Theoretical Design of Environmentally Responsive Clean Coatings

A thesis submitted
in fulfillment of the requirements
for the academic degree of
Master of Applied Science

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March, 2014
Declaration of Candidature

I certify that except where due acknowledgment has been made, this work is that of the candidate alone. This work has not been submitted previously, in whole or in part, to qualify for any other academic award. The content of this thesis is the results of work which has been carried out since the official commencement date of the approved research program. Any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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Acknowledgements

This work would not exist without the contribution, support, guidance and collaboration of many people who deserve to be acknowledged.

Firstly I would like to acknowledge my primary supervisor, Prof. Irene Yarovksy. Thank you for giving me the opportunity to work with you on this project. Your support, patience and guidance have made this research both enjoyable and memorable.

I would also especially like to thank my second supervisor, Dr. George Yiapanis. Thank you for all the help you have given me and the contributions that you have made to this project. Your knowledge, experience and guidance have helped in times of need.

A sincere thank you to my supervisor, Dr. David J. Henry for contributions made throughout the project. Thank you for your supervision predominantly at the beginning of this project. Your comments and suggestions have made this thesis a better piece of work.

I would also like to acknowledge Mr. Kamron Ley. Thank you for all the work you have contributed to this project. Your efforts have been greatly appreciated.

Additional thanks to Adam Makarucha for accepting to read this thesis during the final stages. Your comments and suggestions greatly improved this body of work.

Dr. Evan Evans and Dr. Shane McLaughlin from BlueScope Steel, thank you for the collaboration on the project and the experimental support you have provided.

To the Materials Modelling and Simulations Group, thank you for discussions that have contributed to this work and making this project a very enjoyable experience along the way, I admire you all. These people include but are not limited to: Dr. Michelle Spencer, Dr.
Nevena Todorova, Dr. Andrew Chrisofferson, Dr. Piotr Kowalczyk, Dr. Levi Yeung, Dr. Michael Breedon, Dr. Kester Wong, Dr. Michael Plazzer, Dr. Everson Kandare, and Mr. Patrick Charchar.

To the RMIT physics department, thank you all for making my stay at RMIT a pleasant one and I wish you all the best on your future endeavours.

I would like to thank the Australian Research Council, BlueScope Steel and RMIT University for providing financial support for this project.

I would also like to acknowledge the National Computing Infrastructure (NCI) and the Victorian Partnership for Advanced Computing (VPAC) for providing computational facilities.

I would like to personally thank my family, my mum and dad who have been there for me throughout the hardest of times and provided me with continuous support and love, and all my brothers who I still look up to, for challenging me and providing me with entertainment, fun and laughter.

Finally I would like to thank my friends, many of whom have moved away but still remain a part of my life.
Abstract

In this thesis atomistic level modelling is conducted to investigate the design of an environmentally adaptable self-cleaning polymer paint coating that incorporates biomimetics to remain clean in various environmental settings. This work will be used to aid in the development of stay-clean polymer paint coatings. In Chapter 1, we discuss the motivation for this project and include a concise literature review on recent discoveries in the areas of polymer surface modification and computational modelling. Additional literature reviews are included in the introductory sections of Chapters 3 and 4 pertinent to the subject matter in question. Classical molecular mechanics (force-field methods) is employed to describe the physical interactions between the surfaces and their surrounding environment, and molecular dynamics is used to obtain time-dependent and temperature-dependent properties of surface/environment systems. A detailed description of the computational techniques is included in Chapter 2. In silico nanoindentation between a contaminant particle and engineered polymer surfaces that include functionalised-surface-crosslinked and functionalised non-surface-crosslinked polyesters is included in Chapter 3. The mechanical properties of the surfaces are assessed by monitoring the roughness, density and morphology as the coatings respond to the approaching particle. We show that in environments where mechanical stresses are applied, deformations of the coatings significantly impact on the strength of adhesion between polymer and indenter particle. In Chapter 4 we revisit natural self-cleaning coatings in nature which use brush like formations to remain clean. We investigate the humidity induced de-swelling and swelling of PEGylated surfaces at various temperatures, and show that substrates play a significant role in the response of PEG.
1. Introduction / literature review

1.1 Overview

This chapter reviews the current state of literature on self-cleaning surfaces and describes the motivation for this research (Section 1.2). In Section 1.3 examples of self-cleaning surfaces found in nature and their mechanisms for self-cleaning are discussed. Section 1.4 reviews a biomimetic approach to coating design and commonly encountered obstacles associated with designing such complex systems. The emergence of responsive surfaces, their capability to remain clean in various environments, and limitations encountered will be discussed in Section 1.5. In Section 1.6, a review of previous computational studies of self-cleaning polymer surfaces and interfaces is presented. Lastly, the project aims are presented in Section 1.7.
1.2 Background and motivation

Polymer-based coatings are employed in multiple industrial and architectural applications. Under extreme weathering conditions, ranging from fully immersed through to totally dry, these coatings can become susceptible to soiling and degradation from various sources, particularly atmospheric pollution [1, 2]. Long-term exposure of these coatings to pollution and other harsh environments can result in their deterioration [3]. For example, carbon-based particulates such as soot are not only a major cause of respiratory problems but can also cause discoloration of paints used by building industries. Soot contaminants are generally hydrophobic and can easily adhere to the surface of the hydrophobic polymer coatings. Therefore, with the intention of improving the durability and long-term aesthetic appeal of these coatings, functionalisation with suitable compounds that can prevent or reduce the deposition of unwanted particulates is highly desirable [4]. The ability to modify surface properties of solid materials through surface functionalisation is also critical in other practical applications. In biomedicine, functionalised surfaces are used to manufacture prosthetic devices that replicate functions of human tissues and organs [5, 6], as well as to act as carriers in drug delivery systems [7-10]. In these applications, a solid surface is grafted with oligomers that display non-immunogenicity, non-antigenicity, hydrophilicity and protein-rejection properties to target the issue of protein adhesion. These properties render the material biocompatible.

This research was supported by the Australian Research Council Linkage scheme with contributions by BlueScope Steel as an industry partner. Their flagship product Colorbond®, a multilayered paint system, is used in both residential and commercial buildings. Colorbond® has been developed to contain a multifunctional cured polyester based top-coat that delivers outstanding performance against corrosion and resistance to chipping, peeling and cracking. An enhancement of the current coatings contamination
resistance is believed to be a critical hurdle that is required to be overcome in order to achieve further extension of the lifetime of the product. It is imperative that any improvement in contamination resistance does not impede the current performance of the already outstanding coating. Therefore, improvements in contamination resistance must only be made to the outer-layer while maintaining the current properties of the underlying substrate. To achieve this goal a detailed understanding of the mechanics at the outer-layer of the coating is needed at the atomistic level, which is not achievable by experimental techniques. At this level of resolution we will be able to achieve greater insight into the surfaces and the surrounding environment. This information is obtained through a detailed understanding at the atomic level of the mechanical properties of the surface as it responds to a given environmental setting. Furthermore, a detailed understanding of the surface chemistry (hydrophilicity/hydrophobicity) at the atomistic level is also important for the improvements of contamination resistance at the atomistic level. Therefore molecular dynamics is employed in order to advance understanding of these coatings at the atomic level and to theoretically study surface modifications that will aid in the experimental design and synthesis of a stay-clean coating. Therefore molecular dynamics is employed in order to advance understanding of these coatings at the atomic level and to theoretically study surface modifications that will aid in the experimental design and synthesis of a stay-clean coating.
1.3 Natural self-cleaning surfaces

While there are many examples of naturally occurring materials that have the ability to remain clean, two prominent classes include superhydrophobic and superhydrophilic surfaces [11]. Examples in nature, of self-cleaning superhydrophobic surfaces are lotus leaves, rice leaves, cicada wings and butterfly wings. Leaves of the lotus flower have an ability to remain clean in a harsh environment [12, 13]. The microscopically rough, double pillared, surface structure of the lotus leaf [14] ensures that water droplets roll off the surface, collecting dirt particles and thereby cleaning the surface. This is referred to as the “Lotus effect” (Figure 1 and Figure 2). This cleaning mechanism also protects against plant pathogens such as fungi and bacteria, as germination of fungi and reproduction of bacteria are limited by water access. Rice leaves are also considered superhydrophobic and self-cleaning, however the wetting of these leaves is said to be anisotropic as the superhydrophobicity of the leaf is not the same in each direction along the surface [15]. It is believed that this anisotropic wetting improves the self-cleaning efficiency as water droplets can roll to the edge of the leaf without falling off, thereby remaining on the leaf and collecting all dirt on the leaf’s surface [11]. Cicada wing surfaces [16] also possess anisotropic wetting ensuring that water droplets roll off in the radially outward direction to prevent wetting of the butterfly’s core. This is demonstrated by the fact that when the surface is tilted fully upright, tight pinning of the water droplets occurs [17].
Superhydrophobicity can often be achieved by roughening of regular hydrophobic surfaces to create a Cassie state [18, 19] where on a rough surface, pockets of air can become trapped in the cavities when a water droplet makes contact. A surface is considered superhydrophobic if it has a water contact angle above 150° [11]. A low contact angle hysteresis (difference between advancing and receding contact angles) is also desirable for self-cleaning, normally below 10°. This is exemplified in the previously mentioned lotus leaf which possesses a water contact angle, surface tilt angle (angle which initiates rolling of water) and contact angle hysteresis of approximately 164°, 5° and 3°, respectively [11].

Conversely, superhydrophilic surfaces exhibit a strong affiliation with water and can form a water contact angle well below 10°. Such surfaces also demonstrate an ability to eject contaminants and debris for their surface. In this case, water spreads out creating a thin water layer beneath contaminants which lifts the contaminants off the surface and carries them away (Figure 2). The structures of superhydrophilic surfaces found in nature often contain hydrophilic hairs such as the Spanish moss (Tillandsia usneoides) which uses its superhydrophilic structure for water uptake via absorptive hairs (hydathodes) [13].
Hydrophilic hairs are also present on the self-cleaning Lady’s Mantle surface [20]. The hairs on the Lady’s Mantle are not only hydrophilic but are also considered elastic. In contact with water the plant hairs bundle together due to their elasticity and stick into the water droplet. As a result a water droplet resting on such a bundle of hydrophilic hairs cannot come into contact with the substrate. This bundling effect creates a thin water film using hydrophilic hairs to capture water vapour and clean the surface of the Lady’s Mantle. These inspiring examples demonstrate that surface wettability and surface compliance (in the case of the Lady’s mantle) are essential ingredients in maintaining the clean state of a material.

Figure 2. Schematic illustrations of self-cleaning processes on superhydrophilic surface (a) and superhydrophobic surface (b). On the superhydrophilic surface water droplets spread forming a thin film of water, lifting contaminants from the surface, while on the superhydrophobic surface spherical water droplets roll-off the surface carrying away unwanted contaminant particles as the roll [11].
1.4 Mimicking nature

Surface wettability can be controlled through the addition of hydrophobic or hydrophilic functional groups [21-24]. Fluorine is often considered the material of choice for improving the hydrophobicity of a surface. For example, in a study by Inoue et al. [25] argon ion bombardment of a fluoro-polymer (poly-tetrafluoroethylene, PTFE) was used in an effort to improve the hydrophobicity of the surface. X-ray photoelectron spectroscopy (XPS) and contact angle measurements of the irradiated samples demonstrated a positive correlation between hydrophobicity and the concentration of terminal CF$_2$ and CF$_3$ groups. Similarly, Hong et al., showed the CF$_4$ plasma treatment of ethylene-vinyl alcohol (EVOH) copolymers reduced water retention due to the formation of CF, CF$_2$ and CF$_3$ groups [26]. Wen et al. [27] also demonstrated an improvement in hydrophobicity due to fluorine containing groups on the surface of PET films that had been treated with CF$_4$ plasma. Conversely, many studies [22, 27, 28] have demonstrated that the presence of polar functionality such as hydroxyl (OH) groups can significantly reduce the water contact angle of the surface. These groups can form hydrogen bonds with surrounding water molecules increasing water uptake rendering the surface hydrophilic. In fact one of the properties responsible for Titania’s known superhydrophilic stay-clean behaviour is its ability to generate polar groups via UV induced oxidation [29-31]. The generation of polar groups at the surface ensures that when water droplets land on the surface, they spread to form a thin sheet which helps to reduce surface contamination.

In addition to surface chemistry, the surface morphology can also play an integral part in controlling wettability [18, 32] as previously demonstrated by the example of the lotus leaf. For example, superhydrophobic surfaces have been fabricated through a nanoparticle sol-gel process [33, 34]. In these cases entrapment of air occurs through the generation of the hierarchical surface roughness. In one study [26], PTFE surfaces were
exposed to O$_2$ plasma in the hope of improving the hydrophilic character of the material through incorporation of polar groups. Unexpectedly, an increase in hydrophobicity was noted, due to the fact that the oxygen plasma simply etched the surface and augmented its roughness. In fact a study by Miller et al. [35] demonstrated that changes in roughness even at the nanoscale can result in significant changes in surface wettability.

