Direct Polymer Grafting as a Method of Maintaining the Mechanical Properties of Cellulose Nanocrystals in the Presence of Moisture

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Cellulose nanocrystals (CNCs) are a distinctive nanomaterial derived from cellulose, the most abundant natural polymer on Earth, and the primary reinforcing structural component of cellulose fibrils found within the plant cell wall. These nanocrystals exhibit mechanical properties comparable to synthetic aramid fibers but are advantageous as they are biodegradable, renewable, and can be produced sustainably as they are predominantly extracted from naturally occurring cellulosic materials. These qualities make it a sustainable, highly renewable and environmentally friendly material to be used in place of synthetic materials in a variety of applications. With their high surface area to volume ratio, low level of defect, impressive mechanical stiffness and potentiality for engineered surface chemistries, CNCs have been exploited to develop cheaper, renewable nanocomposite materials with unique capabilities. In these nanocomposites, CNCs serve as the reinforcing filler phase within a synthetic polymer matrix such as acrylic glasses or polystyrene foams. While nanocomposites have been fabricated with CNCs as the reinforcing phase, a number of challenges have presented themselves, including poor dispersion of CNCs and degradation of mechanical properties upon exposure to moisture. One method to address these shortcomings is surface modification of CNCs to inhibit
their hydrophilic nature via direct grafting of synthetic polymer chains in an effort to create high-performance nanocomposites while maintaining moisture-resilient mechanical properties. In this work, the effect of polymer grafting on individual CNCs is investigated using fully atomistic molecular simulation. Using Grand Canonical Monte Carlo (GCMC) simulations, the effect of polymer grafts on moisture adsorption is explored to determine how grafting parameters such as polymer chain length, grafting density, and polymer species impact the adsorption characteristics of CNCs.
NORTHERN ILLINOIS UNIVERSITY
DE KALB, ILLINOIS

AUGUST 2019

DIRECT POLYMER GRAFTING AS A METHOD OF MAINTAINING
THE MECHANICAL PROPERTIES OF CELLULOSE
NANOCRYSTALS IN THE PRESENCE
OF MOISTURE

BY

MARY BREEN-LYLES
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A THESIS SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE
MASTER OF SCIENCE

DEPARTMENT OF MECHANICAL ENGINEERING

Thesis Director:
Robert A. Sinko
ACKNOWLEDGEMENTS

I first would like to thank my research advisor, Dr. Robert (Bobby) Sinko, for all of his guidance and unwavering patience. His expertise in this area and many insights were beyond indispensable, and I am very grateful to have had the opportunity to work with him on this project. I could not have completed it if not for his continuous support of my work in his research area.

I also want to thank my other committee members, Dr. John Shelton and Dr. Kyu Taek Cho, for their advice and their much-appreciated committee participation.

In addition, I need to thank my peer and lab-mate Scott Bishop for all of his help with updating the laboratory computers with the necessary software - an invaluable contribution that certainly expedited the process of obtaining data for this research.

Last, I want to thank my favorite human, Kurt Waldowski, for not only giving incredibly useful advice and help in writing some of my Python scripts for data extraction and organization but also for his endless love and support throughout my time working on this project.
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CHAPTER 1

INTRODUCTION

In the following sections, the concept of composite materials, the functionality of nanocomposite materials, bioinspired materials, cellulose and the nanocrystalline structures it can form, and their applications in novel materials research, as well as the concept of polymer grafting and how it can be applied in this research area, will all be examined. The relevance of these topics to the research discussed in this paper will be touched on in detail, and this introduction should serve as a basic background for the larger topics and research areas that this project concerns.

1.1 Nanocomposites

The influence of nanocomposite materials in the field of materials science is broad and indispensable. The barest bones reduction of the purpose and importance of nanocomposites is that materials with structure at the nanoscale often exhibit novel and unique optical, mechanical, electronic, or thermodynamic properties that are not otherwise present in many traditional composite materials. Simply adding structure at the nanoscale can lead to massive improvements in macroscale properties. Polymer nanocomposites are multiphase solids with at least one phase on the nanometer scale (in the case of cellulose-reinforced composites, that phase would be \( \sim 1-50 \) nm in size for the cellulose), and the mechanical performance of the material is enhanced after a nanoparticulate filler is added [1]. This added material is often referred to as the “reinforcing phase” since it is the addition of this nanophase that ultimately leads to the performance
enhancement in the host material – known as the matrix. The primary reason for the improvement is due to the increased surface area to volume ratio due to the very small (nano/microscale) filler. The reinforcing phase can be made up of fibers, sheets, or particles, all of which are embedded within the bulk matrix. Common matrix materials include polymers, ceramics, and metals. The material enhancement can also, in part, be attributed to the fact that the addition of a nanoscale phase adds a form of structural hierarchy to the material, a secondary phase on a different order of length scale, making it more resistant to deformation and dislocation [1], [2].

The failure rate of such composites is directly affected by the distribution of stresses over the material, as well as the bond distribution throughout the material, making the distribution of the reinforcing phase particularly influential [3]. The routine corrosion of conventional metal, for example (and especially) when used in oil and gas pipelines, is reason enough for nanocomposite development to be made a priority. The high failure rate of traditional materials is another marker of the importance of nanocomposite research. The promise of the nanocomposite material lies in its low defect and failure rate and mechanical and physical properties more diverse and vastly superior to those of traditional grain materials.

1.2 Bioinspired Materials Design

The development of nanocomposite materials has become a cost-effective alternative to many traditional materials for achieving properties that would otherwise not be found in their constituent parts [4]. Right now, the abundance of non-sustainable, non-biodegradable materials poses a direct threat to the environment. To combat the changing environment, it will be
important to focus research on creating stronger, more sustainable materials as well as a sustainable means of developing those materials. Bioinspired design is used in many research areas outside of materials design, such as robotics, sensing, catalysis, optics, and architecture, but the introduction of biological design concepts into the field of engineering materials has led to development of many new high-performance materials using multiple composite types and experimental settings [2], [5], [6], [7], [8]. Research into this topic has also led to improved identification and characterization and more refined understanding/quantification of natural design parameters [5].

With the information that nanoscale structure yields vastly different and often outstanding improvements in the mechanical and physical properties of materials, many researchers turn toward the natural world for inspiration for the innovation of new nanomaterials. It is clear that over millennia, the material properties of natural biological systems and structures have had more than ample time to evolve and transform into the many diverse and mechanically impressive natural materials we study today. They often have their own naturally occurring structures at the nanoscale, generously improving their overall value and application as a material in nature. Investigations into the structure-function relationships within naturally resilient biological materials have given more insight into those structural patterns that yield an ideal material design; thus the processing methods for obtaining such an ideal design can be developed [5].

One such pattern found in naturally strong biological materials that facilitates their strength is a heterogeneous microstructural architecture, allowing the material to withstand non-uniform loads and fulfill a wider variety of mechanical demands [5]. This optimizes the building-
block geometry of the material, which will in turn maximize its functional properties [5]. The primary reason for this comes from a structural hierarchy within the material, with a controlled spatial distribution and orientation of the (micro)structure on multiple length scales [5]. Along with this hierarchy come both strong and weak tunable bonds that work together to spawn adaptable static properties in the natural material [5]. When an external stimulus is then applied to the material, there will be a cooperative response in the material on multiple length scales corresponding to the hierarchy. Hierarchical structuring leads to an increased compressive strength, greater suppression of buckling, and a general increase in the strength to density ratio of the material when higher orders of structural hierarchy are present [9]. One example of a biological material that utilizes this type of structural design is the mollusk shell, which achieves a fracture toughness about 10 orders of magnitude higher (meaning the energy required to cause a fracture is 2 orders of magnitude higher) than that of unstructured calcium carbonate (CaCO$_3$), the component accounting for 95% of the chemical composition of mollusk shell [5]. Another example would be bone, which has almost 10 times the fracture toughness of its unstructured primary phase, hydroxyapatite [5].

