Development of Nanocomposites Based on Functionalization of Polylactic Acid (PLA) and Cellulose Biopolymers

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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**Declaration**

I declare and certify that:

a. Except where due acknowledgement has been made, the work is that of the author alone;
b. The work has not been submitted previously, in whole or in part, to qualify for any other academic award;
c. The content of the thesis is the result which has been carried out since the official commencement date of the approved research program;
d. Any editorial work, paid or unpaid, carried out by a third party is acknowledged;
e. Ethics procedures and guidelines have been followed.

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The scientific theorist is not to be envied. For Nature, or more precisely experiment, is an inexorable and not very friendly judge of his work. It never says 'Yes' to a theory. In the most favorable cases it says 'Maybe,' and in the great majority of cases simply 'No.' . . . Probably every theory will some day experience its 'No.' Most theories, soon after conception." -- Albert Einstein
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Credits

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4. **Mukherjee**, Tapasi, Mark Tobin, Lilijana Puskar, Nhol Kao, Rahul K. Gupta, Nurul Quazi and Sati Bhattacharya, Synchroton based chemically imaging the interfacial region of surface acetylated nanocellulose based PLA matrix (this is the work from Australian Synchroton)

Peer reviewed conference publications:


4

Nomenclature

<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PLA</td>
<td>Poly (lactic acid)</td>
</tr>
<tr>
<td>PBAT</td>
<td>Poly (1,4, butylene adipate)</td>
</tr>
<tr>
<td>MCC</td>
<td>Microcrystalline Cellulose</td>
</tr>
<tr>
<td>NCC</td>
<td>Nanocrystalline Cellulose</td>
</tr>
<tr>
<td>NFC</td>
<td>Nanofibrillated Cellulose</td>
</tr>
<tr>
<td>AC-MCC</td>
<td>Acetylated Microcrystalline Cellulose</td>
</tr>
<tr>
<td>AC-NCC</td>
<td>Acetylated Nanocrystalline Cellulose</td>
</tr>
<tr>
<td>AC-NFC</td>
<td>Acetylated Nanofibrillated Cellulose</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Microscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>ARES</td>
<td>Advanced Rheometric Expansion System</td>
</tr>
<tr>
<td>$d_f$</td>
<td>Fractal Dimension</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Volume Fraction</td>
</tr>
<tr>
<td>$\phi_{per}$</td>
<td>Percolation Threshold</td>
</tr>
<tr>
<td>$\phi_{max}$</td>
<td>Maximum Volume Packing Fraction</td>
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Executive Summary:

Research in material science strongly suggests that even a trace of added nanoscale fillers can significantly improve the properties of a polymer matrix. Reinforcement mechanism needs to be fundamentally understood to establish a successful use of the technology. Nanostructured material research is still a developing area as many aspects of these systems are unclear at present. Literature abounds with numerous works, where the nanofiller reinforcement of polymers leads to numerous mechanical phenomenon including fiber debonding, crack pinning, thin layer yielding and interfacial load transfer. Microreinforcement mechanisms, including crack deflection and filler-polymer debonding, stem directly from reduced filler size and improved dispersions with reduced agglomeration. Other investigations have found evidence that the interface (polymer in contact with another polymer or a non polymer in a bulk phase) between filler and matrix can have long-range impacts on nearby polymer-chains. Overwhelmingly, the research suggests that filler size, loading and distribution dictate the amount of affected polymer. The surface structure and chemistry of the particles dictate the intensity of interaction at the particle / polymer interface. Despite the broadly recognized importance of nanoparticle dispersion, the characterization of dispersion remains largely qualitative and based on subjective interpretations of standard transmission electron microscopy (TEM) images. The successful transfer of nanocomposite technology requires the development of a more fundamental understanding of the reinforcement mechanism. Nanostructured materials are difficult to characterize and many aspects of these systems are unclear at present. The development of a simple and broadly applicable dispersion quantification technique promotes a more fundamental understanding of polymer nanocomposite materials and reinforcement mechanism. By quantitatively measuring dispersion,
systematic studies of processing, loading, particle size, agglomeration and interfacial interaction effects become possible. Optimal dispersion of cellulose as a filler leads to enhanced properties, whereas in the presence of particle agglomerates, a poor material performance will be obtained. It is therefore required to modify the cellulose by some surface treatment to obtain an improved dispersion in biopolymer matrix like PLA to achieve the desired property enhancement. This study is based on the hypothesis that partial substitution of hydroxyl groups on the surface of cellulose by some acetyl groups, eventually will improve the dispersion of nanocellulose in PLA matrix as the acetyl groups will arrest agglomeration of nanocellulose to an extent. As PLA has acetyl groups, it was further assumed that acetyl groups on the surface of cellulose will be more likely to be compatible and disperse in the polymer matrix. Apart from dispersion, this modification can also impart property enhancements of cellulose that could benefit in production of novel products like composites, construction materials, porous materials, fiber web structure, paper and board, coatings, functional surface, functional additives and rheological modifiers in flexible packaging as well as biomedical applications.

This research is focussed on developing a well dispersed nanocellulose based PLA nanocomposite and an in depth investigation of the degree of dispersion by means of all different characterization techniques and examines the fundamentals of nanocellulose dispersion in PLA matrix by using rheology as an effective tool. Further investigations on the enhancement of these nanocomposites in comparison to the composites prepared earlier with cellulose microcrystals are part of the scope of study. Evaluations on the final quality of the dispersion with different surface modifications are conducted by rheological study. This was achieved by preparation of nanocellulose from microcellulose and then surface treating the cellulose by acetylation technique to restrict agglomeration. Evaluations on better dispersion are complemented by morphological and thermal study. The final quality of dispersion is evaluated primarily by evaluating
the rheological percolation threshold and maximum packing fraction, applying the Krieger-Dougherty model.

Successful acetylation of microcrystalline cellulose (MCC) was initially accompanied by acetyl chloride at room temperature as revealed in NMR and FTIR studies. Improvement in dispersion was observed in morphological and rheological tests. This was achieved when composites were prepared by this surface acetylation technique, particularly at a lower filler loading reaching its optimum value around 2.5 wt% (volume fraction: $\emptyset \sim 0.018-0.02$) from the rheological percolation threshold analysis. The observed value indicated that beyond this region, dispersion is affected by agglomeration of the filler. Improved thermal behaviour was observed in DSC thermogram. Further analysis reveals that percent crystallinity is enhanced for all PLA-AC-MCC composites, in comparison to PLA-MCC composites, reaching its optimal value at 2.5 wt% (volume fraction: $\emptyset \sim 0.018-0.02$). This suggests that AC-MCC is a stronger candidate to act as a nucleating agent in comparison to pure MCC in preparing such PLA based composites. Effective surface acetylation on two types of nanocellulose (NCC and NFC) by using acetic anhydride and dimethyl formamide was further achieved. Different types of nanocellulose based (NFC/NCC) and PLA based nanocomposites were prepared by solvent casting technique. Both microscopy and rheological characterization suggested that acetylated NCC yielded nanocomposites with significantly better dispersion in the PLA matrix. In general, low frequency rheological characteristics (loss modulus and storage modulus) increased significantly upon adding the nanofiller. The rheological percolation-volume fraction of $\emptyset \sim 0.018-0.02$ for PLA-AC-NCC composites and $\emptyset \sim 0.052-0.055$ for PLA-AC-NFC composites, respectively - indicates that AC-NCC was a better candidate for better dispersion, probably due to its inherent crystalline rod like structure that helps in forming a network structure in the polymer matrix (Mukherjee et al., 2013). Different values of maximum packing fractions were evaluated as $\phi_{\text{max}} \sim 0.035$, $\phi_{\text{max}} \sim 0.05$, and $\phi_{\text{max}} \sim 0.065$ for
AC-NCC, AC-MCC and AC-NFC, respectively, when the high frequency data was fitted to the Krieger-Dougherty equation (Vermant et al., 2007). The lower value of the maximum fraction leads to a better dispersion of the nanofiller. A direct correlation between the rheological percolation and maximum packing fraction value was also observed. Moreover, when scaling law analysis is performed on AC-NCC and the value is compared with standard clay particles, as obtained from literature, the lower value of $d_f \sim 1.06$ suggested a more open fractal structure to form a pronounced network structure (Puisto et al., 2012). This value also suggests that in comparison to clay particles, the inherent crystalline structure of AC-NCC helps in forming a more organized network in the PLA matrix.

In summary, this research focused on developing a well dispersed nanocellulose based polylactic acid (PLA) nanocomposite and an in depth investigation of the degree of dispersion by using rheology as an effective tool for its evaluation. This was achieved by preparation of nanocellulose from microcellulose and then surface treating the cellulose by acetylation technique to restrict agglomeration. Evaluations on better dispersion are complemented by morphological and thermal study. The final quality of dispersion is evaluated primarily by evaluating the rheological percolation threshold and maximum packing fraction, applying the Krieger-Dougherty model. It was observed that the rheological percolation is directly correlated to the maximum packing fraction. Further to the study, it was also concluded that better dispersion leads to less packing fraction. This factor was used to rank the quality of dispersion. The nature of network formation was further studied by fractal analysis applying scaling laws. The study confirmed a more open network structure.
Chapter 1: Introduction

This section includes overview, justification of the project, research questions and objectives and structure of the thesis.

1.1 Overview

“Green composites” offer hope for designing and developing sustainable products to address ecological concerns, considered as a predominant theme for the 21st century. Inspired by rapid expansion of nanotechnology and its convergence with both biology and ecology, a new class of “green materials” exploits this triple convergence and is an active area of investigation. The challenge lies in improving the efficiency of present system while working to develop new technologies that are inherently more environmentally benign and sustainable (Ahmann and Dorgan, 2007).

Development of polylactic acid or polylactide (PLA) based cellulose nanocomposite is inspired by this paradigm shift in developing composites for biomedical and flexible packaging applications. PLA -nanocellulose composites have been explored in recent years (Jonoobi et al., 2010; Oksman et al., 2006; Peterson et al., 2007; Pei et al., 2010; Braun and Dorgan, 2009) as the key material for nanodevice development.

PLA can be produced from natural resources such as corn, sugar beet, cellulosic waste, and rice starch (Bhardwaj and Mohanty, 2007). Nanocellulose as resourced from the natural fibres is known to be the most chemically versatile, abundant and inexpensive material for reinforcements (Huber et al., 2012). Nanocellulose as available from natural fibres has been much explored as a reinforcing material in PLA. (Sain and Oksman
2006; Gardner et al., 2008; Sequeira et al., 2010; Oksman et al. 2006; Eichorn et al., 2010; Pei et al., 2010; Oka, 2010; Pracella et al., 2010; Tome et al., 2011). Engineers are using PLA’s “green” properties such as biodegradability and selective gas barrier properties in sustainable designing of flexible packaging and biomedical applications such as in ligament fracture and knee injury.

Several factors govern the resulting properties of such composites which include dimension, aspect ratio, geometric and mechanical percolation effect of nanocellulose, to name a few (Dubief et al., 1999). All these factors contribute to the final quality of dispersion and interfacial interaction between the matrix and the reinforcement phase. It is thought that hydrophillic polymers like PLA have the advantage to achieve a strong interface between hydroxyl groups of cellulose whiskers thus resulting in good dispersion. One of the developed processing methods to prepare such composites as referred in the literature is melt compounding (Jonoobi et al., 2010). However, PLA is sensitive to hydrolytic degradation under melt processing conditions in the presence of small amounts of moisture (Oksman et al., 2006), resulting in rapid reduction in final properties. Attempts have been made to blend PLA with elastomers to improve the mechanical properties (Signori et al., 2009). Another route to reduce the hydrolytic degradation is to introduce a long chain branching in PLA or by adding a high molecular weight fraction (Pilla et al., 2009; Mihai et al., 2010). Nanocellulose, too has the tendency to form hydrogen bonds with adjacent nanocellulose due to the high density of hydroxyl groups on their surface, thereby resulting in agglomeration or entanglement (Eichorn et. al., 2010). This phenomenon initiate’s crack causing failure of the composite.

Scientists experimented on variations of the dispersion methods, as practiced otherwise on traditional particles and pigments to overcome the
challenges as mentioned in the above paragraph (Huber et al., 2012). A possible way to achieve a good dispersion during processing is to “switch off” nanocellulose fibre self-interactions by binding with a hydrogen-bond forming solvent. Several “solubilising schemes” have been explored over the last decade to improve dispersibility which include the use of surfactants (Oksman et al., 2006), acetylation (Braun and Dorgan, 2009), silylation (Pei et al., 2010), grafting (Oka. 2010; Pracella et al., 2010) etc.

This research proposal is intended to develop nanocellulose based PLA nanocomposites by exploring the various possibilities to improve the dispersion scheme. This includes but not limited to surface treatment of nanocellulose as well as changing the polymer architecture of PLA by some preliminary grafting techniques. Variations in dispersion methods and an evaluation on the resulting effects of their corresponding PLA composites will be attempted.

1.2. Justification of the Project

The incorporation of nanocellulose into polymers is attractive as it enables the creation of materials with new or improved properties by mixing multiple constituents and exploiting synergistic effects. The broad technological exploitation is however stifled by the lack of effective methods to control the nanocellulose dispersion.

Although the environmental and economic advantages are achieved by using cellulose as filler or reinforcer in bio based composites, the reduction of properties limits its broad scale application and its potential end use. A fully dispersed and a stable state will lead to optimal properties, whereas in the presence of particle agglomerates a poor material performance will be obtained. It is therefore sensible to modify the cellulose by some surface
treatment to attain an improved dispersion in biopolymer matrix like PLA to accomplish the desired property enhancement. This study is based on the hypothesis that partial substitution of hydroxyl groups on the surface of cellulose by some acetyl groups, eventually will improve the dispersion of nanocellulose in PLA matrix as the acetyl groups will arrest agglomeration of nanocellulose to an extent. As PLA has acetyl groups, it was further assumed that acetyl groups on the surface of cellulose will be more likely to be compatible and dispersed in the polymer matrix. Apart from dispersion, this modification can also impart property enhancements of cellulose that could benefit in production of novel products like composites, construction materials, porous materials, fiber web structure, paper and board, coatings, functional surface, functional additives and rheological modifiers in flexible packaging as well as biomedical applications.

Modification of cellulose for property-enhanced cellulose based biopolymer composites has been extensively studied. However, knowledge and information on modification of cellulose that involves improving dispersion for property enhanced application by rheological model is less studied or not reported. The rheological properties, both the linear and non-linear ones, are sensitive to changes in the particulate microstructure, integrated overall length scales. Rheological measurements have hence been used for different types of nanocomposite systems as a complementary, indirect technique to monitor the quality of dispersion, precisely in qualitative terms (Francisco et al., 2011). One of the advantages of rheology is that it offers an integrated picture of the composite samples of macroscopic dimensions, as compared to smaller samples that are prone to micro-scale in homogeneities. With conventional optimal methods, such as microscopy (SEM, TEM and AFM) and light scattering techniques, the investigation is based only on the local microstructure and is unable to adequately capture the relevant levels of dispersion and structure. The alternative approach to
macroscopic dimensions to quantify dispersion offers a global view of the material performance.

1.3. Research Objective, Deliverables and Questions

This research focuses on developing a well dispersed nanocellulose based PLA nanocomposite and an in depth investigation of the degree of dispersion by means of all different characterization techniques and examine the fundamentals of nanocellulose dispersion in PLA matrix. Further investigations on the enhancement of these nanocomposites, in comparision to the composites prepared earlier with cellulose microcrystals, have been part of the scope of this study. Evaluations on the final quality of the dispersion with different surface modifications have been conducted by using rheological study.

Objectives:

- To prepare functionalized PLA/nanocellulose composites.
- To make a systematic rheological measurement of PLA nanocellulose composites.
- To uniformly disperse nanocellulose in their PLA based composite.
- To conduct extensive morphological and rheological analyses.
- To carry out an indepth analysis of dispersion characteristics based on rheological measurements
**Expected Deliverables:**

1. Effective surface acetylation of nanocellulose for a uniform and homogeneous dispersion.
2. Development of a well dispersed nanocellulose based PLA composite
3. Estimation of an optimal loading for a uniform dispersion by fitting data to a rheological percolation threshold model.
4. In depth analysis on characterization of dispersion using maximum packing fraction and scaling laws model.
5. Complimentary morphological analysis to compare the rheological model fit.

**Research Questions:**

1. How to prepare a well dispersed nanocomposite?
2. How will the functionalized nanocellulose disperse in PLA matrix?
3. What is the optimal loading for a uniform dispersion?
4. How will the composite behave in relation to thermal, rheological, and morphological properties?
5. Why is rheological study important in analyzing dispersion?
6. What are the rheological parameters that can be used to predict the dispersion quality?
1.4. Structure of the Thesis

The findings of the end results of the above objectives are presented in Chapters 2 to 7. The Literature review on natural fibres, cellulose, source, biopolymers and cellulose-based complexes, etc. are explained in Chapter 2. This Chapter 2 contains the initial part of the literature review, namely the natural fibre section which is published in Journal of Polymers and the Environment. In addition, a literature review on why dispersion of cellulose in a polymer matrix is important is explained as well in Chapter 2. Experimental Investigations and Errors in Experiment are explained in Chapter 3. Chapter 4 explains the improved dispersion of MCC based PLA composite by surface acetylation. This work is published in Chemical Engineering Science. Chapter 5 characterizes NFC based composites – include PBAT-NFC as well as PLA-AC-NFC based composites. A part of this work is published in Carbohydrate Polymers. Chapter 6 explains the preparation of nanocellulose from MCC with surface treatment and quantifies the quality of dispersion applying the Krieger-Dougherty model. This chapter quantifies dispersion by following rheological protocols and modelling higher frequency and lower frequency data respectively on acetylated nanocellulose crystalline based PLA composites. In Chapter 7, FTIR imaging is used to image the spatial distribution of the functional group chemistry of the composite constituents. In this Chapter it is shown that better interaction is possible due to a better dispersed phase of the nanofiller in the polymer as explained in Chapter 6. Chapter 8 presents the main conclusions and provides some recommendations for future work.
Chapter 2: Literature Review

This section presents a comprehensive literature review on thermoplastic polymers, natural fibres, cellulose, source, biopolymers and cellulose-based complexes. A deeper insight on thermoplastic biopolymer composites based on natural cellulose is presented as well.

Thermoplastic Biopolymer Composites based on Natural Cellulose

There is a growing interest in using natural cellulose–based plastic composites over the last decade from sustainability point of view. Along with the environmental benefits, strength and biodegradability are desirable for the embedded reinforcing fibre and the selected matrix. In this context, it is worthwhile to consider here that the matrix plays a crucial role in the performance of polymer composites. Thermosets and thermoplastics are both attractive as matrix materials for composites, with their advantages and few challenges. In general, thermosets offer a remarkable enhancement in properties over thermoplastic polymers. However, the biggest challenge lies in its formulation, as it is complex because a large number of components are involved. On the other hand, thermoplastic polymers offer many advantages over thermoset polymers. This includes low processing cost along with design flexibility and ease of moulding complex parts (Nabi Saheb and Jog, 1999).

Therefore, selection of a suitable thermoplastic biopolymer matrix is crucial. It is critical to investigate several aspects that are of concern before making the appropriate choice of the polymer matrix for material design.

A biodegradable biopolymer can be processed from either petroleum feedstock as renewable resources. Examples of biopolymer derived from petroleum feedstock include polyester amide (Bayer’s BAK polymer), Polycaprolactone (PCL) and Dupont Biomax copolyester (Mohanty et al., 2001). In comparison to this polymer, examples of polymer that can be
derived from renewable feedstock include poly (lactic acid) (PLA), poly (hydroxyoctanoate) (PHO) and poly (3-hydroxybutyrate) (PHB). These polymers provide significant energy saving and easy degradation of hydrolysis. Another advantage in using these polymers lies in their suitable composite density, mechanical properties and temperature related properties (Van De Velde and Kiekens, 2002). Nevertheless brittleness and slow crystallization of PHB inconvenience its processability. The co-polyester of PHB and poly (3-hydroxyvalerate) (PHV) shows an increasing flexibility. However, high cost has limited PHB and its co-polyester from commercialisation. Furthermore no improvement in the tensile strength of the poly (3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) could be found using hemp cellulose as reinforcing fibre (Keller, 2003). Interfacial properties dominate composite strength and theoretically hemp should improve its strength. This is a recurring problem for most bio composites at present. Therefore, PLA is considered in this project as a polymer matrix.

