Morphological, Mechanical and Rheological Behaviour of Cellulose Nanocrystal-Poly(Methyl Methacrylate) Nanocomposites Prepared by Wet Ball Milling and Melt Mixing

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Applied Science

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Abstract

Cellulose nanocrystals (CNCs) are an ideal reinforcing agent for polymer nanocomposites because they are lightweight, nano-sized, and have a high elastic modulus. To date, using cellulose nanocrystals in common matrices has been generally unsuccessful due to their hydrophilicity and incompatibility with hydrophobic polymers. To overcome the poor compatibility, we have grafted poly(methyl methacrylate) (PMMA) onto the surface of the nanocrystals for the first time using a one-pot, aqueous *in-situ* "grafting from" polymerization reaction with ceric ammonium nitrate initiator to produce poly(methyl methacrylate)-graftedcellulose nanocrystals (PMMA-g-CNCs). We compared the compounding of CNCs and modified CNCs with PMMA using two processing methods; melt mixing and wet ball milling. We examined the morphological mechanical and rheological behaviour of the nanocomposites and found that ball milled composites had lower mechanical and rheological performance compared to melt mixed composites for both CNCs and modified CNCs. Additionally, we found that high (>1 wt. %) loadings of CNCs had a positive effect on the performance of nanocomposites, while low loadings of CNCs and all loadings of PMMA-g-CNCs had no net effect on the performance of the nanocomposites compared to the control. The morphology of nanocomposites showed some agglomeration in the samples with CNCs, but more pronounced agglomeration in samples with PMMA-g-CNCs. This is consistent with the decreased rheological and mechanical behaviour of composites with PMMA-*q*-CNCs compared with CNCs.

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Nomenclature	
AFM	Atomic Force Microscopy
CAN	Ceric Ammonium Nitrate
CesA	Cellulose Synthase
CNC	Cellulose Nanocrystals
CNF	Cellulose Nanofibers
CNs	Cellulose Nanoparticles
CNT	Carbon Nanotubes
CNW	Cellulose Nanowhiskers
MEK	Methyl Ethyl Ketone
MMA	Methyl Methacrylate
N ₂	Nitrogen
NaCl	Sodium Chloride
NCC	Nanocrystalline Cellulose
NH03	Nitric Acid
PEO	Polyethylene Oxide
PMMA	Poly(Methyl Methacrylate)
PMMA-g-CNC	Poly(Methyl Methacrylate)-Grafted-Cellulose Nanocrystals
ROP	Ring-Opening Polymerization
SEM	Scanning Electron Microscopy
ТЕМРО	(2,2,6,6-Tetramethylpiperidin-1-yl)Oxy
TGA	Thermogravimetric Analysis
WPU	Waterborne Polyurethanes
XRD	X-Ray Diffraction

Chapter 1: Introduction

1.1 Cellulose Nanocrystals as Reinforcing Agents for Polymer Nanocomposites

Nanotechnology involves the use of nano-sized particles with unique

properties to produce new technologies, or improve existing ones. Potential applications for these "nanoparticles" are in fields as diverse as medicine, composites, electronics, biomaterials, and energy storage. Cellulose nanocrystals (CNCs) are nanoparticles derived from cellulose, which is the most abundant and renewable polymer in the world. Discovering appropriate applications for this material will facilitate the replacement of more expensive and environmentally harmful or inefficient particles. CNCs have excellent mechanical properties, including an estimated specific Young's modulus comparable to Kevlar and steel [1], and are relatively inexpensive and lightweight. Due to these, and the low density, stiffness, and high anisotropy, CNCs have the potential to replace more traditional inorganic particles in polymer composites and improve mechanical performance.

The commercialization of cellulose nanocrystals has accelerated quickly in the past five years. Companies such as FPInnovations, CelluForce and Alberta Innovates are currently producing industrial quantities of CNCs [2], and major programs aimed at developing CNC products have begun in Canada, the United States, and Finland [3]. High purity CNCs are now commercially available in Canada and the United States from both private and government-supported organizations. Current research on cellulose nanocrystals is focused on finding applications that can take full advantage of their unique physical and chemical properties. To date, CNCs have been primarily investigated as reinforcing agents in hydrosoluble polymer matrices, which are compatible with the hydrophilicity and relatively low degradation temperatures (250 °C) of CNCs [1]. Using CNCs in more common commodity polymers such as polyethylene and poly(methyl methacrylate) (PMMA) has been limited due to the poor interactions between CNCs and polymers, as well as the degradation of CNCs at high processing temperatures. Tuning CNC-polymer interactions and using low temperature composite processing methods are essential to obtaining nanocomposites with good dispersion and improved mechanical properties.

1.2 Research Objectives

The goal of this thesis work is to compare the effect of (1) CNC surface modification, (2) nanoparticle loading, and (3) composite processing methods on the performance of CNC/PMMA nanocomposites.

Surface modification:

This work aims to investigate if the CNCs can be modified by grafting PMMA to the surface using a "grafting-from" approach. We address (i) the grafting of PMMA onto the surface of CNCs to form PMMA-grafted-CNCs (PMMA-*g*-CNCs); and (ii) the characterization of surface modified CNCs including Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and atomic force microscopy (AFM).

