similar strength residues after calcination at 400 and 1050 °C (~ 0.60 ± 0.15 and 0.68 ± 0.12 MPa respectively). Introducing APP:CaCO₃ filler mixture to PVAc showed an expansion in the composite, which affected the strength of the residue making it weaker compared with PVAc:APP:ATH composites, which did not show any expansion, therefore they showed higher residue strength after calcination at 1050 °C.

In addition the results shows that high content of APP combined with ATH (4:1) did not lead to strong fusion of the residues as that seen in PVAc:APP:CaCO₃ (4:1) this is due to the water present in ATH that cools the substrate. In addition it
showed residue strength of 0.70 ± 0.10 MPa. Increasing ATH content in the composite and decreasing APP content (PVAc:APP:ATH 1:4) show a residue strength of 0.66 ± 0.19 MPa that was slightly weaker than PVAc:APP:ATH (4:1). The results in shown in Table 7.2 reveal that PVAc:APP:ATH 1:1 and 2:3 show the highest residue strength (0.87 ± 0.20 and 0.79 ± 0.23 MPa respectively). PVAc:APP:mica 1:1 show residue strength (0.69 ± 0.10 MPa) that was lower than that in PVAc:APP:ATH 1:1 (0.87 ± 0.20 MPa) composite residue this is due to the mica platelet structure that caused the composite to break easily.

A comparison between the PVAc ternary filler mixtures revealed that introducing kaolin to PVAc:APP:CaCO₃ increased the residue strength of the composite (0.86 ± 0.25 MPa) whereas introducing mica decreased the residue strength (0.67 ± 0.30 MPa). Introducing ATH to the composites with varying the filler ratios (1:1:1 and 1.2:1.8:2.0) showed a slight increase in the residue strength for composites with 1.2:1.8:2.0 ratio (0.75 ± 0.30 MPa) compared with 1:1:1 ratio (0.72 ± 0.12 MPa). Replacing ATH with talc (PVAc:APP:CaCO₃:talc) in the composite provided a significant increase in the residue strength (0.79 ± 0.35 MPa).

These results reveal that introducing kaolin or talc to the composite improved the residue strength more than ATH, mica or CaCO₃. This was because kaolin was already calcined and talc showed only 1.63 % mass loss (Chapter 4) therefore no voids were present after the heat treatment. Whereas ATH showed about 32 % mass loss at 277 °C to form Al₂O₃ and CaCO₃ showed about 43 % mass loss at 740 °C to form CaO. The release of water from ATH and CO₂ from CaCO₃ lead to the presence of voids in the composite residues. However after heat treatment weaker residue strength was obtained.

The variability in the mechanical test results for the chars was affected by many factors, include changes in specimen hydration and temperature, structure or type of filler and the structural changes produced during furnace treatment that led to some dimensional changes (shrinkage and expansion) due to formation of carbonaceous char. Some samples were of too little strength after pyrolysis that enabled any measurements.
### Table 7.2: Mechanical properties for break strength of fire retardant PVAc composite

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Ceramic residue strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C (MPa)</td>
</tr>
<tr>
<td>PVAc:CaCO₃</td>
<td>Powder</td>
</tr>
<tr>
<td>PVAc:Talc</td>
<td>0.60 ± 0.50</td>
</tr>
<tr>
<td>PVAc:APP</td>
<td>-</td>
</tr>
<tr>
<td>PVAc:ATH</td>
<td>0.12 ± 0.07</td>
</tr>
<tr>
<td>PVAc:Kaolin</td>
<td>0.56 ± 0.30</td>
</tr>
<tr>
<td>PVAc:Mica</td>
<td>Powder</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>-</td>
</tr>
<tr>
<td>1:1</td>
<td>0.59 ± 0.15</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>0.70 ± 0.30</td>
</tr>
<tr>
<td>1:4</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃</td>
<td>-</td>
</tr>
<tr>
<td>2:3</td>
<td>0.60 ± 0.29</td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>0.11 ± 0.09</td>
</tr>
<tr>
<td>4:1</td>
<td>0.64 ± 0.20</td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>0.62 ± 0.25</td>
</tr>
<tr>
<td>2:3</td>
<td>0.72 ± 0.29</td>
</tr>
<tr>
<td>PVAc:APP:ATH</td>
<td>0.66 ± 0.15</td>
</tr>
<tr>
<td>1:1</td>
<td>0.66 ± 0.15</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:ATH</td>
<td>0.59 ± 0.19</td>
</tr>
<tr>
<td>1:1:1</td>
<td>0.70 ± 0.30</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Mica</td>
<td>0.64 ± 0.19</td>
</tr>
<tr>
<td>1.2:1.8:2.0</td>
<td>0.64 ± 0.40</td>
</tr>
<tr>
<td>PVAc:APP:CaCO₃:Kaolin</td>
<td>0.70 ± 0.20</td>
</tr>
<tr>
<td>1.2:1.8:2.0</td>
<td>0.70 ± 0.20</td>
</tr>
</tbody>
</table>