**Polylactic Acid (PLA)**

Polylactic acid (PLA) can be considered as a well behaved thermoplastic polymer with a reasonable shelf life for most single-use packaging applications, and with proper disposal, will hydrolyze to harmless, natural products. It belongs to the family of aliphatic polyesters commonly made from α-hydroxy acids, and are considered biodegradable and compostable. The basic building block of PLA is lactic acid. The synthesis of lactic acid into high molecular weight PLA can follow two different routes of polymerization, as depicted in Figure 2.1.
The first route includes the condensation process, where lactic acid undergoes a condensation polymerization, to yield a low molecular weight, brittle, glassy polymer, which is generally unusable for any application unless external coupling agents are used to increase the molecular weight of the polymer. A low molecular weight polymer results in the condensation process. This is due to the viscous polymer melt, the presence of water, impurities and statistical absence (low concentration of reactive end-groups and the "back-biting" equilibrium reaction that forms the six-member lactide ring. The second route includes the ring opening polymerization (ROP), that results lactide to yield high-weight-average molecular weight ($M_w > 100,000$) PLA.

The mechanical properties and crystallization behaviour of PLA is very dependent on the molecular weight and stereochemical makeup of the backbone. This stereochemical makeup is very easily controlled by the polymerization with D-lactide, L-lactide, D, L-lactide, or mesolactide, to form random or block stereocopolymers, while the molecular weight is directly controlled by the addition of hydroxylic compounds (Garlotta, 2001). Pure poly (D-Lactide) or poly (L-Lactide) has an equilibrium crystalline melting point of 207 °C, (Raquez et al., 2013) but typically
melting points are in the 170 -180 °C range. The final properties of PLA do not depend on the molecular weight, but more on the content in optical impurities between both lactide enantiomers within PLA chains.

In addition to its biodegradability and renewability, PLA exhibits a Young modulus of around 3 GPa, a tensile strength between 50 and 70 MPa with an elongation at break of ca. 4%, and an impact strength close to 2.5 KJ/m², (Anderson et al., 2008). In comparison to conventional polymers like polyethylene (PE), polypropylene (PP), Polystyrene (PS), and Polyethylene terephthalate (PET), the mechanical properties of semicrystalline PLA are attractive, making it as an excellent substitute for commodity polymers in short-time packaging (Mark, 2009). However, PLA is a brittle material with low impact strength, representing one of its main limitations for the sustainable development of PLA (Auras et al., 2004). However, in addition to this, the main issue about PLA is its low crystallization ability and degree, significantly limiting its industrial implementation in different applications, particularly in durable applications like automotive and electronics (Rasal et al., 2010). A solution largely developed over the past years has consisted to incorporating nano-sized reinforcements within the polymer matrix, yielding so-called nanocomposite materials (Alexandre and Dubois, 2000; Bordes et al., 2009). Various types of fillers have been considered as reinforcing agents to PLA matrix in order to enhance its thermo-mechanical properties as well as to provide additional functionalities like fire-resistance. They include reinforcing PLA with kenaf (Soykeabkaew et. al., 2008), flax (Oksman et al., 2003), jute (Siro and Plackett, 2010), abaca (Shibata et al., 2003), and cordenca rayon fibre (Bax and Mussig, 2008), as reinforcement in order to replace synthetic fibre in polymer composites. A comparative study on the mechanical properties of PLA based composites with different reinforcement fibres as given in Table 2.1, (Mukherjee and Kao, 2011).
Table 2.1 Comparison of the mechanical properties of PLA composites with different reinforcement fibres:

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Source</th>
<th>Fibre type</th>
<th>Fibre proportion in wt%</th>
<th>Charpy impact in %</th>
<th>Tensile strength in %</th>
<th>Young modulus in %</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Bledzki and Jaszkiewicz (2010)</td>
<td>Man Made Cellulose</td>
<td>30</td>
<td>260</td>
<td>175</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>Shibata et al. (2003)</td>
<td>Abaca</td>
<td>20</td>
<td>–</td>
<td>104*</td>
<td>170*</td>
</tr>
<tr>
<td>4</td>
<td>Gangster and Fink (2006)</td>
<td>Cordenka</td>
<td>25</td>
<td>188*</td>
<td>157*</td>
<td>146*</td>
</tr>
<tr>
<td>5</td>
<td>Bax and Mussig (2008)</td>
<td>Cordenka</td>
<td>30</td>
<td>447</td>
<td>130</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>Oksman et al. (2003)</td>
<td>Flax</td>
<td>30/40</td>
<td>63*</td>
<td>106</td>
<td>244</td>
</tr>
<tr>
<td>7</td>
<td>Bax and Mussig (2008)</td>
<td>Flax</td>
<td>30</td>
<td>69</td>
<td>121</td>
<td>202</td>
</tr>
<tr>
<td>8</td>
<td>Plackett et al. (2003)</td>
<td>Jute</td>
<td>40</td>
<td>93</td>
<td>182</td>
<td>271</td>
</tr>
<tr>
<td>9</td>
<td>Nishino et al. (2003)</td>
<td>Kenaf</td>
<td>70</td>
<td>–</td>
<td>286</td>
<td>492</td>
</tr>
<tr>
<td>10</td>
<td>Huda et al. (2005)</td>
<td>Wood Flour</td>
<td>30</td>
<td>–</td>
<td>92*</td>
<td>196</td>
</tr>
</tbody>
</table>
It is noteworthy to mention here that as the values for mechanical properties for pure PLA presented in different papers differ significantly from each other. Percentage change values compared to the value for pure matrix material given in every particular work are presented. Values marked with an asterisk are calculated by using information which was not given in numeric values but in figures.

Bax and Mussig (2008) in their endeavour to prepare Cordenka reinforced PLA composite reached a maximum increase in impact strength in 72 kJ/m² at a fibre mass ratio of 30 wt%, which is approximately 4.5 times higher the value of pure PLA. Bledzki et al (2009) obtained better results as well when they used man made cellulose as reinforcements. A decrease in impact strength is observed in case of jute reinforcements with flax fibres by Plackett et al. (2003). Similar results were observed by Oksman et al., (2003) and Bax and Mussig (2008), when they tried to reinforce PLA based composites with flax. In a publication by Gangster and Pinnow (2006), the impact strength of a PLA/Cordenka composite with a fibre-mass proportion of 25 wt%, was examined with a value of approximately 70 kJ/m².


2.1. Natural Fibre

Natural fibres can either be obtained from plants or animals. Figure 2.2 gives a brief understanding of the type of fibres available based on their sources. Fibres obtained from plants can either be from wood or non-wood sources (Mohanty et al., 2002). Wood plastic composites (WPC) are currently a rapidly growing market (Singh and Mohanty, 2007). They are commonly made by mixing wood flour or fibre with a virgin or recycled plastic to produce a composite product. Study on the effects of fibre length with the processing and properties revealed improved mechanical properties with increased fibre loading (Migneault et al., 2008). WPCs are extensively used in decking and railing systems, fenestration applications (e.g., window lineals, door stiles and rails), mouldings and exterior covering applications like siding and trimming. Non wood fibres can be resourced from plant straw, bast, leaf, seed, fruit or grass. Straw fibres are derived from resources like corn, wheat and rice hull and are characterized as having relatively high strength and stiffness, low density, renewability and carbon storage capacity (Pervaiz and Sain, 2003). Composites from these fibres are used in residential construction materials, especially as deck boards. Bast fibres are derived from the outer cells of the stems of various plants. They have weight specific properties, superior to the corresponding properties of glass fibre reinforcements and perceived as an environmental friendly option. Examples of bast fibres include abaca (Shibata et al., 2003), flax (Oksman et al., 2003), hemp (Singh and Mohanty, 2007), jute (Plackett et al., 2003) and kenaf (Nishino et al., 2003). The type of fibres used plays an important role in adhesion to the matrix and thereby improving the mechanical parameters (Bledzki et al., 2010). Flax, jute and hemp are used in the thermoplastic matrix composite panels for internal structures in the automotive industry (Brahmin and Cheikh, 2007). Hemp is used to prepare sheet moulding compounds for building applications (Hapuarachchi et al., 2007). Identified primary sources of leaf based fibres are primarily sisal (Li et al., 2000). Compared to bast fibres, the fibres show
superior impact properties (Megiatto et al., 2010). The main drawback in using these fibres is their hydrophilic nature thereby causing difficulties in adhesion with the hydrophobic polymer matrix (Mohanty et al., 2006). Examples of fibre derived from fruit and seed are those available from coir (Barbosa et al., 2010), coconut (Brahmakumar et al., 2005), etc., primarily used in non-structural applications. Grass based fibres are those obtained from bamboo (Jiang et al, 2009), elephant grass (Rao et al., 2007) and similar resources. Several investigators have studied the fibre-surface treatment methods and the resultant effects on the physical and mechanical properties of this different fibre matrix composite system.

Figure 2.2 Classification of Natural Fibres (Mukherjee and Kao, 2011)

Natural cellulose fibres provide a wide range of applications in composite materials such as materials for construction (Riedel and Nickel, 1999), automotive parts and interior components (Margurno, 1999; Wotzel et al., 1999) and food packaging (Averous et al., 2001). The strongest potential for cellulose products originates from the combination of their low cost, biodegradability, renewability, and high specific strength. It is very likely that cellulose will be a major chemical resource for the future (Schurz,
One factor that affected the properties of fibre is the part of the plant from which the fibre originated. Bast plants are characterised by long, strong fibre bundles that comprise the outer portion of the stalk. The word ‘bast’ refers to the outer portion of the stem of these plants. Bast plants include flax, hemp, kenaf, ramie and jute. Overall advantages of bast plant are high specific strength, long fibre length and high fibre productivity rates. The choice of the fibre for plastics applications depends on the availability of the fibre in the region and also on the ultimate composite properties needed for the specific application.

Figure 2.3 gives the schematic representation of a cellulose stem. Glucose is the building block of cellulose. The above figure shows the molecular structure of a cellulose unit, showing the β 1-4 glucosidic bond, along with

**Figure 2.3** Schematic Representation of a Cellulose Stem.  
(Ref: Oujai and Shanks. 2005)
the hydrogen bond. As can be seen in the figure, each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability to make hydrogen bonds between cellulose chains govern the physical properties of cellulose (Oujai and Shanks. 2005).

2.2. Non-cellulosic Components

The natural fibres are ligno-cellulosic in nature. Three major non-cellulosic compositions presented in the natural fibre are hemicellulose, lignin and pectin (Oujai and Shanks. 2005). These compositions depended on the type and time of cultivation. The hemicelluloses have linear polysaccharide backbones, often but not always homopolymers, that are composed of linked xylose, glucose, or mannose units; 1,4-glucan, mannan, and acetylated xylan can assume the same two-fold screw axis and 1.03 nm linear repeat unit, which facilitates hydrogen bonding with the microfibrils. Lignin is a complex aromatic polymer with molecular weight of about 11,000 g/mol that is formed by the three-dimension polymerisation of cinnamyl alcohols (derivative of phenylpropane). Lignin is deposited in the wall during secondary wall synthesis and signals the end of cell expansion. The pectin fraction includes the polygalacturonosyl-containing polysaccharides and other polysaccharides that are covalently associated with them. Up to 80% of the carboxyl groups of the galacturonic acid residues exist as methyl ester and some hydroxyl groups may be acetylated.
2.3. Structure of Cellulose

This section provides a relationship between structure and properties of cellulose fibre. There are many factors that affect agro-fibre properties. It is well known that different parts of plants have different chemical and physical properties. Chemical compositions and fibre properties of plant tissue taken from the roots, stem, trunk and leave are different (Marchessault 2003). Cellulose isolated from native sources is always polydisperse, i.e. it consists of a mixture of macromolecules with a wide distribution of chain lengths. Cellulose is a linear syndiotactic homopolymer composed of D-anhydroglucopyranose units (AGU), which are linked together by -glycosidic bond. Each of AGUs possesses hydroxy groups at C-2, C-3 and C-6positions (Figure 2.4). The hydroxy groups at both ends of the cellulose chain show different behaviours. The C-1 end has reducing properties, while the glucose end group with a free C-4 hydroxy group is nonreducing. The bridging and the ring oxygen atom are predominantly involved in intra- and intermolecular interactions, mainly hydrogen bonds, and in degradation reactions. The conformation of the AGU in the cellulose chain is generally assumed to be 4C1 chair conformation. In this conformation the free hydroxyl groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in the vertical position (axial) (Longstaff and McNab. 1986).
2.4. Representative Properties of Cellulose

The mechanical properties of natural cellulose fibre depend on the composition, morphology and crystalline structure. Table 2.2 shows the mechanical properties dependent on type of natural cellulose fibres (Mohanty et al., 2001).

**Table 2.2** Mechanical Properties of Natural Cellulose Fibres

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Density (g/cm³)</th>
<th>E-Modulus (Gpa)</th>
<th>Specific modulus (eModulus/Density) (g Gpa/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass</td>
<td>2.55</td>
<td>73</td>
<td>29</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.48</td>
<td>70</td>
<td>47</td>
</tr>
<tr>
<td>Flax</td>
<td>1.4</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>Jute</td>
<td>1.46</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.33</td>
<td>38</td>
<td>29</td>
</tr>
<tr>
<td>Coir</td>
<td>1.25</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.51</td>
<td>12</td>
<td>8</td>
</tr>
</tbody>
</table>

The fibrillar model suggested that the following relationships exist between fibre morphology and tensile properties. The tensile properties are related to the number of interlinks between the morphological units, the alignment with respect to the fibre axis (degree of orientation) and the perfection of
spatial arrangement (degree of crystallinity) of the molecules composing the fibre structure. The better the lateral arrangement along the fibre axis and the better the spatial arrangement, the more uniformly will a stress be distributed, giving higher tensile strength.

2.5. Dispersion:

2.5.1. Dispersion: Important to Study

Research in material science strongly suggests that even trace addition of nanoscale fillers can significantly improve the properties of a polymer matrix. Reinforcement mechanism needs to be fundamentally understood to establish a successful transfer of the technology. Nanostructured material research is still a gray area as many aspects of these systems are unclear at present. Literature abounds with numerous studies, where the nanofiller reinforcement of polymers contribute to numerous mechanical factors including fiber debonding, crack pinning, thin layer yielding and interfacial load transfer (Khare and Bussir, 2010). Micro reinforcement mechanisms, including crack deflection and filler-polymer debonding, stem directly from reduced filler size and improved dispersions with reduced agglomeration. Other investigations have found evidence that the interface between filler and matrix can have long-range impacts on nearby polymer-chains; commonly known by various names such as interphase, interfacial zone, and interfacial region. Overwhelmingly, the research suggests that filler size, loading and distribution dictate the amount of affected polymer, while the surface structure and chemistry of the particles dictate the intensity of interaction at the particle/polymer interface. Intuition suggests that reinforcement increases as the filler loading increases. Numerous investigators have demonstrated improved properties with increased loadings. Often, however, these benefits are limited to loadings below an optimum whereby additional loadings are detrimental. Qualitatively, the optimums coincide with the emergence of significant agglomeration of the
nanoparticles; there have been no systematic investigations of this effect due primarily to the absence of a robust and quantitative dispersion characterization tool. The literature clearly demonstrates that optimum performance requires an effective distribution of the nanoparticles within the matrix. However, the same scaling effects that make nanoparticles attractive also compete against effective dispersion. Nanoparticles tend to ‘stick’ to one another and are difficult to separate or disperse due to high specific surface area. Higher relative surface area then gives higher energy and higher unstability. In light of thermodynamic perspectives, agglomeration from one side, leads to a decrease in entropy of the system, but from another side it leads to negative enthalpy changes (due to bond formation). As long as the enthalpy factor outweighs the entropy factor, agglomeration can take place, and in this case the overall result is a negative Gibbs energy change which forms the driving force for agglomeration. Once this driving force is eliminated ($\Delta G=0$) the structure becomes thermodynamically stable. The more they interact with one another, the less they interact with the polymer in need of reinforcement. These nanoparticle agglomerations have little cohesive strength and their presence is often detrimental to the properties being targeted for improvement (Lively et al., 2014). Increased loadings of effectively dispersed particles increase the interaction volume and contribute to additional reinforcement. Review articles of the field have consistently cited nanoparticle dispersion as a major challenge area for the advancement of polymer nanocomposite technology. Despite the broadly recognized importance of nanoparticle dispersion, the characterization of dispersion remains largely qualitative and based on subjective interpretations of standard transmission electron microscopy (TEM) images. Myriad quantitative methods have been proposed (Rahatekar et al., 2010), but none have been widely implemented due to deficiencies in generality and simplicity.
The successful transfer of nanocomposite technology requires the development of a more fundamental understanding of the reinforcement mechanisms. Nanostructured materials are difficult to characterize and many aspects of these systems are unclear at present. Prior works have attributed nanofiller reinforcement of polymers to numerous mechanical factors including filler debonding crack pinning, thin layer yielding and interfacial load transfer.

2.5.2 Dispersion: Current Techniques

At present, the dispersion of polymer nanocomposites is characterized by qualitative morphological investigations via electron microscopy accompanied by a series of material property tests like electrical resistivity, dynamic mechanical analysis etc, to support the morphological observations. This is obviously time consuming and fails to provide quantitative statistics of the nanocomposites microstructure. The most commonly used process for the quantitative dispersion of fibrous-filled polymer nanocomposites involves the analysis of binarized two-dimensional (2 D) micrographs. Quantitative dispersion work is also being done involving analysis with the use of scanning electron microscopy (SEM). Transmission light (optical) or electron microscopy (TEM) supplies 2D projections of the nanocomposite microstructure while providing clear distinction between the filler and matrix unlike SEM. Within this field of microstructure study there are two areas of focus: nanodispersion studies via TEM and macrodispersion studies via optical microscopy. However, TEM analysis yields very distinct information about particle morphology but reflects only a localized scale. The use of digital analysis and random sampling from a range of locations enhances the value of the TEM information. Wide Angle X-Ray is also considered as a useful technique for dispersion study. A shift in the WAXS d001-spacing (defined as Δd001=d001,composite - d001,organoclay) has usually been interpreted in
terms of polymer intercalation into the organoclay galleries, and the absence of an X-ray peak has frequently been misinterpreted to mean a high state of exfoliation, although other morphological states may also lead to similar X-ray signals.

Nanodispersion refers to the more traditional definition of nanofiller dispersion by describing the level of filler individualization. Published works use different statistical or stereological principles for obtaining distributions or parameters to quantitatively describe the dispersion of the nanofiller on the nanoscale and relate these to material properties. The benefit of this style of study is the ability to obtain nanolevel spatial statistics for the nanocomposite system. However, nanodispersion studies require expensive microscopic equipment, difficult sample preparation, and ultimately fail to provide a bulk analysis of the nanocomposite. Table 2.3 below summarizes the literature review on dispersion study.