Nanoparticle loading:

This work examines the function of nanoparticle loading on the bulk properties of CNC/PMMA nanocomposites. We address CNC loadings of 0.25 wt. %, 0.5 wt. %, 1 wt. % and 2 wt. % for each of the four sets of samples with different CNC chemistries and nanocomposite mixing methods. These loadings are below the percolation threshold for CNCs (2.4%), and were chosen based on the availability of the CNCs and PMMA-*g*-CNCs. However, since CNCs are a low-density material, the volume fraction is high compared with materials such as glass fibers.

Nanocomposite compounding:

The primary objective is to disperse CNC particles efficiently in a polymer matrix. To investigate this, we examine two compounding methods;, melt mixing and wet ball milling, and test which method will produce CNC/PMMA composites with better mechanical properties. We present (i) the preparation of a series of CNC/PMMA and PMMA-*g*-CNC/PMMA nanocomposites; (ii) the characterization of the nanocomposites, including SEM and optical microscopy; and (iii) the mechanical performance of the nanocomposites by tensile testing and rheology. An overview of the entire project appears in Scheme 1.

1.3 Thesis Outline

The content of this thesis is separated into six chapters, including this Introduction. Chapter 2 of the thesis presents a literature review discussing the preparation, modification and unique properties of cellulose nanocrystals, as well as the dispersion, characterization, compounding methods, and mechanical properties

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of polymer nanocomposites. Chapter 3 summarizes the materials and experimental procedures used over the course of the research. Chapter 4 contains the results and discussion of the PMMA-grafting reaction on cellulose nanocrystals, including general observations, the morphology, and the characterization of the materials. Chapter 5 presents the characterization and discussion of CNC/PMMA and PMMA-*g*-CNC/PMMA nanocomposites, including general observations and morphology, and the performance and discussion of CNC/PMMA and PMMA-*g*-CNC/PMMA nanocomposites, including general observations and morphology, and the performance for the discussion of CNC/PMMA and PMMA-*g*-CNC/PMMA nanocomposites, including resented in Chapter 6.



Scheme 1: The experimental overview of the project, including CNC modification, processing methods and characterization methods.

Chapter 2: Literature Review

2.1 Cellulose

Cellulose, a non-toxic and biodegradable polysaccharide, is the most abundant polymer on the planet due to its widespread availability from renewable sources such as plants, bacteria, marine animals and fungi [1][4]. Annual production of cellulose is estimated to be between 7.5×10^{10} [1] and 1.5×10^{12} tons [5]. The molecular structure of cellulose is composed of a repeating sequence of cellobiose units, which consist of two D-glucose monomers linked together by β -1,4 glycosidic bond, with each cellobiose unit rotated 180° with respect to its neighbors (Figure 1). At either end of each cellulose chain there is a chemically reducing end with a hemiacetal unit (aldehyde functionality) and a nonreducing end with pendant hydroxyl groups [1].



Figure 1: Cellulose chains are made up of repeating cellobiose units. Chain ends have different chemistries, with one end reducing (hemiacetal) and the other end non-reducing (hydroxyl). Figure adapted from [1].

There can be up to 20,000 D-glucose units in the cellulose chains produced by plants, which is defined as its degree of polymerization, however, shorter chains can also exist [1]. Cellulose is considered a semicrystalline polymer due to the ability of cellulose chains to pack regularly and form extensive hydrogen-bonded networks. The specific crystalline allomorph, degree of polymerization and ratio of amorphous to crystalline regions in cellulose is dependent on the biosynthesis mechanism of the organism making it (i.e., the plant, bacteria, or animal). The description of cellulose biosynthesis below focuses on plant sources of cellulose such as cotton, which is the starting material used in this work.

2.2 Biosynthesis of Cellulose

In plants, single cellulose chains are synthesized by the polypeptide cellulose synthase catalytic subunit (CesA). A group of six CesA subunits, each in contact with two other units, form a circular structure called a rosette subunit. In turn, six rosette subunits arrange themselves the same way to form a rosette with 36 CesA polypeptides. Each rosette subunit produces six cellulose chains [6]. Once the cellulose chains exit the CesA units, the oxygen and hydroxyl groups of adjacent cellulose chains form hydrogen bonds. A simplified figure of this process appears in Figure 2. This promotes parallel stacking of several molecules to form elementary cellulose fibrils that aggregate into microfibrils [4]. A visual representation of the build-up of cellulose into fibrils, microfibrils and the plant cell wall structure appears in Figure 3 [7].



Figure 2: Arrangement of CesA into a rosette to produce cellulose microfibrils. Reproduced from Reference [6].



Figure 3: Cellulose microfibril structure and origins in plants. Reproduced from Reference [7].

Biosynthesis of cellulose in different organisms varies, but each source produces high molecular weight cellulose with alternating amorphous and crystalline regions [1]. These crystalline regions can be extracted, and are commonly known as cellulose nanocrystals (CNCs), nanocrystalline cellulose (NCC), or cellulose nanowhiskers (CNWs).