Biomimicry in polymer nanocomposites is necessitated by the fact that these superior microstructural design outcomes are rarely achieved by artificial, non-bioinspired polymer nanocomposites [5]. The exploitation of these nano/microstructural design parameters will enhance the mechanical properties of the overall composite in which they are applied [5]. Other properties that may be enhanced by instituting bioinspired design concepts in polymer nanocomposites include optical, magnetic, sensing, actuating, and interfacial adhesive properties
This project focuses on investigating potential design parameters of multiple types of cellulosic fiber-reinforced nanocomposites.

1.3 Cellulose Nanocrystals

The escalating price of crude oil and petroleum products has led to an increased demand for renewable and sustainable materials [10]. In many situations where a synthetic nanofiller is used, the same desired effects could be achieved or even improved upon by a more sustainable material - such as a modified form of cellulose. The superior material properties and abundance of cellulose make it an attractive candidate as a potentially cheap and structurally durable filler to be used in more sustainable polymer nanocomposites. These properties are especially impressive in cellulose nanocrystals (CNCs) and in fact either rival or surpass those of many synthetic materials [2]. Cellulose nanocrystals are derived from bulk cellulosic material, which is extremely abundant and can be easily obtained from trees, annual plants, tunicates, algae, and bacteria. CNCs are typically extracted via a process of acid hydrolysis [11]. Essentially, the process of acid hydrolysis hydrolyzes the amorphous regions of the cellulose fibers and develops reactive O-H side groups along the nanocrystal surface. This process simply utilizes a hydrogen-rich acid to catalyze a substitution reaction that adds hydrogen and oxygen atoms between two bonded atoms within the cellulose fibers, resulting in the dissolution of the amorphous regions and reactive hydroxyl groups along the surface of the CNC. Following this procedure, some further processing of the cellulose material is required for the cellulose microfibers to break up into CNCs, which are rod-like with a very high aspect ratio, are around 3-5 nm wide, 50-500 nm long, and about 54-88% crystalline [12]. Figure 1 shows the chemical makeup of a single cellulose chain repeat unit and microscopic image of a collection of CNCs.
Figure 1: Structural hierarchy of CNCs.

(a) Chemical structure of single cellulose monomer, showing intrachain hydrogen bonding along dotted lines, and C₁ and C₄ linkage; (b) cellulose microfibril configured in one of multiple potential configurations of crystalline/amorphous phases; (c) CNCs after the amorphous region is dissolved by the acid hydrolysis reaction; and (d) TEM-generated image of CNCs derived from wood. Source: Moon et al. [11].
Specifically, CNCs’ very high axial stiffness, high tensile strength, low thermal expansion and excellent thermal stability up to ~300 °C set them apart from more traditional cellulose-based materials [11]. Due to the abundance of cellulose in nature, cellulose fiber-based nanocomposites are inherently renewable. They can also be produced sustainably, and CNC fibers can replace man-made, unsustainable, harder to make, or more expensive fibers such as glass or Kevlar - in fact the elastic modulus of CNCs is comparable or greater than these [13]. The fibers can be extracted and processed very cheaply and also in large quantities [10], [12]. Additionally, producing CNCs and CNC nanocomposites has few environmental risks compared to other materials [12], very low health and safety risks [12], and low energy consumption [10]. They are low density, making them very lightweight, and their non-abrasive qualities mean that sliding wear in the host material will not be of much concern [10], [13]. Other versatile properties of CNCs make them an even more compelling potential nanofiller. For instance, they already serve as the primary reinforcing phase in many natural composites (e.g., wood). They are mechanically similar to Kevlar but with an even higher elastic and tensile strength and have few material defects due to their high crystallinity [13]. CNCs as a material already exhibit hierarchical structuring themselves, so their application as a nanofiller will lead to an even greater structural reinforcement in the composite [14]. Their high aspect ratio means a higher surface area to volume ratio, making them more likely to have better interfacial interactions as a nanofiller as well. Finally, the fact that their surfaces are peppered with reactive hydroxyl groups makes surface functionalization possible [10]. In addition to CNCs’ intrinsic stability, sustainability, and low health and safety risk, it would also be fairly inexpensive to process them on a large scale in massive quantities [11].
Cellulose nanocrystals are also capable of naturally self-assembling into chiral nematic films, a term used to describe a type of ordering in the assembly patterns of thermotropic liquid crystals, cellulose being one example of a thermotropic liquid crystalline material [2]. Liquid crystals are simply a state of matter with properties of conventional liquid coinciding with properties of solid crystal - flowing as a liquid but having a distinct crystalline molecular orientation. This chiral nematic phase generally occurs when the CNCs have been cast from a solution [2]. The chiral nematic microstructure, also known as the Bouligand structure, is a type of hierarchical ordering, or a form of structural hierarchy, that is also the primary microstructural makeup of bone as well as the dactyl club of the mantis or peacock shrimp, both frequently noted for their exceptional mechanical strength and toughness [8], [15]. In fact, the most commonly observed natural microstructural pattern found in biological materials is the Bouligand structure, seemingly nature’s evolutionarily selected solution for generating high-toughness materials out of materials that, absent of microstructural ordering, could be very weak indeed, such as the calcium carbonate in mollusk shell. This microstructure resembles a twisting helical pattern that is sometimes referred to as the “twisted plywood” structure, citing this observation. The fibers making up the microstructure exist in a system of layers, each consisting of parallel fibers, with each subsequent layer rotated by a fixed angle from the position of the preceding layer. A representation of this structure can be seen in Figure 2. The Bouligand structure aids in the toughening of these materials via shear wave filtering, crack twisting, and crack deflection and arrest [2]. Bouligand arrangement in CNC-reinforced polymer composites has been seen to improve both impact resistance and bending properties of the composite [2]. Additionally, like many composites, Bouligand-arranged CNC-reinforced composites experience deficient
interfacial compatibility and adhesion, and a solution to this problem proposed by multiple sources is to prepare films with polymer-grafted CNCs [2], [16], [17].

Figure 2: Bouligand structure [18].

CNCs have been applied in a variety of contexts, such as non-aqueous formulations, biosensing, catalysis, photovoltaics, drug delivery, filtering, antimicrobial applications, and of course, the primary context with which this project is concerned, composite material reinforcement. All of the previously mentioned properties of CNCs make them an excellent candidate as a nanocomposite reinforcer. The introduction of these nanocrystals as added fillers within multiple types of natural and synthetic polymers has already proven to be an effective means of modifying and improving composite mechanical and thermal properties, among other
properties [6], [11], [16], [17]. An interesting example of this involves the use of cellulose extracted from tunicates, commonly referred to as sea squirts. In the study conducted by Cao et al., the tunicate cellulose was added to epoxidized natural rubber (ENR) [6]. This combination was demonstrated to foster an improvement in mechanical properties as well as self-healing behavior in the rubber [6]. The introduction of dynamic hydrogen-bonded, supramolecular networks between the oxygenous groups within the ENR and the hydroxyl groups on the CNC surface, as well as chain inter-diffusion inside the rubber, promoted this self-healing and mechanical property improvement [6]. In other words, a good CNC-matrix interfacial interaction is the primary cause of the improvement in the material’s performance. There are ways of improving the interfacial interaction within other CNC-filled polymer composites as well, which in effect spawns a greater improvement in the composite mechanical properties and overall performance. These involve taking better advantage of the reactive hydroxyl groups on the CNC surface, in a similar way to how those hydroxyl groups facilitated performance improvement in the material in the Cao et al. study. This will later be discussed in greater detail.