Table 2.3: Literature Review on Dispersion

<table>
<thead>
<tr>
<th>Category</th>
<th>Methods</th>
<th>Estimated</th>
<th>System Studied</th>
<th>Models Used</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEM</td>
<td>Distance between agglomerate</td>
<td>Polycarbonate/carbon nanofiber (CNTs)</td>
<td>Wicksells corpuscle</td>
<td>Lively et al., 2014</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Agglomerate Size</td>
<td>Polycarbonate/carbon nanofiber</td>
<td>Osher's solution to Wicksell's corpuscle problem for sample agglomeration diameter</td>
<td>Livelya et al., 2012</td>
<td></td>
</tr>
<tr>
<td>SEM/TEM</td>
<td>Interspatial distribution of particles</td>
<td>Polycarbonate/Multiwalled carbon nanotubes (MWNT)</td>
<td>N/A</td>
<td>Petra et al., 2004</td>
<td></td>
</tr>
<tr>
<td>Optical Microscopy</td>
<td>AFM</td>
<td>Height of an individual sheet</td>
<td>Poly (vinyl alcohol) (PVA) nanocomposites with graphene oxide</td>
<td>N/A</td>
<td>Liang et al., 2009</td>
</tr>
<tr>
<td>Light Scattering</td>
<td>Raman Light Scattering Intensity</td>
<td>A value of the mean standard deviation (SD) of the Raman light scattering intensity is taken as the dispersion index</td>
<td>Single-walled carbon nanotube (SWNTs) in Poly (methyl methacrylate)</td>
<td>Oxidised Polypropylene wax in polypropylene composite</td>
<td>N/A</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Basal Spacing of wax</td>
<td>Braggs Law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wide Angle X-ray diffraction (WAXD)</td>
<td>Basal Spacing of montmorillonite (MMT)</td>
<td>Polypropylene based montmorillonite nanocomposite</td>
<td>Braggs Law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser Confocal Microscopy Image/X-Ray Diffraction</td>
<td>Frequency and size of agglomeration/Interlayer distance</td>
<td>Carbon nanotube (MWNT)/Polystyrene nanocomposite</td>
<td>Braggs Law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-Ray Diffraction Pattern</td>
<td>Interlayer spacing</td>
<td>Compatibilized polyimide (R-BAPS)/BAPS-modified clay nanocomposites with improved dispersion and properties</td>
<td>Braggs Law</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mechanical Properties</td>
<td>Mechanical Strength</td>
<td>Combination of different mechanical models to rank the degree of dispersion</td>
<td>Epoxy Resin/SWNT</td>
<td>Combination of different mechanical model to estimate the young modulus by taking into account fibre dimension</td>
<td></td>
</tr>
<tr>
<td>Rheology</td>
<td>Percolation threshold/Aspect Ratio/Fractal dimension above percolation</td>
<td>Polypropylene based montmorillonite nanocomposite</td>
<td>Scaling law to calculate fractal dimension beyond percolation, Krieger Dougherty model to calculate effective volume fraction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.5.3. Rheology as a Tool to Evaluate Dispersion

Rheology potentially offers a quantitative macro dispersion analysis, which has been the focus of several different studies in recent years. These macro dispersion style studies are typically performed via optical microscopy. Image analysis is then performed on the micrographs to quantitatively measure the agglomeration within the nanocomposite system. Compared to TEM style nanodispersion assessment, this scale of dispersion analysis requires inexpensive equipment, simpler sample preparation, and covers a more significant area than what is practical with TEM. One commonly discussed drawback to macrodispersion characterization is the lack of quantitative information about the nanoscale dispersion. However, nanodispersion is directly related to the amount of agglomeration within a polymer nanocomposite. With the same components and concentrations, a nanocomposite system with better macrodispersion will have more potential for enhancement to the host matrix compared to a poor macrodispersion system with a higher percentage of no individualized nanofiller.

Rheological measurements have been used for different types of nanocomposite systems as a complementary tool to monitor the quality of dispersion, primarily in qualitative terms, (Vermant et al., 2007). Rheology potentially offers a means to assess the state of dispersion of nanocomposites directly in the melt state. The rheological properties, both linear and non-linear ones, are sensitive to changes in the particulate microstructure, particle size, and shape and surface characteristics of the dispersed phase. The level of linear properties such as the storage and loss
moduli, G’ and G”, are always raised with filler addition. G’ and G” curves can be used diagnostically to assess the state of dispersion, since a flocculated system will show up as an extra low G’ plateau. This usually takes the form of a progressive increase in the level of properties as more filler is added. However, sometimes, a secondary mechanism can be seen such as the development of a plateau usually from a pseudo network set up between flocs or chains of particles (Barnes, 2003). The advantage of using rheology as a technique to measure dispersion is that using samples of macroscopic dimension, it offers an integrated picture of the composite material with increased data reliability, as compared to other methods using small samples that are prone to micro-scale in homogeneities. Different rheological methods can be employed to study the response of the nanocomposite structure to both linear and non-linear deformation. The only disadvantage to these measurements is that it is an indirect method to probe the hybrid microstructure.

Thus to summarize, rheology can be envisaged as a tool that is complementary to traditional methods of material characterization such as electron microscopy, X-Ray scattering, dynamic mechanical analysis and mechanical testing.

Different approaches have been proposed to describe the dispersion quality of the polymer nanocomposites by linear viscoelastic behaviour. Establishment of the power law relationship between elastic property and volume fraction assuming filler as the fractal aggregate is very popular (Schaefer, 1984); Rueb and Zukoski, 1997). Similarly, assuming fractal aggregate, Shih et al. (1990) proposed a scaling relation for the elastic properties that predict a power-law dependency on the volume fraction with the fractal dimension of the network as an exponent. There is also a change in non linear and time dependent rheological behaviour on addition of the nanofiller to the polymer nanocomposites. The changes in behaviour could possibly be related to the quality of dispersion. For example an increase in the steady-state shear viscosities can be observed depending on the
volume fraction and particle shape of the filler (Krieger (1972); Brenner (1994); Larson (1999). The presence of fractal aggregate and a particulate network structure may lead to the development of an apparent yield stress and thixotropic responses. (Mewis (1979), Solomen et al. 2001). Vermant et al., 2007 argued that nanocomposites indeed belong to the class of thixotropic materials and performed transient experiments to provide direct information about the microstructural kinetics under constant shear conditions and at rest. They also cited the work of Mohraz and Solomon (2005), in describing how stress overshoots in aggregate systems in terms of cluster rupture could be explained as a measure of the dispersion quality. The basic concept centers around the hypothesis that when aggregate govern the rheology, the forward flow makes them interlock whereas the reverse flow disentangles them. Supporting these arguments, they assessed the dispersion quality of their nanocomposites from the volume fraction dependency of the plateau modulus and the critical strain that limits the linear response regime. The microstructure was quantified using scaling laws for fractal aggregate networks. Additionally, changes to the high frequency data module were also considered as a means to assess dispersion quality as they enable one to determine the effective hydrodynamic volume of the particles and aggregate over the entire range of volume.

Recently, Vermant et al (2007) explored to what extent rheological methods can be used in a more quantitative manner and evaluated the effect of molecular weight and processing history on clay-polymer nanocomposites. It is important to consider here that in analysing rheology data, it is essential to evaluate the flow history and the resulting thixotropic response. Pre-shearing protocols that allow sufficient rest times between sample loading and experiments are a way in which, at least reproducible initial conditions can be obtained.

- At volume fractions above the percolation threshold, the state of dispersion can be assessed from the volume fraction dependency of
the plateau modulus and the critical strain that limits the linear response regime.

- The microstructure can be quantified using scaling laws for fractal aggregate networks.
- Additionally, changes to the high frequency module were also considered as a means to assess dispersion quality as they enable one to determine the effective hydrodynamic volume of the particles and aggregate over the entire range of volume fractions.

2.5.3.1 Volume Fraction Dependency on the Plateau Modulus: Scaling Laws

At high concentrations, interparticle interactions will become more significant, even though they are not apparent at lower concentrations. They become particularly important even for the definition of phase volume, since small increase in effective phase volume is calculated on the basis of the “core” radius plus a layer thickness has very large effect on viscosity at these phase volumes. The effect of particle size distribution, particle shape and even porosity can all be taken into account by the appropriate choice of the maximum phase volume.

2.5.3.2 Scaling Laws for Fractal Aggregate Network

It was earlier noted that that colloidal suspensions can be either dispersed or flocculated, depending on

i) The magnitude of the particle-particle interaction energy, and
ii) Particle concentration.

Various conditions such as the pH, surfactant, additives and particle size can affect the inter particle interaction energy and thus cause the transition
from the dispersed to the flocculated state. A colloidal gel is a special state of flocculated systems in which a continuous network of particles is formed before settling occurs, with the resulting suspension having a very high viscosity and a finite shear modulus. The gel state occurs most often with small particles (<0.1 µm) and the particle volume fraction in the gel state can be as low as few percent. In polymeric system it is known that gels are formed by crosslinking polymers in semidilute solutions. Colloidal gels are very similar to polymer gels in that both are viscoelastic. Furthermore, colloidal gels are formed by particle aggregation and polymer gels are formed by either polymerization or crosslinking, both of which are also aggregation processes.

The basic concept of the scaling theory for polymer gels is to relate the elastic properties of a gel to its network structure. Near the gel point, the shear modulus of a gel behaves like $G' \sim (\phi - \phi_c)^t$ which is characteristic of a percolation transition. The theory also enables one to extract structural information about the individual flocs, as available from the rheological measurements, such as the fractal dimension of the flocs and the fractal dimension of the elastic backbones of the flocs. In a study conducted by Shih et al., (1990), the scaling behaviours of the elastic properties of colloidal gels that are well above the gelation threshold are studied both theoretically and experimentally. A scaling theory is developed by considering the structure of the gel network as a collection of flocs, which are fractal objects closely packed throughout the sample.

When the particulate networks are above the percolation threshold, scaling of the elastic properties for fractal network, as developed by Shih et al. (1990), can be used for quantitative data analysis. This model conceptually captures the multiscale structure, containing dispersed tactoids, which then aggregate. The model considered the structure of a particulate network as a collection of the fractal aggregates that are elastically linked together. The elastic properties are dominated by the elasticity of the backbones of the aggregates. A decrease of the linearity limit with increasing volume
fraction is associated with inter aggregate links stronger than the aggregates themselves, which corresponds to the strong link regime in the terminology of Shih et al. (1990). In this regime, the value of the plateau modulus is predicted to have a power-law dependence on volume fraction:

$$G_p \sim \phi^{(3+\chi)/(3-d_f)} \ldots \ldots \ldots (2.1)$$

Where ‘$d_f$’ is the fractal dimension of the aggregate network and ‘$\chi$’ is an exponent that connects the particle volume fraction with aggregate size, i.e., $x$ depends on the number of particles per aggregate. Likewise, the critical strain values follow:

$$y_{\text{crit}} \sim \phi^{-(1+\chi)/(3-d_f)} \ldots \ldots \ldots (2.2)$$

Depending on the strength of the links between the flocs, there can be two types of regime, namely, strong link regime and the weak link regime.

In the strong link regime, $\kappa \sim \phi^{(d+\chi)/(d-D)}$ and $y_0 \sim \phi^{-(1+\chi)/(d-D)}$, where $d$ is the Euclidean dimension, $D$ is the fractal dimension of the flocs and $\chi$ is the backbone fractal dimension of the flocs. The main differences in the two regimes are

i) $\kappa$ increases more slowly in the weak link regime than in the strong link regime, and

ii) $y_0$ increases with increasing particle concentration in the weak link regime but decreases with increasing particle concentration in the strong link regime.

Similar observations were obtained by Schaefer et al. (1984), where they measured the fractal dimension, $D$, of colloidal aggregates of small silica particles. A power law decay of the structure factor $[s(k) \sim k^{-D}]$ by both light and x-Ray scattering showing that the aggregates are fractal.
Wu and Morbidelli (2001) extended the model of Shih et al. (1990), to include gels that are intermediate between the strong-link and the weak link regimes. In addition to the modulus, they also considered the critical strain $\gamma_{\text{crit}}$ at which the linear viscoelastic region ends:

$$G' = \phi^A \ldots \ldots \ldots (2.3)$$

$$\gamma_c = \phi^B \ldots \ldots \ldots (2.4)$$

The exponents of A and B are given by:

$$A = \frac{\beta}{d - D_f} \ldots \ldots \ldots (2.5)$$

$$\beta = (d - 2) + (2 + x)(1 - \alpha) \ldots \ldots \ldots (2.6)$$

$$B = (d - \beta - 1)/(d - D_f) \ldots \ldots \ldots (2.7)$$

Where the parameter $\alpha=0$ for a strong link gel, $\alpha=1$ for a weak link gel, and $0<\alpha<1$ for intermediate gels; $\alpha$ is the fractal dimension of the gel’s backbone, and “d” is the Euclidian dimension of the system (usually taken as 3). One obtains for weak links, $B=1/(d - D_f)$, and for strong links, $B = -(1 + x)/(d - D_f)$. Thus, one must have reliable data on modulus and critical strain versus concentration to calculate values of $D_f$ and $\beta$.

In the strong link regime, where the interfloc links are stronger than the intrafloc links, the modulus of a gel is given by that of intralinks. In the weak link regime, where the flocs are more rigid than the interfloc links, the elasticity of the interfloc links determines the elasticity of the gel (Rao, 2007). In the weak link regime, the limit of linearity increases with increasing volume fraction; in contrast to, in the strong link regime it decreases. The exponent $x$, which represents the backbone fractal dimension or tortuosity of the network has a value of 1.0-1.3 for a colloidal gel. A value of $x=1.3$ was used by Wu and Morbidelli (2001) in order to
calculate values of $D_f$, ranging between 1.73 and 2.82, and $\beta$, ranging between 1.0 and 4.4, of several gels. It should be noted that for $x=1.3$, the magnitude of $\beta$ should be between 1.0 and 4.3.

It can thus be concluded that, the parameter $\alpha$ indicates the relative importance of the elastic contributions of both inter- and intra-flocculation links. The parameter $\alpha$ also allows to identify the different gelation regime prevailing in the system (ie. strong-link, transition, or weak-link). Strong-link and weak-link regimes are found for $\alpha = 0$ and $\alpha = 1$, respectively, and transition regimes are found for $0 < \alpha < 1$. This fractal dimension analysis helps one to probe more into the microstructure of the gel.

2.5.3.3 Higher Frequency Moduli as a Means to Assess the Dispersion Quality

At the highest frequencies probed, the polymer matrix contribution dominates over the aggregate contribution. At these frequencies, with increasing volume fraction, the moduli are observed to increase, which can be attributed to an increased effective deformation rate in the matrix. The higher moduli stem from an increase of the matrix contribution due to the hydrodynamic contribution. This can be also used to obtain information about the dispersion quality. In fact, from a methodological point of view, an interesting point is that high frequency data are easier to obtain and might provide a fast route to characterize dispersion. Here the volume occupied by aggregates is probed, even when they are part of a network. The relative high frequency moduli can be obtained by dividing the moduli by the values for the matrix.
Further to the analysis, the evolution of the relative high frequency moduli can be described by the Krieger-Dougherty equation:

\[
G'_{HF,rel} = \frac{G'_{HF}}{G'_{HF,m}} = \left[1 - \frac{\varnothing}{\varnothing_{max}}\right]^{-[\eta]\varnothing_{max}} \quad \text{... (2.8)}
\]

Where \(G'_{HF,rel}\) refers to the high frequency modulus of the nanocomposite, \(G'_{HF,m}\) is the high frequency modulus of the matrix at the same frequency, \(\varnothing\) is the volume fraction, \(\varnothing_{max}\) is the maximum packing fraction, and \([\eta]\) is the intrinsic viscosity. Typically for clay based nanocomposites, more exfoliation means lower \(\varnothing_{max}\).

The maximum solid volume fraction can be calculated by taking a similar approach by Ghosh and Bhattacharya (1984) and Thomas (1965), where the maximum solid volume fraction \((\varnothing_{max})\) in the suspensions was determined by plotting the values of relative apparent viscosity \((\mu_r)\) against the volume fraction \((\varnothing)\). The previous authors suggested that if the values of \((\mu_r-1)^{-1}\) were plotted against \(\varnothing\) and then extrapolate to zero ordinate, it will give the maximum volume packing fraction \((\varnothing_{max})\). Relative apparent viscosity is defined here as:

\[
\text{Relative apparent viscosity } (\mu_r) = \frac{\text{Apparent Viscosity of Nanocomposite } (\eta_{composite})}{\text{Apparent Viscosity of the Polymer Matrix } (\eta_{matrix})}
\]

This apparent viscosity can be measured in strain controlled ARES rheometer by performing standard steady shear single point tests.
Chapter 3: Experimental Investigation, Procedures and Errors

This Chapter aims to discuss and demonstrate the experimental aspects of this research. The raw material characteristics and acquisition; processing procedure and conditions of PLA/cellulose nanocomposites; morphological, thermal and rheological characterization techniques of the samples; steady and dynamic rheological procedures to evaluate the rheological behaviours of the prepared samples; and data analysis techniques employed during the course of this research will be portrayed in this Chapter.

3.1. Polylactic Acid (PLA)

Grade 4032D Poly (L, L-lactide)-PLA was supplied by Nature Works LLC with a density of 1.24 g cm\(^{-3}\) and a melting point of 160 °C was chosen as matrix. Table 3.1 demonstrates the physical, mechanical and molecular characteristics of this grade of PLA.

![Chemical Structure of Polylactic Acid](image)

**Figure 3.1** Chemical Structure of Polylactic Acid
Table 3.1 Technical Specification of Polylactic Acid

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.24 g/cc</td>
</tr>
<tr>
<td>Moisture Vapour Transmission</td>
<td>8.30 cc-mm/m² 24 hr-atm</td>
</tr>
<tr>
<td>Oxygen Transmission</td>
<td>14.0 cc-mm/m² 24 hr-atm</td>
</tr>
<tr>
<td>Carbon Dioxide Transmission</td>
<td>76.0 cc-mm/m² 24 hr-atm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Elongation at Break, TD</td>
<td>100%</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>2.85 GPa</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>44.0 MPa</td>
</tr>
<tr>
<td>Secant Modulus, MD</td>
<td>3.44 GPa</td>
</tr>
<tr>
<td>Secant Modulus, TD</td>
<td>3.784 GPa</td>
</tr>
<tr>
<td>Elmendorf Tear Strength, MD</td>
<td>0.669 g/micron</td>
</tr>
<tr>
<td>Elmendorf Tear Strength, TD</td>
<td>0.551 g/micron</td>
</tr>
<tr>
<td>Film Tensile Strength at Break, MD</td>
<td>103.2 MPa</td>
</tr>
<tr>
<td>Film Tensile Strength at Break, TD</td>
<td>144.5 MPa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>160 °C</td>
</tr>
</tbody>
</table>
### 3.2 Microcrystalline Cellulose (MCC)

Microcrystalline cellulose was supplied by Sigma Aldrich.