### 7.4 Conclusion

The thermal degradation of PVAc composites produced with individual fillers (kaolin, talc, CaCO₃, mica, APP and ATH) were investigated. From the thermogravimetric mass loss observed, it was concluded that introduction of talc,
kaolin and mica to PVAc led to an increase in the thermal stability and the rate of the reaction compared with the pure polymer.

The thermogravimetry results of the binary filler mixtures with the presence of PVAc in the composites revealed that when APP was compounded with ATH or CaCO₃ the thermal stability of the composites were significantly increased, the release of water from ATH or CO₂ from CaCO₃ on decomposition, resulted to the formation of a thermally stable aluminium phosphate or calcium phosphate compounds. This was confirmed with the X-ray results.

The mechanical properties of PVAc composites residues revealed that introducing kaolin or talc to the composite improved the residue strength more than ATH, mica or CaCO₃. This is because kaolin is already calcined and talc showed only 1.63 % mass loss (Chapter 4) therefore no voids will be present after heat treatment. The release of water from ATH and CO₂ from CaCO₃ can lead to the presence of voids in the composites; however after heat treatment weaker residue strength were obtained.

The mechanical properties of the composites residue were improved for the binary and ternary filler mixtures. The results showed an increase in the residue strengths for all of the composites. However the fire performance were enhanced for ternary filler mixtures i.e. when the FR were combined with the mineral fillers.
CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

8.1 Conclusions

Fire retardant (FR) polymer composites were prepared by dispersion of filler particles in aqueous polymer emulsions. The resulting composites were analysed before and after furnace heating regimes to explore the filler interactions and strength development over the critical transitional stage.

Two polymer systems were used as a matrix for ceramifiable filler system and each polymer formed a flexible base for the filled composites:

- Poly(vinyl acetate) (PVAc)
- Butyl acrylate methyl methacrylate co-polymer (BAMMA).

The key thermal degradation reaction mechanisms of individual minerals for structure and FR functionality have been investigated using thermogravimetry (TGA). Structural changes were studied using X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy. Each system was studied with reference to thermal stability and structural changes initiated by temperature and the presence of other components in binary and ternary filler combination systems.

The reactions were studied in ratio of 1:1 or 1:1:1 in binary or ternary filler combinations to maximise the potential interactions that could be found in combustion when these filler combination systems were included in the polymer.
The individual filler degradation mechanisms were established. The simplest degradation mechanisms were those of magnesium hydroxide (MH, Mg(OH)$_2$), aluminium trihydroxide (ATH, Al(OH)$_3$) and talc (Mg$_3$[(OH)$_2$•Si$_4$O$_{10}$]). These all underwent dehydroxylation reactions that were initiated at different temperatures. The metal hydroxides formed thermally stable inorganic residues magnesium oxide (MgO) and aluminium oxide (alumina, Al$_2$O$_3$). The TGA results showed that ATH had lower thermal stability compared with MH. Tale being a layered magnesium silicate had a minor amount of water loss due to dehydroxylation, but functioned by providing structure and platelet morphology for barrier performance through limiting gas and heat transfer. The X-ray diffraction patterns showed that the release of water led to the conversion of monoclinic talc (Mg$_3$[(OH)$_2$•Si$_4$O$_{10}$]) to enstatite (Mg•SiO$_3$). Calcium carbonate (CaCO$_3$) decomposed at high temperatures with release of CO$_2$ and the formation of calcium oxide (CaO).