As discussed in an earlier section, in order for a nanocomposite material to have reliable durability, the matrix-fiber interfacial bond strength must be maximized [3]. Again, cellulose fibers already have superior interfacial interactions within polymer nanocomposites compared with other common nanofillers, and one way to improve on this property even more for cellulose fibers would be to graft alike/identical polymer chains to the surface of the fibers, thus improving the cellulose filler’s compatibility with its polymer matrix.

Unfortunately, some of the usefulness of incorporating CNCs in structural materials is threatened by their tendency to experience structural decay when exposed to moisture, losing
much of their strength and toughness. CNCs are naturally hydrophilic (moisture retaining), which means that the reinforcement of a nonpolar polymer matrix is made much more difficult in the presence of any kind of moisture. In the presence of moisture, the previously exceptional mechanical properties of the cellulose-reinforced composite are significantly diminished due to the decline in the structural integrity of the cellulose fibers dispersed throughout the matrix [19]. This in turn reduces the fibers’ resistance to interfacial shearing stresses between the CNCs, leading to material defects [16]. Even when the material is dried after moisture exposure, the process of drying will lead to filler aggregation, worsening the mechanical performance of the composite as there will no longer be a uniform dispersion of the filler throughout the matrix [17]. This provokes both greater difficulty in attempted redispersion as well as a decline in mechanical performance [17]. As pointed out by Johnsy George et al., even though CNCs tend to maintain good dispersion within hydrophilic composite systems and are a broadly preferred reinforcing component, the primary challenge remains: it is difficult to achieve homogeneous dispersion within the polymer matrix and maintain good matrix-filler interaction. Directly modifying the surface properties of the CNC fillers can improve their compatibility with hydrophobic polymers, maintaining their positive benefits to the overall material structure [20]. To form a high-performance nanocomposite, one must select a nanoscale filler with significantly different functional properties and one that will be dispersed uniformly throughout the material [1]. Poor dispersion (clustering) of the filler creates structural defects within the composite, and for cellulose’s use as a filler, a functionalized surface is key for good dispersion and strong interfacial adhesion [16], [17], [21], [22].
Functionalization of the CNC surface has already proven to be an effective way to improve matrix-fiber dispersibility [3], [16], [17], [23]. This process uses ions or grafted molecules that exploit the reactive OH groups unique to the surface of CNCs, allowing different surface properties to be obtained [12], [16], [17], [22]. There are many benefits to this. Among them are enhanced dispersion within suspensions and polymer matrices, as mentioned; better control over the interfacial properties of the CNC, such as bond strength and adhesion; and an eased and expedited self-assembly process for the composite [3], [17], [19], [24], [25]. Additionally, a surface grafted with a polymer of a similar type should improve its dispersibility within the matrix even more [19], [24]. Polymer grafting is a technique that has been used extensively to improve the performance of inorganic fillers through the development of new surface interactions, and it has also been found that the size and topology of the nanoparticle to which the polymers are grafted plays an integral role in the ultimate polydispersity of the chains themselves and even in the particle’s ability to eventually disperse within the polymer matrix [26], [27], [28].

1.4 Polymer-Grafted Cellulose

Graft copolymerization, or polymer grafting, in general is a popular method of imparting new functional groups to polymer backbones in chemistry and materials research. This, in turn, leads to new mechanical properties in the resulting molecule that can be exploited for many diverse uses. Researchers are interested in graft copolymers partly due to the protection of the polymer backbone exercised by the grafted polymers, which gives rise to a host of new applications, including use as emulsifying or surface-modifying agents, interfacial compatibilizers within polymer blends, and as coating materials [29]. In fact, one of the most
often applied uses of graft copolymers is as these compatibilizers inside polymer blends and multiphase systems, and they have been shown to improve the properties of starch/polylactic acid blends to a greater extent than other conventional agents [30]. Polymer-grafted silica nanoparticles have also been successfully used as drug carriers, with the grafted copolymer acting as a gatekeeper at the porous regions of the silica nanoparticles [31]. This allows the drug to be loaded into the pores at low temperature when the copolymer conformation leaves the “gate” open, and when the pore entrances close at higher temperatures, the drug can then have a delayed release [31]. There are many other applications of graft copolymers and evidence of their usefulness in improving interfacial compatibility in polymer blends and as agents in surface modification of a primary polymer backbone. This is part of what makes polymer grafting so interesting in the context of CNC fillers applied to polymer matrices, in addition to the improvements they can add to the matrix-filler relationship discussed above.

There are two methods to explore when considering modification of the CNC surface: ion-exchanged surfaces and polymer-grafted surfaces. In one experimental simulation that tested the surface functionalization of CNCs using ions, it was found that the use of ions may result in greater aggregation of the CNCs within the matrix, causing poorer dispersion [17]. It was also found that the presence of moisture for the ion-shielded CNCs reduced the interfacial adhesion between CNC and polymer [17]. However, in this study, it was noted that MePh₃P⁺-exchanged CNCs did, in fact, have reduced adsorption of water molecules to the CNC [17].

Polymer-grafted surfaces should theoretically be able to overcome some of the shortfalls of using ion-exchanged surfaces for several important reasons. It is possible that the use of polymer-grafted surfaces instead of ion-exchanged surfaces would help with the issue of
interfacial adhesion as a polymer composite is more likely to have increased interaction with a material more like itself, and the improvement in filler dispersibility as a result of this effect has already been documented [11], [28]. It is predicted that grafting a large-enough volume of polymer to the CNC surface will also improve surface-shielding effects, enhancing the overall hydrophobicity of the surface. Since the polymers would also be bound covalently to the CNC surface, their connection to the CNC would be much stronger than the ionic bonds present in the previous study, and thus more likely to have sustained, uniform effects on the surface chemistry and its interaction with the composite.

The primary intent of this project is to investigate methods of mitigating the moisture degradation phenomenon observed in cellulose-based materials by testing the viability and effectiveness of polymer-grafted CNCs at eliminating or reducing the moisture interaction with the CNC. The strategy of grafting polymers to CNCs has already been used as a means of enhancing the mechanical properties of CNC-reinforced composites [28]. Using this method to reduce moisture-related degradation was investigated via three-dimensional computational simulation and proved to be a semi-effective means of maintaining the mechanical properties of the cellulose in the presence of moisture [17]. Another key intention of this research is to determine which quantitative variables pertaining to the polymer-grafted nanocrystals are most effective at facilitating this effect. These variables will become important design parameters should this filler material be used inside a real-world composite in the future. The primary variables investigated in this project were polymer type and chemistry, grafting length, and grafting density.
In order to determine the potential for structural preservation and the nature of the adsorption properties of each unique system of polymer-grafted CNCs, these materials have been simulated in three dimensions over several MD software platforms. This approach enables an expedited process of analysis and evaluation of the broad design possibilities and eases the exploration of the variables listed above and their effects on the overall moisture dependency of the material's mechanical properties.
CHAPTER 2
INITIALIZATION OF MOLECULAR SYSTEMS

In the following sections, we will discuss the methods used to obtain the initial grafted polymer systems, the methods of initializing and then analyzing those preliminary system states, simulating the insertion of water molecules into those systems, and finally the methods used to analyze the results of those simulations.

2.1 Generating Polymer-Exchanged CNCs for Simulation

This investigation sought to evaluate and quantify the efficacy of the use of polymer grafts to a cellulose nanocrystal for obtaining a moisture repulsion effect in the molecule. The key deliverable of this project was to identify some specific design parameters for optimizing the thermomechanical and moisture-responsive properties of a polymer-grafted CNC.