A significant obstacle associated with modification of polymeric surfaces is stability. The mobility of polymer chains enables polymer surfaces to respond rapidly by altering their chemical surface composition to match their environment. Through rotational and translational movement of the chain segments, the interfacial free energy between the polymer and its environment can be reduced. For example, in a non-polar dry environment, polymers can reduce the concentration of polar groups at the surface via hydrophobic recovery, whereas in a polar aqueous environment, it is more energetically favourable for the surface to become enriched in polar-groups, with hydrophobic moieties driven away from the surface into the bulk. Modification of a polymer surface typically creates a non-equilibrium state. It is therefore unstable and loses within hours or days, partially or completely, the properties conferred by surface treatments. Li et al. [36] modified polypropylene (PP) via oxygen capacitively coupled plasma (CCP) and aged the freshly modified surfaces in air at temperatures of 20 °C, 60 °C and 90 °C at a humidity of approximately 60 % during a time up to 25 h. Aging of the modified superhydrophilic PP surface at 20 °C resulted in a slight decrease in hydrophilicity, while aging at 60 °C and 90 °C assisted in transitioning the surface into superhydrophobic states. The conversion of wettability was mainly ascribed to the surface restructuring of the chemical compositions in the top layer of the polymer at depths of a few angstrom. Wen et al. [27] also demonstrated the destabilisation of plasma treated polyethylene terephthalate (PET) films. Their results showed that the fluorine-containing groups with hydrophobic characteristics could migrate from the surface into the inner layer and reduce the water contact angle after dipping into
KOH aqueous solutions. Rather surprisingly, an opposite trend was encountered in certain instances where the polymer surface was enriched with low-molecular oxidised material. That is, an increase in water contact angle after exposure to a polar environment. The reason for this was due to the removal of low molecular weight polar groups from the surface. This indicates that degradation and detachment of polymer chains at the surface can also play an important role in the long-term self-cleaning ability of a coating and its stability against environmental degradation.
1.5 Responsive surfaces

Adaptive surfaces [37, 38] that can transition between hydrophobic and hydrophilic states have the potential to remain clean in a more diverse range of environments [39] and for longer periods than traditional hydrophobic or hydrophilic coatings. Some stimuli responsive surfaces adapt to the environment to continually provide low adhesion with contaminants [39-41]. For example Shivapooja et al. developed an environmentally responsive surface which consisted of an electro-active anti-fouling coating that was able to dynamically deform when exposed to an electric field [42]. Repeated deformation of the coating resulted in the removal of 95% of biofilms consisting of the bacterium Cobetia Marina which is found in sea-water. Furthermore, they found that it was the repeated deformation of the coating that resulted in the removal of the biofilm as an increase in the electric field did not have any direct impact on the biofilm.

Adaptive surfaces make use of a combination of stimuli responsive polymers such as polyethylene glycol (PEG) [43] and polydimethylsiloxane (PDMS) to alter their wettability in air and water environments. In air, hydrophobic components rise to the surface and provide a low adhesion by reducing the interfacial tension, while in water, hydrophilic component rise to the surface, again minimising the interfacial tension. This combination of hydrophobic and hydrophilic components provides low interfacial adhesion in both air and water environments.

Stimuli-responsive surfaces provide a means to overcome soiling from oil-based solvents. In a study by Howarter et al. [44] polyethylene glycol with short perfluorinated end caps (f-PEGs) were grafted to silica to create a solvent-sensitive stimuli-responsive surface. Dynamic water contact angle measurements revealed a unique case in which the receding contact angle of a low surface energy fluid (hexadecane) was greater than the advancing contact angle of water. This resulted in a surface where water was energetically driven to
undercut the oil droplets and freely float on top of the water. As the glass slide was tilted, the oil and excess water was completely removed from the surface leaving behind only a film of water. It was also proposed that the rapid rearrangements in response could be attributed to an optimal grafting density, where ease of motion may be promoted due to free volume inherent in the structure.

PEG is one of the most commonly used surface protectors, as in addition to its responsive and anti-fouling behaviour can render a surface biocompatible. Kuroki et al. [38] investigated 3D polymer grafting (grafting throughout surface and substrate) of non-biocompatible poly(2-vinylpyridine) (P2VP) with a biocompatible polymer, poly(ethylene oxide) (PEO), to implement long-lasting anti-fouling properties. The pH-responsive poly(2-vinylpyridine) films with 3D grafting of poly(ethylene oxide) showed a 4-fold increase in longevity of anti-fouling behaviour in comparison to their 2D grafted counterparts. This demonstrated in 3D-grafted surfaces anti-fouling properties remained intact even if the material undergoes stimuli-triggered changes.
1.6 Computational studies of polymer surfaces and interfaces

It has been consistently shown that force-field based methods provide a valuable tool to obtain an atomic level understanding of complex systems such as those described in this work. A detailed knowledge of the molecular structure and dynamics is critical for the successful design of self-cleaning coatings highly desirable for the BlueScope Steel’s Colorbond® product. One of the most influential computational studies associated with industrial coating design was the work of Yarovsky et al. [45]. In their work a method to construct atomistic models of crosslinked polymer networks using classical molecular dynamics was developed, that enabled a realistic coating model to be studied (Figure 3) [46-53]. Specifically, in [45] the authors applied their method to create a model of crosslinked low molecular weight epoxy resins with tributoxymethyl melamine and tetramethylol glycoluril crosslinkers. Furthermore, they examined barrier properties, shrinkage, and adhesion with an alumina substrate. Their results demonstrated that the systems with a high number of unreacted crosslinking sites produced improved barrier properties and created a higher adhesion with the alumina substrate in comparison to systems where every crosslinking site was reacted. This was primarily attributed to hydrogen bonding between unreacted sites to both small penetrant molecules and the alumina substrate.

Figure 3. Schematic diagram showing indentation of a polyester layer using a fullerene C_{60} particle.
Another theoretical study of polyester based paint coatings was undertaken by Henry et al. and Yiapanis et al. [46-50], in which they used classical force-field methods to investigate the interfacial adhesion between modified surfaces and amorphous carbon (a representative surface of a hydrophobic contaminant). In their work they attempted to lower the interfacial adhesion between amorphous carbon and polyester surfaces by modifying polyester models with hydroxyl, carboxyl and fluorine groups to increase atomic surface roughness and to alter the surface chemistry. Their results showed that augmentation of the atomic-level surface roughness using functional groups resulted in significant reductions in contaminant adhesion. However, these reductions were short-lived due to aging or hydrophobic recovery particularly prevalent in flexible substrates. The authors therefore suggest that making the substrate more rigid prior to functionalization would maintain functional groups in close proximity to the opposing surface of the contaminant resulting in longer-lived contamination resistance [51].

Work has also been made into theoretical surface crosslinked polyester models and simulated nanoindentation. The authors [52] presented a simulation methodology to chemically cross-link the surface of polymer models and simulate nanoindentation using a C_{60} fullerene nanoparticle to probe the hardness of different regions and calculate the work of adhesion between probe and polymer (Figure 3). The purpose of their work was to create and probe surface crosslinked polyester models which could then be used as a base for chemical modification with functional groups as this was suggested as a possible means to reducing aging and improving the durability of modification effects. In their work polyester surfaces were cross-linked with hexamethylene di-isocyanate (HDI) and isophorone di-isocyanate (IPDI) molecules. Simulated nanoindentation was then carried out using the C_{60} fullerene particle to determine hardness and interfacial adhesion parameters. The results showed that HDI cross-linked polyester possessed a flexible top surface layer which was able to envelope the particle by wrapping around its periphery and resulted in a higher adhesion.
In contrast, surfaces cross-linked with IPDI resulted in a significant hardness at the topmost layer which both lead to “stick-slip” behaviour and maintained a lower adhesion in comparison to unmodified polyester. Furthermore, this “stick-slip” behaviour was found to be purely a characteristic feature of the loading curve of IPDI crosslinked coating and is particularly prevalent for hard and atomically rough surfaces. In this thesis, we extend previous work to include surface functionality and the effect of cross-linking as these effects both increase surface roughness and alter the surface wettability both of which are important parameters in the design of self-cleaning surfaces. Furthermore, this thesis is predominantly focused on investigating the role of responsive mechanisms of coatings to changes in the environment either changes in mechanical, chemical or wettability properties.

Trends in the literature are beginning to demonstrate that to achieve lower interfacial adhesion a combination of surface roughness, hydrophobic or hydrophilic chemical modification and substrate rigidity is needed. Furthermore, in the case of responsive surfaces, reversibility of the physical or chemical surface composition may also play an important role. For example, Yiapanis et al. employed molecular dynamics to investigate the effects of substrates on the mechanical response and adhesion of PEGylated surfaces [53]. In their study, the attachment of PEG chains (PEGylation) to hard substrates (silica) and soft substrates (polyester) was undertaken via a simulated condensation reaction to terminal hydroxyl (OH) groups. These substrates were then subjected to an in silico loading procedure to evoke a mechanically induced response, while simultaneously measuring the adhesion between contaminant and surface. Results demonstrated that PEGylation of a hard surface reduced adhesion to the approaching hard surface, while PEGylation of a soft, flexible substrate enhanced adhesion due to significant rearrangement of the subsurface and carpeting of tethered chains which reversed the initial surface roughness and, hence, its anti-contamination resistance.
1.7 Project aims

The aim of this project is to apply classical all-atom molecular dynamic techniques to further investigate the atomistic mechanisms that provide surfaces with self-cleaning properties. This knowledge is intended to be implemented to aid in the design of surface coatings that increase contamination resistance. The specific aims of the project are:

- Examine the role of hydrophobic and hydrophilic surface treatments for contamination protection of surface-crosslinked polymer coatings.
- Examine the role of surface stability and surface crosslinking in the protection against contamination.
- Investigate the dynamics behaviour of functional chains grafted onto polymer coatings and its influence on surface protection.
- Examine responsive surfaces at the atomistic scale and identify the mechanisms that drive their response during a change in environment from wet (aqueous) to dry (vacuum) conditions.
- Identify molecular design parameters for self-cleaning of polymer coatings that can be applied to industrial paint coatings such as Colorbond®.
2. Computational Techniques

2.1 Overview

Molecular modelling is increasingly becoming accepted as a complementary technique to experiments. At the nanoscale level, where experimental techniques become limited, molecular modelling becomes effective, and indeed the two complement each other. In this work, we use atomistic level modelling to provide mechanistic insight into nano-functionalised surfaces with the aim of achieving contamination resistance. In this section, molecular mechanics (force-field) methods are discussed, with a focus on the potential energy expression and molecular dynamic simulations. The applicability of these methods to accurately model organic surfaces and interfaces is also assessed. The energy minimisation procedure and algorithms that follow time evolution of molecular systems (molecular dynamics) are described. Finally, the procedures employed to generate rigorous thermodynamic ensembles are discussed.
2.2 Introduction to molecular modelling

Molecular modelling is a collective term for the computational techniques that are applied to model the structure and time dependent behaviour of molecules. Experimental techniques while useful in determining properties of a material, are limited in resolution for studying phenomena at the atomic scale and in short time intervals. Specifically, molecular modelling enables us to isolate and investigate specific features of a material. Therefore computer simulations can be advantageous in characterising and examining molecular and atomistic detail under controlled conditions, in domains where experimental techniques are unable to do so.

Molecular modelling can be classified into several categories based on the studied representation of interacting particles, system size and time-scale, Figure 4. The most accurate methods are based on quantum mechanics and are defined as “from first principles” or \textit{ab initio}, and involve solving the Schrödinger equation for calculation of the electronic structure. These methods are used to investigate processes which involve bond breaking and formation as well as force-field parameterisation.

![Figure 4. Diagram of the accessible time and length scale for different types of simulation techniques.](image-url)

For larger systems sizes and longer simulation time scales, force-field based methods can be particularly useful. Force-field methods ignore the formation and breaking
of covalent bonds and instead evaluate the energy of the molecular system by combining pair or multibody potentials that describe bonded and non-bonded interactions occurring between all atoms of molecules within the system. Force-field methods are computationally more efficient in comparison to \textit{ab initio} techniques. The combination of these properties enables the calculation of physical interactions with a decreased cost in computational time in comparison to \textit{ab initio} techniques albeit with a decreased accuracy.

At the large length and longer time scale are coarse-graining methods [54, 55]. In these methods instead of explicitly representing every atom of the system, “pseudo-atoms” are used to represent groups of atoms. For example, instead of treating all four atoms of a CH$_3$ methyl group explicitly, the whole group is represented by a single interaction site. The interaction between sites is then evaluated using pair potentials. The use of grouped atoms allows large complex systems to be simulated at timescales currently inaccessible to atomistic methods. The pseudo-atom types must, of course, be properly parameterized so that its interactions with other groups have the proper distance-dependence. Furthermore, hydrogen atoms are typically eliminated, except for those participating in hydrogen bonds.
2.3 Quantum mechanics

2.3.1 Quantum mechanics

In quantum mechanics, the time independent Schrödinger equation describes the quantum state of a physical system [56] and takes the following form;

$$ E\Psi = \hat{H}\Psi, $$  \hspace{1cm} (2.1)

where $\hat{H}$ is the Hamiltonian operator, $\Psi$ is the wave function and $E$ is the total energy of the system. The Hamiltonian operator is composed of a kinetic and potential energy operator and its application upon a wave function yields the total energy of the system. The wave function describes the quantum state of a particle and its square gives a corresponding probability density of finding a particle in a given place at a given time. Although the Schrödinger equation can, in principle, be used to describe any physical system with a near perfect accuracy, solving for a system with a large number of particles is immensely complex. Therefore, for larger systems a number of approximations are required.