Reaction mechanisms became significantly more complex for ammonium polyphosphate (APP) ([NH$_4$•PO$_3$]$_n$) and zinc borate (2ZnO•3B$_2$O$_3$•3H$_2$O). Both of these components were used for their char enhancing reactions, although individually their decomposition led to different final products. APP was a linear crystalline polyphosphate that underwent transformation to a highly crosslinked polyphosphoric acid (ultraphosphate) with the release of ammonia and water, converting to a polyphosphoric acid and sublimated with increasing temperature. The type of polymer and filler interactions modified the behaviour of the fillers in composites; APP promoted charring and intumescence, and resulted in the entrapment of acid or other products. Zinc borate was used for char enhancing properties and it underwent several changes; dehydroxylation leading to an amorphous structure before crystallising and further melting at elevated temperature, leading to less thermally stable zinc borate (3ZnO•B$_2$O$_3$).

The binary combination of inorganic powders, ATH and/or CaCO$_3$, had the potential to improve the FR action of APP. The combination showed interactions that would have an impact on increasing the char yield and improving the insulation properties of the char. APP:ATH or CaCO$_3$ mixtures on heating led to the formation of new thermally stable aluminium phosphate (AlPO$_4$) and/or
calcium phosphate ($Ca_2P_2O_7$), respectively. These new compounds showed good intumescence properties because of the gas released during conversion to the char product. Ternary combinations of inorganic fillers increased the thermal stability according to thermogravimetric mass loss curves, in addition the combination of the three fillers APP:ATH:CaCO$_3$ produced residues that were found to be tricalcium phosphate alumina ($Al_2O_3\cdot Ca_3(PO_4)_2$). The presence of mica in the composite (APP:CaCO$_3$:mica) caused a shift in the mass loss steps to higher decomposition temperatures more than the other inorganic fillers, due to the formation of calcium phosphate silicate ($Ca_5(PO_4)_2\cdot SiO_4$). Pure mica formed a platelet amorphous structure of mullite ($3Al_2O_3\cdot 2SiO_2$) during degradation.

The thermal decomposition of pure PVAc and PVAc composites produced with individual fillers APP, CaCO$_3$, ATH, mica, kaolin and talc were studied using TGA. The degradation of PVAc led to the elimination of acetic acid, followed by a smaller mass loss from scission of the polymer back-bone. In addition these unsaturated sequences re-arranged and decomposed to aromatic and aliphatic hydrocarbons. This was confirmed using FTIR analysis.

The thermal stability of the PVAc–individual filler composites was enhanced. Introducing the binary (APP:ATH or CaCO$_3$, mica) and ternary (APP:CaCO$_3$:talc, mica or kaolin) filler combinations to PVAc significantly increased the thermal stability of the composites; this was due to the formation of aluminium phosphate ($AlPO_4$), calcium phosphate ($Ca_2P_2O_7$), calcium phosphate silicate ($Ca_5(PO_4)_2\cdot SiO_4$), and tricalcium phosphate alumina ($Al_2O_3\cdot Ca_3(PO_4)_2$). These new compounds can lead to the formation of a surface protective layer that provided increased thermal stability by delaying the degradation of the composites. The structural changes that occurred during transformation were confirmed by X-ray diffraction patterns.

The thermal decomposition of PVAc composites produced with kaolin or talc as filler with FR MH and zinc borate revealed that the first mass loss of PVAc i.e. the elimination of acetic acid overlapped with the decomposition of the fillers by dehydration. This indicated that the endothermic release of water from the
hydrated fillers absorbed heat, while water formed and vapourised thereby cooling the substrate and causing polymer decomposition to shift to a high temperature due to volatiles being absorbed on the filler surfaces. A higher stabilisation of talc compared with kaolin composites was observed.

The flexural strength of the ceramic char formed after heating the (PVAc:kaolin:MH:zinc borate) composites to 1050 °C in a furnace showed that kaolin improved the flexural strength of the ceramic residues from the composites because kaolin had small particle size, and in addition it was already calcined so less water was released during decomposition. However composites that contain talc (PVAc:talc:MH:zinc borate) showed lower residue strength due to the talc platelet structure and larger particle size that increased the wettability by PVAc causing more microvoids after pyrolysing the polymer. This resulted in weakening of the ceramic residue.