The different grafting parameters applied to each polymer-grafted CNC can be found in Table 1, which catalogs the two polymer types used for grafting – PMMA and PS – and the varied number of monomer units repeated to form a single chain (10, 20, and 50), the varied grafting densities used for each different chain length, and the total number of chains grafted to the CNC surface due to the grafting density. There were 18 CNC-polymer systems plus one nongrafted CNC system in total. The two polymers that were considered were poly(methyl methacrylate) or PMMA, the popular thermoplastic used in acrylics, and polystyrene or PS, another very popular thermoplastic. PMMA and PS were chosen for this investigation because
they both happen to be very common nanocomposite matrix materials, they are mechanically similar, and they have both been grafted successfully in an experimental setting [28]. Further, it will be useful to compare PMMA, a naturally hydrophilic molecule with a potentially good CNC interaction due to this similarity in their reaction to water, to polystyrene, a naturally hydrophobic molecule with a less predictable CNC interaction. All systems will be visualized using VMD or OVITO [32], [33]. Using the LAMMPS software package, insertion/deletion trials of water molecules were conducted on the system via a Grand Canonical Monte Carlo (GCMC) method [34]. These simulations took place over a span of several million time steps, each a femtosecond long, and each individual simulation takes several thousand processing hours. For this reason, most of these simulations took place over Northern Illinois University’s high-performance computing cluster, Gaea.

Table 1
System Types

<table>
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<th>-PMMA or -PS</th>
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</tr>
<tr>
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</tbody>
</table>
These simulations were intended to show that surface functionalization via direct polymer grafting reduces the number of water molecules retained by the CNC-polymer aggregate. By tracking the water adsorption of each system and measuring the dynamics of the accepted water molecules, core insights can be made into the dynamic properties of the adsorption process exhibited by these materials and how to influence them.

To accomplish this, a CNC made up of four 10-unit cellulose chains by four 10-unit cellulose chains was developed, and two different synthetic polymers (PMMA, PS) were grafted to the CNC at the varying densities and lengths listed above. CNCs were generated using the Cellulose-builder toolkit, an incredibly versatile crystal generation software tool for several cellulose polymorphs [35]. A 4x4 chain CNC is used because it is closest in size to that of naturally extracted CNCs, having cross-sectional dimensions on the order of 2-3 nm by 2-3 nm [36]. A schematic of the base CNC and both polymer types can be found in Figure 3. In order to graft each polymer chain to its respective grafting site in experiments, a technique known as atom transfer radical polymerization (ATRP) is often used. In our work, the initiator compound alpha-bromoisobutyryl bromide is used for this process as it has been successfully utilized to experimentally graft both PMMA and PS to CNCs in the past [37]. This compound is an initiator molecule meant to catalyze a reversible-deactivation radical polymerization in the CNC-graft polymer system, which is a fancy way of saying that it facilitates the creation of a strong carbon-to-carbon bond between a carbon atom on the PMMA or PS chain and a carbon atom on the CNC, and it is a popular method of inducing polymer chain growth.
(a) Thousands of cellulose repeat units combine through covalent and hydrogen bonding, as well as Van der Waals attraction, to form much larger CNC molecules, following the typical hierarchical structure of a CNC, from cellulose monomer all the way to I-β CNC. (b) A complete polystyrene (PS) 10mer grafted cellulose nanocrystal at 10% grafting density (10% of grafting locations utilized), showing how the PS repeat units are configured on the molecule. A complete PMMA-grafted CNC will have a similar appearance.
In total, 19 systems were generated – all those indicated in Table 1 as well as an unmodified CNC to be used as a baseline case. All force field parameters used in the simulations conducted using LAMMPS come from CHARMM, a molecular mechanics set of force fields. For the cellulose in the simulations, the CHARMM force field for carbohydrates was used, and for the polymers, the generalized CHARMM force field was used. These force fields were necessary for generating all of the structure and parameter files necessary to run simulations. These statistical mechanical parameters were needed to solve the equations of motion necessary for the molecular dynamics computations and configurations made by LAMMPS to take place.

Every system was simulated with periodic boundary conditions along the z-axis for the purpose of creating a closer approximation to a real-world experimental CNC nanofiller, generally closer to 500-5000 Å in length than the ~100 Å directly modeled inside the simulation cell. To generate these systems, scripts written in Tcl (Tool Command Language), an embedded scripting language provided in the standard distribution of VMD, were used to graft CHARMM-based polymer molecular structures to the surface of CHARMM-based CNCs. Gathering the necessary configurational information to generate these compositions prior to the grafting process also required Materials Studio, VMD’s psfgen feature, and LAMMPS’s charmm2lammps tool.

2.2 Minimization and Annealing

After the initial grafted systems were created, equilibration and annealing processes were conducted over each system in LAMMPS. This was to ensure that the subsequent GCMC simulations were run with the systems starting in an equilibrium condition prior to the entrance of any water molecules into the simulation. It is imperative that the introduction of moisture to the CNC systems be as close to a real-world context as possible. This requires an energy
minimization as well as a relaxing of the overall structure of the CNC-polymer arrangement. The minimization is needed first to bring the systems into a local energy minimum and local entropy maximum, followed by an annealing simulation to hopefully overcome any potential energy barriers that would have prevented the minimization simulation from bringing the systems to their global energy minimums.

Utilizing LAMMPS, each system was initially minimized to within an energy change tolerance of $1 \times 10^{-4}$ and a force tolerance $1 \times 10^{-6}$ Kcal/mole-Angstrom; i.e., LAMMPS brings the configuration to a local potential energy minimum until it approximates a critical point of the objective function:

$$E(r_1, r_2, \ldots, r_N) = \sum_{i,j} E_{\text{pair}}(r_i, r_j) + \sum_{ij} E_{\text{bond}}(r_i, r_j) + \sum_{ijk} E_{\text{angle}}(r_i, r_j, r_k) + \sum_{ijkl} E_{\text{dihedral}}(r_i, r_j, r_k, r_l) + \sum_{ijkl} E_{\text{improper}}(r_i, r_j, r_k, r_l) + \sum_i E_{\text{fix}}(r_i)$$

which simply sums all pairwise, bond, angle, dihedral, and improper interactions as well as energy associated with any fixes used in LAMMPS, such as the NVT fix also used in these simulations. All of the MD simulations, which includes the minimization, annealing, and GCMC simulations, were conducted within a canonical NVT ensemble, and a Nose-Hoover thermostat was used to unite each system with a heat reservoir. When this type of fix is employed, LAMMPS performs a time integration on the Nose-Hoover style of non-Hamiltonian equations of motion that generates positions and velocities sampled from the canonical ensemble, then updates the atoms inside the simulation with those positions and velocities every time step. A constant temperature of 300 K and time step size of 1 fs were used, and the carbon atoms comprising the CNC cellulose were tethered to their initial positions via a harmonic force of 10 Kcal/mole-Angstrom. The NVT ensemble uses a constant temperature, chemical potential and
volume. The volume of each specific system varied, but the volumes for each system remained constant over the lives of each simulation performed. The chemical potential during the minimization and annealing simulations was -13 Kcal/mole.

After energy minimizations were performed on each system, an annealing simulation was then performed. A stepwise function for annealing temperature was utilized, as shown in Figure 4. Each molecular system followed this function over the 3,650,000 fs simulation. Once each system had been minimized, they were then heated to 1000 K twice. The CNC-polymer configurations were heated from 300 K to 1000 K twice, equilibrated for 50,000 fs every ±50 K, and equilibrated for 250,000 fs both times the maximum annealing temperature was reached and both times the minimum temperature was reached. The CNC carbon backbone was again tethered to its initial position for the annealing simulations. A visualization of a fully minimized and annealed CNC-polymer system can be found in Figure 5.