Specification details are highlighted below:

<table>
<thead>
<tr>
<th>TEST Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance (Colour) White to Off-White</td>
</tr>
<tr>
<td>Appearance (Form) Powder</td>
</tr>
<tr>
<td>Infrared spectrum Conforms to Structure</td>
</tr>
<tr>
<td>Loss on Drying &lt; 7.0 %</td>
</tr>
<tr>
<td>Residue on Ignition &lt; 0.1 %</td>
</tr>
<tr>
<td>Heavy Metal (as Lead) &lt; 0.001 %</td>
</tr>
<tr>
<td>pH -4.5 - 7.5</td>
</tr>
<tr>
<td>C=11%, Aqueous Slurry</td>
</tr>
<tr>
<td>Particle Size Distribution &lt; 10 %</td>
</tr>
<tr>
<td>+60 Mesh</td>
</tr>
<tr>
<td>Particle Size Distribution &gt; 40 %</td>
</tr>
</tbody>
</table>

![Chemical Structure of Microcrystalline Cellulose](image)

**Figure 3.2** Chemical Structure of Microcrystalline Cellulose
3.3 Nanofibrillated Cellulose

**Figure 3.2** Photograph of Nanofibrillated Cellulose Suspension in water as a medium
**Table 3.2** Technical data sheet of Nanofibrillated Cellulose Suspension

<table>
<thead>
<tr>
<th>Description:</th>
<th>1-5% nanocellulose suspension in distilled water made from soft wood pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Features:</td>
<td>Highly viscous and absorbent; high fibre aspect ratio; translucent and well dispersed</td>
</tr>
<tr>
<td>Suggested Applications:</td>
<td>Rheological additive for paints and coatings</td>
</tr>
<tr>
<td></td>
<td>Reinforcement filler for thermalsets and thermal plastics</td>
</tr>
<tr>
<td></td>
<td>Making high strength nanofilms for gas barrier products or transparent nanocomposites</td>
</tr>
<tr>
<td></td>
<td>Fillers for paper and paperboard products</td>
</tr>
<tr>
<td></td>
<td>Fracturing fluid for oil recovery or drilling mud</td>
</tr>
<tr>
<td></td>
<td>Hygiene and absorbent products</td>
</tr>
<tr>
<td>Typical Physical and Chemical Properties:</td>
<td></td>
</tr>
<tr>
<td>Appearance:</td>
<td>Translucent gel</td>
</tr>
<tr>
<td>Density:</td>
<td>1.01g/cc @ 0°C (32°F)</td>
</tr>
<tr>
<td>Cellulose Content:</td>
<td>83% (based on dry weight)</td>
</tr>
<tr>
<td>Fibre Diameter:</td>
<td>10-25nm (majority)</td>
</tr>
<tr>
<td>Degree of Polymerization:</td>
<td>1200</td>
</tr>
<tr>
<td>Crystallinity:</td>
<td>71%</td>
</tr>
<tr>
<td>Degradation Temperature:</td>
<td>310°C (on-set); 340°C (maximum weight loss)</td>
</tr>
<tr>
<td>Property</td>
<td>Specification</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Film Strength</td>
<td>≥ 200MPa (film density: 1.3g/cm³)</td>
</tr>
<tr>
<td>Film Modulus</td>
<td>≥ 13GPa (film density: 1.3g/cm³)</td>
</tr>
<tr>
<td>Film Transparency</td>
<td>20%@600nm (film density: 1.3g/cc, film thickness: 40μm)</td>
</tr>
<tr>
<td>Storage</td>
<td>Store in a cool, dry place in sealed containers.</td>
</tr>
<tr>
<td>Precaution</td>
<td>Please refer to the material safety data sheet (MSDS) prior to the use of this product.</td>
</tr>
<tr>
<td>Disclaimer</td>
<td>All information in this data sheet is believed to be accurate, but all recommendations are made without warranty since the conditions of use are beyond the control of the Centre for Biocomposites and Biomaterials Processing (CBPP). The reported properties included in this data sheet are illustrative only and are based on laboratory testing, which is not intended for design purposes. CBPP disclaims any liability in connection with the use of the information, and does not warrant against infringement by reason of the use.</td>
</tr>
</tbody>
</table>
3.4 Poly (1, 4-butylene adipate) (PBAT)

![Chemical Structure of Poly (1,4-butylene adipate (PBAT))](image)

**Figure 3.2** Chemical Structure of Poly (1,4-butylene adipate (PBAT))

**Table 3.3** Technical data sheet of Poly (1,4-butylene adipate (PBAT))

<table>
<thead>
<tr>
<th>Related Categories</th>
<th>Esters, Hydrophobic Polymers, Materials Science, Polymer Science, Polymers More…</th>
</tr>
</thead>
<tbody>
<tr>
<td>form</td>
<td>chips</td>
</tr>
<tr>
<td>mol wt</td>
<td>average $M_w \sim 12,000$ by GPC</td>
</tr>
<tr>
<td>transition temp</td>
<td>$T_g -68 \ ^\circ C$</td>
</tr>
<tr>
<td></td>
<td>$T_m 54 \ ^\circ C$</td>
</tr>
<tr>
<td>density</td>
<td>1.019 g/cc at 25 °C (Signori et al. 2009)</td>
</tr>
</tbody>
</table>
3.5 Processing

3.5.1 Preparation of Nanocellulose:

![Figure 3.3 Process adapted for hydrolysis of Cellulose](image)

Acid hydrolysis of MCC was performed by standard procedure as mentioned elsewhere (Bondeson et al., 2006). Hydrolysis was carried out with 64% (w/w) sulfuric acid at 45°C for 45 min with constant stirring. Typically, 40 g of filter aid (dried at 105°C for 30 min) was treated with 700 mL of acid. Immediately following the acid hydrolysis, the suspension was diluted 10-fold with deionized water to quench the reaction. The suspension was centrifuged at 6000 rpm for 10 min to concentrate the cellulose and to remove excess aqueous acid. The resultant precipitate was rinsed, recentrifuged, and dialyzed against water for 5 days until constant neutral pH was achieved. Acid hydrolyzed nanocrystalline cellulose (NCC) is eventually freeze dried to produce a powdered form of the crystals, which is later surface acetylated.
3.5.2 Acetylation of Nanocellulose

In a one litre round bottom flask, 15 g of freeze dried nanocellulose and 100 ml of dimethyl formamide were stirred at 60 °C for half an hour. Sodium Hydride (7 g, 60 % dispersion in mineral oil) was added portion wise in the reaction mixture and stirring was continued overnight (16 h) in a nitrogen atmosphere. Next day, acetic anhydride (10 ml) was added and stirred for further 3 hours.

The above reaction mixture was cooled to room temperature with continuous stirring. Finally ethanol (50 ml) was added carefully to deactivate excess sodium hydride. The reaction mixture was poured into 400 ml of water and stirred; the solid was collected by filtration and washed with water and acetone, dried at 80 °C in a vacuum oven, to give the acetylated NFC (~15g).

![Reaction Scheme for Surface Acetylation](image)

**Figure 3.4** Reaction Scheme for Surface Acetylation

3.5.3 Preparation of Composites

Composites were prepared by solvent casting technique, using dichloromethane (DCM) as the medium. The desired amount of AC-MCC was added along with 20.0 g of PLA into DCM to produce a mixture. Although DCM is considered to be category 5 carcinogenic, it has low boiling point and rapidly evaporates. The mixture was then conditioned overnight to eliminate bubbles and was then casted into a petri dish. The DCM was allowed to evaporate at ambient temperature (25 °C) for 24 h. Finally the
solidified films, with a thickness of around 1 mm, were vacuum dried overnight, and then kept in a desiccator containing silica gel.

![Figure 3.5 Photograph of solvent casted sample in a petridish](image)

### 3.6 Characterization

#### 3.6.1 Fourier Transform Infrared Microscopy

FTIR-KBr spectroscopic studies were carried out in drift mode on the samples with a PerkinElmer FTIR spectrophotometer (TA 8000). A total of 32 scans per sample were taken, starting from 4000 cm\(^{-1}\) to 450 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\). The spectrum was analysed with Perkin Elmer Spectrum Software (Mukherjee et al., 2012). The samples for FT-IR analysis were prepared by grinding the dry blended powders with KBr, often in the ratio of 1:100(Sample: KBr), using a pestle and a mortar. For the drift spectra, a Perkin-Elmer diffuse reflectance (DR) sampling cell was used.
3.6.2 Fourier Transform Microspectroscopy

Approximately a 10 µm thick cross-sections were cut from the films with a microtome and used for the FTIR analysis. High spatial resolution maps were recorded at the IRM beamline. The beamline collects infrared radiation from a bending magnet of the Australian Synchrotron storage ring, and couples this light into a Bruker V80v vacuum FTIR spectrometer, coupled to a Bruker Hyperion 2000 IR microscope (Bruker Optics, Ettlingen Germany). The microscope is equipped with a 36x (0.5 numerical aperture) objective and condenser and 50 x 50 micron single element, narrow band mercury cadmium telluride detector. This detector is sensitive in the mid-IR spectral region, with a cut-off at 750 cm\(^{-1}\). The infrared synchrotron beam is focused onto the sample with a beam spot size of approximately 8 x 8 microns, and the area of analysis can be further refined using apertures to about 3 x 3 microns. A motorized stage allows spectral mapping of the sample by raster scanning the sample through the focused beam. For the work reported here the aperture size for analysis was 5x 5 microns and the mapping step size was 10 x 10 microns. Spectra were co-added for 256 scans at each position, with a spectral resolution of 4 cm\(^{-1}\). Data collected at the beamline were analyzed using the Bruker software OPUS 7.2.

3.6.3 Nuclear Magnetic Resonance Imaging

Solid State NMR study was conducted to confirm the surface acetylation of NCC. The CP/MAS 13C-NMR spectra were recorded on a VNMRS 600 MHz NMR spectrometer equipped with 4 mm CPMAS triple resonance probe. The 13C frequency was 150.8 MHz and the chemical shift resonances were referenced to the adamantane chemical shifts obtained with a similar pulse sequence. Acquisition was performed with a CP pulse sequence using a 5.25 ms proton n/2 excitation pulse, a spectral width of 50 kHz, an
acquisition time of 25 ms using a SPINAL-64 decoupling scheme of 70 kHz strength and a 5 s delay between transients. The Hartmann-Hann match was optimized on the -1 sideband at a MAS speed of 8 kHz with a contact time of 500 ms and a linearly ramped-CP field of 30±0.8 kHz. Typically, 12000-16000 transients were accumulated at 25ºC. A line broadening of 50Hz and zero filling to 65k points were used to process the spectra.

3.6.4 Scanning Electron Microscopy

Morphology of MCC and the fractured surface of the MCC based PLA composites at different loading of weight percentage, were examined using an FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM), at an acceleration voltage of 30 kV and pressure of 0.50 Torr. MCC powder was sprayed on a carbon tape to study its morphology. The fractured surface was prepared by immersing the specimen in liquid nitrogen and manually fracturing the specimen. Samples were then mounted on to a sample holder with the fractured surface facing upwards. The sample holder was then placed in the ESEM sample chamber. Various sample surfaces were scanned to obtain a visual impression of fibre fracture, distribution and the appearance of the fibre/polymer interface (Mukherjee et al., 2012).

Morphology of cryo-sectioned samples of PLA-NFC nanocomposites at different loading of weight percentage (1-5 wt %) were examined using the FEI Nova Nano SEM (2007) in immersion mode, using the STEM detector, at an acceleration voltage of 15-20 kv. Samples were cryo-sectioned to produce ultra-thin film specimen of 60 nm thick, at -120 ºC and then placed in a TEM grid. They were then negatively stained by uranyl acetate to produce better contrast in imaging. TEM grids were then mounted in the STEM holder which was then attached to the microscope for imaging. Various sample surfaces were scanned to obtain a visual impression of fibre fracture, distribution and the appearance of the fibre/polymer interface.
3.6.5 Transmission Electron Microscopy

Morphology of NFC is characterized by Transmission Electron Microscopy (TEM) in a JEOL 1010 instrument at an accelerated voltage of 100 kv. The main purpose of doing a TEM study was to zoom into the nanofibril network to provide clear visualization of ultra-fine morphological development of the entangled nanofibrils. NFC was dispersed in distilled water. A drop of the dispersion was deposited on a carbon-coated TEM grid and allowed to dry prior to imaging.

3.6.6 Atomic Force Microscopy

The morphology of nanocellulose was further investigated by atomic force micrography technique. The images (512 × 512) were recorded using scanning rates of 0.250 Hz. The drive frequency and amplitude was 280.02 Hz and 186.0 mV. NFC powder was dispersed in distilled water. A drop of the solution was deposited on a silicon wafer and allowed to dry prior to imaging.

3.6.7 Crystallinity Study by X-Ray Diffraction (XRD)

XRD patterns were obtained using a Bruker D4 Endeavor X-ray diffractometer in the angular range of 6° to 90° (2θ) at a voltage of 40 KV and current of 100 mA. Peak intensities were every 0.02° at sweep rates of 1.0° 2θ/min, to see the change in crystallinity after acetylation, if any.
3.6.8 Thermal Study-Modulated Differential Scanning Calorimetry (MDSC)

Thermal property characterization of the samples was performed by modulated temperature differential scanning calorimeter (MDSC) with via TA Instrument Model 2920. Samples were heated and cooled in nitrogen atmosphere. Samples of approximately 7-9 mg in weight were encapsulated in aluminium pans. An empty sealed aluminium pan and lid was used as the reference. The first heating scan was run at 5 °C min\(^{-1}\) and modulated at ± 0.5 °C/40sec from 0 °C up to 200 °C. The samples were held at this temperature for 2 minutes, and then the first cooling scan was run at 5 °C min\(^{-1}\) down to 0 °C. The second heating scan was also run from 0 to 200 °C at 2 °C min\(^{-1}\). The first scanning cycle was applied to erase the thermal history of the samples. In order to minimize the possible effect of non-uniformity of the micro-size DSC specimens, the reproducibility of the result was examined through three specimens in each sample.

Figure 3.6 Photograph of DSC machine
3.3.4 Shear Rheology

Dynamic Frequency Sweep tests were conducted using ARES Rheometer (TA Instrument) based on constant strain rate. The tests were conducted using a 25 mm parallel plate at temperature of 170 °C. This temperature was chosen as the temperature close to the melting temperature of PLA (180 °C), where degradation of the polymer starts to begin. All measurements were performed using a force transducer with a range of 0.2 to 200 g-cm torque. Prior to any tests, the zero gaps between the parallel plates were calibrated at the required temperature. After the sample loading, the test samples were allowed to rest until they reached the temperature (170 °C) at which the rheological measurements were carried out. A delay of 5 mins was necessary to erase the thermal and mechanical histories of the sample under investigation. Dynamic Strain Sweeps were conducted at 1, 10 and 100 rad/s at 0.1-100 % strain, to check the linear viscoelastic region (LVR) of prepared PLA/nanocellulose composites at different loading of nanocellulose (1-5 wt%). A critical strain $\gamma_c$ was determined at 10 rad/s. Dynamic frequency sweep tests were conducted in the LVR region at 10 rad/s, between the frequency of 0.1 and 100 rad/s at 170 °C.

- A critical strain $\gamma_c$ was determined at 1 rad/s as the strain where $G'/G'_0=0.9$.
- Dynamic frequency sweep experiments were then performed in the linear viscoelastic region of each material with frequency between 0.1 and 100 rad/s.
- A waiting time after loading or after a pre-shear was used to eliminate the effects of loading history. This waiting time was a compromise between the time required for the structure to “anneal” the effects of pre-shear or loading and the limitations set by the thermal stability of the material.
- In transient flow experiments, a cone and plate geometry was used (R=12.5 mm, cone angle = 0.1 rad)
- The thermal stability of the polymer was assessed by checking the high frequency moduli when using dynamic experiments.
- To avoid interference between changes in the network structure and effects of thermal degradation on the matrix, the measurements were performed at high frequencies (100 rad/s) where the matrix contribution is predominantly probed.

![Figure 3.7 Photograph of ARES Rheomete](image)

### 3.4 Error Analysis

The inaccuracies involved with the experimental tasks of research studies could be initiated from different sources of error; i.e. human errors, systematic errors and random errors. Human errors are the result of the imprecisions occurred by the performer of the experiments while the systematic errors are caused by the intrinsic inaccuracies in the experimental set-ups. The systematic errors could be reduced via proper calibration of the instruments prior to the commencement of the experiments. The random errors are the inevitable results of the absence of utter accuracy during any types of experimental procedures and they
can be minimized via considering the repeatability and averaging the final outcomes of the experimental procedures.

The possible sources of error during this research are as follows:

**3.4.1 FTIR Error Analysis**

Apertures can be the largest source of errors in the IR microscopy and can lead to the detector. The detector also samples the secondary lobes of the diffraction pattern. Thus, spectral information from the delineated area is spread over a larger area than the aperture. Quantitative analysis requires that spectra be measured from samples that are non-luminous, their absorbance be invariable with changes in concentration, their absorption be invariable with changes in concentration, the absorption coefficient of the species be independent of the intensity of incident radiation, the spectral response be uniform across the radiation cross-section, the instrument be devoid of stray light and respond in a linear manner to different levels of light intensity. Some or many of the factors above are violated by sample non-uniformity, instrumental factors and the behaviour of chemical species (interactions) leading to incorrect measurements. The effects of deviations can be theorized, quantified and experimentally verified. Errors may also arise during use due to improper location of the spot to be mapped, substrate optical effects that shift the beam focus and loss of accuracy in system alignment over time.

**3.4.2. Error analysis of MDSC**

The main source of error in MDSC comes from the minute size of the samples (4-7 mg) as well as the encapsulation of such small samples before the start of the thermal analysis procedure. However, this source of error
could be minimized through averaging the weight of the samples in addition to inspecting the reproducibility and repeatability of the data produced by the instrument. The second source of error in this characterization technique could rise from the thermal history of samples due to the variations in samples’ aging, processing and storage conditions. In order to utterly eliminate the thermal history of the samples, all specimens were subjected to the first heating and cooling cycles in advance of their exposure to the main (second) heating and cooling cycles.

### 3.4.3. Shear Rheological Error Analysis

The major sources of error in rheological measurements may occur due to the thermal degradation of the samples at elevated temperature; poor calibration of the rheometer before the measurements; inaccurate zeroing of the gaps between the parallel plates, and inconsistencies with the software programming due to the human errors. Moreover, the lack of precision in placing the samples between the parallel plates in less than 15 seconds (to avoid the significant temperature drop) could also contribute to the final error in shear rheological measurements.

In order to minimize the mentioned errors, the following points were required to be considered:

- Neat PLA was dried properly before the processing stage and the final samples were stored in vacuum oven prior to the experimental analysis. Furthermore, Standard desiccators were utilized to carry the samples to the testing locations.
- The lab Technical Officers were asked to calibrate ARES instrument before the shear rheological analysis of the samples.
• The zeroing of the gap between parallel plates was carefully performed at least three times previous to the start of the tests.

• Loading of samples between parallel plates was carefully monitored and its duration was kept below 15 seconds. After loading the samples, the oven was locked for 5 minutes to create thermal steady state and equilibrium between the oven and the samples. The shape and the state of the specimens were inspected frequently from the provided lenses on the oven wall.

• To avoid programming discrepancies by the software, consistent testing programs were developed and employed for all samples in the ARES instrument’s Orchestrator software.
Figure 3.7 represents the repeatability of the storage modulus data of acetylated microcrystalline cellulose based PLA composite (1.5 wt % loading). The storage modulus is plotted against the various frequency range in the linear viscoelastic region. The experimental condition is repeated three times under the same condition. As observed from the figure, the repeatability test is consistent without much variation. For the rest of the samples, random spot check of the measurement is adopted to check its consistency.
Chapter 4: Rheological Percolation to Characterize Improved Dispersion of Microcrystalline Cellulose in PLA Biopolymer

This Chapter discusses the partial substitution of microcrystalline cellulose (MCC) fibre by acetyl groups by using acetyl chloride at room temperature. The primary motivation behind this study was to improve the dispersion of MCC in PLA matrix by surface acetylation. Emphasis was laid to characterize the behaviour of dispersion at different level of loadings, ranging from 1-5 wt%. Beyond 5 wt% loading, filler-filler interactions were observed. Composites were prepared with this surface acetylated MCC, using PLA as base matrix by solution casting technique and dichloromethane as the solvent (Mukherjee et al., 2012). Acetylation is confirmed by FTIR and NMR study. The behaviour of dispersion is characterized by XRD, DSC, and shear rheological tests. A rheological percolation threshold is calculated to quantify the level of dispersion and the optimal loading for a uniform dispersion. This Chapter is part of the publication in the Journal of Chemical Engineering Science.

4.1. Acetylation of MCC:

Acetylated cellulose was characterized by Fourier Transform infrared (FT-IR) and solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS 13C-NMR) spectroscopy. The reaction scheme with acetyl chloride is shown in Figure 4.1. Figure 4.2 illustrates the FT-IR absorbance spectra of unmodified cellulose and acetylated cellulose resulting from the two reactions. For the pure MCC, as reported in literature, a strong band around 3, 434 cm\(^{-1}\) is observed which is attributed to the stretching of hydroxyl groups (Das et al., 2010). In comparison, the spectrum of acetylated cellulose shows successful evidence of acetylation with ester bond appearing around 1756 cm\(^{-1}\).
Another important aspect in the acetylated MCC spectrum is the decreasing absorption peak at 3,434 cm\(^{-1}\), assigned to stretching vibration of hydroxyl groups, as compared to pure MCC (Mukherjee et al., 2012). **Figure 4.3** represents the spectral curve by 13 C solid state NMR. With acetylation, there were two chemical shifts located at 172 ppm and 20 ppm, as assigned to –C=0 and –CH\(_3\) stretching, thus confirming the successful acetylation of MCC. The results obtained were similar to the observation made by Lin et al. (2011), where acetylation was performed on cellulose nanocrystals. The percentage of acetyl content as calculated by conductometric titration was 5.5.