2.3 Cellulose Nanocrystals (CNCs)

Cellulose nanocrystals are rigid, rod-like particles with all dimensions in the nanoscale. The width of CNCs can range from 5-10 nm and the length from 50several micrometers [4]. Cellulose nanocrystals are typically extracted from these sources via controlled acid hydrolysis, which preferentially breaks down the more accessible amorphous regions of the fibers into small polysaccharides and sugars. Due to their high crystallinity, the CNCs are resistant to degradation during the hydrolysis, and can be separated from the acid and saccharide mixture by centrifugation and dialysis. Rånby et al. were the first to report stable CNC suspensions in water using sulfuric acid hydrolysis in 1949 [8]. Other forms of nanosized cellulose can be extracted using milder and/or different synthetic approaches. For example, cellulose nanofibrils (CNFs), are high aspect ratio fibers that are made by mechanically breaking down the multi-level organization of the cellulose fibers using high shear. CNF preparation does not remove the amorphous regions, but instead delaminates the fibers into flexible, nanofibrils, which have diameters of 3-5 nm and lengths in the micrometer range [4].

Cellulose can exist in four different crystalline structures, I, II, III, and IV, which differ in the inter and intramolecular hydrogen bonding of the cellulose chains. Cellulose I is most commonly found in nature, and has two distinct polymorphs; I α and I β . I α is found in algae and bacteria, while I β is dominant in plant cell walls, including cotton. Different processing methods can produce other cellulose crystal structures from cellulose I. Cellulose II is the most thermodynamically stable structure of cellulose, and is produced from regeneration or mercerization of cellulose I, cellulose III can be made from cellulose I and II by liquid ammonia treatments, and cellulose IV is formed from thermal treatments of cellulose III [4].

Different types of cellulosic nanomaterials (CNs), or nanocelluloses, have been described in the literature but the terminology is often inconsistent. Recent efforts to standardize terminology and test methods for nanocellulose have been undertaken by the Canadian Standards Association (CSA Z5100-14), TAPPI and the International Standards Organization (ISO TC 6 and TC229). The main categories of cellulosic nanomaterials, and a summary of their properties, are listed in Table 1.

Name	Other Names	Preparation Method	Length (µm)	Degree of Crystallinity (%)	Reference
Cellulose Nanofibrils (CNF)	nanofibrillated cellulose (NFC), microfibrillated cellulose (MFC), microfibrils	Mechanical treatment under high shear	0.5-10's	51-69	[4]
Cellulose Nanocrystals (CNCs)	NCC, CNW, crystallites, microcrystals	Acid hydrolysis or oxidation	0.05- 0.5	>80	[1][4][9]
Bacterial Cellulose (BC)	microbial cellulose, biocellulose	Bacteria production	0.1-1.5	65-79	[10][4]

Table 1: Terminology, preparation methods and physical characteristics for cellulosic nanomaterials.

2.3.1 Preparation Methods

Cellulose nanocrystals are isolated from plant sources in two stages to remove impurities like hemicelluloses and lignin, and then amorphous cellulose. First, the source material is pretreated to purify and homogenize the particles for a more uniform reaction. The exact steps depend on the composition of the source material, and on the preferred morphology of the CNCs. Pretreatment of wood is typically done using the Kraft bleaching process that is used in pulp and paper processing [4][11][12]. Following pretreatment, sulfuric acid hydrolysis is the most common method for producing CNCs, though hydrochloric, hydrobromic, and phosphoric acid have also been used [1]. Sulfuric acid hydrolysis is the most widely used because it leaves negatively charged surface sulfate ester groups. These charged surface groups stabilize the CNCs in aqueous suspension through electrostatic repulsion [13], and as a result, the CNCs do not aggregate and form a stable colloidal suspension. Hydrochloric and hydrobromic acid produce uncharged CNCs which do not form stable suspensions, and instead the nanoparticles flocculate in water [14].

2.3.2 Physical and Chemical Properties

CNCs have high mechanical strength properties relative to their size; the specific elastic modulus of CNCs is comparable to steel, but they are almost five times less dense and have a large surface area [4]. This strength, low density, and high aspect ratio combination make CNCs an ideal reinforcing agent for polymer nanocomposites. However, most commercial polymers are hydrophobic, and the highly hydrophilic CNCs tend to aggregate in nanocomposites due to the lack of interfacial compatibility [12][15]. The hydrophilicity of cellulose nanocrystals is due to the presence of the three hydroxyl groups on each glucose unit [16]. The contact angle of CNC films ranges from approximately 13-25°, depending on sample preparation [17]. The polymeric nature and high hydrophilicity contribute to the poor solubility of CNCs in most solvents, though they can be dispersed/suspended in certain organic solvents with strong sonication [16].