2.3 Analysis of System Initiation

The process of energy minimization in the simulations is what causes the contracting effect seen in the long polymer chains extending outward from the surface of the CNC when comparing the structure shown in Figure 3 to that shown in Figure 5. During the simulation, the lowest energy configuration is approached, which causes the polymer chains to move to a lower energy position in relation to the CNC, drawing the chains in closer until they eventually lay against the CNC surface, or to cluster against the surface and each other. More clustering was seen in the minimized PMMA systems than in the PS systems. This was in part due to the smaller overall volume of PMMA when compared to polystyrene, owing to its stronger
electrostatic interaction with itself, as well as the CNC. The results of these simulations were fairly standard, with the total energies measured throughout each simulation decreasing to approach an asymptote presumably near the equilibrium energy state. This looks similar to the sample shown in Figure 6, which shows the total energy of the 20% PMMA 20mer grafted CNC, approaching an equilibrium around \( \sim 81.5 \times 10^3 \) Kcal/mol. Further, the end-to-end distances and radii of gyration of the grafted polymer chains, acting as measures of the overall relaxation of each system, also appear to equilibrate, as shown in Figure 7.
Figure 5: Example of initialized system.

Fully minimized and annealed polystyrene-grafted CNC (20mer PS at 50% grafting density): a) top view, b) side view.
Figure 6: Sample of tracked minimization energy.
Figure 7: End-to-end distances and radii of gyration for minimizations.

The similar trends of end-to-end distance and radius of gyration for grafted polymer chains of PMMA (a and c, respectively) and polystyrene (b and d, respectively). Not every system is represented, but the trends reflect that each system approaches an equilibrium as the curves smooth out toward the end of the simulation.
During the annealing simulations, the systems are gradually heated from a lower temperature (300 K). As the temperature inside the simulation rises, the polymer chains begin to extend and expand out from their resting position against the CNC surfaces. During the 250,000 fs equilibration at the highest annealing temperature (1000 K), the chains remain mostly extended and far more dynamic in this higher energy configuration than in their lower energy configuration at the 300 K baseline temperature. Then as the temperature gradually decreases, the free polymer chains begin steadily recoiling back toward the CNC surface once again. A schematic illustration of this process can be found in Figure 8, showing the progression of an annealing cycle on a polystyrene-grafted CNC (20mer PS at 20% grafting density). Initiating at the starting baseline temperature 300 K, the PS chains begin to expand as the temperature increases to 600 K, become most extended at the maximum annealing temperature 1000 K, and again begin to contract toward the CNC surface until reaching 300 K once more. During the equilibration periods that occur each time the temperature is increased, part of the calculation being performed within LAMMPS due to the NVT fix being invoked comes from a minimization of the Helmholtz free energy, the thermodynamic potential associated with closed, isothermal, isochoric thermodynamic systems such as the NVT ensembles used here. Each time the temperature increases or decreases 50 K, a 50,000 fs equilibration is performed that effectively minimizes the Helmholtz free energy of the system, and for the maximum annealing temperature of 1000 K and baseline temperature of 300 K, this equilibration period lasts 250,000 fs.
Part of the purpose of running annealing simulations on these pre-minimized systems is to ensure that they have the most even distribution of polymer chains encapsulating the CNC. The PMMA especially had a lot of clustering of polymer chains after the initial minimization, but the PS systems did also have some non-uniform polymer chain distributions over the surface. An annealing simulation, which involves heating the systems to a much higher temperature and then slowly cooling back down from that high temperature, will allow the polymer chains more time to expand, orientate themselves, and relax into a somewhat more even distribution over the CNC surfaces. This will help to improve any potential surface-shielding effects that may be seen when
water is introduced to the systems later. This effect is visualized to a certain extent in Figure 8. In
the Step 5 side visual, which is taken from the very end of the annealing simulation, there are
fewer exposed CNC sites than in the Step 1 side visual. More of the redder CNC sites are
covered and blurred by the blue, overlapping polystyrene chains. Of course, this process will
certainly not guarantee a uniform chain distribution over the surface. PMMA in particular had a
tendency to adhere more to itself than to the surface of the CNC, but the effect of the annealing
did lead to a noticeable before-and-after effect in terms of even dispersal of the polymer chains
over the CNC.

The end-to-end distances and radii of gyration of the free polymer chains in each system
throughout the complete annealing process were calculated and stored and can be observed in
Figure 9. It can be seen from the average end-to-end distances of the polymer chains in each
system that these values follow the expected pattern of increase and decrease throughout the
duration of annealing, as displayed in Figure 9. As the temperature inside the simulation
increases, between 0 fs and 700,000 fs and between 1,850,000 fs and 2,500,000 fs, the polymer
chains will gain greater and greater kinetic energy, allowing them to stretch out from the body of
the CNC. This will lead to a net increase in the average end-to-end distance of each polymer
chain, since an uncoiled polymer chain will have more distance from tip to tip than a cooler,
more compacted set of polymer chains. As the systems subsequently cool, they will re-condense
and settle back down toward the CNC surface. Each system repeats this process once more
before settling into its final configuration prior to the GCMC water molecule insertion
simulation.
Figure 9: End-to-end distances throughout annealing.

Average end-to-end distances of polymer chains in each system configuration (varying polymer type, length, and grafting density) – comparisons between a) 10%, b) 20%, and c) 50% grafting densities.
The peak end-to-end distances occur when the systems are at the maximum annealing temperature (1000 K). It is especially noticeable for the 50mer polymer chains. For the shorter 10mer and 20mer polymer chains, however, the peak around the maximum annealing temperature is far less pronounced, although the increased fluctuation in the average end-to-end distance that occurs at higher temperatures can still be seen in the higher temperature time steps for those systems. The discernible effect of the longer polymer chains experiencing larger fluctuations in the average end-to-end distances of the chains, both during the higher temperature periods and in general, is due to the fact that a polymer chain having a greater length will have more additional length to spread out when higher amounts of kinetic energy are added to the system and more length to shrivel up when there is less kinetic energy in the system. The shorter polymer chains will generally not coil up as much as the longer chains because there is not as much physical length there for coiling. These shorter chains can also only extend themselves as long as the individual units in the chain will allow the chain to stretch, so the end-to-end distances of these chains are limited by their shorter physical length. The average end-to-end distances for these systems will therefore fluctuate by smaller amounts around their initial values, whereas the end-to-end distances for the longer 50mer chains have much more length available to expand and contract, thus the average end-to-end distance curve will have higher peaks about the higher temperature time steps and more pronounced fluctuations in general.

Once again, in the graphs depicting the trends in the polymer chains’ radii of gyration, found in Figure 10, the effects appear to be partly segregated by polymer chain length. For the longest polymer chains, the average radii of gyration at similar grafting densities are the largest, and for the shortest polymer chains, the average radii of gyration are generally the shortest. This
Figure 10: Radii of gyration throughout annealing.

Average radii of gyration about the polymer chains’ axes of rotation, separated by grafting density (proportion of functionalized grafting sites): a) 10%, b) 20%, and c) 50%.
can again be explained by the physical length each chain has available to coil up or fully extend. However, there is a distinct difference in the magnitude of the fluctuation of the polymer chain radii of gyration observed for each different grafting density. The least dense graft, at 10%, observes the largest magnitude of fluctuation in the radius of gyration, while the most dense graft, at 50%, observes the smallest magnitude of fluctuation, with the 20% grafts falling somewhere in the middle. For each system, there are still more fluctuations concentrated around the periods with higher temperature as the chain positions are be more dynamic when more kinetic energy is present, but the magnitude of that fluctuation is simply much larger for the smallest grafting densities. This could be due to the fact that a smaller grafting density leaves more open space in the immediate vicinity of each free polymer chain to move around, thus at higher temperatures when the amount of kinetic energy present in the system is larger, the motion of the polymer chains is far less impeded by adjacent chains. At larger grafting densities, the polymer chains are packed in more closely to each other and therefore will not be able to cluster in a way that puts the center of mass very far away from the average atom in the chain because each chain is more or less obstructed by neighboring chains taking up potential rotation space. With the chains more densely packed, there is less opportunity for the distribution of the mass in each chain to change by very much. Since the average radius of gyration of a given set of chains is based on the radial distribution of mass of each individual chain, the average radius of gyration for the chains belonging to the various CNC-polymer systems will be dependent on how densely packed the polymer chains are.
CHAPTER 3
GCMC SIMULATIONS

In the following sections, the methods of simulating water molecule insertions and methods of analyzing those simulations will be discussed at length. Finally, a concluding explanation of the results presented here will be made, and suggestions for types of further study that could be made into this subject area will be speculated.