**Figure 4.1** Reaction scheme of acetylation of cellulose by acetyl chloride
Figure 4.2 FT-IR study of AC-MCC as compared to MCC
Figure 4.3 \(^{13}\)C CP-MAS NMR spectra of pure MCC and acetylated MCC

4.2. Morphological Study

Environmental Scanning Electron Microscopy (ESEM) was used to investigate the morphology of the cellulose microcrystals embedded in PLA matrix. The untreated MCC in Figure 4.4 (a) had a rod like morphology with an aspect ratio of 4.5-7.5. After acetylation of MCC, the rodlike shape was still preserved as shown in Figure 4 (b). But its size slightly decreased, with a reduced aspect ratio of 3.5-6.5. From the image, it is also evident that the image of acetylated MCC is slightly blurry, which is possibly due to the partial solubilization of cellulose molecules, similar to the observation made by Lin et al. (2011), for acetylated cellulose nanocrystals, retaining its intrinsic morphology. Figure 4.4 (c-i) shows
the fractured surface of neat PLA and composites reinforced with pure and acetylated MCC at different loading. Similar to the micrographs as reported by Frone et al. (2011), the addition of MCC influenced the fracture mechanism of PLA at cryogenic temperature. ESEM images show a smooth fracture surface in the case of PLA (as shown in Figure 4.4 (c)), but an uneven fracture surface in the case of PLA composites, suggesting a significant matrix deformation after the addition of MCC. The images indicate that the treated fibres were better distributed in the polymer matrix in comparison with composites obtained from pure MCC. Figure 4.4 (d) and Figure 4.4 (e) represent PLA-MCC and PLA-AC-MCC composites, both at 1.5 wt% respectively. Cellulose nucleation with agglomeration starts at 2.5 wt% of MCC, as indicated in Figure 4.4 (f). Agglomeration is more evident at a higher loading of MCC (5 wt%) as shown in Figure 4.4 (h), which is reduced to an extent in PLA-AC-MCC as shown in Figure 4.4 (i) (Mukherjee et al., 2012). This observation is similar to the results as observed by Huda et al. (2007), where they studied the SEM micrographs of silane treated talc reinforced PLA/Newspaper composites. Regularity in the fibre dispersion is observed in the matrix with less large size aggregate of cellulose. Frone et al. (2011) also observed effect similar to that of surface treatment on MCC crystals in their dispersion of silane coupling agents in PLA. The ability of AC-MCC to reduce the filler-filler interactions through the reduction of surface energy can result in better filler dispersion (Lin et al., 2011).
Figure 4.4 ESEM images of (a) Neat Fractured Surface of PLA
(b) Morphology of MCC
(c) Morphology of AC-MCC
(d) PLA-MCC (1.5 wt%)
(e) PLA-AC-MCC (1.5 wt%)
(f) PLA-MCC (2.5 wt%)
(g) PLA-AC-MCC (2.5 wt%)
(h) PLA-MCC (5 wt%)
(i) PLA-AC-MCC (5 wt%)
4.3 Crystallinity Study by X-Ray Diffraction (XRD)

In XRD analysis, neat PLA was mainly comprised of the amorphous polymer structure with intermittent crystalline structure characteristics, as shown in Figure 4.5. As reported in the literature, it exhibited three diffraction peaks located at about 16.4°, 19.1° and 22.6° and there is an appearance of another peak at 44.2° of 2θ as indicated in the figure (Lin et al., 2011). Four main peaks correspond to different crystal structures (Furuhashi et al., 2012 and Chen et al., 2011). Acetylated MCC, when introduced at a different loading (1-5 wt%), improved the crystallinity of neat PLA overall, as indicated by growing intensity of the peak located at 16.4° and 22.6° in Figure 4.6. X-Ray diffraction patterns did not change after the addition of the filler, indicating that the crystalline structure of the polymer is unaltered. With increase in level of loading, the acetylated cellulose microcrystals exhibited two distinct diffraction peaks located at around 64° and 82.6° of 2θ, particularly at a loading above 1 wt%. The peak around 44.2° became more significant above that loading as well. Biopolymers like PLA contains both crystalline and amorphous phase arranged randomly. When acetylated MCC were introduced to the PLA matrix, the uniform distribution of rigid microcrystals in the matrix restricted the motion of the polymer chains, as indicated by the intensified peak located at 16.4° and 22.6°. These results can be compared to Lin et al. (2011), where the crystalline property of the nanocrystals exhibited the growth of two diffraction peaks located at about 16.4° and 22.6° of 2 θ. As reported in a similar study on composite system, the appearance of the new peak in the amorphous phase may be due to increasing polymerization in the amorphous phase, thereby inducing a quazi crystalline phase in the system (Rahman et al., 2012).
Figure 4.5 Neat PLA X-Ray Diffraction Pattern
4.4 Thermal Analysis (Differential Scanning Calorimetry)

DSC thermograms of PLA-MCC composite and PLA-AC-MCC composite are shown in Figure 4.7 and Figure 4.8. The data for the glass transition (T_g), cold crystallization (T_{cc}), melting temperature (T_m), heat of fusion (\Delta H_m), and the degree of crystallinity within the PLA fraction (X_c) of the composites are summarized in Table 4.1 and Table 4.2 for the PLA-MCC and PLA-AC-MCC composites, respectively. From the data it is evident that the T_g is higher in all the composite materials, as compared to that of pure PLA (62.73 °C), indicating that the polymer relaxation is delayed in the presence of reinforcements. Mathew et al. (2006) had similar observations on PLA-MCC composites, where they concluded that the restriction of the chain mobility is due to increased crystallinity. Further to the analysis, T_g reaches its optimal value at 2.5 wt% for acetylated MCC based PLA.
composites, thereby showing maximum constrain of polymer relaxation due to improved dispersion. The value for $T_m$ remains almost constant at 170 °C. It will also be interesting to interpret as to how the MCC dispersion affects the nucleation and growth geometry of the crystals. This can be partially achieved by closely observing the values of $T_{cc}$ data. Cold crystallization value of pure PLA is slightly higher than those of the composites. The value of cold crystallization is observed to reduce after acetylation. Similar trend is observed by Reinsch and Kelley (1998) on wood fibre reinforced PHB composite, where they concluded that the enhancement of the nucleation rate is likely responsible for reduced cold crystallization temperature and thereby an overall cold crystallization rate.

Percentage crystallinity is calculated by applying Equation (4.1):

$$
\Delta X_c = \frac{\Delta H_m - \Delta H_c}{93(1-X_{mcc})}
$$

The percentage crystallinity obtained from Equation (4.1) indicates that crystallinity of pure PLA is slightly higher (approx. 36.13 %) than that for PLA–MCC composites, which have almost same crystallinity. Comparatively, PLA-AC-MCC composites have higher crystallinity reaching its optimal value at 2.5 wt% (29 %). This result is comparable with Pei et al. (2010), where the percentage crystallinity values increased slightly by using surface silylated cellulose nanocrystals in PLLA matrix. They concluded that the nucleating effect of the filler in the polymer matrix is enhanced if homogeneous dispersion of cellulose in poly (lactic acid) matrix is achieved.
Figure 4.7 DSC thermo grams of PLA-MCC composites (1.5-5 wt %)
Figure 4.8 DSC thermo grams of PLA-AC-MCC composites (1.5-5 wt%)
Table 4.1: DSC data analysis of PLA-MCC Composites

<table>
<thead>
<tr>
<th>% of MCC</th>
<th>Sample Wt (mg)</th>
<th>Tg (°C)</th>
<th>ΔHg (J/g)</th>
<th>Tcc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Xc</th>
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<tr>
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<td>63</td>
<td>0.25</td>
<td>103</td>
<td>10</td>
<td>171</td>
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<td>36</td>
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<tr>
<td>1.5</td>
<td>13.3</td>
<td>63</td>
<td>0.26</td>
<td>102</td>
<td>21</td>
<td>170</td>
<td>28</td>
<td>30</td>
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<tr>
<td>2.5</td>
<td>9.59</td>
<td>64</td>
<td>0.39</td>
<td>101</td>
<td>22</td>
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<td>27</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>9.45</td>
<td>63</td>
<td>0.65</td>
<td>98</td>
<td>21</td>
<td>171</td>
<td>28</td>
<td>30</td>
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</tbody>
</table>

Table 4.2: DSC data analysis of PLA-AC-MCC Composites

<table>
<thead>
<tr>
<th>% of AC-MCC</th>
<th>Sample Wt (mg)</th>
<th>Tg (°C)</th>
<th>ΔHg (J/g)</th>
<th>Tcc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Xc</th>
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<tr>
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<tr>
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<td>10.5</td>
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<td>0.21</td>
<td>100</td>
<td>20</td>
<td>171</td>
<td>34</td>
<td>37</td>
</tr>
</tbody>
</table>
4.5 Shear Rheology

Rheological measurements are complementary to traditional polymer nanocomposite analysis technique and may serve as an analytical tool to differentiate the degree of dispersion (Zhao et al., 2005). In this work, the quality of the degree of dispersion of MCC in PLA matrix is evaluated using dynamic frequency sweep tests, by associating their storage modulus and complex viscosity parameters to their dispersion. In earlier work on polymer nanocomposites, it is well established that the rheological behaviour is indicative of the level of interaction of nanoclay with the polymer matrix and is intimately related to the clay type, its surface treatment and affinity with the polymer matrix (Ray and Okamoto, 2003; Dan et al., 2006). Figure 4.9 compares the storage modulus (G’) of the PLA-MCC composites at various loadings, ranging from 1.5-5 wt% at 170 °C, when subjected to dynamic frequency sweep tests. Figure 4.10 compares the G’ of the acetylated MCC reinforced PLA based composites at different level of loading ranging from 1.5-5 wt% at 170 °C. Figure 4.11 and Figure 4.12 compare the G’ of acetylated MCC with that of pure MCC and neat PLA at 2.5 wt% and 5 wt% respectively. Figure 4.13 and Figure 4.14 compare the complex viscosity (η*) of pure and acetylated MCC at different loadings. In all dynamic frequency sweep tests, the frequency is varied from 0.1 rad/s to 100 rad/s. The minimum frequency used is 0.1 rad/s as the data based on lower frequency beyond this point produced instrumental error resulting in data distortion. From these figures it is evident that the enhancement of storage modulus (G’) of PLA-MCC composites as compared to neat PLA is significant at a comparatively lower level of loading (1.5-2.5 wt%) than that at a higher level of loading. The optimal loading reached at 2.5 wt%. From Figure 4.10, Figure 4.11, and Figure 4.12, it is also observed that acetylation did improve the G’ of the composites as compared to the composites from pure MCC as well as neat PLA up to a loading of 2.5 wt%, in the lower frequency range sweep. At higher loading above 2.5 wt%, there is an exponential drop in G’ value.
(Mukherjee at al., 2012). It is also evident from the curve, that at lower frequency, the composites behaved more solid like, whereas at a higher frequency, the composites behaved more liquid like. This is probably because at higher frequency, cellulose is highly deformable, leading to decrease in storage modulus. On the other hand, lower frequency leads to increase in storage modulus, due to low deformation of cellulose. This phenomenon could be possibly explained by analysing the microstructure of the polymer matrix. Non acetylated cellulose microcrystals (MCC), being hydrophilic in nature, has polar –OH groups that facilitate intra as well as intermolecular hydrogen bonding in the PLA matrix. However, PLA is a hydrophobic non polar thermoplastic polymer. PLA and MCC thus have the tendency to repel each other and therefore not compatible as compared to acetylated derivatives of MCC. On the other hand, when MCC is acetylated, they have limited -OH group, and as a result, intra as well as intermolecular hydrogen bonding is restricted. Therefore, acetylated MCC (AC-MCC) is more compatible in the PLA matrix and stay together in the polymer chain constraints, possibly bonded by a weak vander Walls force. This led to an improvement in dispersion and thereby an increased storage modulus up to a loading of 2.5 wt%. At a comparatively higher loading, the storage modulus eventually deteriorates, as they affect the interactions between crystalline and amorphous domains of the polymer chain.

Complex viscosity and its reciprocal, complex melt fluidity, is a significant parameter to study structure relationship in polymer composites (Verney and Michel. 1989). Cox-Merz rule, a well-known hypothesis states that the functional dependence of complex viscosity’s magnitude, expressed as a function of frequency, is identical to the functional dependence of the steady shear viscosity expressed as a function of shear rate (Cox and Merz.1958). From Figure 4.13 and Figure 4.14, it is observed that complex viscosity (η*) is slightly higher than pure PLA for all the composites up to a loading of 2.5 wt%, indicating better dispersion of the filler. With increasing loading beyond 2.5 wt%, the value of η* is reduced, reaching its
minimal value at 5wt %. It is further observed that PLA-AC-MCC 2.5 wt% exhibited reduced shear thinning behaviour, probably due to chain scission mechanism. Reduction in complex viscosity at a higher loading could be possibly due to a small decrease of polymer molecular entanglement density as a function of the filler aggregate, causing disruption in the polymer chain entanglement network (Hatzikiriakos et al., 2005).

The rheological study thus indicates that best enhancement of rheological properties occurs for a loading of 2.5 wt %, when the dispersion is at its optimum level.

**Figure 4.9** Dynamic Frequency Sweep of PLA-MCC Loading (1.5-5 wt %) Comparision of Storage Modulus at Different Loading at 170 °C
Figure 4.10 Dynamic Frequency Sweep of PLA-AC-MCC Loading (1.5-5 wt %) Comparision of Storage Modulus at Different Loading at 170 °C
**Figure 4.11** Comparison of Storage Modulus (G’) of acetylated MCC with that of pure MCC and neat PLA at 2.5 wt % loading at 170 °C
Figure 4.12 Comparison of Storage Modulus (G’) of acetylated MCC with that of pure MCC and neat PLA at 5 wt % loading
Figure 4.13 Comparison of Complex Viscosity at Different Loading of PLA-MCC (1.5-5 wt %)
Figure 4.14 Comparison of Complex Viscosity at Different Loading of PLA-AC-MCC (1.5-5 wt %)

Figure 4.15 Slope \((n')\) for storage modulus \(G'\) at low frequency against vs PLA-AC-MCC composite at different loading. The experiment is carried out at 170°C.
Further to the analysis, slope of G’ at lower frequency, which is represented as n’ is plotted against various loadings (1.5 to 5 wt %) of PLA-AC-MCC composites, shown in Figure 4.15. This figure evaluates the rheological percolation threshold for a uniform dispersion. From the figure, it is observed that around 2.5 wt% loading, a region of minimum slope exists and indicates that beyond that region, dispersion is affected by agglomeration. This empirical study is indicated to quantify the degree of dispersion and evaluate the optimal loading for a uniform dispersion of MCC in PLA matrix. Similar trend in result is observed in morphological study, where the micrograph shows the tendency of MCC and AC-MCC to agglomerate beyond a loading of 2.5 wt%.

4.6 Summary

From this study it can be concluded that successful acetylation of microcrystalline cellulose (MCC) was accompanied by acetyl chloride at room temperature as revealed in NMR and FTIR studies. Improvement in dispersion was observed in morphological and rheological tests, when composites were prepared by this surface acetylation technique, particularly at a lower loading reaching its optimum value around 2.5 wt% from the rheological percolation threshold analysis, indicating that beyond this region, dispersion is affected by agglomeration of the filler. Improvement in crystalline structure was observed in XRD study, when MCC was incorporated into the matrix. Acetylation did not affect this crystalline structure. Improved thermal behaviour was observed in DSC thermo gram. Further analysis reveals that percent crystallinity is enhanced for all PLA-AC-MCC composites, in comparison to PLA-MCC composites, reaching its optimal value at 2.5 wt%. This suggests that AC-MCC is a stronger candidate to act as a nucleating agent in comparison to pure MCC in preparing such PLA based composites.
Chapter 5: Dispersion Study of Nanofibrillated Cellulose based PLA and PBAT Composite

This Chapter presents an investigation on the Improved Dispersion of Nanofibrillated cellulose (NFC) based polybutyrate adipate terephthalate (PBAT) and Polylactic Acid (PLA) Composites. In case of PLA composites, surface acetylation on NFC is performed. PBAT is primary known for its high flexibility and ductility. This property in contrast with the material property of PLA, which is known for its brittle nature. PBAT is used here for understanding trend in results for contrasting property material. This work has been published in Carbohydrate Polymers and part of this work has been submitted to Composite Science and Technology journal.

Result and analysis in this Chapter is divided primarily into two sections. In the first section, a series of bio-nanocomposites were developed by reinforcing NFC from regenerated wood fiber into Poly (butylene adipate-co-terephthalate) PBAT by injection moulding. Then the degree of dispersion is evaluated by morphological, rheological and thermal tests. In the second section, acetylation of NFC is performed to prepare acetylated NFC based PLA composites. The composites were then characterized to estimate the acetyl content, to observe the morphology of the nanofibrill distribution and to measure the rheological properties of the composite.

5.1. PBAT-NFC Composite

This section presents the rheology and morphological study of PBAT-NFC composite. The primary motivation to prepare NFC based biopolymer composites was to use a water soluble polymer like Poly (butylene adipate-co-terephthalate) PBAT by injection moulding and understand the behaviour of interface and interphase. The second stage of research was to surface acetylate the filler and use the treated filler in PLA matrix.
5.1.1. Morphological Study

Figure 5.1 (a) shows the formation of nanofibril network under TEM and AFM imaging, respectively. Image J software was used to roughly estimate the size of the nanofibrils. From the imaging, it is apparent that the morphology was formed by the internal fibrillation of submicron or large nanofibrils of several hundred nanometers to small nanofibrils of 10-30 nm, which probably resulted from external fibrillation. Figure 5.1 (b-e) shows the TEM image of PBAT-NFC composite (0.2-1 wt %). From this figure, it is evident that, at 0.2 wt %, fine dispersion of NFC is visible at a high magnification of 100 nm. The observation coincides with rheology and thermal study as discussed in the subsequent sections. With the addition of 0.5-0.75 wt % NFC, the filler still exhibited good miscibility with the matrix. Meanwhile, addition of NFC did not destroy the original structure of PBAT, which is again confirmed by the XRD study as discussed in the subsequent sections in this Chapter. However, with a continuous increase in the loading level of NFC, some agglomerates emerged as shown in Figure 5.1 (d) and Figure 5.1 (e), which is mainly attributed to self-aggregation of the superfluous nanofiller. This observation is similar to a study on organomodified clay based PBAT composites, where big agglomerates of micrometre size appear (Bittman et al., 2012). Aspect ratio as determined from this network fractal study on 0.2 wt % NFC composite is ranging from 1-2.5
Figure 5.1 (a) TEM and AFM Image of the Structure of Nanofibrillated Cellulose Network
Figure 5.1 (b) Structure of PBAT-NFC (0.2 wt %) (c) PBAT-NFC (0.5 wt %) (d) PBAT-NFC (0.75 wt %) (e) PBAT-NFC (1 wt %)
In XRD analysis, as shown in Figure 5.2, neat PBAT exhibited five different diffraction peaks, with a combination of amorphous and crystalline structure. The crystal peaks are observed at 16.4°, 17.4°, 20.6°, 23.2° and 24.7°. This is similar to the study performed by Chivrac et al. (2007) where five characteristic peaks are also observed at the same values for all PBAT-NFC nanocomposites. From these observations, it can be inferred that there is no important transcrystalline phase in the system interface. Therefore there is few or no change in the PBAT crystal structure as induced by nanofiller incorporation.