The Born-Oppenheimer approximation alleviates the formidable task of computing the energy and the wave function of molecules. There are two main assumptions associated with the Born-Oppenheimer approximation. The first is that the mass of the nuclei are significantly larger than the electrons and as a consequence, the nuclear motion is so much slower than electron motion that nuclei are considered to be fixed or stationary from the electrons reference frame. The second assumption is that the velocity of the electrons is much greater than that of the nuclei and therefore the nuclei perceive a smeared out potential from the fast electrons. The implication of the Born-Oppenheimer approximation is that it allows for the motion of the electrons to be decoupled from the motion of the nuclei.
Therefore, eq. (2.1) can be solved by keeping the position of the nuclei constant and determining the energy of the system for a given set of nuclei coordinates. Once the nuclei are repositioned to a new set of coordinates, the equation is recalculated. Calculations based on Schrödinger equation enable electronic properties and reactivity information of the system to be determined.
2.4 Atomic simulation methods

2.4.1 Force-field method

In molecular mechanics or force-field base methods the energy of the system is evaluated by a combination of pair or higher order potentials describing the bonded and non-bonded interactions between atoms within the system. In this approach, the form of the interaction potential is based on Newtonian laws and any electronic information is provided through parameters or constants in the potential energy expression. The parameters can be derived from both experimental empirical fitting or through higher level \textit{ab initio} calculations. These parameters typically include values for atomic mass, van der Waals radius, partial charge, equilibrium bond lengths, angles, torsion angles and effective spring constants. The force-field approach can describe physical (non-chemical) interactions in the system, and reproduce structural, conformational, thermo-physical and vibrational properties.

This work aims to investigate properties of the surfaces driven by physical interactions, as opposed to chemical, and these types of interactions are suitably studied using the force-field method. If \textit{ab initio} methods were to be employed in this thesis intricate detail of the formation and breakage of chemical bonds within the system could be studied. Additionally, the models used in this work comprise of approximately 5000 particles, and are far too large to be modelled by \textit{ab initio} methods. In comparison the force-field approach can calculate properties of fully atomistic models in a fraction of the computer time. Also, longer simulation times can be investigated using the atomistic force-field approach to obtain time-dependent properties, which are of most interest to this work. Therefore, classical all-atom force-field approach was chosen for the simulations implemented in this thesis, and is described in greater detail than other modelling methods.
2.4.2 Force-field energy expression

The force-field energy expression refers to the mathematical function used to describe the potential energy of a system of particles. In this work the force-field chosen is the COMPASS force-field [57], a second generation force-field whose energy expression includes cross-coupling terms and parameterized for a variety of molecules in the condensed phase. The COMPASS force-field has the following functional form:

\[
V_{\text{total}} = \sum_b [k_2(b - b_o)^2 + k_3(b - b_o)^3 + k_4(b - b_o)^4] \tag{1}
\]

\[
+ \sum_\theta [k_2(\theta - \theta_o)^2 + k_3(\theta - \theta_o)^3 + k_4(\theta - \theta_o)^4] \tag{2}
\]

\[
+ \sum_\phi [k_1(1 - \cos \phi) + k_2(1 - \cos 2\phi) + k_3(1 - \cos 3\phi)] \tag{3}
\]

\[
+ \sum_\chi k_2 \chi^2 + \sum_{b,b'} k(b - b_o)(b' - b'_o) \tag{4} \text{and (5)}
\]

\[
+ \sum_{b,\theta} k(b - b_o)(\theta - \theta_o) \tag{6} \text{(2.3)}
\]

\[
+ \sum_{b,\phi} (b - b_o)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] \tag{7}
\]

\[
+ \sum_{\theta,\phi} (\theta - \theta_o)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] \tag{8}
\]

\[
+ \sum_{\theta',\theta} k(\theta' - \theta'_o)(\theta - \theta_o) \tag{9}
\]

\[
+ \sum_{\theta,\theta',\phi} k(\theta - \theta_o)(\theta' - \theta'_o) \cos \phi \tag{10}
\]

\[
+ \sum_{i,j} \frac{q_i q_j}{\varepsilon \tau_{ij}} + \sum_{i,j} \varepsilon_{ij} \left[ 2 \left( \frac{\tau_{ij}^0}{\tau_{ij}} \right)^9 - 3 \left( \frac{\tau_{ij}^0}{\tau_{ij}} \right)^6 \right] \tag{11} \text{and (12)}
\]
The functions can be divided into two categories, the valence terms and the non-bonded terms. Valence terms describe the energy contribution due to the internal coordinates of the system, such as the bond length ($b$), bond angle ($\theta$) and torsion angle ($\phi$). The non-bonded terms describe long range interactions, which include van der Waals and Coulombic interactions.

Valence terms of the force-field equations are described by terms (1-10). Term (1) describes the energy change due to the compression or stretching of bonds using a fourth degree polynomial extension of Hooke’s Law, where $b$ is the interaction distance or bond length and $k$ and $b_o$ are the spring constant and equilibrium length of the bond respectively. Term (2) describes the energy associated with the angle $\theta$ formed between triplets of consecutively bonded atoms, where the parameters $k$ and $\theta_o$ describe the stiffness and equilibrium angle respectively. Terms (3) and (4) describe the energy contribution due to the torsion ($\phi$) and out-of-plane ($\chi$) angles respectively, while terms (5-10) are described as cross-coupling terms and define the energy change due to coupled valence-type interactions. For example, bond length stretching is found to decrease neighbouring valence angles in order to reduce the increased interaction caused by bond stretching. Cross-coupling terms are required to accurately predict vibrational frequencies and structural variations associated with conformational changes. These cross-coupling terms are specific to second generation force-field and increase the accuracy of the force-field.

Non-bonded terms of the force-field equation are described by terms (11) and (12). The electrostatic interaction (11) is modelled using Coulomb’s law, where $q_i$ and $q_j$ are the point charges of atoms $i$ and $j$ respectively, $\varepsilon$ is the relative permittivity, and $r_{ij}$ is the inter-atomic distance. The point charges are chosen carefully to reproduce the electrostatic properties of the molecule and represent the partial charge of the atom. Term (12) describes the van der Waals (vdW) interactions using a Lennard Jones 9-6 potential. The Lennard-
Jones 9-6 potential is considered a “soft” potential, the $r^{-9}$ term represents the short range Pauli repulsion interaction while the $r^{-6}$ represents the longer range dispersion interactions, which arise due to instantaneous dipoles in the electron cloud. Again $r_{ij}$ is the interatomic distance, $r_{ij}^0$ is the characteristic distance between two atoms when the potential energy between them is at a minimum, and $\epsilon_{ij}$ governs the depth of the minimum.
2.4.3 Force-field parameterization

In the force-field method, each atom is assigned to a particular type depending on the atomic element and its chemical environment. In the COMPASS force-field the atom type consists of the elements symbol and a number indicating the coordination number or number of bonds. For instance, an atom type of c4o indicates a carbon atom with four bonds, one of which is an oxygen atom (an α-carbon in ethers or alcohols). In force-field parameterization, each atom type is assigned its own set of parameter values describing the chemical bonding that the particular atom type is involved in. It essentially involves assigning numerical values to the constants of the force-field energy expression, such as atomic mass, and atomic partial charges for individual atoms as well as the equilibrium values of bond lengths, bond angles, and dihedral angles for pair, triplets and quadruplets of bonded atoms. Parameterization of the COMPASS force-field, was undertaken by Sun et al. [57-60] and involved a common hybrid procedure consisting of \textit{ab initio} parameterisation and empirical optimisation. \textit{Ab initio} parameterisation of the COMPASS force-field consisted of determining atomic partial charges and valence parameters. The atomic partial charges were derived based on \textit{ab initio} calculations of the electrostatic potential energy (ESP), where the ESP is the potential energy arising from the Coulombic force acting between point charges.

\textbf{Empirical optimisation of the force-field involves refining parameters values to yield good agreement with experimental data. Many valence parameters of the COMPASS force field were transferred from the PCFF force field. For those functional groups that were not available, new parameters were derived using the same CFF development method.}#ref The valence parameters were validated against high-quality experimental data, which were
based on intramolecular properties of isolated molecules, such as molecular structures, molecular dipole moments and vibrational frequencies. In most cases, the calculations were full-energy minimization using a general Newton-Raphson algorithm. For conformational properties, torsion-force minimization was performed in which one or more dihedral angles were fixed while all other degrees of freedom were relaxed. The calculated results were compared with high-quality experimental data or ab initio data calculated at the MP2 level with various basis sets (DZ2P to TZ2PF) or DFT method with the VWN functional and DNP basis set. Finally, Lennard-Jones 9-6 parameters were subjected to refinement using molecular dynamics simulations of molecules in condensed phases, which was then used to calculate and compare physical properties of the molecular liquids, such as densities and cohesive energies at given temperatures and pressures.

Compatibility and transferability of parameters among different functional groups is essential in making a general force-field. The central issue in parameterising a general force-field is to use as few parameters as possible so that the parameters can then be transferred across a broad range of molecules. A path of parameterisation for the COMPASS force-field is that the most common functional groups are parameterised first followed by the least common. The COMPASS force-field has been parameterized for a wide range of organic compounds including alkanes and esters, as well as inorganic molecules and materials. In the interest of this study, the COMPASS force-field has been used to model condensed phase polymeric systems and tested for a wide range of organic and inorganic interfaces [46, 47, 61, 62]. Further details of the parameterization of the COMPASS force-field can be found in the study of Sun [57].
2.5 Energy minimisation

The potential energy of a system of atoms can be represented as a multidimensional surface known as the “potential energy surface”, with atomic positions as variables. Stable states of the molecular system correspond to the minima on the potential energy surface, with the lowest energy corresponding to the global minima, Figure 5. For a large system with many atoms the potential energy surface becomes rather complex, since it must take into account every possible orientation of the system. To attain an initial geometry configuration that corresponds to a closest energy minimum, an algorithm known as energy minimisation is used [63, 64]. In other words, energy minimisation results in minimum potential energy configuration attained by the most efficient movement of the atoms in the system.

A common energy minimisation method is the steepest descent method which involves moving atoms according to the total net force acting on them. In particular, the force on an atom is calculated as the negative gradient of the total potential energy of the system. The direction of the negative gradient indicates where a minimum is located, and the magnitude of the gradient indicates the steepness of the energy slope. During minimization a line search modifies the coordinates to generate a new, lower-energy state. This is achieved by choosing an arbitrary direction on the energy surface and calculating the minimum in that particular direction. Once the minimum is found a new direction, perpendicular to the previous, is chosen for the new line search. In this iterative way, the minimisation of the system is achieved when convergence occurs, i.e. when the potential
energy of the system decreases below a specified criterion. Although the gradient decent method is numerically stable, it is very time-consuming in comparison to other minimization methods as it suffers from a “zigzagging” behaviour on energy surfaces with narrow valleys.

Another minimisation method is the conjugate gradient method. The conjugate gradient method makes use of previous line searches to improve the next step. Specifically, each successive step continually refines the direction towards the minimum. This is achieved through an algorithm that produces a complete basis set of mutually conjugate directions to calculate each successive step from previous steps. Therefore, each line search is a conjugate to all previous line searches, hence the term conjugate gradient. This method improves the gradient decent method by reducing “zigzagging” behaviour. For this reason, when stringent minimisation and high convergence criterion is required, the conjugate gradient method is often a preferred option, as the local energy minimum can be attained in far fewer steps. In this study, the first order derivative minimisation methods of gradient descent and conjugate gradient are used. Furthermore, all molecules whether constrained or not underwent a minimisation procedure prior to molecular dynamics.
2.6 Molecular dynamics

Molecular dynamics (MD) involves simulating the motion of atoms and molecules in a system. It is employed to determine the time evolution of velocities and positions of atoms and molecules by numerically solving Newton’s equations of motion for a system of interacting particles, where the forces between the particles and the potential energy are defined by the force-field and parameter set. Specifically, for a particular system, Newton’s second law takes the form,

\[ F = -\frac{dV_{\text{total}}}{dr} = m \frac{d^2r}{dt^2} = ma, \]  \hspace{1cm} (2.4)

where \( V_{\text{total}} \) is the potential energy determined from the force-field energy expression (eq. 2.4), \( r \) is the vector that contains \( x, y, \) and \( z \) coordinates of the particles, and \( F \) and \( a \) are the force and acceleration vectors respectively. The classical equations of motion are deterministic, as such the initial coordinates and velocities determine the coordinates and velocities at a later time.

Numerous algorithms have been developed for solving Newton’s equations of motion. Variants of the Verlet [65] algorithm for integrating the equations of motion are perhaps the most widely used methods in molecular dynamics. One particular variant employed in this study is the velocity Verlet algorithm [66]. In the velocity Verlet algorithm the position \( (r) \) and velocity \( (v) \) vectors after time step \( (\Delta t) \) are defined as follows:

\[ r(t + \Delta t) = r(t) + \Delta t v(t) + \frac{1}{2} \Delta t^2 a(t) \] \hspace{1cm} (2.5)
The position (eq. 2.5) is evaluated as a Taylor series expansion. To calculate the new velocity from (eq. 2.6), values of the acceleration at times (t) and (t + Δt) are required concurrently (a(t) and a(t + Δt)). Therefore, the velocity Verlet method is implemented as a three stage process. Firstly, the new position vector \( r(t + Δt) \), is determined (eq. 2.5). In this equation, the initial values of the velocities \( v(t) \) are randomly chosen from a Maxwell-Boltzmann distribution for a given temperature, and the acceleration \( a(t) \), determined from the derivative of the potential (eq. 2.3). Secondly, the atomic positions are propagated to their new coordinates and again with the use of the interaction potential (eq. 2.3), the new values of the acceleration are determined (a(t + Δt)). Finally, values of a(t) and a(t + Δt) are used to determine the new velocity vector \( v(t + Δt) \). The velocity Verlet algorithm assumes that the acceleration is dependent on the position of the particles and not on their velocities. By undertaking a large number of time steps the time evolution of the system is obtained.