CNC thermal stability may be problematic for applications that require high temperature processing, such as melt mixing or thermal injection. The typical onset of thermal degradation for CNCs is between 200 and 300 °C, depending on the heating rate and surface modification [4]. These are common processing temperatures for many polymers that may be compatible with CNCs. CNCs produced by sulfuric acid hydrolysis, such as the ones used in this work, degrade around 260 °C. It is well known that CNCs with fewer surface sulfate ester groups are more thermally stable and that the rate of heating can also affect the onset of thermal degradation [10]. The loss in thermal stability due to the presence of sulfate ester groups arises because when heated, sulfate groups are freed from the surface and become sulfuric acid, which degrades the cellulose through a continued hydrolysis reaction. Impurities and small polysaccharides adsorbed onto CNCs may also hinder thermal stability and cause discoloration when subjected to heat.

2.3.3 Commercial Use

Cellulose nanocrystal production is a relatively inexpensive and scalable process compared with other nanomaterials such as carbon nanotubes. Pilot scale

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plants have been adopted by several companies with the hope that the material can be more economical than industrial multi-walled carbon nanotubes, which are between \$100 and \$250 per kilogram (AlphaNano Technology Co.).

Despite the abundance and potential of cellulose nanocrystals, most applications for the material are still under lab-scale investigations. High energy consumption required for production, as well as the moisture sensitivity and incompatibility with most polymers are drawbacks that have prevented more commercial incorporation of CNCs into paper and plastic material. Some applications, including pharmaceutical binders, food packaging films, and flexible solar cell panels are currently under investigation. The market for nanocellulose is expected to be worth \$250 million in North America by 2020, with between 2600 and 5500 tons produced. Current production rates are between 350 and 380 tons, 34% of which is CNCs. This is still small compared with the market for CNTs, which is projected to be worth almost \$2.4 billion by 2018 [18].

2.4 Modification of Cellulose Nanocrystals

2.4.1 Introduction and Background

In order to expand the use of CNCs commercially some of their properties, namely the hydrophilicity, must be tuned for specific applications. This can be done through chemical or physical modification using small molecules, monomers, or surfactants [16]. However, the scope of the modification is limited because the chemical composition of cellulose is largely determined by biosynthesis, and cannot be modified in the same way as a commercial synthetic polymer [16].

Modification of the surface hydroxyl groups on cellulose nanocrystals is ideal because it acts to remove hydrophilicity while potentially adding hydrophobicity and new chemical functionality. The increase in particle cost depends on modification conditions like solvent, surface group choice, and the initiator. Theoretically, these modifications should improve compatibility between CNCs and non-polar and hydrophobic solvents or polymers. These surface hydroxyl groups are also highly reactive, abundant, and easily accessible. Surface modifications with both covalent and noncovalent bonds have been explored in order to examine the effect on CNC dispersion and compatibility in different solvents and polymer matrices or to impart new chemical properties for various applications. For example, a physical modification of CNCs may use neutral or positively charged surfactants that adsorb to the CNC surface by van der Waals forces or electrostatic interactions [1][19]. However, chemical modification of CNCs is more versatile and includes (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO)-mediated oxidation [14], cationization, esterification, acetylation, silylization and polymer grafting [1]. A summary of some successful surface functionalization reactions for CNCs is shown in Figure 3 [20].



Figure 4: A visual diagram of the versatility of CNC modification reactions. Reproduced from Reference [20].

Grafting polymers onto the surface of CNCs is possible by two methods, namely "grafting to" and "grafting from", as shown in Figure 4. The "grafting to" strategy involves attaching a pre-synthesized polymer to one of the hydroxyl groups using a coupling agent, while the "grafting from" strategy involves initiating the surface of the CNC using an initiator and growing the polymer *in-situ* [1]. Habibi et al. were the first to report the "grafting from" technique using polycaprolactone and a ring-opening polymerization (ROP). Further "grafting from" reactions using CNCs have used atom transfer radical polymerization (ATRP) or oxidative polymerization which often require multiple steps and in the case of ATRP, a pre-synthesis step to attach the initiator to the surface of the CNCs [1].



Figure 5: Schematic diagram of a) "grafting to" and b) "grafting from" approach to CNC modification. Reproduced from Reference [21].

One of the main challenges in CNC modification is that many of the reactions take place in organic solvents. Since CNCs are insoluble and do not form colloidal suspensions in most organic solvents, many modification reactions require a temporary solvent exchange to suspend them in the organic medium, and another to re-suspend them back into water [21]. The process is tedious and induces agglomeration, and so modification reactions that use aqueous media are ideal. An example of such a reaction is the oxidative polymerization of polyaniline to CNCs *in-situ* in an acidic solution using ammonium peroxydisulfate [1].