3.1 How Water Molecules Are Inserted

After each CNC-polymer system had been fully minimized and annealed, they were finally introduced to moisture for performance testing. To simulate the presence of the water molecules within the system, GCMC exchanges were computed using the LAMMPS software. In each system, water molecules were introduced based on a Grand Canonical Monte Carlo (GCMC) method. This method requires an imaginary ideal gas reservoir at a specified temperature and chemical potential, and Monte Carlo (MC) exchanges of H₂O molecules are made to and from the reservoir based a calculation that accounts for the total potential energy of the reservoir and the total potential energy of the simulation cell. This is largely related to the chemical potential, which is defined as:

\[ \mu = \mu^{id} + \mu^{ex} \]

where \( \mu^{ex} \) represents excess chemical potential that results from energetic interactions, such as those occurring within the simulation cell, but it is zero for the ideal gas reservoir. The chemical
potential for the simulation cell and gas reservoir are the same, but the value of $\mu^{ex}$ is not, typically making the densities of the two regions very different, which facilitates exchange. Part of the purpose of using an MC simulation with LAMMPS is to simulate the introduction of atoms or molecules to a system while faithfully preserving the equilibrium Boltzmann probability distribution (canonical ensemble). Whenever a water molecule added from the reservoir is to be accepted or deleted, the change in potential energy is calculated, and an acceptance criterion known as the Metropolis criterion is used to determine the fate of the molecule. The Metropolis criterion essentially does the following:

1) If $\Delta U < 0$, accept the molecule.

2) If $\Delta U > 0$, calculate,

$$P^{acc} = e^{-\Delta U / T}$$

Then, draw a random number $r$ between 0 and accept the addition only if the condition $P^{acc} > r$ is satisfied.

Monte Carlo translations were enabled for the simulations as well. These allowed the water molecules in the system to move within the cell based on a calculation similar to the MC exchange, such that a move is either accepted or rejected based on the acceptance criterion that ensures the full molecular configuration inside the simulation cell is sampled from the canonical ensemble distribution – simply, a probability distribution describing potential states of the system. So ultimately, aggregated over many MC steps, the molecular configuration of the simulation will obey the canonical ensemble distribution. Thus, the probability of the system falling into any given configuration will eventually be:

$$\varphi (r^N) \propto e^{-U(r^N) / T}$$
where T represents the temperature of the system, and N represents the number of atoms present in the system.

### 3.2 Water Adsorption

The systems were simultaneously equilibrated during the insertion simulations using a μVT ensemble at constant temperature 300 K, fixed volume in each simulation (once again, specific volume of the simulation cell varied from system to system), and constant chemical potential -10.96 Kcal/mole making relative humidity 100%. Rather than using the NVT canonical ensemble as the previous simulations did, these simulations must employ the grand canonical ensemble to account for the changing number of atoms present in the simulation cell. The boundary conditions along the z-axis were also periodic, as previously mentioned, for the purpose of ensuring a close approximation to a real-world CNC-polymer system by simulating effects over longer, unbroken CNCs.

It was anticipated that the molecules containing PMMA grafts would not perform as well as those containing polystyrene grafts. This is due to the fact that, despite being a technically hydrophobic molecule, PMMA is known to be more hydrophilic than polystyrene in most contexts [38]. That characteristic is likely to impede its ability to shield the very hydrophilic cellulose that comprises the nanocrystal from interacting with water molecules once it is exposed. Thus, it was expected that polystyrene would have the best potential for reducing the adsorption of water molecules to the surface of the CNC.

Throughout each simulation, the number of adsorbed water molecules was tracked, and the plots in Figure 11 appear to reflect the prediction that the PMMA grafts would not lead to a substantial improvement compared to polystyrene. The grafting of polystyrene is clearly causing
Figure 11: Adsorption plots.

Water molecule adsorption by CNCs grafted with PMMA (top) and PS (bottom). The thick black line indicates a bare CNC with no polymer grafts. Curved lines are coded identically between each graph.
a significant reduction in the extent of moisture exposure to the CNC, reducing the moisture adsorption by a full order of magnitude. The best shielded polystyrene-grafted CNCs, PS 50mer grafts at 20% and 50% and 20mer grafts at 50%, had the lowest levels of overall moisture adsorption, far lower than anything found in the PMMA grafts. PS 20mers grafted at 20%, 50mers grafted at 10%, and 10mers grafted at 50% do appear to be extremely close seconds to the perfectly shielded CNCs. This is likely due to these systems being the second best shielded, although they are still very much on par with the perfectly shielded systems in terms of their response to moisture.

The most interesting thing about the polystyrene-grafted systems, in fact, was that not only is the polystyrene effective when it forms a full shell around the CNC, but it also appears to be effective in reducing the moisture response by merely being present at the surface, even when multiple gaps in the polymer shell exist, exposing the cellulose to a moisture-filled region. Even the PS 10mers graft at 20% density and 20mers graft at 10% density appear to have a limiting effect on overall moisture adsorption. This suggests that the benefits of using a polystyrene graft to inhibit moisture adsorption don’t simply come from a basic shielding effect - they also come from the natural hydrophobicity of the styrene polymer. Therefore, if this were the polymer of choice for a polymer-CNC graft to improve moisture resistance, a quantity of the polymer large enough to shield the entire CNC would not necessarily be required.

The PMMA adsorption trends clearly show little to no effect of the PMMA presence on moisture adsorption. There was not a single type of PMMA-grafted CNC system that performed better than the plain, nongrafted CNC. If anything, the presence of PMMA at the surface of the CNC seems to result in increased moisture adsorption, especially for the densest grafts with the
thickest polymer shells. Based on Figure 11, the PMMA 20mers grafted at 50%, and 50mers grafted at 50% and 20% appear to be the top water-collecting systems, where the 50mers at 50% clearly have the biggest adsorption effect and vastly accelerate the adsorption rate of the CNC. The less shielded systems have effects somewhat closer to the behavior of the bare CNC, though they still accept significantly more water molecules on average than the bare CNC. This suggests that PMMA might be somewhat more hydrophilic than cellulose in this context.

Table 2, Figure 12, Table 3, and Figure 13 are meant as a supplement to Figure 11 in order to help identify the relevant trends in the beginning of the GCMC simulations. In Table 2, which shows slope trends for PMMA-grafted CNCs during the first 1,000,000 fs of the GCMC simulation, i.e., the initial adsorption rate for PMMA at different grafting parameters, and Figure 12, it appears that for PMMA-grafted systems the adsorption rates tended to increase with grafted polymer length. It can be inferred from Figure 11 that PMMA has more electrostatic (van der Waals) interactions with water than the cellulose because the more the CNC is coated in PMMA, the more water is attracted to it than to a regular CNC. So as polymer lengths increase and grafting densities increase, so will the adsorption rate. However, they also seem to have highest adsorption rates for 50% grafts and 10% grafts, with 20% grafts having the lowest adsorption rate for the three density values for 10mers and 20mers. This is likely again due to the electrostatic forces present in PMMA. For the smaller polymer lengths, there is less polymer material available to interact with water molecules, and 10 and 20mers are smaller compared to 50mers. For the smaller polymer lengths, there is less polymer material available to interact with water molecules, and 10 and 20mers are closer in size compared to 50mers. It is likely that for the smallest 10mers 10% system, enough of the surface of the CNC was exposed to have an
increased adsorption compared to the 10mers at 20%. Again, these systems are somewhat similar in size compared to the 50mer systems, so any small fluctuation like this does not necessarily betray the general trend that grafting more of the PMMA polymer to the surface leads to a higher adsorption rate and higher overall adsorption of water molecules.