There are many examples where MD has been used to probe the dynamics of many organic and inorganic interfaces, including those of interest to this work [45, 48, 61, 67, 68].
2.7 Periodic boundary conditions

Periodic boundary conditions (PBC) are typically used to simulate large systems by modelling a small part of the system and replicating it in specific directions. In theory these boundary conditions allow for a system of “infinite” size to be modelled [63, 64]. Particles are enclosed in a unit cell of geometry suitable for three-dimensional tiling. As a particle passes through one face of the unit cell, it reappears on the opposite face with the same velocity, Figure 6. This makes the tiled copies of the unit cell “images” of the original cell and each atom within the unit cell all “unique” atoms of the system. For example, assuming a particle has a position and velocity of the vector \( r \) in a unit cell, when periodic boundary conditions are applied, the particle is replicated infinitely in the following manner,

\[
r_{\text{image}} = r + la + mb + nc
\]

(2.7)

where \( l, m \) and \( n \), are integers ranging from \(-\infty\) to \(+\infty\), and \( a, b \) and \( c \) are the vectors corresponding to the unit cell. The vector \( r_{\text{image}} \) from (eq. 2.7), represents the coordinates of the “image particles”. Effectively, each particle is now considered to be interacting not only with other particles within the unit cell, but also with image particles in neighbouring boxes. Periodic boundary conditions are particularly useful to eliminate surface effects near boundaries which can lead to erroneous results. This is in fact the greatest advantage of implementing periodic boundary conditions. However, the size of the simulation box must also be large enough to prevent periodic artefacts from occurring. These artefacts occur in a box that is too small, a macromolecule may interact with its own image in a neighbouring box, which is functionally equivalent to a molecule's "head" interacting with its own "tail".
Figure 6. A two-dimensional representation of periodic boundary conditions.
2.8 Non-bonded interactions

During molecular dynamics simulation the calculation of non-bonded interactions (van der Walls and coulombic) [63, 64] is computationally expensive, in comparison to bonded interactions, due to their pair additive nature. To deal with the expensive computational cost associated with the evaluation of non-bonded interactions a minimum-image convention [69] is applied. In the minimum-image convention any particle that leaves the simulation box on one side enters back on the other, the distance between each atom is then recalculated. Essentially the minimum-image convention is a form of PBC particle bookkeeping in which each individual particle in the simulation interacts with the closest image of the remaining particles.

In molecular dynamics simulations a cutoff method of non-bonded interaction is often employed to improve computational efficiency. The atom based cutoff method calculates non-bonded interactions to a cutoff distance, when atom pairs are separated by a distance greater than the cutoff value their interactions are neglected. This is because the greatest contributions from non-bonded interactions arise from the closest particles. A limitation of this technique results in discontinuities in the energy as since atom pairs that move in and out of the cutoff range between successive steps result in “energy jumps” where non-bonded energies are included in one step and excluded from the next. Often, a smoothing function is employed to alleviate discontinuities by smoothly ‘turning off’ interactions between atoms separated by a distance larger than the cut-off criteria. The Ewald technique [70, 71] alleviates some of the problems associated with discontinuities. Specifically this method introduces a convergence function which is a summation of short and long range interactions. The sum of the short range interactions quickly converge in real space, while the sum of the long range interactions quickly converge in Fourier space. The Fourier transform of long range interactions results in faster convergence.
2.9 Thermodynamic ensembles

2.9.1 Canonical ensemble

An ensemble is a collection of a large number of virtual copies of a system each of which represents a possible state that the real system might be in. In other words it is a probability distribution for the state of the system. In the canonical ensemble (NVT), the number of particles (N), the volume (V) and the temperature (T) are conserved. A molecular dynamics simulation employing the canonical ensemble (NVT), under periodic boundary conditions, evolves at constant volume and temperature [63, 64]. In principle, this is achieved by surrounding the system with a very large heat bath at a user defined target temperature ($T_0$). Any change to the temperature of the system away from $T_0$ of the bath will always be countered by the bath and so the system will relax to $T_0$. The temperature of a system can be calculated from the average kinetic energy of the particles.

To control the temperature a number of algorithms have been developed. The direct velocity scaling approach [72] is used to maintain the user defined target temperature ($T_0$), by simply multiplying the velocities by a factor $\lambda$ corresponding to the desired temperature change. This method is used for rapid equilibration of a system at which point, a more rigorous algorithm is used. Another algorithm is the Berendsen method [73], which provides a gentle exchange of thermal energy between the system and a heat bath through the introduction of a time constant ($\tau$). However both of these temperature control methods do not generate rigorous canonical averages whereby the probability that a configuration of energy $E$, is proportional to the Boltzmann distribution factor. An alternative is the Andersen thermostat [74] which generates the correct canonical ensemble based on stochastic collisions between particles. The velocities of the particles are adjusted to produce a predefined collision frequency. The Andersen thermostat is used in this work as it has been demonstrated to predict water diffusion coefficients accurately [75].
2.9.2 Isothermal-isobaric ensemble

In the isothermal-isobaric ensemble (NPT), the number of particles (N), the pressure (P) and the temperature (T) are conserved. As previously discussed, molecular dynamics simulations employing the canonical ensemble evolve at constant volume and temperature, while in the isothermal-isobaric ensemble a molecular dynamics simulation, under periodic boundary conditions, evolves at constant pressure and temperature. Simulations in the isothermal-isobaric ensemble are most relevant to experimental conditions, since experimental techniques are generally carried out at constant temperature and pressure. To maintain constant reference pressure \( P_0 \) rescaling of the simulation cell is undertaken. Any change to the reference pressure of the system away from \( P_0 \) will be countered by adjustment of the volume of the simulation cell.

Various algorithms have been developed to control the pressure of the system [73, 74, 76]. The Berendsen algorithm [73] maintains pressure at a constant value by rescaling the atomic coordinates and box vector every step with a scaling factor \( \mu \), which has effects on the first-order kinetic relaxation of the pressure towards a given reference pressure \( P_0 \):

\[
\frac{dP}{dt} = \frac{P_0 - P}{\tau_p}
\]

where \( \tau_p \) is the coupling constant and \( P \) is the pressure value of the system. Other algorithms include the Andersen [74] and Parrinello-Rahman [76] implement similar techniques.
3. Molecular simulations of surface crosslinking and functionalisation

3.1 Overview

We have applied a theoretical modelling approach to aid in the rational design of contamination resistant coatings. Using \textit{in silico} nanoindentation characterisation of the adhesion between a contaminant particle and engineered polymer surfaces that include functionalised-surface-crosslinked and functionalised non-surface-crosslinked polyesters has been undertaken. The roughness, density and morphology of the surfaces were dynamically monitored as the coatings responded to the approaching particle. Our results suggest that surface crosslinking provides a stable platform for incorporation of functional groups that would otherwise migrate into the bulk substrate upon aging. However surface crosslinking with rigid cyclic curing agents renders the coatings far too stiff, which can result in slip whereby surface crosslinkers shift to the side of the incoming contaminant particle, leading to both the exposure of the flexible substrate and the envelopment of the contaminant. Modification of surface crosslinked with rigid cyclic curing agents increases the magnitude of this slip behaviour and as such has a negative effect on contamination resistance. This type of deformation negates steric repulsions of the functional groups, crucial for preventing undesirable adhesion. In contrast, functionalisation combined with flexible acyclic surface crosslinks results in superior contamination resistance.
3.2 Introduction

A solution to soiling and degradation of polymer surfaces from various sources of contamination is highly desirable, and a compelling option may be provided through surface functionalisation [77-79]. It has been shown that functionalisation of polyester coatings with polar groups such as OH, CO$_2$H and F improves the contamination resistance both in a dry and in a fully hydrated environment [47-51]. However, this improvement is short-lived with subsequent aging of these functionalised surfaces in a dry environment resulting in migration of polar groups into the coating (hydrophobic recovery) and loss of contamination resistance. In fact one of the biggest obstacles facing purpose driven modification of polymer surfaces is that of stability highlighted by the extensive literature on polymer aging [50, 51, 80, 81]. In addition, previous studies have shown that when contaminant particles come in contact with flexible polyester surfaces under dry conditions, they access small cavities on the coating surface and become deeply embedded. Subsequent hydration is then ineffective at removing these particles.

To address the issue of surface stability, surface crosslinking has been proposed as a means to increase the hardness of the outer layer and reduce the mobility of the functional groups [52]. This previous study showed that surface crosslinking of unmodified polyester with hexamethylene di-isocyanate crosslinkers increased the hardness at depths greater than 1 Å, but maintains a top surface with significant mobility. On the other hand crosslinking with isophorone di-isocyanate was found to increase the hardness at the top surface while maintaining a flexible core region. In this section of the thesis the investigation is extended to determine if these changes in surface mobility affect the performance of functionalisation. This involved altering the surface chemistry of the crosslinked polymer coatings by the addition of hydrophobic and hydrophilic functional groups. In silico
nanoindentation was then carried out to test the mechanical properties of the modified coatings.

This molecular dynamics study investigates and assesses how flexible polymer surfaces which have been surface crosslinked and functionalised, mechanically respond to an approaching particulate. The methodology involves in silico nanoindentation of polymer films to firstly identify the mechanical properties of the surface and secondly to calculate free energy change via force integration. The study focuses on the role of surface hardness (achieved via crosslinking), chemical functionalisation and morphology on the ability of a surface to resist adhesion of hydrophobic particulates. Comparisons of theoretical results with experiments are made where available.
3.3 Computational details

3.3.1 Polymer surface model

Three polyester models were chosen as substrates for modification. The first of these substrates is a non-surface-crosslinked (soft) polyester composed of polyester chains that contain on average 15 units of 2-butyl-2-ethyl-1,3-propanediol, 2 units of trimethylolpropane, and 16 units of isophthalic acid, denoted Polyester [46, 48]. A detailed description of the procedure used to construct the model is presented in the theoretical study by Yarovsky and Evans [45], Figure # depicts the Polyester structure. In addition to the soft polyester substrate, two surface cured (hardened) coatings denoted Polyester15HDI and Polyester14IPDI were also examined, whose polyester surface chains have been crosslinked with hexamethylene di-isocyanate (HDI) or isophorone di-isocyanate (IPDI), respectively [52]. The crosslinker molecules chosen represent two distinct classes of curing agents, Figure # depicts the crosslinker structure/composition. HDI belongs to a class of acyclic compounds that are considered quite flexible while IPDI belongs to the family of cyclic compounds and is considered much more robust and rigid. Details of the crosslinking procedure can be found elsewhere [52].

Figure # Structure of resin and crosslinker molecules: (a) CYMEL 1158: Tributoxymethyl-melamine, (b) CYMEL 1172: tetramethylol glycoluril, (c) Phosphated epoxy resin: $P0 - n = 0$; $P1 - n = 1$
Surface functionalisation of the three polyester substrates was performed similar to previous studies [47-51], by adding fluorine (F) or hydroxyl (OH) groups as substituents for the outermost hydrogen atoms to a depth ranging from −0.6 to −1.2 nm at a surface coverage of 5.3 functional groups per nm², resulting in six functionalised polyester surface models (Table 1). While the surface depth of functionalisation is smaller than typical length scales of plasma modification it is comparable to previous molecular dynamics (MD) studies [47-51, 82]. In the functionalised crosslinked models, 96 % of modifiers were introduced on the crosslinks, while in the case of the non-surface-crosslinked polyester all functional groups were introduced directly on the polyester surface [47-51]. Following modification, the surfaces were energy minimized thereby relieving any introduced strain.

All models were created in a periodic cell of dimensions of 37 Å, 38 Å and 70 Å in the x, y and z directions, respectively. They displayed a surface area of −14 nm² and a surface depth of −25 Å. Each surface contains areas of a varying degree of crosslinking and functionalisation, resulting in different local densities that may in turn impact local surface properties. It is therefore important to characterise these areas individually.
Table 1 Surfaces represented by model system.