2.4.2 Using Ceric Ammonium Nitrate

Ceric ammonium nitrate (CAN) is a useful redox initiator for cellulose because it is effective in water. CAN has been used to graft vinyl monomers (using the "grafting from" method) onto bulk cellulose, starch, and poly(vinyl alcohol) [22]. Historically, CAN was described to work only in the more accessible amorphous cellulose regions of bulk cellulose which would imply that CNCs may be too crystalline for grafting with CAN to be effective. To the contrary, our research group has recently reported using CAN to graft poly(4-vinyl pyridine) and poly(Nisopropylacrylamide) onto the surface of CNCs [21]. The specific mechanism of CAN and cellulose is still debated, but researchers suspect that it works by the oxidative cleavage of the cellulose backbone at the vicinal diol (C₂ and C₃) to create reactive aldehydes (see Figure 1 for cellulose structure carbon numbering) [23][22]. In this mechanism, shown in Scheme 2 with the methyl methacrylate monomer, the cellulose backbone is oxidized by CAN and free radicals are formed. A single electron is transferred from the hydroxyl group of cellulose to the ceric ion, and graft polymerization from this site begins [24][25]. The ceric ion forms a chelated complex with the cellulose backbone and electrons are transferred to Ce(IV) from cellulose, leading to Ce(III) and a radical site on the backbone. This radical electron transfers to the double bond of the monomer and the polymerization propagates until termination.



Scheme 2: Simplified mechanism for CAN-initiated "grafting from" reaction with methyl methacrylate to form PMMA-*g*-CNCs, showing initiation, propagation, chain growth, and the final products.

Though oxidation at the C_6 hydroxyl is also possible, model studies into the relative oxidation rates reveal that oxidation is more likely to occur at the C_2 - C_3 position [26]. Oxidation at the end of the cellulose chains, at the hemiacetal unit, is also possible and oxidation is actually 360 times more likely to occur there [27]. Due to the disparity of hemiacetal sites compared with the C_2 - C_3 sites along the cellulose backbone, however, this should not impact the structure of the polymer graft significantly.

2.5 Polymer Nanocomposites

2.5.1 General Overview

Polymer nanocomposites are a class of composites that have a polymer matrix and nano-sized particles dispersed within the matrix to add strength or functionality [28]. Most polymer composites are made to combine the strength of the reinforcement filler with the overall properties of the polymer matrix, as seen in Figure 6 [29]. Using nanoparticles instead of larger fillers is advantageous in theory because nanoparticles can improve composite properties with only a fraction of the loading. Adding nanoparticles to polymer matrices has the potential to create composites that have improved strength, thermal endurance, barrier properties, and abrasion resistance [30][31]. However, the nanoparticles tend to form aggregates due to their high specific surface area and surface energy [32]. These aggregations reduce the benefits obtained from the small particle size. Obtaining uniform dispersion is crucial for exploiting the full potential of nano-sized fillers, and there are several methods to accomplish this, either with additives or solvents, or without.

There are two main models that predict composite reinforcement; the Halpin-Kardos model and percolation theory. The Halpin-Kardos model predicts composite strength based on the Young's modulus, fiber aspect ratio, volume fraction, Poisson's ratios, and shear modulus of the nanocomposite components [30]. This model is not suitable for CNCs because it discounts all fiber-fiber interactions, so percolation theory is often used instead [33]. Nanoparticles with high aspect

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ratios will drastically improve nanocomposite strength, theoretically, once they are above the percolation threshold [34], though nanomaterials are still capable of reinforcement below this threshold. The percolation threshold occurs where the nanoparticles form an interconnected network, and is highly dependent on nanoparticle aspect ratio. In theory, CNCs with lengths of ~100 nm should have a percolation threshold of 2.4% [35]. This value is for perfectly dispersed nanocrystals, and aggregation of particles will increase the percolation threshold.

The reinforcement potential of nanocomposites can be estimated using the law of mixtures, which combines the volume fraction of the nanoparticle and matrix with their respective Young's modulus [30]. For CNCs and PMMA, which have Young's moduli of about 105 and 2 GPa respectively, a 2.7 vol. % CNC loading (equivalent to 2 wt. %) would more than double the Young's modulus of the nanocomposite to 4.77 GPa [4].



Strain

Figure 6: A generalized stress-strain curve showing the mechanical properties of the polymer matrix, the reinforcement and the resulting composite. Reproduced from Reference [26].

2.5.2 Nanocomposites with PMMA Matrices

Poly(methyl methacrylate), commercially made as Plexiglass^{™,} Acrylite®, Lucite^{™,} and Perspex^{™,} is a relatively common plastic used as a glass substitute due to its thermal stability, optical transparency, low density, and high impact strength [36][37]. As a result of its versatile applications in medical devices [38], optical lenses [36], and in building materials, PMMA is often used as a matrix for nanocomposites with clays [38][39], carbon nanotubes (CNT) [40][41], and inorganic crystals [42]. Often the fillers are used for reinforcing the plastic or to add electrical conductivity, as is with carbon nanotubes. Over 100 publications on PMMA nanocomposites have been published in 2014 alone on applications related to packaging, bio-sensing, synthetic bone materials, and UV-shielding lenses. The favorable properties of PMMA, including easy melt processing, as well as its low cost make it an ideal and popular matrix for nanocomposites.