![X-Ray Diffraction Analysis](image)

**Figure 5.2** X-Ray Diffraction Analysis of PBAT-NFC thermograms at various NFC concentrations

### 5.1.2. Thermal Study

**Table 5.1** summarizes DSC results. From the data it is observed that there is a slight shift of the glass transition on addition of NFC to the PBAT matrix reaching its maximum at 0.2 wt% indicating optimal dispersion. The
uniform dispersion of the NFC filler restricts the polymer chain mobility, thereby increasing the $T_g$ value. With further loading, agglomeration of NFC starts to begin, due to hydrogen bonding and thereby filler-filler interaction dominates, which eventually decreases the $T_g$ value. The observed value complements morphology study by TEM, where an optimal dispersion was observed at 0.2 wt%. The correction for diluents effect linked to the nanocellulose incorporation into the PBAT matrix, as shown in Equation (5.1) and Equation (5.2), is taken into account to calculate the corrected values of enthalpy, where $\varnothing$ is the fraction of cellulose content:

$$\Delta H'_c = \frac{\Delta H_c}{1-\varnothing} \text{(5.1)}$$

$$\Delta H'_m = \frac{\Delta H_m}{1-\varnothing} \text{(5.2)}$$

It is also apparent, that the corrected values of heat of fusion ($\Delta H_m'$ and $\Delta H_c'$) as calculated from Equation (5.1) and Equation (5.2) are higher in comparison to the values obtained from the thermograms, as the effect of diluent is taken into account in this equation. The corrected values are equivalent and both are into the range of 10.1-15.7 J/g, similar to the study performed by Madera-Santana (2009) on agar based PBAT particles. However, the incorporation of NFC did not induce any significant effect on the crystallization temperature ($T_c$). The percentage of crystallinity ($X_c$) increases with increasing content of NFC, which is unlike those reported in literature on clay and natural filler based PBAT composites. This indicates the potential of NFC as a nucleating agent on the PBAT matrix.
Table 5.1: Summarized DSC Data indicating the thermal behaviour of PBAT-NFC Composites

<table>
<thead>
<tr>
<th>NFC</th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_g$ (J/g)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_m'$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\Delta H_c'$ (J/g)</th>
<th>$X_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-33.93</td>
<td>0.23</td>
<td>116.6</td>
<td>7.65</td>
<td>7.65</td>
<td>79.74</td>
<td>7.53</td>
<td>7.53</td>
<td>6.71</td>
</tr>
<tr>
<td>0.2</td>
<td>-25.3</td>
<td>0.2</td>
<td>116.69</td>
<td>11.58</td>
<td>11.60</td>
<td>80.17</td>
<td>9.8</td>
<td>9.82</td>
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</tr>
<tr>
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<td>11.76</td>
<td>81.66</td>
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<td>9.35</td>
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<td>13.33</td>
<td>13.47</td>
<td>79.27</td>
<td>10.3</td>
<td>10.40</td>
<td>11.81</td>
</tr>
</tbody>
</table>

Thermogravimetry (TGA) was performed to confirm composition and establish thermal stability of PBAT composites in a nitrogen atmosphere. Figure 5.3 reflects the mass change and degradation temperatures. As evident from this figure, TGA shows a one-step mass loss that indicates degradation started at approximately 320 °C and was completed by approximately 465 °C, which is similar to the study performed by Madera-Santana et al., (2009) on agar based PBAT particles. Pure PBAT had a higher decomposition temperature. Adding NFC reduced the decomposition temperature by 1-3 °C, in a non-linear fashion. Notably, the TGA curve showed no other deflection indicating that NFC was well dispersed in PBAT or consisted of too little of the mass to be detected. Thus adding NFC to PBAT only slightly decreased its heat resistance, which is desirable as low heat resistance can make moulding, disposal and reprocessing easier.
5.1.3. Shear Rheology

Investigation on dispersion, network formation and microstructural changes of NFC in the PBAT matrix at melt state is performed by oscillatory measurements. **Figure 5.4 (a), Figure 5.4 (b) and Figure 5.4(c)** compare the storage modulus (G'), loss modulus (G'') and complex viscosity (η*) of PBAT-NFC composites at various loadings, ranging from 0.2-1 wt% at 150 °C, when subjected to dynamic frequency sweep tests. From these figures, it is evident that the enhancement of storage modulus (G'), loss modulus (G'') and complex viscosity (η*) is significant at all frequencies for all PBAT-NFC composite in comparison to neat PLA, reaching its optimal value at 0.2 wt %, particularly at the lower frequency range. At higher frequency, this difference is minimized due to the hydrodynamic force. The result is similar to the observation made by Madera-Santana et al. (2009) on their PBAT-Agar composite, where at a lower frequency; the influence of agar particle increased the storage modulus. The complex viscosity data showed a shear thinning behaviour. As expected, the
influence of the NFC filler on the complex viscosity is observed at a lower frequency, when the hydrodynamic force is not very dominant. This enhancement is probably due to the uniform dispersion of NFC in PBAT matrix at 0.2 wt % loading, as observed in the TEM study.

The phase homogeneity in polymer solutions and melts is often derived from Cole-Cole plot where the imaginary part of the complex viscosity η” is plotted as function of the real part η’ (Warren et al., 1973, Cole and Cole. 1941). Generally, in a melt, at very low frequencies solid like behaviour is observed, whereas at higher frequencies liquid like behaviour prevails. In this formation, G*(ω) = G’ (ω) + iG”(ω), a modified Cole-Cole plot can be obtained by plotting G’ against G” (Park et al., 2007). Figure 5.4 (d) represents a modified Cole-Cole plot of PBAT and PBAT-NFC composite using the G’ and G” data from Figure 5.4 (a) and Figure 5.4 (b). The plot (Figure 5.4 (d)) indicates a right shift in the elastic modulus (G’) for a loading of 0.2 wt % NFC indicating a predominant viscous behaviour. This is probably due to the weak interaction between the filler and the matrix. With increasing concentration of NFC (0.5 -1.00 wt %), the curve collapsed into a single line with a slope of 1.15. This suggests that there are few structural changes like agglomeration of the filler, as the NFC concentration increased. It will be interesting to note here that the Cole-Cole plot is also complementing the complex viscosity data in Figure 5.4 (c), where there is an optimal increment of the storage modulus at 0.2 wt % loading of NFC. The observed trend is similar to the trend observed by Park et al. (2007) on polystyrene clay nanocomposite.

It is well known that the storage modulus (G’) at low frequency range is more sensitive to the structural changes in the polymer nanocomposites (Mabrouk et al., 2011). Thus the slope of dependence of G’, denoted as n’, is plotted against different loading of NFC (0.2-1 wt %) at the low frequency range (0.01-1 rad/s) in Figure 5.4(e). This figure evaluates the rheological percolation threshold for a uniform dispersion. From the figure, it is observed that around 0.2-0.5 wt% loading, a region of minimum slope
exists and indicates that beyond that region, dispersion is affected by agglomeration. This empirical study has been conducted to quantify the degree of dispersion and evaluate the optimal loading for a uniform dispersion of NFC in PBAT matrix.

**Figure 5.4(a)** Comparison of Storage Modulus ($G'$)
Figure 5.4(b) Comparison of Loss Modulus (G")

Figure 5.4(c) Comparison of complex viscosity (η*)
Figure 5.4(d) Cole-Cole Plot

Figure 5.4(e) Slope (n’) for storage modulus G’ at low frequency for PBAT-NFC composites
5.1.4. Discussions on Dispersion, Structure and Property

Dispersion is the key factor in improving the strength of the nanocomposites, as homogeneous separation of nanoscale particles is responsible for high interface of contact between the fibre and the matrix. A good fiber matrix adhesion creates a synergistic effect, leading to the overall property improvement of the polymer material. The homogeneous dispersion of NFC in the PBAT matrix is challenging due to the high polarity of the cellulose surface (Ten and Vermerris, 2013). In this study, the degree of dispersion is evaluated by morphological, rheological and thermal tests. TEM analysis indicates an optimal dispersion of PBAT-NFC (0.2 wt %) composite. This uniform dispersion is contributing to the shift of glass transition and crystallinity in DSC and enhancement of storage modulus in shear rheological tests. Notably, the TGA curve shows no deflection meaning that NFC is well dispersed in PBAT or makes up too little of the mass to be detected. A quantitative approach has been used to evaluate the degree of dispersion by evaluating the rheological percolation threshold. This evaluation indicates a percolation around the region of 0.2-0.5 wt %. Further to the study, the Cole-Cole plot suggests that viscous behaviour is more predominant at 0.2 wt %, probably due to the weak interaction between the filler and the matrix. Beyond that loading agglomeration and few structural changes are apparent.

5.2 PLA-AC-NFC Composite

This section presents the rheology and morphological study of PLA composites acetylated with NFC.

5.2.1 Morphology Study

Figure 5.5 (a-d) shows the SEM image of PLA-NFC composite (1.75-5 wt%). From this figure, it is evident that, at 1.75 -2 wt %, fine dispersion...
of NFC was apparent. Meanwhile, addition of NFC did not destroy the original structure of PLA. However, with a continuous increase in the loading level of NFC, some agglomerates emerged as shown in Figure 5(c) and Figure 5(d), which is mainly attributed to self-aggregation of the superfluous nanofiller. This result is similar to the study by Fernandes et al. (2010), where the random orientation and the good dispersion of the nanofibrillated cellulose in the chitosan matrices were evident. From the SEM study on the composites, it is also apparent that the filler is locally ordered like clay particles in tactoids organized aggregate on a large scale. The average aspect ratio of these tactoids as measured by taking several SEM micrographs is about ~6.

![Figure 5(c)](image)

![Figure 5(d)](image)
In XRD analysis, neat PLA in Figure 5.6 was mainly comprised of the amorphous polymer structure, with intermittent crystalline structure characteristics. As reported in the literature and in Chapters 4 and 6, it exhibited four main different peaks located at about 16.4°, 19.1°, 22.6° and 44.2°, with the appearance of a less intensified peak around 64° and 82.6°. These four main peaks correspond to different crystal structures (Furuhasi et al., 2012; Chen et al., 2011). Acetylated NFC, when introduced at a different loading (1-5 wt%), improved the crystallinity of neat PLA in overall, as indicated by growing intensity of the peak located around 44.2°, 64° and 82.6° in Figure 5.6, particularly at a loading above 1 wt%. X-Ray diffraction patterns did not change after the addition of the filler, indicating that the crystalline structure of the polymer is unaltered. This behaviour is unlike the observation made by Lin et al. (2009), where the original structure of the PLA matrix was cleaved to a greater extent. The peak around 44.2°, 64° and 82.6° became more significant above that loading as well. Biopolymers like PLA contains both crystalline and amorphous phase arranged randomly. When acetylated NFC was introduced to the PLA matrix, the uniform distribution of rigid microcrystals increased the
crystalline property of the composites, as indicated by the intensified peak located around 44.2°, 64° and 82.6°. These results can be compared to that of Lin et al. (2011), where the crystalline property of the nanocrystals exhibited the growth of two diffraction peaks located at about 16.4 and 22.6 of 2θ.

**Figure 5.6** PLA-AC-NFC Composite X-Ray Diffraction Pattern with different weight percent as indicated in the index
5.2.2. Shear Rheology

Investigation on dispersion, network formation and microstructural changes of AC-NFC in the PLA matrix at melt state is performed by oscillatory measurements in the linear viscoelastic region.

In this study, rheology is envisaged as a tool to assess the quality of dispersion by applying two techniques. They include analyzing the rheological percolation at low frequency moduli and probing to fit the higher frequency data using the Krieger-Dougherty model. Rheological data for different loadings of the filler, as referred before in percentage weight, is now converted to volume fraction, which will help in further analysis of the maximum packing fraction. Thus, the new volume fraction of the earlier weight percent (1.75/2.5/3.5/5) corresponds to 0.022/0.031/0.043/0.061, respectively. The volume fraction is calculated using the solid densities of NFC and PLA as 1.01 g cm$^{-3}$ and 1.27 g cm$^{-3}$, respectively, as available from the technical data sheet and Equation (5.3) as described below.

\[ V_f = \frac{W_f / \rho_f}{\rho_f + (1-W_f) / \rho_a} \] ..........................(5.3)

Where \( W_f \) and \( \rho_f \) correspond to the weight and solid density of NFC, While \( \rho_a \) represents the solid density of neat PLA.

In all dynamic frequency sweep tests, the frequency is varied from 0.1 rad/s to 100 rad/s. In general, the classical viscoelastic behaviour of a homogeneous polymer solution / melt is distinguished by (G$''$ > G$'$), where at low frequency (terminal region) G$'$~ $\omega^2$ and G$''$~ $\omega$ (Larson, 1998). In general from the experimental study, it is observed that the PLA sample showed liquid like behaviour at low frequency (G$''$/G$'$), where the slopes of G$'$ and G$''$ were 1.28 and 0.94, respectively. Deviation from the exponent of 2 and 1 for loss and storage moduli could be attributed to the
polydispersity of the commercial PLA resin, probably due to the presence of the two lactide form (L-lactide and D-lactide).

**Figure 5.7(a) and Figure 5.7(b)** compare the storage modulus (G’) and loss modulus (G”) of PLA-AC-NFC composites at various loadings, ranging from 0.02-0.06 volume fraction (Ø) at 170 °C, when subjected to dynamic tests. From these figures it is evident that the enhancement of storage modulus (G’) of PLA-AC-NFC composites as compared to neat PLA is significant at all levels of loading, up to a loading of Ø ~0.04. It is also apparent from the curve, that at lower frequency, both storage and loss moduli increased by incorporation of the NFC filler in the PLA matrix. It was further observed that storage modulus was more sensitive to the presence of NFC filler than loss modulus, thus following similar trend as reported for other polymer nanocomposite systems (Bhattacharya et al., 2008; Litchfield et al., 2006). Furthermore, the slopes of both loss and storage moduli versus angular frequency in the terminal region were lowered by the addition of NFC to PLA. This is similar to previous study as reported earlier on PLA and acetylated cellulose microcrystals as reported in Chapter four.

### 5.2.2.1. Fitting lower frequency data to obtain rheological percolation model

The level of linear properties, such as the storage and loss modulli, G’ and G” curve can be used diagnostically to assess the state of dispersion, since a flocculated system will show up as an extra low G’ pleateau. This usually takes the form of a progressive increase in the level of properties as more filler is added (Barnes, 2003). The basic concept of the scaling theory for polymer gels is to relate the elastic properties of a gel to its network structure. Near the gel point, the shear modulus of a gel behaves like $G’ \sim (\Phi - \Phi_c)^t$ which is characteristics of a percolation transition.
Based on the concept of rheological percolation as mentioned above, the slope of $G'$ at lower frequency, which is represented as $n'$, is plotted against various loadings ($\bar{\omega} \sim 0.02-0.04$) of PLA-AC-NFC composites, shown in Figure 5.7(c). This figure evaluates the rheological percolation threshold for a uniform dispersion. From this figure, it is observed that around $\bar{\omega} \sim 0.05$ loading, a region of minimum slope exists, which indicates that beyond that region, dispersion is affected by agglomeration. This empirical study is used to quantify the degree of dispersion and evaluate the optimal loading for a uniform dispersion of AC-NFC in PLA matrix. As compared to AC-MCC in Chapter four, the percolation threshold reached at a comparatively higher loading (for AC-MCC it was observed that the region of minimum slope exists around $\bar{\omega} \sim 0.02$). A detailed comparison of percolation is presented in Chapter six.

5.2.2.2 Fitting Higher Frequency Data to the Krieger-Dougherty Model.

The rheological study clearly indicates that at high frequency, there is a dominance of the polymer matrix contribution over the aggregate contribution. It is observed that at higher frequencies, moduli are increased with increasing volume fraction. This is probably due to an increased effective deformation rate in the matrix due to the hydrodynamic contribution. The higher frequency data is further used in the analysis in the later part to assess the quality of dispersion. The relative high frequency moduli can be obtained by dividing the moduli of the composites by the values of their matrix. The Krieger-Dougherty equation, as described in Equation (5.4), is used to further analyze this data.

$$G'_{HF,rel} = \frac{G'_{HF}}{G'_{HF,m}} = \left[1 - \frac{\bar{\omega}}{\bar{\omega}_{max}}\right]^{-[\eta] \bar{\omega}_{max}} \quad \ldots \ldots \ldots (5.4)$$
Where $G'_{HF,rel}$ refers to the high frequency modulus of the nanocomposite, $G'_{HF,m}$ is the high frequency modulus of the matrix at the same frequency, $\phi$ is the volume fraction, $\phi_{max}$ is the maximum packing fraction, and $[\eta]$ is the intrinsic viscosity. The basic concept applied in the analysis and explanation is that, the more pronounced network of the NFC filler will lead to an increased average aspect ratio and thereby a lower packing fraction. Thus determining the effective maximum packing fraction ($\phi_{max}$) will give an opportunity to quantitatively rank the dispersion quality of different samples (Vermant et al., 2007).

In this study, rheological measurements have been used as an effective tool to measure the effective hydrodynamic ratio and compared it to the measured aspect ratio of the NFC tactoids from SEM study by fitting the higher frequency data to the Krieger-Dougherty equation. In order to calculate the effective hydrodynamic aspect ratio, Ren et al (2000) expression will be used, which is rewritten in terms of the average aspect ratio of the tactoids ($A_f$):

$$A_f = \frac{3\phi_R}{4\phi_{per}} \ldots \ldots \ldots (5.4)$$

Using the percolation threshold volume fraction for randomly packed overlapping spheres ($\phi_R=0.30$), Isichenko (1992) and the experimentally obtained percolation threshold $\phi_{per}$ from Figure 5.7(c), the value of $A_f \sim 4.5$ is obtained. The value obtained here is in line with that obtained from SEM study. The difference in the value is indicative of the fact that rheological methods probe an effective “hydrodynamic” aspect ratio.
In earlier study by Vermant et al., (2007) the state of dispersion is evaluated by quantitatively ranking the maximum volume packing fraction from the Krieger-Dougherty equation fit. According to that study, the lower the packing fraction, the better the dispersion quality as this will allow a structured network formation of the filler in the polymer matrix. Further to that study, an attempt has been made here to fit the higher frequency data to the Krieger-Dougherty equation, as mentioned earlier. Two sets of data, namely the high frequency data set of PLA-AC-NFC, as available from Figure 5.7(a) and the high frequency G’ data set of acetylated microcrystalline cellulose based PLA composite (PLA-AC-MCC) from earlier study in Chapter four, are fitted to the Krieger-Dougherty equation in Figure 5.7(d), respectively. In earlier study, as referred to here, cellulose microcrystals were surface acetylated and the reported percolation at approximately around a volume fraction of 0.02. The intrinsic viscosity was estimated by using the Brenner approach (Brenner (1974) of the rheology of axysymetric Brownian particles. The relative parameters for the intrinsic viscosity were obtained by simulating the Brenner’s expression for oblate spheroidal particles. Applying the Brenner approach for intrinsic viscosity for oblate spheroids and $A_f$ found from Equation (5.5) (Brenner (1974), values of $[\eta]$ $\sim$6.85 and $[\eta]\sim$4.09 for AC-MCC and AC-NFC were determined, respectively. These values are only approximate. The measured data points at the highest volume fraction deviated. Excluding the deviated data point and fitting the Krieger-Dougherty equation, as shown by the lines in Figure 5.7(d), yields an effective maximum packing fraction of $\sim$0.065 and $\sim$0.05 for AC-NFC and AC-MCC, respectively. These values give a fair indication of the fact that microcrystalline cellulose, when surface acetylated, was better dispersed than AC-NFC in the PLA matrix probably because of their native crystalline shape to build a structured network. This result is also indicative of the fact that shape and size of the filler is a strong determining factor on the quality of their dispersion in the
polymer matrix as reported elsewhere (Mihut et al., 2013). It can also be suggested that percolation has some phenomenological effect on maximum volume packing fraction. For acetylated MCC presented in Chapter four, the percolation reached much earlier around a volume fraction of $\phi_{per} \sim 0.028$, whereas in the present case with AC-NFC, the percolation reached at a comparatively higher volume fraction $\phi \sim 0.05$. Similarly with the shift in percolation volume fraction value $\phi_c$, there is a shift in maximum volume packing fraction ($\phi_{max}$). Again from percolation theory on nanofiller, it is known that lesser the value of $\phi$, the better the dispersed state of nanofiller. Thus by manipulating the value of $\phi_c$, the $\phi_{max}$ value can be minimized, which will eventually lead to a better dispersed state of the nanofiller in the polymer matrix.

![Figure 5.7(a)](image)

**Figure 5.7(a)** Comparison of the storage modulus of PLA-AC-NFC composites
**Figure 5.7(b)** Comparison of the loss modulus of PLA-AC-NFC composites

**Figure 5.7(c)** Rheological percolation based on G’ data at lower frequency.
Figure 5.7(d) Relative high frequency modulus as a function of volume fraction for PLA-AC-NFC and PLA-AC-MCC composites. The lines represent the Krieger-Dougherty (KD) equation.
5.2.3. Discussions on Dispersion, Structure and Property

The behaviour of dispersion is characterized here by morphological (Scanning Electron Microscopy (SEM)), X-Ray Diffraction (XRD) study and shear rheological tests. SEM micrographs give an idea on how AC-NFC is locally dispersed in the PLA matrix and provide means to assess a rough estimate of the aspect ratio and nature of the network formation, if any. XRD study gives an idea on whether there is any change in the inherent structure of the polymer after the addition of the filler or there is any improvement in crystallinity, if any. Rheology plays a significant role in quantifying the state of dispersion. Rheological measurements have been used for different types of nanocomposite systems as a complementary tool to monitor the quality of dispersion, primarily in qualitative terms, (Vermant et al., 2007). A rheological percolation threshold is calculated to quantify the level of dispersion and the optimal loading for a uniform dispersion. Moreover, high frequency linear viscoelastic behaviour is analysed and the data is fitted to the Krieger-Dougherty equation to determine the maximum packing fraction.