Table 2
PMMA Adsorption Rates

<table>
<thead>
<tr>
<th>Grafting Parameters (Polymer length_density)</th>
<th>Rate of Adsorption (molecules/ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10_0.1</td>
<td>121</td>
</tr>
<tr>
<td>10_0.2</td>
<td>96.97</td>
</tr>
<tr>
<td>10_0.5</td>
<td>136.8</td>
</tr>
<tr>
<td>20_0.1</td>
<td>136.3</td>
</tr>
<tr>
<td>20_0.2</td>
<td>126.1</td>
</tr>
<tr>
<td>20_0.5</td>
<td>168.8</td>
</tr>
<tr>
<td>50_0.1</td>
<td>143.2</td>
</tr>
<tr>
<td>50_0.2</td>
<td>189.1</td>
</tr>
<tr>
<td>50_0.5</td>
<td>290.1</td>
</tr>
<tr>
<td>Naked CNC</td>
<td>118.8</td>
</tr>
</tbody>
</table>
Figure 12: Adsorption rates for PMMA.

Table 3

PS Adsorption Rates

<table>
<thead>
<tr>
<th>Grafting Parameters (Polymer length_density)</th>
<th>Rate of Adsorption (molecules/ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10_0.1</td>
<td>77.96</td>
</tr>
<tr>
<td>10_0.2</td>
<td>30.44</td>
</tr>
<tr>
<td>10_0.5</td>
<td>8.764</td>
</tr>
<tr>
<td>20_0.1</td>
<td>52.12</td>
</tr>
<tr>
<td>20_0.2</td>
<td>29.34</td>
</tr>
<tr>
<td>20_0.5</td>
<td>13.15</td>
</tr>
<tr>
<td>50_0.1</td>
<td>20.525</td>
</tr>
<tr>
<td>50_0.2</td>
<td>3.651</td>
</tr>
<tr>
<td>50_0.5</td>
<td>10.056</td>
</tr>
<tr>
<td>Naked CNC</td>
<td>118.8</td>
</tr>
</tbody>
</table>
For the PS-grafted systems, the trend is very clear. Based on the information in Table 3, which shows slope trends for PS-grafted CNCs during the first 1,000,000 fs of the GCMC simulation, i.e., the initial adsorption rate for PS at different grafting parameters, and Figure 13, the adsorption rate vastly decreases with grafting density – another manifestation of the primary mechanism by which water adsorption is decreased for polystyrene-grafted systems: surface shielding. There is also a clear decrease in adsorption rates when longer polystyrene chains are used. Overall, the clear trend for polystyrene is that its natural hydrophobicity means larger grafts covering more of the CNC will lead to more of a decrease in water adsorption.

Figure 13: Adsorption rates for PS.
3.3 Characterizing Water Adsorption

For simplified data processing, Tcl and Python scripting was utilized to transform text files and assorted output data into organized data sets for direct plotting and analysis. Solvent-accessible surface areas of reactive hydroxyl groups on the surface of the CNC, adsorption rates for H\textsubscript{2}O molecules to the different molecular systems, as well as radial distribution functions of H\textsubscript{2}O oxygen to CNC oxygen, were all computed using Tcl scripts (run using the Tk Console extension provided by VMD) operating on modified data files [32]. In conjunction with these Tcl scripts, certain computations provided by the standard distribution of VMD along with TopoTools, one of the available plugins for VMD, were also utilized within the Tcl scripts [32], [39].

3.3.1 Solvent-Accessible Surface Area

For a better interpretation of the data on adsorption by PMMA- and PS-grafted systems, it is useful to take a look at the solvent-accessible surface area for each system. The solvent-accessible surface area, or SASA, is a measure of the surface area that will be available with which a solvent may interact. VMD measures the SASA for whichever range is selected by extending the radius of each atom in the selection by the specified solvent radius to find the points on the sphere that will be exposed to the solvent.

For these systems, the SASA was calculated for the reactive hydroxyl groups at the CNC surface because it is these surface groups specifically that will interact most strongly with the water molecules present near the surface. A larger number of unobscured hydroxyl groups available at the surface increases the chances of water reacting with the CNC to produce
structural decay. It is useful to know the availability of these groups for extrapolating how water will interact with each molecular system. SASA should vary considerably with grafting density as the closeness of polymer chains is the primary determining factor of whether or not the system will be encapsulated by a full shell. Table 4 shows the solvent-accessible surface areas for the PMMA- and PS-grafted CNCs after annealing was completed and systems were in their initial states prior to water introduction. From Table 4, it is apparent that PMMA and PS systems have nearly identical SASAs for each grafting type. This is not out of line with expectations as the longer annealing process should have put each system with similar grafting parameters within a similar extent of CNC coverage. Figure 14 is the plot of Table 4 and shows the SASA based on grafting density for different polymer types and graft lengths. From Figure 14, the trend is made even more clear, as well as the fact that polymer length does not cause a variation in SASA. The sole determining factor is the density of the graft, independent of polymer type or length. This data set is yet a further indication of the significant role of shielding for decreasing water adsorption for polystyrene. The density and thickness of the polystyrene shell is a major determinant of the volume of water that will be able to interact with it. For PMMA, despite having an essentially identical shielding effect, however, the adsorption of water molecules was almost not decreased at all, which as discussed earlier is a result of PMMA’s stronger electrostatic interactions with water.
Table 4

Solvent-Accessible Surface Area

<table>
<thead>
<tr>
<th>Type_Density</th>
<th>PMMA (Angstrom²)</th>
<th>PS (Angstrom²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10_0.1</td>
<td>10320</td>
<td>10365</td>
</tr>
<tr>
<td>10_0.2</td>
<td>9145</td>
<td>9196</td>
</tr>
<tr>
<td>10_0.5</td>
<td>5791</td>
<td>5791</td>
</tr>
<tr>
<td>20_0.1</td>
<td>10347</td>
<td>10392</td>
</tr>
<tr>
<td>20_0.2</td>
<td>9201</td>
<td>9204</td>
</tr>
<tr>
<td>20_0.5</td>
<td>5791</td>
<td>5718</td>
</tr>
<tr>
<td>50_0.1</td>
<td>10384</td>
<td>10329</td>
</tr>
<tr>
<td>50_0.2</td>
<td>9199</td>
<td>9219</td>
</tr>
<tr>
<td>50_0.5</td>
<td>5791</td>
<td>5791</td>
</tr>
</tbody>
</table>

Figure 14: SASA.
3.3.2 Water Molecule Distribution Over the CNC Surface

In attempting to discern how each unique system behaves in the presence of moisture, in addition to understanding the physical magnitude of water molecules entering the systems, it is also very important to understand if the water molecules are reaching the CNC surfaces as this will determine their likelihood of surface interaction, and thus the likelihood and extent to which the CNC’s mechanical strength will be preserved. If they do not stay on the surface and instead burrow deeper into the polymer chains, then the shielding effect of the polymer chains is diminished. As previously indicated by Figure 11, surface shielding plays an important role in reducing the quantity of water molecules interacting with the system, but if water molecules were to routinely penetrate that polymer shell, the CNC underneath would still be at risk of exposure to moisture, reducing its overall structural integrity within the composite and potentially leading to dispersion issues. It was expected that due to the hydrophobicity of polystyrene there would not be a substantial penetration effect. Due to the demonstrated hydrophilicity of and prominent electrostatic forces within PMMA, however, a notable penetration effect of water molecules was predicted.