2.5.3 Polymer Nanocomposites Reinforced with CNCs

As mentioned previously, CNCs are small, with a high surface area, good tensile strength, and a low density, which makes them an ideal reinforcing agent for polymer nanocomposites. The major challenge in incorporating CNCs into nanocomposites is finding compatible matrices. CNCs have a tendency to aggregate due to the strong interactions of surface hydroxyl groups and potential for hydrogen bonding [43]. Many groups have studied CNC nanocomposites with water soluble polymers such as waterborne polyurethanes (WPU) [44], PEO [43], poly(vinyl alcohol) [43], and polysaccharides [29]. Water soluble polymers are most commonly used for CNC nanocomposites because they provide the easiest processing method, which is simply mixing and then casting the aqueous suspensions of CNCs with dissolved polymer [43]. The mixture can also be freeze-dried or hot pressed. Due to strong interfacial adhesion between CNCs and hydrophilic matrices, the CNCs are dispersed and the nanocomposites have improved mechanical properties.

One way to avoid the need for water-soluble polymers is to create CNC nanocomposites via *in situ* polymerization of the matrix, where the nanocrystals are impregnated with a monomer that is then polymerized. This process has several advantages, including being solvent- and surfactant-free, and requiring virtually no post reaction work up [43]. However, this method has not been tested to a great extent and the CNCs need to be stable within the monomer used; successful examples reported in the literature include poly(lactic acid) [45][46][47][48], polystyrene, polypyrrole, and poly(furfuryl alcohol) [43]. For commonly used commercial polymers with highly toxic monomers, like MMA and styrene, other

methods are preferable. Dispersion of CNCs into these non-compatible polymers is more challenging and surface modifications or solvent exchanges are often necessary, depending on the polymer matrix. Melt mixing CNCs into polymers is another alternative and Chapter 2.5.5.2 is dedicated to this information.

2.5.4 Dispersion in Nanocomposites

Nanomaterials are highly sought after for reinforcing composites because the same, or better, reinforcing capabilities can be achieved using significantly less material. One of the main challenges in making nanocomposites is getting adequate dispersion of nanoparticles [49]. Extensive research has been done on polymer nanocomposites with carbon nanotubes, which are promising conductive reinforcing agents, but their full potential has been limited due to dispersion issues. Cellulose nanocrystals have similar complications, with high aspect ratio particles, a large surface area, and high surface energy in non-polar media.

Preventing aggregation of nanomaterials in composites is challenging because the high specific surface area encourages the particles to "stick" to one another due to strong interparticle interactions. This cohesion will reduce interactions with the matrix and create agglomerates in the system. The benefits of the nano-dimensions are diminished once agglomeration occurs because agglomerates have less reinforcing strength [32], there is less surface area available for reinforcement, and the percolation threshold is increased. Good dispersion of nano-sized materials will minimize the domains of unreinforced polymer and therefore limit weak points in the nanocomposites from more compartmentalized

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damage [32]. Dispersion is dictated by filler size and loading, which inherently affect the volume of the reinforced polymer. Surface interaction intensity, by contrast, is dictated by the surface structure of the particles as well as the chemistry [32]. Visually, this is represented in Figure 7 as smaller particles (17 nm) fill the uniform matrix more effectively than particles twice the size, at 1 wt. % and 4 wt. % loading. Halving the size of the nanoparticles while retaining the loading will lead to a 96% reduction in unreinforced domain, the same as increasing the loading by four times. Thus, reducing particle size is more effective for polymer reinforcement than simply adding more material. In fact, reducing the particle size by one order of magnitude leads to a reduction in the volume of unreinforced polymer by three orders of magnitude [32].



Figure 7: A visual representation of the scaling and loading effects on nanocomposite dispersion using particles and loadings of (a) 35 nm, 1 wt. %, (b) 35 nm, 4 wt. %, (c) 17 nm, 1 wt. %, (d) 17 nm, 4 wt. %. In perfectly uniform dispersions, (a) contains the largest domains of unreinforced polymer. Increasing the loading by 4 times has the same reduction in volume of unreinforced polymer as reducing the filler size by 50%. Adapted from [32].

The effect of the change from micro- to nano-scale filler on the three dimensional volume of unreinforced polymer is obvious when particles are used as an example in computer modeling, as shown in Figure 8. Particles of different sizes (blue) are modeled in 3-dimensional matrix space (grey) with the same loading. As particle size decreases, the volume of unreinforced polymer decreases significantly. Large aluminum oxide particles (~0.1 mm diameter) in a 1 mm³ volume leave a majority of the polymer matrix unreinforced at a loading of 0.1 vol. %, while carbon nanotubes (~10 nm width by 10,000 nm length) do not [49].



Fig. 3. Distribution of micro- and nano-scale fillers of the same 0.1 vol.% in a reference volume of 1 mm3 (A: Al₂O₃ particle; B: carbon fiber; C: GNP; D: CNT).

Figure 8: Comparison of the distribution of (A) Al₂O₃ particles, (B) carbon fibers, (C) gold nanoparticles and (D) carbon nanotubes, assuming a constant volume . Figure reproduced from Reference [40].