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyester75F</td>
<td>Fluorinated Polyester</td>
</tr>
<tr>
<td>2</td>
<td>Polyester15HDI75F</td>
<td>Fluorinated HDI Crosslinked Polyester</td>
</tr>
<tr>
<td>3</td>
<td>Polyester14IPDI75F</td>
<td>Fluorinated IPDI Crosslinked Polyester</td>
</tr>
<tr>
<td>4</td>
<td>Polyester75OH</td>
<td>Hydroxylated Polyester</td>
</tr>
<tr>
<td>5</td>
<td>Polyester15HDI75OH</td>
<td>Hydroxylated HDI Crosslinked Polyester</td>
</tr>
<tr>
<td>6</td>
<td>Polyester14IPDI75OH</td>
<td>Hydroxylated IPDI Crosslinked Polyester</td>
</tr>
</tbody>
</table>
3.3.2 Nanoindentation model

Nanoindentation of the surface models was performed by simulating the approach of a $C_{60}$ indenter towards the surface in the direction normal to the plane of the substrate as shown in Figure 7. A $C_{60}$ fullerene of radius 3.48 Å was chosen as an indenter particle, as it displays a similar surface structure to soot particles, and therefore can serve as a model of a carbon contaminant [47, 83]. The chosen indenter also has a higher elastic modulus than the substrates being tested, which is a requirement for indentation experiments. Prior to indentation, a graphene layer was introduced underneath each polyester layer to mimic an underlying bulk substrate. This constrained graphene layer was used to prevent migration of the indented polymer away from the indenter particle during the indentation process. The indenter was initially positioned at approximately 20 Å above the surface where the interaction between surface and particle is negligible. The particle was then displaced towards the surface, initially by step sizes of 2 Å. At each step, molecular dynamics (MD) was undertaken in the NVT ensemble (constant volume and temperature) for 0.5 ns at 298 K, to enable the polymer to respond to the approaching particle. The maximum speed at which the particle was displaced towards the surface was 0.4 m/s. Over the final 0.25 ns the force ($F_z$) and separation (d) between $C_{60}$ particle and surface were measured in the direction perpendicular to the plane of the substrate. When the change in force between successive steps exceeded 0.02 nN, the step size was halved until a minimum step size displacement of 0.25 Å was reached. During molecular dynamics, the $C_{60}$ particle was kept at a fixed geometry through the entire loading procedure while the unconstrained surface was free to respond to the applied load. Atoms of the $C_{60}$ particle carry zero partial atomic charge and therefore all interfacial forces are governed solely by the van der Waals (vdW) interactions. The loading procedure was terminated when the indenter particle was advanced well past the point of interfacial equilibrium, defined as the position where the net force between indenter and substrate is zero. A detailed description of the nanoindentation procedure can
be found in a previous study [52]. The loading procedure was used to generate a force-separation curve, from which the following parameters were obtained: the equilibrium separation of the interface $d_0$, and the work of adhesion $W_{adh}$, defined as the energy required to separate the interface into two isolated surfaces [84, 85]. In the context of this study these two interaction parameters provide a quantitative measure of the contamination-rejecting properties of each surface. For each substrate, five separate indentation experiments were carried out, with the $C_{60}$ particle driven into different regions of the surface, in order to identify effects of local surface properties on contamination resistance. A detailed description of the indented regions where the $C_{60}$ particle was placed in the XY plane prior to the indentation process can be found in a previous study [#ref]. Once positioned above the polymer the indentation process was then carried out at each of the given XY coordinates. In addition, unloading hysteresis was examined by generating force separation curves during retraction of the indenter particle from the surface. We commenced retraction at a separation below the equilibrium position with step sizes of 0.25 Å.
Figure 7. Schematic diagram displaying indentation of modified crosslinked polyester using a fullerene $C_{60}$ particle.
3.3.3 Surface morphology and roughness

To monitor the mechanical response of each functionalised substrate to the indenter, three-dimensional surface profiles of the indented surface regions were generated during loading. These contour maps provide a visual representation of the topography of the indented surface regions and of induced physical changes as a result of loading. Each surface profile is produced relative to the centre of mass coordinates (x and y = 0.0 Å) of the indenter particle and encompasses an area along the surface plane of ~400 Å². The area along the surface plane is significantly less than the unit cell, 14 nm², as the surface plane is a region within the unit cell. Each mapped area was then further subdivided into 49 square grids of ~8.16 Å². Within each of these grids the maximum height (z_i) of the substrate’s surface atoms was averaged over the last 50 ps of MD, forming a three-dimensional surface topography map. This map was subsequently used to determine the surface boundary, roughness, and local density of the examined region. The boundary of the surface z_{avg} was determined by averaging the height (z_i) across all grids of the map. The root mean squared surface roughness R_{RMS} was determined according to:

\[
R_{RMS} = \left[ \frac{\sum_{i=1}^{n} (z_i - z_{avg})^2}{n} \right]^{1/2}
\]

where z_i is the maximum height of surface atoms within the i^{th} grid, z_{avg} is the surface boundary, and n is the number of grids. The atomic density of each indented region was defined as the number of atoms per unit volume where the volume of each substrate is calculated as the surface area of the examined region (~400 Å²) multiplied by its average
thickness. The thickness was obtained by calculating the upper and lower surface boundaries of the polymer film from topography maps.
3.3.4 Computational details

Inter- and intra- molecular interactions were evaluated using the COMPASS force-field [57] which was previously demonstrated to adequately describe adhesion properties between carbonaceous and polymer surfaces in dry environments [46, 48]. During the geometry optimisation, the non-bonded interactions were calculated using the Ewald procedure with an accuracy of $\sim 0.042$ kJ/mol and an update width of 1.0 Å. Energy minimization was achieved using the conjugate gradient algorithm, with a convergence criterion of $\sim 0.042$ kJ/mol/Å. For MD procedures, non-bonded interactions were calculated using the atom-based summation method with a cutoff radius of 15.5 Å, a spline width of 5.0 Å and a buffer width of 2.0 Å. A long-range tail correction was applied for non-bonded interactions larger than the cutoff radius. A 1.0 fs time step was used for the NVT dynamics at a temperature of 298 K. The Andersen thermostat [74] was employed to control the temperature with a collision ratio of 1.0. All systems were equilibrated to ensure that no total energy drifts occur during the data collection stage of MD.
3.4 Results and discussion

3.4.1 Surface classification

Using the techniques described in the computational method section, we assessed the mechanical response of the surfaces to the approaching contaminant by examination of the force, density and roughness during loading. As each of the six surfaces was indented in five regions, a total of thirty loading curves were generated and can be found in the appendix of this thesis (AT1). From the qualitative analysis of each curve, three surface classes were identified with distinct characteristic features:

- Class A – “soft” surface regions characterised by a limited slippage of the top layer and elastic-like behaviour
- Class B – “stiff” surface regions with an outer-layer that exhibits low elastic deformation, notable slippage and secondary adhesion
- Class C – “tough” surface regions similar to Class B but without secondary adhesion

This classification technique is generic and, in principle, can be applied to any deformable surface to assess its mechanical stability and self-cleaning ability. Below is a detailed discussion of the response of each surface class to an approaching contaminant which led us to identify criteria needed for contamination resistance.
3.4.2  Class A: soft surfaces

As the indenter particle approached the surface, the force in the z-direction (normal to the plane) was calculated, Figure 8. On this force curve, positive values indicate a net repulsion, while negative values indicate a net attraction. The shape of the curve resembles a typical force plot obtained from Atomic Force Microscopy (AFM) measurements, although on a different length scale [86]. At large separations (~10.0 Å to ~4.3 Å), the attractive component of the force dominates with an increase in the net attraction as the indenter advances towards the surface. At a distance of ~4.3 Å, the repulsive component is detected at a separation known as the point of contact and marked by a change in curvature of the force curve [87, 88]. For two non-deformable surfaces the point of contact usually occurs at the bottom of the force basin. However, the outer-layer of a Class A surface is easily deformable which results in force fluctuations, relatively small in magnitude but making it difficult to precisely determine the point of contact. We define contact as the position where instabilities are first noted (~4.3 Å). After contact is attained the repulsive and attractive components continue to increase at a rate that is dependent on the deformability of the surface [89]. Studies have shown [90, 91] that when two highly deformable surfaces are brought into contact with one another, the attractive component of the force may increase at a faster rate than the repulsive component. The result of this is that the strength of attraction between the deformable surfaces continues to rise with decreasing interfacial separation, despite the fact that the surfaces are in contact. This is indeed the case for Class A surface regions as exemplified in Figure 8. In particular, we observe, a non-monotonic increase in the net attraction between separations of ~4.3 Å and ~3.0 Å, highlighting the surface’s ability to conform and alleviate steric repulsions from the incoming particle. This non-monotonic increase in the net attraction is slight but none the less still apparent as the force fluctuations exceed the standard error of the force (0.07 nN) during the indentation process. Eventually, from ~3.0 Å to ~2.5 Å, the repulsive component grows faster with
decreasing separation, cancelling out the attractive component until a state of equilibrium is reached. At equilibrium the sum of all forces acting in the z-direction on the indenter particle equates to zero. Any further decrease in the separation results in a significant increase in repulsive forces between the particle and surface.

The surface density was also monitored during indentation to produce the density curve displayed in Figure 8. This plot shows that prior to contact, long range attractive forces induce expansion of the surface evident by a decrease in substrate density observed from ~10.0 Å to ~4.3 Å. After the C_{60} particle attains contact with the surface short range repulsive forces induce a non-monotonic compression of the surface, shown by an overall increase in density from ~4.3 Å to ~2.0 Å. Slight expansions of the surface at interfacial separations of ~3.5 Å and ~3.0 Å, are associated with surface atoms gradually wrapping around the edges of the particle creating openings. Specifically, a Class A region exhibits both slight changes in the force combined with significant changes in the density. This again highlights the inherent deformability (adaptability) of Class A regions.

The three-dimensional surface profiles of Figure 9 provide a visual representation of the region’s morphology in response to the approaching particle. The region’s morphology does not indicate whether or not a cross-linker or functional group is beneath the C_{60} indenter particle. This is due to the fact that cross-linking and functionalization is not uniform over the entire surface. The surface morphology ignores differences in functionalization and crosslinking and instead focuses on the mechanical response of the surface itself. From the unperturbed state (Figure 9a) to the point of contact (Figure 9b) an increase in surface roughness is observed as a result of interfacial attractive forces drawing surface atoms towards the indenter particle in the positive z-direction. Upon further approach of the indenter (Figure 9c), a decrease in the surface roughness is observed. Here, flattening of the surface occurs as steric repulsive forces compress surface atoms. Finally at
short separations where the surface transitions to an equilibrium state (Figure 9d), an increase in surface roughness occurs due to cavity formation and particle envelopment. Variations in the mean roughness displayed in Figure 9 are orders of magnitude greater than the standard error in the roughness (0.006 Å), which demonstrates the significance of these changes.

The modulus of elasticity, defined as the gradient of a stress-strain curve in the elastic region of deformation [92] can be inferred from changes in force and density. Figure 8 shows that Class A regions exhibit a large change in density with relatively little corresponding change in force, suggesting that this type of region possesses a low elastic modulus. Further evidence of the elastic character/nature of a Class A region is observed in the unloading curve of Figure 8. Upon retraction of the particle, we observe a notable absence of loading/unloading hysteresis indicating an elastic response of the surface. Furthermore, since the speed at which the particle was displaced towards the surface is consistent across all loading experiments the presence or absence of a loading/unloading hysteresis is entirely dependent on the elastic properties of the surface. We therefore classify surfaces with such a response to deformation as “soft”.

![Figure 8. Plots of normal force on the C\textsubscript{60} particle and density of the indented region during loading and unloading for a Class A region. The standard errors for the density and force are 0.06 atoms per nm\textsuperscript{3} and 0.07)](image-url)
nN respectively. The errors are not shown for clarity but are an order of magnitude less than the variations observed, indicating the significance of the results.

Figure 9. Surface profiles of Class A (soft) region at specific separations during indentation including corresponding roughness value ($R_{RMS}$) (a) unperturbed state, (b) contact state, (c) state between contacting and equilibrium, and (d) equilibrium state. Standard error in roughness (not shown for clarity) is 0.006 Å.
3.4.3 Class B: stiff surfaces

Figure 10 shows typical force and density plots for nanoindentation of a Class B region. Similar to Class A at long ranges, the attractive component of the force dominates, resulting in an increase in the net attraction as the indenter advances towards the surface. However, in this case, the increase occurs at a faster rate compared to Class A. Less fluctuations in the force curve are observed, which suggests improved stability compared to the soft regions of Class A. In addition, the net attraction at contact is lower due to an earlier onset of repulsive forces. These observations indicate the presence of a rigid outer layer. At separations just beyond contact (~6.4 Å to ~4.5 Å), the force displays a sharp rise. This rise reflects a build-up of steric repulsive forces at the interface, which induces a high level of stress throughout the surface. This stress in the surface continues to increase with decreasing interfacial separation, until a threshold is reached, beyond which repulsive forces induce a lateral displacement of the outer-layer. This displacement enables a release of the stress and is accompanied by a rapid drop in force. Such a phenomenon is known as “slip” [93, 94] and is generally observed for surfaces composed of a rigid outer-layer combined with a flexible sub-surface. Slip of the outer-layer exposes a soft sub-surface similar to Class A regions, resulting in envelopment of the particle as it is advanced further into the surface. The abrupt lateral displacement of surface chains may be classified as a plastic deformation due to the fact that when the C_{60} particle is withdrawn, [95] the surface does not regain its original structure resulting in a large loading/unloading hysteresis (see Figure 6) [96]. Such behaviour differs significantly from the elastically deformable region of Class A which exhibits no abrupt displacements, but rather a gradual rearrangement of surface atoms. Furthermore, the slip event is significant in magnitude compared to the small force fluctuations that were observed during the indentation of a Class A region. After the slip event, in Class B regions, secondary adhesion between indenter and surface is observed. At separations below ~3.0 Å, further advancement of the indenter towards the surface leads to a rapid rise in the
repulsive component of the force. At an interfacial separation of \( \sim 2.5 \text{ Å} \), equilibrium is attained.

As indicated in Figure 10, prior to contact, the surface exhibits little change in density, owing to its robust outer-layer. The rigidity of the outer-layer is further evident from 3D surface profiles (Figure 11) which demonstrate that as the surface transitions from its unperturbed state (Figure 11a) to contacting state (Figure 11b), the roughness remains relatively unchanged. Following the establishment of contact, from \( \sim 6.4 \text{ Å} \) to \( \sim 4.6 \text{ Å} \), the density of the surface is increased slightly, and the surface roughness is marginally reduced (Figure 11b and c). These small changes are in striking contrast to the large morphological variations observed for the soft surface region of Class A. After a separation of \( \sim 4.6 \text{ Å} \) is reached, we observe a significant reduction in density (Figure 10) as a result of plastic deformation (lateral displacement of the surface chains) with subsequent envelopment of the particle (Figure 11d).

In the elastic region of deformation (\( \sim 6.0 \text{ Å} \) to \( \sim 5.0 \text{ Å} \)) for a Class B surface, we observe negligible variation in density but a large increase in force inferring a high elastic modulus and low elastic deformation. We classify surfaces with such response to loading as “stiff”.