Dispersion is the key factor in improving the strength of the nanocomposites, as homogeneous separation of nanoscale particles is responsible for high interface of contact between the fibre and the matrix. A good fibre matrix adhesion creates a synergistic effect, leading to the overall property improvement of the polymer material. The homogeneous dispersion of NFC in the PLA matrix is challenging due to the high polarity of the cellulose surface (Ten and Vermerris, 2013). Surface acetylation of NFC has been attempted here to partially overcome this challenge. In this study, rheology is mainly envisaged as a tool to quantify the degree of dispersion. Morphology and crystallinity study are used to evaluate the aspect ratio for data fit. SEM analysis indicates fine dispersion of the filler.
at 1.75-2 wt%. Meanwhile, addition of NFC did not destroy the original structure of PLA. However, with a continuous increase in the loading level of NFC, some agglomerates emerged which is mainly attributed to self-aggregation of the superfluous nanofiller. From the SEM study on the composites, it is also apparent that the filler is locally ordered like clay particles in tactoids organized aggregates on a large scale. The average aspect ratio of these tactoids, as measured by taking several SEM micrographs, is about ~6. X-Ray diffraction patterns did not change after the addition of the filler, indicating that the crystalline structure of the polymer is unaltered. When acetylated NFC was introduced to the PLA matrix, the uniform distribution of AC-NFC increased the crystalline property of the composites, as indicated by the intensified peak located around 44.2°, 64° and 82.6°. When rheological percolation threshold for a uniform dispersion is evaluated using lower frequency G’ data as obtained from shear rheology, it is observed that at around 0~0.05 loading, a region of minimum slope exists indicating this beyond percolation region, dispersion is affected by agglomeration. When higher frequency data is plotted to the Krieger Dougherty equation, an effective maximum packing fraction of ~0.065 is obtained. This value of maximum packing fraction is compared to the derived maximum packing fraction for acetylated microcrystalline cellulose and an attempt has been made to quantitatively rank the quality of dispersion, based on the value of effective maximum packing fraction. AC-MCC, as reported earlier in Chapter four, has a rod like crystalline morphology. As a result, it has more reactive surface available for acetylation, in comparison to the fibrillated network, as present in AC-NFC. Thus AC-MCC will be more surface acetylated than AC-NFC. AC-MCC will therefore have more chance of carbonyl-carbonyl interaction with the PLA matrix and will have more chance of making a better interface which eventually will lead to a better dispersion quality. Hence, the objective is to lower this value as this figure suggests how well the filler is dispersed in the polymer. The lower packing fraction value will give better network formation of the filler and thereby better dispersion.
5.3 Summary

A series of bio-nanocomposites were initially developed by reinforcing NFC from regenerated wood fiber into Poly(butylene adipate-co-terephthalate) PBAT by injection moulding. The incorporation of NFC in PBAT matrix (0.2-1 wt%) increased the storage modulus (G’) and dynamic viscosity (η’) as revealed by shear rheology, indicating a percolation threshold around 0.2-0.5 wt% region. DSC analysis showed similar improvement with slight improvement of glass transition (T_g) and crystallization temperature (T_c). Percentage crystallinity, as calculated from heat of fusion equation and taking into account 100 % crystallized PLA data, reflected an optimal improvement at 0.2 wt % loading. This indicates NFC has a good potential to act a nucleating agent in the PBAT matrix.

Further to the study, a series (1-5 wt %) of bio-nanocomposites were also developed by reinforcing acetylated NFC from regenerated wood fibre into Polylactic Acid (PLA) by solvent casting technique. The degree of acetylation as evaluated by saponification procedure is found to be around 0.22. Acetylation is further confirmed by NMR study. Rheology is used as an effective tool to quantify the degree of dispersion of the filler in the polymer matrix. Rheological measurements offered an integrated picture of the composite material with increased data reliability. Addition of the acetylated NFC did not change the overall structure of PLA as revealed in X-Ray diffraction. When rheological percolation threshold for a uniform dispersion is evaluated using lower frequency data as obtained from shear rheology, it is observed that around Ø~0.05 loading, a region of minimum slope exists and indicates that beyond that region, dispersion is affected by agglomeration. When higher frequency data is plotted to the Krieger Dougherty equation, an effective maximum packing fraction of Ø_{max}~0.065 is obtained from data fit analysis. This effective maximum packing fraction parameter is then used to evaluate and rank the quality of dispersion. This
was done by comparing the trendline with acetylated cellulose microcrystal based PLA composite, as reported earlier.
Chapter 6: A Comparative Analysis on the Degree of Dispersion of Different Types of Cellulose based PLA Composites

In this Chapter rheology is envisaged as an effective tool to evaluate the state of dispersion of acetylated nanocrystalline cellulose (NCC) in Polylactic Acid (PLA) based biopolymer. Microcrystalline cellulose (MCC) is acid hydrolyzed to produce nanocrystalline cellulose (NCC) for effective nano-reinforcement. Similar surface acetylation on another variety of nanocellulose as regenerated from wood fibre, referred to as nanofibrillated cellulose (NFC), has been performed and the composites made from this filler are compared to that of AC-NCC and AC-MCC (from previous Chapters). A comparative analysis has been performed to rank the quality of dispersion from different varieties of nanocellulose, to show the correlation with native shape, size and crystalline forms of nanocellulose to their dispersion quality.

6.1 Different Approaches

Different approaches have been proposed to describe the dispersion quality of the polymer nanocomposites by linear viscoelastic behaviour. Establishment of the power law relationship between elastic property and volume fraction assuming filler as the fractal aggregate is very popular, (Stauffer, 1981; Aranguren et al., 1992; Rueb and Zukoski, 1997). The basic concept of the scaling theory for polymer gels is to relate the elastic properties of a gel to its network structure. Near the gel point, the shear modulus of a gel behaves like $G' \sim (\bar{\rho} - \bar{\rho}_g)^t$, which is characteristic of a percolation transition. The theory also enables one to extract from the rheological measurements structural information about the individual flocs, such as the fractal dimension of the flocs and the fractal dimension of the elastic backbones of the flocs. The rheological model is well explained in
Chapter 2. In this Chapter, the aforementioned modelling approach will be applied to the derived results.

### 6.2 Morphological Studies by Microscopy: (SEM/TEM/AFM)

Figure 6.1 (a) and Figure 6.1 (b) show the inherent crystalline structure of acetylated crystalline nanocellulose morphology and formation of nanofibril network in AFM study. It is observed in Figure 6.1 (a), that acid hydrolyzed NCC still retained the rod like morphology with a reduced aspect ratio of 4 and equivalent volume diameter of approximately 12.58 nm, as calculated from the micrographs. From the imaging on NFC as revealed in Figure 6.1 (b), it is apparent that the core structure was formed by the internal fibrillation of submicron nanofibrils of 10-30 nm, to several hundred nanometers, which probably resulted from external fibrillation.

![Figure 6.1(a) AFM Image of Nanocrystalline Cellulose](image)
In comparison to MCC, it is certainly evident that there is a subtle particle reduction which eventually leads to poor de-agglomeration and dispersion of the NCC particles, as indicated in Chapter four. A comparative analysis on the state of dispersion of the different nanocomposites at 2.5 wt% is compared, where the cell nucleation and agglomeration starts to begin. The state of dispersion of AC-NCC in PLA is very similar to that of AC-MCC. This is evident from SEM micrograph in Figure 6.2 (a) and TEM micrograph in Figure 6.2 (b). Similar to the previous study, it is observed that cell nucleation with agglomeration starts at 2.5 wt % in Chapter four. Figure 6.2 (c) shows the AC-NFC morphology in the matrix, as derived from SEM micrographs in STEM mode. The addition of fillers did not affect the original structure of PLA. However, with a continuous increase in the loading level of the fillers, as observed in Figure 6.2 (d) (3.5 wt % AC-NCC) and Figure 6.2 (e) (3.5 wt % AC-NFC), some agglomerates emerged, which is mainly attributed to self-aggregation of the superfluous nanofiller. This result is similar to the study by Fernandes et al. (2010), where the random orientation and the good
dispersion of the nanofibrillated cellulose in the chitosan matrices were evident.

Figure 6.2 ESEM Morphology of (a) AC-NCC (1.5 wt%) (b) AC-NCC (2.5 wt%) (c) AC-NCC (3.5 wt%) (d) AC-NCC (5 wt%)
Figure 6.2
ESEM morphology of
(e) AC-MCC (2.5 wt%)
TEM Morphology of
(f) AC-NCC (2.5 wt%)
(g) AC-NFC (2.5 wt%)
(h) AC-NCC (3.5 wt%)
(i) AC-NFC (3.5 wt%)
6.3. Rheological Measurements

The rheological properties, both linear and non-linear ones, are sensitive to changes in the particulate microstructure, particle size, and shape with surface characteristics of the dispersed phase. The level of linear properties such as the storage and loss moduli, $G'$ and $G''$ can be used diagnostically to assess the state of dispersion (Mabrouk et al., 2011). The advantage of using rheology as a technique to measure dispersion is that using samples of macroscopic dimension, it offers an integrated picture of the composite material with increased data reliability, as compared to other methods using small samples that are prone to micro-scale in homogeneities. Investigation on dispersion, network formation and microstructural changes of AC-NCC in the PLA matrix at melt state is performed by oscillatory measurements in the linear viscoelastic region.

The new volume fraction of the earlier weight percent (1/1.5/1.75/2.5/3.5/5) corresponds to (0.008/0.013/0.015/0.022/0.031/0.042), respectively. The volume fraction is calculated using the solid densities of NCC and PLA as 1.25 g cm$^{-3}$ and 1.46 g cm$^{-3}$, respectively, as available from the technical data sheet and Equation (6.1) as described below.

$$V_f = \frac{W_f / \rho_f}{W_f / \rho_f + (1 - W_f) / \rho_a} \ldots \ldots (6.1)$$

Where $W_f$ , and $\rho_f$ correspond to the weight fraction and solid density of NCC.
Figure 6.3 (a) Comparison of Storage modulus of PLA-AC-NCC Composite
From Figure 6.3 (a) and Figure 6.3 (b), it is also evident that the enhancement of loss modulus (G") is more predominant than storage modulus (G') of PLA-AC-NCC composite. It was also observed that at lower frequency range, the nanocomposites behaved more solid like, while at higher frequency range, where the hydrodynamic force is more evident, the composites behaved liquid like. This is similar to the results as reported earlier in Chapter four. It was further observed that it lower frequency, storage modulus was more sensitive to the presence of NCC filler. Similar trend is also observed in case of PLA-AC-NFC composites as shown in Figure 6.3 (c) and Figure 6.3 (d).
Figure 6.3 (c) Comparison of Storage modulus of PLA-AC-NFC Composite

Figure 6.3 (d) Comparison of Loss modulus of PLA-AC-NFC Composite

From Figure 6.3 (a) and Figure 6.3 (c), it is also evident that enhancement of storage modulus ($G'$) of PLA-AC-NCC and PLA-AC-NFC
composites, as compared to neat PLA, is significant at all levels of loadings up to a loading of $\phi \sim 0.061$. Furthermore, it was also observed that the slopes of both loss and storage moduli versus angular frequency in the terminal region were lowered by addition of AC-NCC and AC-NFC to PLA. This is very similar to the previous study, as reported earlier on PLA and acetylated cellulose microcrystals in Chapter four.

### 6.3.1 Fitting Lower Frequency Data to Obtain Rheological Percolation and Scaling Law:

**Rheological Percolation:**
Further to the analysis, the slope of $G'$ at lower frequency, which is represented as $n'$, is plotted against various loadings ($\phi = 0.008 - 0.04$) of PLA-AC-MCC, PLA-AC-NFC and PLA-AC-NCC composites, as shown in **Figure 6.4.** Data for PLA-AC-MCC composite is derived from Chapter four. This figure evaluates the rheological percolation threshold for a uniform dispersion. From this figure, it is observed that around $\phi \sim 0.018 - 0.02$ for PLA-AC-NCC, $\phi \sim 0.028 - 0.03$ for PLA-AC-MCC and $\phi \sim 0.052 - 0.055$ for PLA-AC-NFC composites, respectively, a region of minimum slope exists and indicates that beyond that region, dispersion of the nanofiller is affected by agglomeration. This empirical study is used to quantify the degree of dispersion and evaluate the optimal loading for a uniform dispersion of AC-MCC, AC-NFC and AC-NCC in PLA matrix, respectively.
Figure 6.4 A Comparative Analysis on the Rheological Percolation taking Lower Frequency Data
6.3.2 Scaling Law Application for Fractal Study

The value of the fractal dimension $d_f$ can also be used to evaluate the quality of dispersion of the nanofiller, beyond the level of percolation. A lower value of $d_f$ suggests a more open network and thus a better quality of the dispersed state of the network. Comparitively, a higher value of the fractal dimension, suggests a closer network with a possible agglomeration, and thereby a poor dispersed phase of the nanofiller. As evident earlier, surface treatment of the nanofiller helps in better dispersion and this is reflected by reduced value of $d_f$. Surface modification thus prevents their agglomeration leading to better dispersion and a more organized network structure. The fact that surface chemistry has a very strong effect on the morphology of dispersions is studied well by Paquien et al., (2005), where they showed the change in value of the fractal dimension by changing the surface chemistry of fumed silica-polydimethylsiloxane suspensions.

Only the data points above the percolation threshold were considered in the fits, as scaling law by Shibata et al. (1990) is applicable beyond the gelation point that happens in polymer gel, after the percolation is reached. Analysis is only performed on PLA-AC-NCC composites here, as the data beyond percolation is not available for other composites. The power law exponents were obtained from a similar linear regression analysis and Equation (2.1) and Equation (2.2) were solved simultaneously to give $d_f = 1.06$, as shown in Figure 6.5. Comparitively, a lower value of calculated $d_f$ could be compared to the results obtained by Paquien et al. (2005), where they studied the fractal dimension of unmodified and surface modified silica/PDMS composites, applying similar power laws for a tactoid filler. In their study, they demonstrated that the fractal dimension is very sensitive to the surface silica modification as $d_f$ can decrease from a value of 2.3 to 1.4, by surface modification of the silica particles. Like cellulose, the strong interaction of the surface hydroxyl groups of fumed silica
nanoparticles tends to form a strong aggregate. Surface modification prevents their agglomeration leading to better dispersion and a more organized network structure. Contrary to this Puisto (2012), reported a fractal dimension $d_f \sim 2.75$ for nanofibrillated cellulose suspension, as calculated by applying similar power law model for the tactoid filler. As mentioned before, the value of $d_f$ is believed to be associated to the internal restructuring of the aggregate. According to the model, as developed by Shih et al. (1990), an increase in fractal dimension ($d_f$), results in a more compact cluster and a denser network. The internal restructuring of the aggregate could also be related to the state of dispersion beyond the percolation. This state of dispersion contributes to the viscoelastic properties of the nanocomposite system and is an important area of study. The better state of dispersion beyond percolation will eventually lead to form a more open fractal structure to form a pronounced network structure.
6.3.3 Fitting Higher Frequency Data to the Krieger-Dougherty Equation

In order to calculate the effective hydrodynamic aspect ratio, Ren et al (2000) expression will be used, which is rewritten in terms of the average aspect ratio of the tactoids \(A_f\):

\[
A_f = \frac{3\phi_R}{4\phi_{per}} \quad \ldots \ldots \ldots \ldots \ldots \ldots (6.2)
\]

Using the percolation threshold volume fraction for randomly packed overlapping spheres \(\phi_R=0.30\) Isichenko (1992), and the experimentally obtained percolation threshold \(\phi_{per}\) from Figure 6.4, the values of \(A_f\sim 4.2\) for AC-NCC, \(A_f\sim 4.5\) for AC-NFC, and \(A_f \sim 7.5\) for AC-MCC are obtained. The values obtained here are in line with that obtained from SEM and AFM study in morphology as observed. The difference in the value is indicative of the fact that rheological methods probe an effective “hydrodynamic” aspect ratio.
Further to the study by Vermant et al., (2007), an attempt has been made here to fit the higher frequency data to the Krieger-Dougherty equation, as mentioned earlier. Three sets of data, namely the high frequency data set of PLA-AC-NCC and PLA-AC-NFC composites, as available from Figure 6.3(a) and Figure 6.3 (c) respectively, and the high frequency G’ data set of acetylated microcrystalline cellulose based PLA composite (PLA-AC-MCC) from earlier study in Chapter four, are fitted to the Krieger-Dougherty equation in Figure 6.6. In earlier study, as referred to here, cellulose microcrystals were surface acetylated and the reported percolation at approximately around a volume fraction of $\Omega \sim 0.028$. Applying the Brenner equation for intrinsic viscosity for oblate spheroids and $A_f$ found from Equation (6.2) Brenner (1974), values of $[\eta] \sim 6.85$, $[\eta] \sim 9.01$ and $[\eta] \sim 4.09$ for AC-MCC, AC-NCC and AC-NFC were determined, respectively. These values are only approximate. Fitting the Krieger-Dougherty equation, as shown by the lines in Figure 6.6, yields an effective maximum packing fraction of $\Omega_{max} \sim 0.05$, $\Omega_{max} \sim 0.035$ and $\Omega_{max} \sim 0.065$ for AC-MCC, AC-NCC and AC-NFC, respectively. As mentioned earlier, the lower value of maximum packing fraction leads to a better dispersion of the nanofiller, according to the Krieger-Dougherty model. These values give a fair indication that microcrystalline cellulose and nanocrystalline cellulose, when surface acetylated, were better dispersed compared to that of AC-NFC. It was also observed that acetylated nanocrystalline cellulose was better dispersed than microcrystalline cellulose, as evident from the least value of maximum packing fraction. A list of the values of rheological percolation and maximum value packing fraction is shown in Table 6.1. This result is also indicative of the fact that shape and size of the filler is a strong determining factor of the quality of their dispersion in the polymer matrix as reported elsewhere (Mihut et al., 2013). It can also be suggested that percolation has some phenomenological effect on maximum volume packing fraction. For acetylated MCC in earlier study in Chapter four, the percolation reached much earlier around a volume fraction of $\Omega \sim 0.028$, whereas in the present case with AC-NCC, the percolation reached at a
comparatively lower volume fraction $\phi \sim 0.02$, while for AC-NFC, the percolation reached at a comparatively higher value of $\phi \sim 0.05$. Similar to the shift in percolation volume fraction value $\phi$, a shift in maximum volume packing fraction ($\phi_{\text{max}}$) is also observed. Again from the percolation theory on nanofiller, it is known that the lower the value of $\phi$, the better the dispersed state of nanofiller (Bhattacharya et al., 2008). It can thus be concluded that by manipulating the value of $\phi$, the $\phi_{\text{max}}$ value can be minimized, which will eventually lead to a better dispersed state of the nanofiller in the polymer matrix.

**Figure 6.6** Relative high frequency modulus as a function of volume fraction for PLA-AC-NCC, PLA-AC-MCC and PLA-AC-NFC composites. The lines represent the Krieger-Dougherty (KD) equation. Here a third system AC-NCC is used in addition to the data as represented in Figure 5.7
Table 6.1 A comparative analysis on percolation value and maximum value packing fraction for different types of cellulosic fillers.

<table>
<thead>
<tr>
<th>Filler</th>
<th>$\phi_{per}$</th>
<th>$\phi_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-NCC</td>
<td>0.018</td>
<td>0.035</td>
</tr>
<tr>
<td>AC-MCC</td>
<td>0.028</td>
<td>0.05</td>
</tr>
<tr>
<td>AC-NFC</td>
<td>0.055</td>
<td>0.065</td>
</tr>
</tbody>
</table>

6.3.4 Discussion on Dispersion and Rheology

Similar to any other nanocomposite research, filler size, loading and distribution of the reinforcing nanocellulose filler dictate the amount of affected biopolymer, while the surface structure and chemistry of the nanocellulose dictate the intensity of interaction of the particle/biopolymer interphase shape. Morphological study like the conventional microscopy is an effective mean to assess the state of dispersion of the biopolymer matrix. However, the mesoscopic structure is still not understood well with these methods, as they only offer a means to characterize the local view of the morphology. Rheology plays a significant role in quantifying the state of dispersion in nanocomposite system in mesoscopic scale. Rheological measurements have been used for different types of nanocomposite systems as a complementary tool to monitor the quality of dispersion, primarily in qualitative terms, (Vermant et al., 2007). In this study, a rheological percolation threshold is calculated to quantify the level of dispersion and the optimal loading for a uniform dispersion. Scaling law is
applied beyond the percolation value, to probe into the microstructure of the filler that helps eventually in network formation. Moreover, high frequency linear viscoelastic behaviour is analysed and the data is fitted to the Krieger-Dougherty equation to determine the maximum packing fraction.