2.5.5 Nanocomposite Compounding Methods

2.5.5.1 General Overview

Nanocomposite polymer processing is an area that has been extensively studied due to the potential for strong reinforcement from cellulose nanocrystals and clay nanoparticles, as well as the conductive properties of carbon nanotubes. Researchers in this area are working to overcome particle aggregation while maintaining the desirable properties of the nanoparticles. For carbon nanotubes alone, processing methods have included solution chemistry to functionalize the nanotube surface, polymer coating of the nanotube surface, *in situ* polymerization, ultrasonic dispersion in solution, melt processing, surfactant/dispersant use, electrospinning, electrode chemistry, and gelation processing [50]. For polymerinorganic particle nanocomposites, functionalization, the use of dispersants and coupling agents, melt compounding by twin screw extrusion, in situ polymerization, solution blending, high shear mixing, and three roll milling have all been used to disperse nanoparticles [50]. With the large number of processing methods available, it is important to use one or more methods that are most compatible with the system in question. For CNC nanocomposites, many of the compounding methods are viable choices for dispersion because the chemistry of CNCs is tunable. Melt compounding and wet ball milling are the two methods chosen for this work.

2.5.5.2 Melt Mixing and CNCs

Melt mixing involves mixing polymers and nanomaterials at high temperatures; above the glass transition temperature, T_g, of amorphous polymers, and above the melting temperature, T_m, for semi-crystalline polymers [51]. For polymer nanocomposites, melt mixing can become problematic due to the high temperatures required to melt the polymers. Cellulose nanocrystals have thermal stability issues when heated, and degrade at temperatures exceeding 260 °C. As a result, low processing temperatures are required [43]. In addition, CNCs must be dried before being added to the polymer melt. Since drying induces agglomeration and even permanent aggregation if all water is removed [52] this can complicate dispersion further. Another downside to melt-processing methods is that the structural integrity of CNCs after processing may be compromised. Alloin et al. extruded CNCs with PEO and found that the lengths of the nanocrystals decreased from about 200 nm to 120 nm, and reported a significant narrowing of the CNC length distribution [43].

CNCs have been incorporated into nonpolar matrices using melt mixing, typically extrusion, but require processing aids, such as surface adsorbed PEG or PEO, to improve compatibility. Polyethylene and PLA are non-compatible polymers that have been used for matrices in CNC nanocomposites. Starch, a more compatible polymer for CNCs, can be melt mixed and extruded without the use of processing aids [43].
2.5.5.3 Wet Ball Milling and CNCs

Wet ball milling is a dispersion method that is commonly used in ceramic composite processing. It involves mixing aggregated or fragile particles in a chamber with a solvent and hard, inert spheres. The spheres, usually called balls, can be made of metal, stone, or polymer, and can have different sizes depending on conditions [53]. Dry, or solvent-free, ball milling has been used to grind materials into powders for pharmaceutical solids, metallurgy and cement [54][55][56][57]. Using solvents, which have lower surface tension than air, allows particles to be ground faster by keeping them stuck to the surface of the balls, which collide [58]. A schematic diagram of both methods appears in Figure 9. Wet milling is advantageous for mixing because it can be done using ambient temperatures and is applicable to all classes of nanomaterials [59]. However, to the best of our knowledge there are no examples in the literature of wet ball milling with CNC and polymers.

In the 1990s, researchers at Eastman Kodak Company successfully used polymeric balls in wet milling to break up pigment agglomerates. They found that weak aggregates (1.6-4.6 µm) and strong agglomerates (70-600 nm) had been broken up into individual particles (12 –100 nm) after 24 hours [53]. The monotone shift towards smaller particle size indicates clearly that the particles are breaking without significant re-aggregation. Hussain et al. (1996) reported that epoxy/aluminum oxide composites mixed by wet ball milling in ethanol had significantly less agglomeration and better performance compared with samples that had been dry ball milled or mechanically stirred [59].

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Figure 9: Schematic representation of (A) wet and (B) dry ball milling for particle dispersion and aggregate reduction. Adapted from Reference [58].

2.5.6 Mechanical Testing of Polymer Nanocomposites

Since polymer nanocomposites are generally designed to improve the physical properties of the matrix, specifically to increase the material strength and toughness, the most common method to test polymer nanocomposites is tensile testing. During tensile testing, a well-defined sample is subjected to a controlled tension force until it breaks [60]. From this test, which is relatively fast and inexpensive, information about the material's Young's modulus, the toughness, the strain, and the ultimate tensile strength can be obtained. This data gives an indication about the dispersion of the nanomaterials, and if the particles are effective reinforcing agents. Other mechanical tests for polymer nanocomposites include dynamic mechanical analysis and nanoindentation [61].

2.5.7 Rheology of Polymer Nanocomposites

The rheology of polymer nanocomposites is well studied and can give good insight into the reinforcing capabilities of a filler by measuring changes in the shear viscosity, η . Nanocomposite fillers such as clays, carbon nanotubes, and CNCs can increase the melt shear viscosity as well as the tensile strength, τ , and are measured by a rheometer. Rheology is a common characterization technique for CNTcontaining nanocomposites [62][63], and results of these studies show changes to the viscosity and shear modulus (G') from nanoparticle interconnectivity. Molecular modeling experiments have also been done to understand the effect of nanoparticle size and nanoparticle-polymer interactions on the viscosity of polymer nanocomposites.