The particle size distribution (PSD) of MH, zinc borate and talc revealed that talc had broad PSD, with a small proportion with large particle size. The PSD curve of MH showed a broad peak with the largest area compared with zinc borate and talc. Zinc borate showed one main distribution of particle size corresponding to the presence of large particles and two smaller distributions corresponding to small particle size. Whereas MH showed the smallest particle size compared with zinc borate and talc.

PSD of BAMMA (BAMMA:MH or zinc borate or talc) composites showed results that are similar to the PSD of the pure fillers. MH loading increased the area of peak 1 (corresponds to small particle size) therefore the number of small particles that corresponded to diameter range from 0.26-1.67 μm increased. Introducing talc to the composites increased the area of peak 2 (1.67-4.77 μm) (corresponds to small particle size with small proportion of large particle size) and peak 3 (corresponds to large particle size) in the diameter range from 1.67-62.99 μm. The results revealed that introducing zinc borate to the composites caused peak 3 to shift to a range of larger diameters (4.77-62.99 μm).
Ceramic chars were observed by scanning electron microscopy (SEM). The stacking density of the filler was relatively high for kaolin composites whereas talc composites showed more cracks and microvoids. This concludes that kaolin with the presence of MH and zinc borate in the polymer has the ability to promote the formation of the ceramic-like residue of adequate strength while polymer undergoes decomposition more than talc.

The flexural strength of the ceramic residue was decreased with the presence of the individual fillers, CaCO₃ or ATH, when these were the major fillers components in the composite. PVAc:CaCO₃ gave powdery residues and PVAc:ATH gave very low residue strength (0.30 MPa). However, the flexural strength of the ceramic char for the binary (PVAc:APP:ATH or CaCO₃) (~0.68-0.79 MPa) and ternary (PVAc:APP:CaCO₃:talc or, mica, kaolin) (~0.86 MPa) filler systems were improved and showed higher residue strength compared with that of the composites with individual fillers. This was because the individual fillers showed only loss of water or gas such as CO₂, whereas the binary and ternary combinations showed new crystalline phases that formed a rigid ceramic char.

The thermal decomposition of BAMMA composites were studied using TGA. The interaction between the FR fillers MH and zinc borate were found to increase the thermal stability of the composite due to the formation of magnesium borate. The X-ray diffraction patterns of BAMMA composite residues after heating in the furnace at 1050 °C revealed the structural changes with temperature that occurred during composite degradation. Fire performance investigated by cone calorimetry showed an expanded rigid ceramic residue.

The X-ray diffraction patterns after the cone calorimetry calcination regime showed that zinc borate reinforced MgO by changing it from a powdery structure by forming magnesium orthoborate (3MgO·B₂O₃) resulting in the expansion rigid ceramic residue. The X-ray patterns revealed sharper and better defined peaks, compared with the X-ray patterns of BAMMA composites after heating in a furnace due to the BAMMA co-polymer burning readily once ignited in the cone calorimeter, giving purer residues.
In comparison with the pure BAMMA co-polymer, the FR performance of BAMMA composites (BAMMA:MH:zinc borate or talc) was characterized by a decrease in heat release rate (HRR) peaks due to the formation of a ceramic char that acted as an insulating barrier that slowed the gaseous emission produced by polymer combustion.

Introducing MH to the BAMMA composites increased the time to ignition (TTI) due to the dehydration of MH, as heat was absorbed to eliminate water. The water vapour acted by diluting the volatile compounds in the gaseous phase. MgO remained in the condensed phase and acted as an insulating barrier for the underlying polymer protecting it from the heat source, as well as limiting the diffusion of gases to the combustion zone. Zinc borate played the role of a binder (flux agent) in formation of the MgO-based ceramic. Magnesium borate (3MgO•B2O3) formed at the surface of the substrate and then functioned as a physical/thermal barrier that caused a slow degradation of the polymeric matrix and reduced the flow of the flammable molecules.