When the lower frequency data was analyzed by plotting the storage modulus against volume fraction, it is observed that around volume fraction $\phi \sim 0.018-0.02$ for PLA-AC-NCC composites and $\phi \sim 0.052-0.055$ for PLA-AC-NFC composites respectively, a region of minimum slope exists and indicates that beyond that region, dispersion of the nanofiller is affected by agglomeration. These values were then used to evaluate the average aspect ratio of the filler in the melt state. Intrinsis viscosity parameters applicable for the Krieger–Dougherty equation were then calculated from the available aspect ratio. When the high frequency data were fitted to the Krieger–Dougherty equation, different values of maximum packing fractions were obtained as $\phi_{\text{max}} \sim 0.05$, $\phi_{\text{max}} \sim 0.035$ and $\phi_{\text{max}} \sim 0.065$ for AC-MCC, AC-NCC and AC-NFC, respectively. It was also observed that percolation has some phenomenological effect on maximum volume packing fraction as reflected in Table 6.1. As observed from the morphological study, MCC and NCC has rod like crystalline structure while NFC has an inter-fibrillated network structure. The rod like crystalline structure probably has more chance of forming an organized network in the polymer matrix than that of inherent fibrillated network structure of the NFC filler. This could be one of the reasons as to why the percolation value of AC-MCC and AC-NCC is lower than AC-NFC. Moreover, smaller size of the nanofiller facilitates in better dispersion. This is proved by the lower value of percolation for AC-NCC, in comparison to AC-MCC.

Moreover, when scaling law analysis is performed on AC-NCC and the value is compared with standard clay particles, the less value of $d_f \sim 1.06$ suggests a more open fractal structure to form a pronounced network structure, suggesting that in comparision to clay particles, the inherent
crystalline structure of AC-NCC, helps in forming a more organized network in the PLA matrix.

6.4. Summary

Effective surface acetylation on two types of nanocellulose (NCC and NFC) by using acetic anhydride and dimethyl formamide. Different types of nanocellulose based (NFC/NCC) and PLA based nanocomposites were prepared by solvent casting technique. Both microscopy and rheological characterization suggested that acetylated NCC yielded nanocomposites with significantly better dispersion in the PLA matrix. Linear viscoelasticity tests are very sensitive to filler dispersion in the polymer matrix. In general, low frequency rheological characteristics (loss modulus and storage modulus) increased significantly upon adding the nanofiller. The different values for rheological percolation indicate that AC-NCC were better candidate for better dispersion, probably due to their inherent crystalline rod like structure, that helps them in forming a network structure in the polymer matrix. Different values of maximum packing fractions were evaluated as $\varphi_{\text{max}} \sim 0.05$, $\varphi_{\text{max}} \sim 0.035$ and $\varphi_{\text{max}} \sim 0.065$ for AC-MCC, AC-NCC and AC-MCC respectively, when the high frequency data was fitted to a Krieger-Dougherty equation. The lower value of the maximum fraction leads to a better dispersion of the nanofiller. A direct correlation between the rheological percolation and maximum packing fraction value was also observed. Moreover, when scaling law analysis is performed on AC-NCC and the value is compared with standard clay particles, the lower value of $d_f \sim 1.06$ suggests a more open fractal structure to form a pronounced network structure. This also suggests that in comparison to clay particles, the inherent crystalline structure of AC-NCC helps in forming a more organized network in the PLA matrix.
Chapter 7: Syncrotron Based Chemical Imaging

The primary motivation to present this Chapter in this thesis is to show how a better dispersed phase helps in forming a better interface and interphase in the polymer matrix. It was earlier shown in Chapters 4, 5, and 6, that acetylation of cellulose nanocrystals helps in better dispersion as compared to pure cellulose in the PLA matrix. Taking this concept into account, AC-NCC-PLA interfacial zone is compared to that of pure NCC-PLA interfacial zone by infrared analysis at the Australian Synchrotron beamtime.

The interfacial zones and surface characteristics play a predominant role for designing specific morphologies like the dispersion state in such composite system. Overwhelmingly, research in this area suggests that filler size, loading and distribution dictate the amount of affected polymer, while the surface structure and chemistry of the particles dictate the intensity of interaction at the particle/polymer interface (Khare and Bussir, 2010). A better dispersed phase of the nanofiller will eventually lead to a better formation of interface (“In the bulk state, a polymer may be in contact with another polymer, called a polymer blend interface or in contact with a non-polymer such as a filler”) and interphase (“an interphase is a region of space occupied by both molecular species, often of the order of 6-12 mer lengths. Clearly a gradation of composition exists between the two phases on either side”), that will eventually help in the reinforcement mechanism (Sperling, 1995). The successful transfer of nanocomposite technology requires the development of a more fundamental understanding of the reinforcement mechanisms.

Fourier Transform Infrared (FT-IR) microscopy is a well-established method for the chemical identification of particles or contaminants. This technique also helps in visualizing the distribution of certain substances in complex compounds. Typical applications of FT-IR microscopy include chemical identification of particles and smallest contaminations, the
examination of the homogeneity of coatings and the analysis of the
distribution of a multitude of different components in a complex mixture.
In this study, FTIR imaging is used to image the spatial distribution of the
functional group chemistry of the composite constituent. The matrix
chosen for such purpose is such that where the acetylated NCC is more or
less uniformly dispersed in the PLA matrix. The main objective of the study
reported here was to understand how the variation of the densities in the
ester linkages from the polymer matrix to the AC-NCC filler relates to the
interfacial interaction between the fibre and the matrix, thereby improving
the overall adhesion and mechanical properties of the composites. A
second derivative analysis on the carbonyl peak is performed to resolve
the chemical interaction of the carbonyl group at the interfacial region of
the matrix.

7.1. FTIR Absorption Spectra:
When the FTIR absorption spectra of NCC, AC_NCC and pure PLA are
mutually compared as shown in Figure 7.1 (a) and Figure 7.1 (b), it was
observed that while a strong carbonyl peak around 1744 cm\(^{-1}\) and 1756
cm\(^{-1}\) are significant for pure PLA and AC-NCC, respectively, is subdued for
pure NCC. This indicates that the location of carbonyl stretch for PLA and
AC-NCC is different and they are significant around 1744 cm\(^{-1}\) and 1756
cm\(^{-1}\), respectively. The observed result is similar to the study on acetylation
of cellulose microcrystals as reported earlier in Chapter four. The
characterization of the position of carbonyl peak stretch is later used for
further understanding the interaction of carbonyl peak in the second
derivative analysis. It is to be noted here that multiple spectra are shown
for each material to illustrate the uniformity in pattern relating to the peak
position.
Figure 7.1 (a) FT-IR Absorption Spectra of NCC and AC-NCC
Figure 7.1 (b) Magnified spectra of carbonyl peak in comparison to PLA peak

7.2. Chemical Imaging

The most straightforward method of FTIR spectral data analysis is to generate functional group maps based on band intensities, band areas or band ratios. In this univariate mode, the FTIR maps/images represent the inherent contrast associated with the unique chemical bonds of the components within the analyzed specimen. A chemical map/image of each component is created by plotting the unique frequencies as a function of spatial position and spectral intensity. A colour scheme can be applied to the intensity values to permit the creation of a “false-colour composite” image. While these methods can provide information on the distribution and relative concentration of a particular functional group, they are not very useful in terms of classifying chemical and histopathological features within the specimen matrix. In addition, using these univariate methods, it becomes very difficult to keep track of minor changes in spectra across the specimen. These subtle spectral differences may be the key to the chemical
differentiation of areas such as carious dentin regions (Wang et al., 2010). Under these conditions second derivative analysis may be helpful.

**Figure 7.2 (a)** Visible light image with spectra of the selected points in PLA-NCC microtomed section
**Figure 7.2 (b)** Visible light image with spectra of the selected points in PLA-AC-NCC microtomed section
Figure 7.2 (c) Second derivative analysis of PLA-AC-NCC section of the second shoulder around the carbonyl peak around 1756 cm\(^{-1}\) and 1740 cm\(^{-1}\)
Figure 7.2 (d) Second derivative resolved carbonyl peak of PLA-NCC section.

Figure 7.2 displays the first chemical and spectral information as obtained from FTIR imaging. Figure 7.2 (a) and Figure 7.2 (b) show the visible light micrograph of the cross section of the PLA-NCC/PLA-AC-NCC (10 wt %) laminate, along with spectral intensity distribution of the carbonyl peak around the matrix. The selected points with specified color indicate the point of selection from where the spectra has been chosen from the matrix. The colour scale bar in the image indicates the intensity of the functional group with blue/black and red/orange, being the lowest and highest intensity. From Figure 7.2 (a), it is further observed that slight carbonyl stretch is observed for spectral region around NCC filler, as present in the matrix. This is probably because of the inherent contribution of carbonyl stretch for PLA matrix. The carbonyl peak is further resolved as second derivative in Figure 7.2 (c) to understand the pattern of shoulder change in the peak due to possible interaction of the filler with the polymer if any. From the magnified image of the derivative curve, it is observed that there is a shift of peak towards 1750 cm\(^{-1}\) which would
otherwise be 1740 cm\(^{-1}\), apart from the minimum slope around 1760 cm\(^{-1}\), which was evident in Figure 7.2 (b) as well. It should also be noted here, that as there is clear evidence of carbonyl peak present around 1750 cm\(^{-1}\) with no other peak around 1740 cm\(^{-1}\) in Figure 7.1 (b), it can be inferred that whatever shift in peak, as observed in secondary derivative analysis, is primarily due to AC-NCC. A second derivative of the carbonyl peak, as shown in Figure 7.2 (c) and Figure 7.2 (d) for PLA-AC-NCC and PLA-NCC composite is performed, for a comparative analysis. It was observed that the shoulder peak in case of PLA-NCC is not that predominant as that of PLA-AC-NCC composite around 1750 cm\(^{-1}\). The optical image of the section under study with integration of map around 1753 cm\(^{-1}\)-1740 cm\(^{-1}\) is shown in Figure 7.2 (c) as well. This integration map indicates that there is slight interaction of –C=O group present in AC-NCC with that of lactic acid molecule as present in PLA. This possible interaction could possibly be explained by carbonyl-carbonyl interaction as reported earlier. It was earlier investigated by Barlett et al. (2005), that main chain carbonyl group engages in a C=O….C=O interaction with another main chain carbonyl group in common secondary structures. Possibly, this type of weak n-n* interaction (Kamer et al., 2013) with the carbonyl group present in PLA and that present in the acetylated NCC at the fibre matrix interface, has resulted in shift of peak, as revealed in second derivative analysis. The possible indication of the carbonyl group interaction would result in a strong fiber-matrix interface region, thereby enhancing stress transfer mechanism between the cellulose and the PLA matrix. The better interaction of PLA with AC-NCC, thus forming a better interface is only possible because of a better dispersion of AC-NCC is the PLA matrix as explained in Chapter 6, by comparing the values of maximum packing fraction.
In a recent publication, Newsberry and Raines (2013) reported on the possibility of the carbonyl $n\rightarrow n^*$ interaction as present in PLA as indicated in Figure 7.3, where they concluded that this type of interaction predominates over the possible hydrogen bond. It is therefore quite likely that when the acetyl groups are partially substituted on the surface of the NCC particles and thereby used as a filler, they could also possibly engage in such $n\rightarrow n^*$ carbonyl interaction. It is known that by chemically manipulating the nature of interphase, Gibbs free energy is minimized to reach the equilibrium state, thereby facilitating the interfacial adhesion between the fiber and the matrix (Flory. 1941). If steric repulsion caused by the acetyl groups attached to the NCC surface overcomes NCC-NCC interaction, then modified NCC is more likely to be dispersed well in the hydrophobic matrix like PLA. In other words, by manipulating the chemical nature of the interface, the fibre-matrix interfacial tension can be minimized to reach the equilibrium state, thereby improving the interfacial adhesion (Lin et al., 2011; Pei et al., 2010). It was also reported elsewhere that the increase in the density of ester linkages from the polymer matrix to the cellulose nanocrystal interface contributed to the average increase in elastic
Thus determining the spatial distribution of the different components of the composites would be essential in understanding the behaviour of network formation and the improvement in mechanical properties of the composite (Clemons et al., 2013).

7.3. Summary

A spatial distribution of the different functional group chemistry of the acetylated nanocrystalline cellulose based PLA composite (10 wt%) by FTIR chemical imaging at the Australian Synchrotron. The method was used to better understand the variation in the density of ester linkage. A weak carbonyl group interaction at the interface region seems to occur eventually as revealed in second derivative analysis. This kind of interaction is a possible indication of enhanced stress transfer mechanism between cellulose and the PLA matrix, as reported earlier. Better interaction is possible due to a better dispersed phase of the nanofiller in the polymer as explained in Chapters 4, 5 and 6. This helps in further understanding on how a better interphase is formed because of better dispersion of the nanofiller and thereby a possibility for a better interaction of the nanofiller with the polymer matrix. AC-NCC, in comparison to pure NCC was better dispersed in the polymer matrix and this resulted in better interaction with the available carbonyl groups of PLA, thereby resulting in better formation of the ester linkage in the interfacial zone.
Chapter 8: Conclusions and Recommendations

Evaluations on the final quality of the dispersion with different surface modifications are conducted by rheological model. Successful acetylation of microcrystalline cellulose (MCC) suggested that AC-MCC is a stronger candidate to act as a nucleating agent. Similarly, study on dispersion of nanofibrillated cellulose (NFC) based PLA and PBAT composite suggested that NFC, too, acts as a better nucleating agent in the PBAT matrix. It was further observed that around Ø~0.05 loading, a region of minimum slope exists for PLA-AC-NFC composite, and indicates that beyond that region, the quality of dispersion is affected by agglomeration. An effective maximum packing fraction of Ø~0.065 is also obtained for PLA-AC-NFC composites. When a comparative analysis on the degree of dispersion of different types of cellulose is performed, a rheological percolation around volume fraction of Ø~0.018-0.02 for PLA-AC-NCC composites and Ø~0.052-0.055 for PLA-AC-NFC composites are obtained. Similarly, different values of maximum packing fractions were evaluated as, Ø_max~0.035, Ø_max~0.05 and Ø_max~0.065 for AC-NCC, AC-MCC, and AC-MCC respectively, when the high frequency data was fitted to the Krieger-Dougherty equation. Study on synchrotron based chemically imaging the the interfacial region of surface acetylated nanocellulose based PLA matrix also suggested that a better interface is formed because of better dispersion of the nanofiller and thereby a possibility for a better interaction of the nanofiller with the polymer matrix.
The main findings are Chapter specific and were summarized within the respective Chapters: this section synthesizes the findings to answer the following research questions:

a. Improved Dispersion of Surface Acetylation of Microcrystalline Cellulose - where the better surface acetylation of microcrystalline cellulose gave a better dispersion in the PLA matrix. Thermal, rheological and morphological characteristics of the composites are well explained. Optimal loading for a uniform dispersion is explained by rheological percolation model. Research questions 1-4 (page 19) are well explained in this context. From this study it was concluded that successful acetylation of microcrystalline cellulose (MCC) was accompanied by acetyl chloride at room temperature as revealed in NMR and FTIR studies. Improvement in dispersion was observed in morphological and rheological tests. This suggested that AC-MCC is a stronger candidate to act as a nucleating agent in comparison to pure MCC in preparing such PLA based composites.

b. Dispersion study of nanofibrillated cellulose based PLA and PBAT composite - where the better surface acetylation of nanofibrillated cellulose in PLA matrix is compared to nanofibrillated cellulose based PBAT matrix. Thermal, rheological and morphological characteristics are well explained. In addition to this, why rheological study is important is well explained here by analysing the data with rheological percolation threshold and fitting the higher frequency data with the Krieger-Dougherty model. Apart from research questions 1-4, research questions 5 and 6 are addressed here as well. The incorporation of NFC in PBAT matrix (0.2-1 wt%) increased the storage modulus (\(G'\)) and dynamic viscosity (\(\eta'\)) as revealed by shear rheology, indicating a percolation threshold around 0.2-0.5 wt%
region. This indicated that NFC acts as a better nucleating agent in the PBAT matrix. Similarly, addition of acetylated NFC did not change the overall structure of PLA. When rheological percolation threshold for a uniform dispersion is evaluated using lower frequency data of PLA-AC-NFC composite, as obtained from shear rheology, it is observed that around $\phi \sim 0.05$ loading, a region of minimum slope exists and indicates that beyond that region, dispersion is affected by agglomeration. When higher frequency data is plotted to the Krieger Dougherty equation, an effective maximum packing fraction of $\phi \sim 0.065$ is obtained from data fit analysis.

c. A comparative analysis on the degree of dispersion of different types of cellulose based PLA composites - this Chapter mainly addresses research questions 5 and 6. Apart from rheological percolation threshold and fitting the higher frequency data to the Krieger-Dougherty model, fractal study including scaling law is used to explain the nature of the network formation of the nanofiller as well. In the main key finding, a rheological percolation around volume fraction $\phi \sim 0.018-0.02$ for PLA-AC-NCC composites and $\phi \sim 0.052-0.055$ for PLA-AC-NFC composites, respectively, indicates that AC-NCC were better candidate for better dispersion, probably due to their inherent crystalline rod like structure, that helps them in forming a network structure in the polymer matrix. Different values of maximum packing fractions were evaluated as, $\phi_{\text{max}} \sim 0.035$, $\phi_{\text{max}} \sim 0.05$ and $\phi_{\text{max}} \sim 0.065$ for AC-NCC, AC-MCC, and AC-MCC respectively, when the high frequency data was fitted to a Krieger-Dougherty equation. The lower value of the maximum fraction leads to a better dispersion of the nanofiller. A direct correlation between the rheological percolation and maximum packing fraction value was also observed. Moreover, when scaling law analysis is performed on AC-NCC and the value is compared with standard clay particles, the
lower value of $d_f \sim 1.06$ suggests a more open fractal structure to form a pronounced network structure. This also suggests that in comparison to clay particles, the inherent crystalline structure of AC-NCC helps in forming a more organized network in the PLA matrix.

d. **Synchrotron based chemically imaging the interfacial region of surface acetylated nanocellulose based PLA matrix** - this Chapter includes synchrotron based chemically imaging the interfacial region of surface acetylated nanocellulose based PLA matrix. A spatial distribution of the different functional group chemistry of the acetylated nanocrystalline cellulose based PLA composite (10 wt%) by FTIR chemical imaging at the Australian Synchrotron. The method was effective to understand the variation in the density of ester linkage. A weak carbonyl group interaction at the interface region seems to occur eventually as revealed in second derivative analysis. This kind of interaction is a possible indication of enhanced stress transfer mechanism between cellulose and the PLA matrix, as reported earlier. Research question 2 (page 19) is well explained here by the synchrotron study. This helps in further understanding on how a better interface is formed because of better dispersion of the nanofiller and thereby a possibility for a better interaction of the nanofiller with the polymer matrix. AC-NCC, in comparison to pure NCC was better dispersed in the polymer matrix and this resulted in better interaction with the available carbonyl groups of PLA, thereby resulting in better formation of the ester linkage in the interfacial zone.
8.2. What is the PhD novelty and Contributions?

a. Devised a new method of surface treating nanocellulose for optimal dispersion. Acetylation is performed here by using sodium hydride. This method is slightly different from using conventional acetic anhydride in large volume of pyridine. Pyridine is highly toxic and not very industrially friendly.

b. Attempt to chemically image the distribution of the functional groups in the matrix. This is done with the support of the Australian Synchroton facility. Images taken help in directly interpreting how the interface/interphase is formed. This made an in depth investigation on the degree of dispersion of such biopolymer nanocomposites by using rheology as an effective tool. Rheology offers a mean to evaluate the mesoscopic view of dispersion unlike the local view as offered by conventional morphological study. This added new knowledge in understanding the fundamentals of dispersion of such nanocomposites.

8.3. Recommendations

This research is restricted to plant based resources and further exploration on characterization of the mechanical properties of such composites is recommended. Degree of surface acetylation for optimal dispersion needs further study as well. Quantification of dispersion quality by further morphological image analysis could have been another area of research complementing this research study. While PLA was the only biopolymer used for this study, further research on other biopolymer matrix could have further strengthened this research as well.
Key areas for recommendation are highlighted below:

- Modifications of cellulose by other means by experimenting with other functional groups.
- Preparation of other biocomposites using other biopolymer rather than PLA/PBAT.
- Thermal study for crystallization analysis. The relationship between structural features and crystallization kinetics in addition of the nanofiller to the polymer matrix is required from a fundamental viewpoint for isothermal and non-isothermal processing operations. Addition of cellulose has some nucleating effect on PLA matrix which needs to be further explored.
- Further fractal study and applying scaling law to understand the structure of the network.
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