![Figure 10. Plots of normal force on the \( C_{60} \) particle and density of the indented region during loading for Class B region. Standard errors in each density and force (removed for clarity) are 0.06 atoms per nm\(^3\) and 0.07 nN respectively.](image-url)
Figure 11. Surface profiles of Class B (stiff) region at specific separations during indentation including corresponding roughness value ($R_{\text{RMS}}$) (a) unperturbed state, (b) contact state, (c) flattening state and (d) equilibrium state. Standard error in each roughness (not shown for clarity) is 0.006 Å.
3.4.4 Class C: tough surfaces

Force and density plots for indentation of a typical Class C region are shown in Figure 12. As for the other classes, initially an increase in the net attraction occurs as the indenter advances towards the surface (~10.0 Å to ~5.4 Å). The point of contact occurs at a large separation compared to Class A. After contact, a rise in the force is observed (~5.4 Å to ~4.0 Å). This smooth rise indicates structural stability due to a robust outer-layer that resembles the stiff surface of Class B. Variations in force are observed from ~4.0 Å to ~2.5 Å, attributed to lateral displacement of surface chains, which in turn results in a loading/unloading hysteresis (plastic deformation). However, the stress between particle and surface is sustained over a greater range than for Class B, indicating that the degree of slip is smaller. We classify surfaces with such response to loading as “tough”. The “toughness”, attributed to the presence of a relatively stable sub-surface, ensures that secondary adhesion is significantly smaller in magnitude compared to the stiff surface region of Class B. In addition, equilibrium is reached at a higher separation, ~4.3 Å.

From the unperturbed state to the point of contact a significant increase in density occurs (Figure 12), however compression of the surface from the indenter particle is not possible since contact has yet to be established. Therefore, a possible explanation for this increase in density is a lateral movement of the surface due to long-range vdW attraction. Evidence of this shift can be obtained from the surface profile changes from ~9.3 Å to ~5.4 Å (Figure 13), where distinct features, such as the peaks and troughs, move in the positive Y direction. This observation corresponds to the phenomenon known as “jump to contact”, whereby surface atoms extend to meet an incoming particle, that not only occurs in the vertical plane but can also occur in the lateral plane [89, 97]. The lateral movement of surface atoms during loading is particularly evident when the primary length scale of the surface features is comparable to the size of the incoming particle. The density continues to
increase after contact from ~5.4 Å to ~4.0 Å (Figure 12), due to compression of the outer-layer. However, this increase is negligible compared to the soft surfaces of Class A, yet notable relative to the stiff region of Class B. We therefore expect that elasticity of Class C surfaces to be somewhere between Class A and B. From separations of ~4.0 Å to ~2.0 Å we observe fluctuations in density as a result of slip.

Figure 12. Plots of normal force on the C_{60} particle and density of the indented region during loading for a Class C region. Standard errors in density and force are 0.06 atoms per nm$^3$ and 0.07 nN respectively. The error bars have been removed for clarity.
Figure 13. Surface profiles of a Class C (tough) region at specific separations during indentation including corresponding roughness value ($R_{\text{RMS}}$) (a) unperturbed state, (b) contact state, (c) state between contacting and equilibrium, and (d) equilibrium state. Standard error in roughness is 0.006 Å. The errors bars have been removed for clarity.
3.4.5 Distribution of classes and effects of surfaces properties on adhesion

Our classification technique was applied across all simulated surface regions, to obtain a percentage distribution of the mechanical properties for each coating, Figure 14. Due to the amorphous nature of the surfaces, a co-existence of soft, stiff and tough regions was observed. The data from functionalized surfaces was combined as no significant difference was observed between adding either fluorine and hydroxyl groups to the surface. The non-surface-crosslinked polyester, denoted Polyester75X (where “X” represents a functionalized surface), was found to be predominantly soft (80 %) highlighting its elastic-like behaviour. In contrast, the IPDI crosslinked surface, cured with a cyclic curing agent, is largely populated with regions of high stiffness (50 %) and has a high proportion of tough regions (40 %), while the HDI crosslinked surface, cured with an acyclic curing agent, is found to be predominantly tough (70 %). These results suggest that surface crosslinking not only increases the film’s elastic modulus [98] but also renders the surface plastically deformable in agreement with experiment [96]. In addition, we found that the nature of the curing agent can affect the mechanical properties of the surface [52]. Specifically, surface crosslinking with an acyclic curing agent such as HDI, lowers the elastic modulus and reduces the extent of surface displacement (plastic deformation) compared to its cyclic counterpart. This is in qualitative agreement with experiment [99] showing that HDI crosslinked polyurethanes endure a greater elongation and display a reduced elastic modulus during tensile strength testing compared to their IPDI counterpart. This difference was attributed to the cyclic/asymmetrical nature of IPDI that enhanced interchain steric hindrance [100].

The interaction parameters obtained during loading are shown in Figure 15: the equilibrium separation at the particle/surface interface ($d_0$) and the work of adhesion ($W_{adh}$), which is the free energy required to separate this interface. For comparison, interaction parameters for surfaces [52], which have not been functionalised, are also included.
(Polyester, Polyester14IPDI and Polyester15HDI). Figure 15 shows that as the adhesion increases, the equilibrium separation decreases and vice-versa, highlighting a strong coupling between these two parameters. Functionalisation of non-surface-crosslinked polyester leads to a ~12 % reduction in adhesion and a ~0.6 Å increase in equilibrium separation in comparison to the non-functionalised polyester. However, these changes are contained within the standard error suggesting that F or OH functionalisation of soft surfaces does not result in significant improvement in contamination resistance. In contrast modification of HDI crosslinked polyester results in a notable reduction in adhesion (~27 %) and a prominent increase in equilibrium separation (~0.9 Å) in comparison to non-functionalised polyester crosslinked with HDI. Finally, functionalisation of IPDI crosslinked polyesters results in a ~26 % increase in adhesion, in comparison to its non-functionalised counterpart. Overall, our results suggest that functionalisation combined with curing by a flexible surface crosslinking molecule (HDI) results in superior contamination resistance, as this surface maintains functionality, possesses significant surface roughness, and provides low adhesion, all of which are important components for contamination resistance.

To explain these trends one must first elucidate the role of surface functionality in the context of contamination resistance. Studies have shown that the location of functional groups in relation to the position of the approaching particle or contaminant has a significant effect on the particle-surface interactions [47-49, 51, 101]. Functional groups located directly between the particle and surface endure a strong compression upon approach which in turn induces an opposing repulsive force and renders the surface contamination resistant [49]. However, an increase in dispersive interactions may be evident if functional groups are positioned away from the particle i.e. not directly between particle and surface [51]. Our simulations explain the experimental observations which suggest that these steric effects, and in turn interfacial adhesion [102], may be further influenced by the mechanical properties of the substrate [95]. The soft outer-layer in Class A systems, typically
found on non-surface-crosslinked polyester, displays significant elastic deformation. The surface functional groups of these soft films therefore exhibit significant mobility [49] which in turn negates their steric repulsions. This explains why functionalisation of non-surface-crosslinked polyester leads to only limited improvement in contamination resistance.

Functionalisation of non-elastic Class B and C films, such as those that have been surface crosslinked, leads to a completely different behaviour. They show limited surface mobility during contact with the particle due to an increase in the Young’s modulus, which in turn enhances the steric effects and exposure of functional groups. These films also provide a stable platform for incorporation of surface modifiers that would otherwise migrate into the bulk material upon aging [50, 51]. However, the induced stress between the particle and functional groups may be alleviated via lateral displacement of surface crosslinks, provided that the crosslinks are commensurate with the incoming particle. This behaviour is common to the stiff surface regions of Class B, typically found on surfaces crosslinked with a cyclic curing agent, such as IPDI. These surfaces are characterised by local regions of hardness [52] while the underlying substrate remains rather deformable. As the contaminant adheres to the crosslinked region, the mobility of the underlying substrate allows for significant lateral displacements (plastic deformation) of the rigid crosslink molecules (IPDI), which in turn exposes the non-surface-crosslinked regions, leading to notable secondary adhesion with the particle. This results in a significant reduction in the surfaces contamination resistance.

Tough regions like those of Class C, also display limited surface mobility, yet exhibit an ability to resist significant surface displacement (plastic deformation). Class C surfaces would be typically crosslinked with flexible acyclic crosslinks (HDI), which have been shown to increase hardness over greater surface depths in comparison to IPDI [52], resulting in a more stable platform for grafting surface modifiers. When functional groups are added to
these tough regions along the surface, steric effects are not only enhanced but endured, leading to superior contamination resistance.

Figure 14. Percentage distributions of classes for indentation of modified crosslinked surfaces.

Figure 15. Average work of adhesion energy ($W_{adh}$) and equilibrium separation ($d_0$) for each class.
3.5 Conclusion

In this section, simulation of the nanoindentation process was carried out on functionalised-crosslinked and functionalised-non-surface-crosslinked polyester, to determine the effectiveness of these modifications on improving contamination resistance. Adhesion parameters and surface characteristics were determined, including the work of adhesion, equilibrium separation, surface roughness, surface densities and surface morphology. Our results suggest that neither hydrophobic (F) nor hydrophilic (OH) functionalisation of soft non-surface-crosslinked polyesters result in significant improvement in contamination resistance. The soft surface allows for significant re-arrangement of the functional groups during approach of the contaminant particle. Deformation of the surface hinders the exposure and negates steric repulsions of the functional groups, which are considered important in preventing undesirable adhesion. Slippage of the outer-most surface layers during loading, a common behaviour for a surface crosslinked with cyclic rigid curing agents, also negates the effects of the grafted segments, as it effectively positions functional groups away from the incoming particle. In contrast, functionalisation combined with flexible acyclic crosslinks results in superior contamination resistance. Crosslinks of this type render the surface tough providing a more stable platform for grafting surface modifiers and as a result, the effects of functionalisation are not only enhanced but endured. These findings provide guidance and design criteria for a rational engineering of stable contamination resistant surfaces.
4. Molecular simulations of responsive surfaces

4.1 Overview

We have described in the previous section that while modification using surface crosslinking combined with functionality imparts contamination resistance to the surface, it also results in a coating that is far too brittle. This is a competing factor when dealing with coated steel products which needs to remain flexible during rolling processes. Therefore we revisited natural self-cleaning surfaces which use flexible brush like formations to remain clean. Depending on the composition of these brush formations and intended environment, they may also display responsive behaviour, and therefore display a potential to remain clean in a more diverse range of environments. This is the motivation behind the use of poly(ethylene glycol) (PEG) as a surface protector.

In this section we present a molecular dynamics study investigating the humidity induced de-swelling and swelling of PEGylated surfaces at various temperatures. PEG chains grafted onto silica substrates exhibit dehydration induced collapse that is far more pronounced compared to those grafted onto polyester. The difference between the silica and polyester substrates is particular notable at low coverage densities where the chains are adequately isolated from one another. PEG chains grafted onto silica generally display an “extended” to “mushroom” transition during dehydration, with the extent of collapse reduced at temperatures close to the low critical solution temperature (LCST). When the dried films are immersed in water they exhibit negligible swelling, indicating a slow response to solvation after the chains have collapsed onto the surface in dry environment. Compared to polyester however, silica based substrates display a finite degree of swelling at PEG coverage densities of 0.20-0.54 chains per nm$^2$ which represents the lowest density enabling penetration of water through the grafted film.
4.2 Introduction

One of the most successful approaches in protecting solid surfaces from contamination or other undesirable adhesion is through poly(ethylene glycol) (PEG) or (PEO) grafting (Figure 14). PEG displays a unique ability to change conformation in response to various triggers [103] which in turn can assist in excluding foreign materials such as organic contaminants including proteins, from its proximity [104, 105]. Experimental work by Sheparovych et al. examined composite polyethyleneoxide PEO surfaces using AFM in both air and water environments to calculate adhesion between samples surface and AFM tip [40, 41]. The authors developed responsive mixed brush films with low adhesive properties in different media, where the mixed brushes display layer segregation in air and water. Major findings showed that in water PEO dominates the outer layer while in air polydimethylsiloxane (PDMS) dominates. Furthermore, the low interfacial energies of PEO in water and PDMS in air combine to generate a low adhesive property of the mixed brush PEO-PDMS in both media by the spontaneous rearrangement of polymer chains. Studies have shown that PEG molecules grafted onto metal substrates using surface-initiated polymerization reduce cell adhesion [106, 107]. This surface-initiated polymerization technique has the advantage of attaining a high grafting density and film thickness, factors which are considered important in controlling undesirable adhesion. Silanated PEG molecules have also been grafted onto glass substrates using solution-based techniques, again resulting in reduced cell adhesion [108]. These examples illustrate that PEG’s unique ability to reject proteins and other contaminants combined with its non-toxic and anti-genetic properties is a justification of its extensive use as a surface protector for biomedical and industrial applications.
It is believed that the protein-rejecting property of PEG is associated with two main mechanisms [109]: steric repulsions and hydration via formation of a structured water layer. However, these models present an incomplete description of a more complex reality since adhesion of proteins, contaminants or other foreign materials is influenced by many parameters. Firstly, the chemistry, morphology and mobility of the underlying substrate collectively define the extent to which a surface can resist adhesion [110]. For example, single-chain mean field theory has been used to investigate protein adsorption on PEGylated substrates [111, 112]. Adsorption trends were shown to be influenced by interactions between substrate and grafted PEG chains in agreement with experiment [111], with these interactions playing an important role in the conformation and stability of the grafted layer [113]. In a recent study, a pre-treatment procedure was introduced to remove low molecular weight non-crosslinked polymeric chains from the surface of the substrate prior to PEGylation [114], with the aim of improving the long-term stability of the grafted PEG chains. Furthermore, it has been demonstrated that the ability of PEG to protect a solid surface is dependent on its molecular weight and grafting density [115]. Taking these factors into consideration and PEG’s extensive use as a surface protector, a better understanding of the fundamental behaviour of PEG chains grafted on different substrates at the atomic level is essential.
Experimentally, density profiles and conformational states of PEG grafted layers have been measured using neutron reflectivity [116, 117] and x-ray photoelectron spectroscopy [118]. Atomic force microscopy has also been used to investigate the conformational of grafted PEG films [118-120]. However experimental characterisation of the dynamic behaviour of PEG is limited by its small length scale and extreme flexibility [119]. This hurdle is particularly prevalent in the case of low molecular weight PEG oligomers (e.g. pentamers) which are of particular interest for self-cleaning surface design. The difficulty in experimental characterisation combined with the desire to better understand the surface grafted behaviour of this ‘popular’ polymer has instigated the use of computational modelling and in particular classical force-field molecular dynamics [43, 121-124]. However, the majority of molecular dynamics studies have so far concentrated on the conformation, chain dimension and overall behaviour of isolated PEG chains in solution. To the best of our knowledge, there has been no fully-atomistic molecular dynamics study investigating the hydration induced transition of low molecular weight grafted PEG chains.