Figures 15 and 16 give a basic visualization of the difference in concentration of water molecules near the CNC surface between PMMA and polystyrene. While most of the water molecules present in the polystyrene visualization do appear near the surface, there are still exceedingly fewer total water molecules present than for PMMA, thus the assertion can still be made that PS is a decent inhibitor of adsorption overall. And yet, based on these figures, the PMMA-grafted systems appear to be doing something interesting. They seem to be trapping water molecules farther away from the CNC surface, thereby ensnaring them and preventing
them from advancing much further toward the CNC. This effect could still prove to be useful for fulfilling the original objective of reducing CNC surface exposure to moisture. The polystyrene grafts are good for reducing the overall presence of moisture, but not preventing the water molecules that are present from migrating to the CNC surface, while the PMMA grafts are good at preventing a large volume of water molecules from actually reaching the CNC surface, but still not useful for reducing the total quantity of water molecules with which the complete system must interact.

Figure 15: $H_2O$ distribution for a medium shell.

Visualization of the $H_2O$ distribution over the CNC for a) polystyrene 20mers grafted at 20% density and b) PMMA 20mers grafted at 20% density. These systems have a medium-thickness polymer shell.
3.3.3 Radial Distribution Function

In order to determine, within a reasonable degree of certainty, where exactly the water molecules were ending up on the surfaces of the CNC-polymer systems, a partial radial distribution function (RDF) was computed for each system between the oxygen atoms present at the CNC surface and the oxygen atoms belonging to the H$_2$O molecules. Partial RDFs, also known as pair distribution functions (PDF), are a description of the density probability of locating a chemical species $\beta$ at different radial distances from a different chemical species $\alpha$. 

Visualization of H$_2$O Distribution over the CNC for a) polystyrene 50mers grafted at 50% and b) PMMA 50mers grafted at 50%. These systems have the thickest polymer shell and therefore the best CNC shielding of all 18 systems.
PDFs and RDFs differ slightly in that RDFs are computed independently from molecular orientation, but practically, they have roughly the same general form. The radial distribution function is computed via the following equation in statistical mechanics:

$$g_{ab}(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|r_{ij}| - r) \rangle$$

where $N_a$ and $N_b$ represent the number of atoms in species $\alpha$ and species $\beta$, respectively. This function will give a distribution of the distances, $r$, between the pair $\alpha$ and $\beta$.

Used in the context of interpreting molecular trajectory data output from each GCMC simulation, the partial RDFs of the two types of oxygen atoms will give an idea as to roughly how far from the surface of the CNC the water molecules are ending up. If they are falling close to the CNC surface despite being well coated in a polymer shell, then this attenuates the polymer shielding effect of reducing moisture exposure for the CNC.

The radial distribution functions for 20mer polymer grafts at 20% grafting density and 50mer polymer grafts at 50% grafting density – the same systems visualized in Figures 15 and 16 – can be found in Figures 17 and 18, respectively. These are the time-average, normalized RDFs for each system. The value $g(r)$ is a reflection of the magnitude of $g(r)$ at each value of $r$ relative to the maximum value of $g(r)$. This is done for the purpose of providing a normalized comparison, as the actual values of $g(r)$ do not analogously reflect the true quantity of water molecules present when directly compared to the magnitudes of the function for the other corresponding systems. For the purpose of making a direct comparison between relative concentrations of water molecules within each system, a normalized RDF can be utilized.
Figure 17: RDF of 20mers at 20% grafting density.

Radial distribution functions for PMMA 20mers (blue/top line) and PS 20mers (red/bottom line) grafted CNCs at 20% grafting density, compared with a plain, nongrafted CNC (yellow/middle line).
Radial distribution functions for PMMA 50mers (blue/middle line) and PS 50mers (red/bottom line) grafted to CNCs at 50% grafting density, compared with a plain, nongrafted CNC (yellow/top line).

In these figures, the location of CNC surface is placed around where \( r = 2.5 \) Å because this is where the largest concentration of water molecules is for the nongrafted CNC as \( \sim 2.5 \) Å is the location of the largest peak for the nongrafted CNC. This is to be expected as one would predict that the water molecules introduced to the nongrafted CNC system can get as close to the surface as possible. As it happens, based on these RDFs, the surface of the CNC is also the location of the largest concentration of water molecules for the PMMA as well as the polystyrene grafts because the largest peaks for both coincide at the same location as the largest peak for the nongrafted CNC.
3.3.4 Actual Surface Adsorption

The total reflects the total number of water molecules present in the system, while the numbers “at the CNC surface” reflect the number of water molecules that are within 5 Angstrom of the CNC surface. The red horizontal line indicates the average number of water molecules at the surface of the non-grafted CNC (239 molecules). Now, taking a look at the average number of water molecules close to the CNC surface toward the end of the GCMC simulations in Figure 19, the results between PS and PMMA reflect the stark difference in the way each type of system handles the presence of water molecules. The polystyrene appears to simply adsorb the water molecules directly to the surface of the CNC as they enter the simulation. The netting effect of PMMA is quite clear, however. For the thickest PMMA shells with 50mer chains and especially for high grafting densities, the number of water molecules able to get close to the CNC surface is much smaller than the total number of water molecules present in the system. The hydrophilic PMMA chains, despite not being able to reduce the total number of water molecules interacting with the system, appear to be at least somewhat effective at slowing down or stopping the water molecules from reaching the surface of the CNC and are instead absorbing and holding the water molecules inside the PMMA shell itself. The PMMA is effectively acting as a shield for the CNC by capturing water molecules before they are able to make it to the CNC surface. Overall, PMMA seems to still be fairly good at preventing the CNC from interacting with water. Although it is about half as effective as using polystyrene to do this, it can still do its job to a certain extent.
Figure 19: Adsorption comparison.

Comparing total vs. CNC surface adsorption by a) PMMA-grafted CNCs and b) PS-grafted CNCs.
3.4 Conclusion

PMMA did not prove to be of particular use for culling the total substantial adsorption of water molecules to the filler molecule. It is still apparent that the PMMA is at least capable of withholding a certain amount of the water molecules present from reaching the CNC surface itself, which is the most important job of the graft polymer since the extent of CNC surface contact with moisture determines its mechanical properties. This will need to be investigated at greater depth to determine the full effects of this phenomenon and its usefulness for creating a nanofiller that is more resistant to the effects of moisture. Grafting polystyrene to a cellulose nanocrystal, however, has proven to be a highly effective means of reducing the overall moisture exposure of the CNC in the standard environment used within the simulations detailed in this paper. Use of polystyrene grafts at a broad range of polymer chain lengths and grafting densities proved to reduce total water adsorption by a full order of magnitude in most cases when compared to a non-grafted CNC.

Most of the water molecules that were able to penetrate the molecule did still reach the CNC surface, but the quantity of water molecules that made contact with the surface of the CNC in the PS-grafted systems was still smaller than the quantity of water molecules able to reach the surface in most PMMA-grafted systems. This filler structure could have many broad applications for use as a semi-water-resistant nanofiller in reinforced polymer nanocomposites. It will be important to consider, however, that some moisture interaction may still exist in polystyrene-grafted systems and that over a longer time interval these systems may eventually see some decline in mechanical performance due to compounded moisture interaction over a period of time. However, the overall effectiveness of polystyrene grafts on the reduction of moisture
adsorption on a CNC is very promising, and more research will need to be conducted to identify more specific design parameters for creating an ideal nanofiller using this method. Something that could be tested is the effect of grafting a hydrophilic polymer like PMMA to the end of a hydrophobic polymer like PS, and then grafting the hydrophobic end of that resulting copolymer to a CNC in a manner similar to that used in this project. This molecule would have all the benefits of the PS but with the additional benefits of an intermediate moisture-catching PMMA layer that would also make the resulting molecule more compatible with a hydrophilic bulk matrix.
REFERENCES