The synergies between combinations of one or a number of different fillers in a polymer were investigated. There was evidence of a synergism between MH and talc. This was confirmed with the weight difference curves where the interactions between the fillers were observed. The degradation of those composites in the range of ~ 250-420 °C was higher than expected due to the expected decomposition of MH, and in the range of 420-800 °C the weight loss was lower than expected showing that the interaction between the fillers led to the stabilization of the material over this temperature range due to the protective effect of MgO.

This study has developed FR composites with the optimum selection of fillers. The filler systems that successfully achieved the high char and intense ceramic were based on the combination of zinc borate, MH and kaolin; and the combination of APP, ATH and CaCO3. These filler combinations were found to improve the ceramifying ability (by forming magnesium borate, aluminium phosphate and calcium phosphate) of the compounds by slowing the evolution of degradation gasses, which in turn led to reduction of porosity and gave high
residue strength. Zinc borate and MH filler combination was successful in both polymers (PVAc and BAMMA), however in BAMMA polymer a significantly higher flame retardance was achieved.
8.2 Recommendations for future work

The fire testing process could be extended to include techniques that can accurately characterise the flammability, toxicity and by products of combustion. Techniques could include limiting oxygen index (LOI), thermogravimetry-evolved gas-mass spectrometry analysis (TGA-EGA-MS) and gas chromatography-mass spectroscopy (GC-MS).

LOI determines the relative flammability of polymeric materials, by measuring the minimum oxygen concentration that will support flaming combustion in a flowing mixture of oxygen and nitrogen. This method could be used to systematical investigate the relative flammability of fire retarded materials, commonly comparing the effectiveness of fire retardants (FR) and fire retardancy mechanisms.

Thermal analysis is a widely used analytical technique for materials research. However, thermal analysis with simultaneous evolved gas analysis describes the thermal event more precisely and completely. Among various gas analytical techniques, mass spectrometry has many advantages. An ultra high vacuum (UHV) compatible mass spectrometry based evolved gas analysis (EGA-MS) system can be developed. A commercial TGA analyser can be interfaced to it. Additional mass flow based gas/vapour delivery system and calibration gas inlets can be added to make it a versatile TGA-EGA-MS facility. This system gives complete information on weight change, heat change, nature and content of evolved gases can be used for (i) temperature programmed decomposition (TPD), (ii) synthesis of nanocrystalline materials, (iii) gas-solid interactions and (iv) analysis of gas mixtures.

GC-MS is a technique that could be used to analyse the volatilisation products evolved on heating the composites. In addition GC could be used for separation components of a mixture. Since polymer formulations usually consist of additives, residual monomer and solvents, polymer identification of additives is greatly assisted by their separation so that a spectrum can be obtained for each component in a mixture.
CHAPTER 8 CONCLUSIONS

The fire testing using cone calorimetry technique could be extended for PVAc composites to accurately characterise the flammability, toxicity and by products of combustion.

Nanocomposites technology is beginning to be used in FR applications, such as aircraft interiors. Nano-scale fillers have small particle size with large surface area that allows them to adsorb volatiles. The use of nano-scale fillers in polymer composites forces solutes traversing the filler layers to follow a tortuous path through the polymer matrix surrounding the filler particles, thereby increasing the effective path length for diffusion. The use of nano-scale fillers may lead to synergistic improvements in the FR and char forming nature of the polymer composites, and could lead to improvements to the ceramifying ability of the compounds developed in this study.

Various polymer matrices could be used to prepare FR composites such as polyamide-6 (PA-6) and phenolic resins. PA-6 plays both roles of a polymeric matrix and of a carbonisation agent. PA-6:APP mixture could lead to fire properties of interest by developing an intumescent shield. The association of APP as the acid source and polymeric PA-6 as a carbonisation agent can be used directly as a FR intumescent additive in any polymer matrix. Phenolic polymers are good char formers. The particular combination of thermo-chemical and thermo-physical properties of these char forming polymers have made them a special interest as high temperature resistant FR polymeric materials. Phenolic resin composites are ablative-resistant polymer materials. The ablative properties of phenolic resin composites at high temperatures are outstanding under conditions of high heat flux due to their high heat of sublimation and low ablation rates, phenolic resins can provide excellent ablative cooling in the temperature range of 600 to 1000 °C.
References


REFERENCES


REFERENCES


REFERENCES