In this work, we use force-field molecular dynamics to investigate the hydration induced response of PEGylated substrates at various temperatures. Substrates included inorganic and organic films in the form of silica and polyester respectively, with various PEG coverage densities examined. These interfaces are prominent in both biological and non-biological systems [125], as shown by some of the examples described above, and understanding the behaviour and interactions in these systems at the nanoscale [85, 126, 127] will facilitate design of responsive surfaces for applications in chemistry, biology and medicine.
### 4.3 Computational Details

#### 4.3.1 Models of PEG grafted silica and polyester substrates

The inorganic substrate used for PEGylation is a realistic model of a vitreous silica surface [46, 48, 50, 128-132], containing terminal hydroxyl groups at a density of 4.2 OH groups per nm$^2$. This represents a highly hydrated silica surface as a fully hydrated surface contains a silanol density of ~5.0 OH groups per nm$^2$ [133]. The silica substrate displays a density of 2.6 g per cm$^3$ (comparable to experiment), an average film thickness of 17 Å (in the z direction) and lateral dimensions of 27 Å (in both x and y directions). The film was packed in a periodically replicated three-dimensional cell (PCB). For all subsequent simulations the surface OH groups remained free to move, while the underlying SiO$_2$ atoms were kept fixed (constrained) at their initial x, y and z coordinates.

The polyester substrate employed for PEGylation comprised polyester chains that contain 15 units of 2-butyl-2-ethyl-1,3-propanediol, 2 units of trimethylolpropane and 16 units of isophthalic acid. Tributoxymethyl-melamine crosslinks were reacted with polyester chains to form the polyester substrate. Details of the construction procedure can be found elsewhere [45]. The polyester substrate exhibited a density of 1.3 g per cm$^3$, compatible with experiment, an average film thickness of 15 Å, equilateral dimensions of 37 Å in the x and y directions, and was packed in a three dimensional cell with PBC. Unlike silica, the polyester model lacks hydroxyl groups at the outer surface layer and therefore an initial attachment of hydroxyl residues onto polyester substrates was required [49, 52, 78], enabling subsequent covalent tethering of PEG derivatives [6].

PEGylation of both silica and polyester substrates was undertaken via a condensation reaction, fusing the oxygen of surface hydroxyl (OH) groups, with terminal oxygen of the PEG molecule, in line with experiment [6]. To incorporate PEG functionality to the polyester surface, the “grafting from” and “grafting to” approaches were considered. To
simulate a “grafting from” method, whereby PEG chains are grown from all available nucleation sites [134], PEG molecules were attached to all available surface OH groups on the polyester substrate, leaving no OH groups unreacted. In contrast, for the “grafting to” method, fully grown chains typically react with only a portion of available nucleation sites [57], and therefore the PEG molecules were attached to randomly identified OH groups on the polyester surface, leaving a portion of unreacted OH groups. The “grafting to” approach was also employed to generate PEGylated silica models.

The PEGylated polyester and silica substrates that have a finite number of OH groups unreacted (“grafting to” approach), are denoted PolyOH-σPEGₙ and SiOH-σPEGₙ respectively, while Poly-σPEGₙ denotes PEGylated polyester surfaces that have zero OH groups unreacted, attained from the “grafting from” method. The parameter σ represents the grafting density of PEG chains in units of PEG molecules per unit area, and the subscript (n) represents the degree of oligomerization. We examined varying grafting densities, by tethering PEG pentamers (n=5) which displays a free chain radius of gyration of ~4.8 Å and PEG octamers (n=8) with a radius of gyration of 6 Å [43] to polyester at a surface density ranging 0.29-1.00 PEG/nm², while for silica a coverage density range of 0.13-0.94 PEG/nm² was considered. A summary of all substrates examined is presented in Table 2.
Table 2. Summary of examined substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Description</th>
<th>Unreacted OH coverage density (OH groups per nm$^2$)</th>
<th>PEG coverage density (PEG per nm$^2$)</th>
<th>PEG chain length</th>
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</thead>
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<tr>
<td>Poly-σPEG$^5$</td>
<td>PEGylated polyester without OH sites</td>
<td>n/a</td>
<td>0.29-1.00</td>
<td>5</td>
</tr>
<tr>
<td>Poly-σPEG$^8$</td>
<td>PEGylated polyester without OH sites</td>
<td>n/a</td>
<td>0.29-1.00</td>
<td>8</td>
</tr>
<tr>
<td>PolyOH-σPEG$^5$</td>
<td>PEGylated polyester with OH sites</td>
<td>4.36-5.07</td>
<td>0.29-1.00</td>
<td>5</td>
</tr>
<tr>
<td>PolyOH-σPEG$^8$</td>
<td>PEGylated polyester with OH sites</td>
<td>4.36-5.07</td>
<td>0.29-1.00</td>
<td>8</td>
</tr>
<tr>
<td>SiOH-σPEG$^5$</td>
<td>PEGylated silica with OH sites</td>
<td>3.23-4.04</td>
<td>0.13-0.94</td>
<td>5</td>
</tr>
<tr>
<td>SiOH-σPEG$^8$</td>
<td>PEGylated silica with OH sites</td>
<td>3.23-4.04</td>
<td>0.13-0.94</td>
<td>8</td>
</tr>
</tbody>
</table>
4.3.2 Computational Details

Inter- and intra-molecular interactions were evaluated using the COMPASS force field [57], which was previously optimised for the simulation of condensed phase polymers and organic/inorganic interfaces. The COMPASS force field has also been demonstrated to predict cohesive properties of an extensive number of polymers including polyethylene glycol oligomers [135]. Energy minimisation was performed to relieve any induced strains prior to MD of all simulations and a flexible simple point charge (SPC) model [57] was used for the water molecules. For energy minimization, non-bonded interactions were calculated using the Ewald procedure with an accuracy of 0.01 kcal mol\(^{-1}\) and an update width of 1.0 Å. The conjugate gradient algorithm was used for energy minimization, with an energy convergence criterion of 0.01 kcal mol\(^{-1}\) Å\(^{-1}\). For MD procedures, non-bonded interactions were calculated using the atom-based summation method with a cutoff radius of 15.5 Å, a spline width of 5.0 Å and a buffer width of 2.0 Å. A long-range vdW tail correction was applied for non-bonded interactions larger than the cutoff radius. A 1.0 fs time step was used for the NVT dynamics, utilising the Andersen thermostat [74] to control the temperature with a collision ratio of 1.0. All systems were equilibrated by ensuring that no energy drifts occur during the data collection stage of MD. The change in chain height \(\Delta h\) was averaged over the final 1 ns of equilibrium MD.
4.3.3 Simulating the hydration induced response of PEG grafts

Having prepared the PEGylated substrates, we then utilized a molecular dynamics (MD) procedure that emulates the wetting (hydration) and drying (de-hydration) of the grafted films [134]. In this work we use a water environment to represent a fully hydrated state and a vacuum environment to emulate a de-hydrated state. PEG chains were initially aligned in an extended direction normal to the surface plane prior to MD in a hydrated state, where a ~20 Å water layer was added above each substrate with water density of 1 g cm⁻³, as shown in Figure 17a and 15d. A ~30 Å vacuum spacer was also added above the water layer. Simulation of these systems was then undertaken via MD for 2 ns at a temperature of 298 K and 370 K. After simulations in the water (W) environment, the PEG chains were subjected to dehydration conditions by removing the water molecules and undertaking MD of the PEGylated films in a vacuum (V) environment. A schematic diagram of the setup is shown in Figure 17b and 15e. Simulation of these systems was again undertaken via MD for 2 ns at a temperature of 298 K and 370 K. Once simulated in the vacuum environment, the resultant systems were transitioned back to a fully hydrated environment (Figure 17c and 15f) by undertaking molecular dynamics in water for 2 ns at temperatures of 298 K and 370 K. This change of simulation environment mimics an experimental study that exposed surfaces coated with mixed PEO-PDMS brushes to air and water environments [40].
We monitored the height of the grafted PEG chains in both dry and wet environments. This height was defined as the vertical distance from the anchor point (reacted O atoms) to the uppermost atom of the PEG. A change in chain height ($\Delta h$) was then determined according to the following:

\[ \Delta h = h_w - h_v \]

where $h_w$ and $h_v$ represents the chain height in the water and vacuum states respectively.

During dehydration ($W\rightarrow V$ transition), a positive change in chain height ($\Delta h$) indicates a collapse of the grafted molecules, while the hydration induced transition ($V\rightarrow W$ transition)
is expected to result in swelling of the grafts. We also monitored the shape of the tethered PEG chains by calculating the radius of gyration in the xy plane as a function of distance from their individual anchor points in the direction normal to the surface (z axis). These profiles were then mirrored about the z-axis providing a visual representation of the chain conformation.

4.4 Results and Discussion

The majority of the results presented henceforth are focused on PEGylated pentamer surface, with octamer results in appendix of this thesis (AF2, AF3, AT4 and AT5). This has been undertaken to focus the discussion on qualitative trends common to pentamer and octamer systems. Any difference in behaviour observed between pentamer and octomer systems will be highlighted.

4.4.1 De-swelling of PEGylated surfaces

When the hydrated tethered PEG chains are subjected to dry conditions (W→V transitions), they exhibit a collapse manifested by a change in chain height (Δh). Figure 16 shows that the extent of collapse is strongly dependent on the chemical nature of the substrate. Grafted silica substrates demonstrate a significant collapse particularly within the low coverage density range (σ) of 0.13 – 0.5 PEG per nm². PEG chains grafted onto polyester substrates ("grafting to" or "grafting from") still exhibit a dehydration induced collapse, but far less pronounced compared to silica. The difference between the silica and polyester substrates is particularly notable at coverage densities below 0.5 PEG per nm² where the chains are adequately isolated from one another. This is in agreement with previous experimental studies which have suggested that in the low grafting density regime, the response of the grafted chains is strongly dependent on the nature of the substrate [136, 137]. The conformation of the chains is depicted in Figure 17 which displays the radius of gyration of
the chains in the xy plane, as a function of vertical distance from their anchor point. It can be seen from Figure 17a and b that the de-swelling of PEGylated silica can be characterised by two types of extreme conformational transitions during dehydration; an extended to mushroom transition at high grafting densities (0.94 PEG per nm$^2$) and an extended to pancake transition at low grafting densities (0.13 PEG per nm$^2$) [ref]. Slight oscillations are observed in the extended curves, Figure 17a, and possibly arise from slight variations in the radius of gyration measurements in the lateral plane. Furthermore, these variations increase as the chain form more brush like conformations and deviate away from a perfectly extended chain. Albeit this is consistent with the change in height values observed for silica at high and low grafting densities. In contrast, dehydration of PEGylated polyester (Figure 17c and d) is characterised by a slight collapse of the chains in the lateral direction and limited de-swelling perpendicular to the surface. Thus, PEG chains tethered onto polyester, display a globule-like conformation in both wet and dry environments which explains the limited response observed for these systems. These qualitative trends detected for pentamer chains were also observed for octamers, although for the latter, the collapse was greater due to the longer tethered segments (AF2).

![Graph](image.png)

**Figure 18.** Change in PEG height ($\Delta h$) during de-swelling as a function of coverage density for PEG$_5$ grafted substrates simulated at 298 K. Error bars represent the standard deviation.
Dehydration of the PEGylated films can also induce changes in surface morphology which can be quantified using root-mean-squared (RMS) roughness, obtained as previously discussed in Chapter 3 of this thesis [53, 138]. Presented in Figure 18 are the RMS roughness values for PEGylated films as they transition from an aqueous to dry environment. During this transition, we observe a decrease in surface roughness for silica based substrates, while for polyester we observe no notable change. Furthermore, the roughness of silica is consistently higher than for polyester in both wet and dry environments and across all coverage densities. This is despite the fact that the end-grafted chains on both silica and polyester can adopt globule-like conformations (see Figure 17b and d). Previous studies have shown [6, 53] that polyester is far more flexible than silica and is richer in surface irregularities. In fact the RMS roughness for silica is \( \sim 2.02 \, \text{Å} \), while for polyester it is \( \sim 2.20 \, \text{Å} \). Moreover the flexibility of the polyester substrate provides a means for the formation of surface cavities as previously discussed in Chapter 3 of this thesis [49, 138]. The natural flexibility of the polyester substrate allows for significant rearrangement of tethered chains, while asperities along the surface of the polyester provide ample volume for the tethered
chains to sink into. The end result is that PEG chains adopt a more compacted, denser arrangement on polyester compared to silica, in both aqueous and non-aqueous environments. To confirm this finding we present density profiles of PEGylated substrates in dry environments (Figure 19). The equivalent profiles for aqueous environments can be found in the appendix of this thesis (AT2). The solid lines in the profiles depict the atomic density along the perpendicular axis of the grafted films and the perforated lines mark the substrate/PEG interface boundary. Namely, the dashed line on the graphs depicts the density profiles of the underlying substrate without PEG. Furthermore, the zero distance on the graphs represents the outermost atoms of the surface layer. Along the solid line, the point at which the density begins to decrease marks the onset of the surface boundary, around ~15 Å for silica (A) and ~18 Å for polyester (B). For PEGylated polyesters, we observe that the tethered chains display a surface profile that overlaps the substrate boundary, indicating penetration of the polyester by the PEG chains. This overlap occurs from ~0 Å to ~15 Å for the PEGylated polyester systems and is particularly evident from the presence of polyester (perforated line) up to the outermost a layer. In contrast, the concentration profiles for PEGylated silica systems are characterised by a distinct peak away from the substrate boundary (around ~19 Å), associated with the protruding tethered chains (C) and an absence of the underlying silica (perforated line) from ~8 Å to the outermost layer, ~0 Å. Furthermore, for polyester surfaces, the concentration of atoms at the substrate-chains interface increases significantly, indicating a more compacted, denser surface film (B). These trends were also detected for octamer tethered chains which can be found in the appendix of this thesis (AF3 and AT5).
Figure 20. Surface RMS roughness as a function of coverage density during de-swelling for SiOH-PEG₅ (blue and red) and Poly-PEG₅ (green and purple). Simulated at 298 K in wet and dry environments.
Our simulations indicate that the dehydration induced collapse of PEG, is dependent on temperature. Specifically at 370 K, the extent of collapse is reduced relative to the room temperature transition (Figure 20), and this is particularly prevalent for octamer tethered chains (see Figure 20a). This behaviour is observed for both silica and polyester grafted films and is associated with the conformation of the grafted chains in water. At 370 K, the chains adopt a partially collapsed state in water (Figure 21a) while at 298 K, they display a much more extended chain conformation (Figure 21b). This temperature induced collapse, is a result of expulsion of interfacial waters and the breaking of intermolecular hydrogen bonds between water and PEG segments. This is shown in Figure 22 where we observe an increase in the inter-molecular hydrogen bonding between water and PEG chains for systems simulated at 298 K in comparison to systems simulated at 370 K. Such temperature sensitive solubility usually originates from the existence of a lower critical solution temperature (LCST) beyond which the polymer becomes insoluble in water. PEG has indeed been shown to exhibit a low critical solution temperature of \( \sim 371 \) K [139], which is one of the temperatures explored in our simulations (370 K). Interestingly, the LCST has been shown to decrease with increasing molecular weight [139, 140], which explains why the octamer tethered chains are more sensitive to this temperature induced transition compared to their pentamer counterparts (Figure 20b).

![Figure 21. Atomic density profiles of PEGylated silica (a-c) and polyester (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG, chains and simulated in vacuum at 298 K.](image-url)
Figure 22. Change in PEG height ($\Delta h$) for $W\rightarrow V$ transition as a function of coverage density for (a) SiOH-$\sigma$PEG$_5$ and (b) SiOH-$\sigma$PEG$_8$ systems simulated at both 298 K and 370 K. Error bars represent the standard deviation.

Figure 23. Radius of gyration profiles for PEG in the lateral (x-y) plane as a function of (z) for PEGylated silica during de-swelling in water at (a) 370 K and (b) 298 K for low, intermediate and high coverage densities.

Figure 24. Average number of inter-molecular H-bonds per PEG between available donor-acceptor pairs in PEG and water as a function of coverage density for SiOH-$\sigma$PEG$_8$ systems simulated at 298 K and 370 K.
4.4.2 Swelling of PEGylated surfaces

We note that the simulations were carried out in sequence, by first simulating the dehydration induced collapse of the tethered chains, followed by swelling of the chains as they transition from a dry to aqueous environment. When the dried films are immersed in water they exhibit negligible swelling within the timeframe of our simulation (Figure 23), indicating a slow response to solvation after the chains have collapsed onto the surface in dry environments. This is particularly the case for PEGylated polyesters. It appears that the energy requirements for reversible response depend on the initial physical state of the system. We reason that the water extended brushes exhibit a quick collapse when dehydrated. This collapsed layer forms a densely packed zone near the substrate which slows down diffusion of water into the film. This is shown in Figure 24a where we observe an increase in the density of water near the PEG film boundary, the penetration of water into the PEGylated polyester provides a coexistence region of 15 Å. In comparison prior to de-swelling (Figure 24b) we observe water molecules moving deeper into the film, this provides a coexistence region of 17 Å. For silica based substrates a finite degree of swelling is observed at PEG coverage densities of 0.20-0.54 PEG per nm$^2$ where the film presents a relatively low density, promoting diffusion and penetration of water through the grafted film (Figure 24c). In comparison, at higher coverage densities of 0.94 PEG per nm$^2$ (Figure 24d) a densely packed PEG layer near the substrate again suppresses water diffusion into the film; this is presented as an increase in water concentration near the PEG film boundary. We stress that this collapsed layer under an aqueous environment most likely does not correspond to equilibrium but constitutes a kinetically trapped conformation of the layer
within the time-frame of our simulation that were extended to 40 ns for V→W transition and still did not reach equilibrium.

Figure 25. Change in PEG height (Δh) during swelling as a function of coverage density for PEGs grafted substrates simulated at 298 K. Error bars represent the standard deviation.

Figure 26. Atomic density profiles of PEGylated polyester (a, b) and silica (c, d) at intermediate (a, b and c) and high (d) coverage densities. PEGylated with pentamer chains and simulated in water during swelling (a, c and d) and de-swelling (b) at 298 K.
4.4.3 Optimal PEGylated surface for contamination resistance?

A previous study employed micro cantilevers to monitor conformational changes in grafted PEG layers for different solvent conditions [141]. In a good solvent environment, the PEG chains adopted an extended conformation which in turn resulted in long-range repulsive interactions with the incoming particle while in a poor solvent environment PEG adopted a collapsed form, which resulted in a weak repulsion. In light of these experimental observations and the results presented here, we can suggest that silica grafted with PEG pentamers at a coverage density of ~0.54 PEG/nm² presents the most promising candidate for the design of a contamination resistant coating. For this particular system, the grafted chains display a transition from extended to globular during dehydration and are stable even under high temperature (370 K). They also exhibit a finite degree of swelling during subsequent wetting. Quite importantly for this system, the surface roughness is maintained in both aqueous and dry environments, which can ensure a repulsive behaviour.
4.5 Conclusion

In this molecular dynamics study we investigated the responsive behaviour of various PEGylated substrates during wetting and drying. The substrates tested include flexible organic polyesters and a rigid inorganic silica surface tethered with PEG chains. The results of our simulated procedure that emulates transition from wet to dry environment showed that when PEG is attached to a rigid substrate it exhibits a significant de-swelling behaviour. This was primarily attributed to the rigidity of the underlying substrate. In contrast PEG attached to the flexible polyester substrates resulted in a significant collapse in both wet and dry environments, which in turn resulted in limited hydration/dehydration response for these systems. In addition, we have demonstrated that these substrate effects were found to be more pronounced at coverage density where the chains are adequately isolated from one another. Finally at high temperatures, the extent of de-swelling was reduced specifically at a temperature close to the low critical solution temperature of PEG attributed to the breaking of inter-molecular hydrogen bonds between PEG and water. We suggested that silica grafted with PEG pentamers at intermediate coverage densities presented the most promising candidate for the design of a contamination resistant coating. This study was able to provide insights into the mechanisms behind responsive behaviour of PEG-grafted surfaces at the atomistic scale during the exposure to external environmental triggers (wetting/hydration).
5. Conclusion

Self-cleaning surfaces found in nature provide grounds for a biomimetic approach to coating design. These natural self-cleaning surfaces predominantly employ superhydrophobicity and superhydrophilicity to remain clean. The surface wettability of a manufactured coating can be controlled through the addition of hydrophobic or hydrophilic functional groups. Adaptive surfaces have the ability to transition between hydrophobic and hydrophilic states and have the potential to remain clean in a more diverse range of environments. A detailed knowledge of the molecular structure and dynamics is critical for the successful design of self-cleaning coatings. Atomistic simulations provide a useful tool to gain such insight and help design surfaces where stay-clean properties are highly desirable. Here, using classical molecular mechanics and dynamics we explored the properties of polymer surfaces in order to understand design requirements for self-cleaning industrial paint coatings. A crosslinked polyester surface model was functionalised, based on hydrophobic or alternatively hydrophilic surface treatments of a realistic cured paint coating. We demonstrated that the deformation of the surface disrupts the contamination resistant properties imparted by crosslinking and functionalisation. Functionalisation of surfaces that were able to resist deformation resulted in a notable ~27% reduction in adhesion. These tough surfaces provided a more stable platform for grafting surface modifiers and as a result, the effects of functionalisation were not only enhanced but endured. While modification using surface crosslinking combined with functionality imparts contamination resistance to the surface it also results in a coating that is far too brittle. We also revisited natural self-cleaning coatings in nature which use responsive brush like formations to remain clean. The natural flexibility of the polyester substrates allows significant rearrangement of tethered chains. We
concluded that silica grafted with PEG pentamers at intermediate coverage densities presented the most promising candidate for the design of a contamination resistant coating.

6. Appendix

TABLE CAPTIONS

AT1 : Loading curves for each indentation, including class (Soft, Stiff or Tough). Series abbreviations refer to surface crosslinking type (H – hexamethylene di-isocyanate, I – isophorone di-isocyanate and P – non-surface-crosslinked), functionalization type (F – fluorine, O – hydroxyl) and indented region (A, B, C, D, E).

AF1 : Percentage distributions of Classes for indentation of unmodified crosslinked surfaces.

AF2 : Change in PEG height (∆ℎ) during de-swelling as a function of coverage density for PEG₈ grafted substrates simulated at 298 K. Error bars represent the standard deviation.

AF3 : Surface RMS roughness as a function of coverage density during de-swelling for SiOH-οPEG₈ (blue and red) and Poly-οPEG₈ (green and purple). Simulated at 298 K in wet and dry environments.

AT2 : Atomic density profiles of PEGylated silica (a-c) and polyester (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG₅ chains and simulated in water at 298 K in an extended state (water for the W→V transition).

AT3 : Atomic density profiles of PEGylated silica (a-c) and polyester (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG₅ chains and simulated in water at 298 K in a collapsed state (water for the V→W transition).
AT4 : Change in PEG height ($\Delta h$) for $W \rightarrow V$ transition as a function of coverage density for PEG$_5$ systems (a) SiOH-oPEG$_5$ (b) PolyOH-oPEG$_5$ and (c) Poly-oPEG$_5$ simulated at 298 K and 370 K. Error bars represent the standard deviation.

AT5 : Atomic density profiles of PEGylated silica with octomer chains in water for $W \rightarrow V$ transition (a-c) and $V \rightarrow W$ transition (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG$_8$ chains and simulated in water at 298 K in a collapsed state (water for the $V \rightarrow W$ transition).

AT1. Loading curves for each indentation, including class (Soft, Stiff or Tough). Series abbreviations refer to surface crosslinking type (H – hexamethylene di-isocyanate, I – isophorone di-isocyanate and P – non-surface-crosslinked), functionalization type (F – fluorine, O – hydroxyl) and indented region (A, B, C, D, E).
AF1. Percentage distributions of Classes for indentation of unmodified crosslinked surfaces.

AF2. Change in PEG height ($\Delta h$) during de-swelling as a function of coverage density for PEG$_8$ grafted substrates simulated at 298 K. Error bars represent the standard deviation.

AF3. Surface RMS roughness as a function of coverage density during de-swelling for SiOH-PEG$_8$ (blue and red) and Poly-PEG$_8$ (green and purple). Simulated at 298 K in wet and dry environments.
AT2. Atomic density profiles of PEGylated silica (a-c) and polyester (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG_5 chains and simulated in water at 298 K in an extended state (water for the W→V transition).
AT3. Atomic density profiles of PEGylated silica (a-c) and polyester (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG₅ chains and simulated in water at 298 K in a collapsed state (water for the V—W transition).
AT4. Change in PEG height ($\Delta h$) during de-swelling as a function of coverage density for PEG$_2$ systems PolyOH-σPEG$_n$ (a and c) and Poly-σPEG$_n$ (b and d). Simulated at 298 K and 370 K. Error bars represent the standard deviation.

![Graphs showing change in PEG height vs coverage density for PolyOH-σPEG$_n$ and Poly-σPEG$_n$ systems at 298 K and 370 K.](image-url)
AT5. Atomic density profiles of PEGylated silica with octamer chains in water for $W \rightarrow V$ transition (a-c) and $V \rightarrow W$ transition (d-f) at low (a and d), intermediate (b and e) and high (c and f) coverage densities. PEGylated with PEG$_8$ chains and simulated in water at 298 K in a collapsed state (water for the $V \rightarrow W$ transition).
7. References


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