The shear viscosity is largely affected by polymer chain bridging. When there are polymer-particle interactions and there is good dispersion, the nanoparticles act as a rigid template and the viscosity of the nanocomposite increases [64]. Clusters of rigid nanoparticles would lead to a smaller increase in the viscosity. The shear modulus, G', is the amount of energy stored elastically in the polymer melt, and it is also affected by nanoparticle-polymer interactions, particularly as nanoparticles form percolating networks. The more restraint present on polymer chain mobility, the larger the G' value at low frequencies and the smaller the slope of G' [64]. Perfect percolating networks of long nanomaterials like CNTs would reach theoretically flat slopes at low frequency, and research into CNT nanocomposites has found this to be true in high loading (>15%) CNT nanocomposites [63][62]. Since G' is largely dependent on fiber-fiber interactions, and therefore the length of fillers, CNCs (100 nm) are not expected to have as significant an impact as CNTs (several hundred nanometers) on the decreasing slope of the G' curve.

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Chapter 3: Materials and Methods

3.1 Materials

Cerium (IV) ammonium nitrate (CAN), sodium chloride (NaCl), inhibitor removers, poly(methyl methacrylate) (PMMA, $M_w = 120,000 \text{ g/mol}$), and methyl methacrylate (MMA) were purchased from Sigma-Aldrich. Nitric acid (70 wt. %) was obtained from EMD Chemicals, polyallylamine hydrochloride (PAH, Mw = 120,000-200,000 g/mol) was purchased from Polysciences, Inc, sulfuric acid (96 ± 0.15 wt. %) was purchased from Fischer Scientific and sodium hydroxide (NaOH, 0.1 M) and hydrochloric acid (HCl, 0.1 M) were purchased from LabChem Inc.

3.2 Preparation of Cellulose Nanocrystals

Suspensions of CNCs were prepared by sulfuric acid hydrolysis as described in [10]. 40 g of cotton filter aid (Whatman ashless filter aid, catalogue no. 1700025, GE Healthcare Canada, Mississauga, ON, Canada) was treated with sulfuric acid (700 mL, 64 wt. %) at 45 °C for 45 min with mechanical stirring. Following hydrolysis, the suspension was diluted 10-fold with purified Type I water (resistivity of 18.2 M Ω , Barnstead NANOpure Diamond system, Thermo Scientific, Asheville, NC) to quench the reaction. The resulting suspension was centrifuged for 10 min at 6000 RPM to concentrate the cellulose, while acid and excess water were removed. The precipitant was rinsed in purified water and re-centrifuged until the suspension could not be decanted further. Following this, the suspension was dialyzed in purified water until a constant neutral pH was achieved. The suspension was sonicated with an ice bath once for 15 minutes (Sonifier 450, Branson Ultrasonics, Danbury, CT) at 60% output. The final suspension was approximately 1 wt. % cellulose by weight and the key CNC characteristics are summarized in Table 2 below.

Characteristic	Instrument	Value
рН	pH meter	3.5
Size (microscopy)	AFM	~100 nm
Size (diameter)	DLS	119 ± 9 nm
Mobility	Zetasizer	- 3.4 (μ/s)/(V/cm)
Zeta Potential	Zetasizer	- 40 mV
% Sulfur	Conductometric Titration	0.53 ± 0.04 %

 Table 2: Summary of lab-made CNC properties.

3.3 Preparation of PMMA-g-CNCs

Suspensions of poly(methyl methacrylate) grafted from cellulose nanocrystals (PMMA-*g*-CNCs) were prepared using the following method. First, the MMA monomer was passed through an inhibitor column. Next, 20 mL of a 1 wt. % CNC suspension was added to a 50 mL round bottom flask with 0.75 mL of 70 wt. % HNO₃ and 1.17 mL of MMA. Under N₂ atmosphere, the mixture was sonicated at 60% output (Branson 450 sonifier) for 15 minutes in an ice bath, at which point 131 mg of CAN was dissolved in 1 mL of purified type I water and added to the mixture. The resulting mixture was sonicated continuously for 2 hours in an ice bath, then left stirring overnight at room temperature under N₂ atmosphere. Excess acid and homopolymer PMMA were removed by filtering with an ultrafiltration stirred cell (Millipore solvent-resistant stirred-cell, catalog #XFUF07601 with 76 mm

ultrafiltration discs, EMD Millipore, Billeria, MA) first with water, then with methyl ethyl ketone (MEK). The PMMA-*g*-CNC suspension was filtered through glass microfiber filter paper to remove any metal particles from the sonicator probe, and dialyzed against acidic water (pH 2). After dialysis, the PMMA-*g*-CNC suspension was ultrafiltrated at 3500 RPM with 100 kDa ultrafiltration tubes for 15 minutes to yield a 1 wt. % PMMA-*g*-CNC suspension, which was then stored in the refrigerator. In order to produce the required amount of PMMA-*g*-CNCs for the nanocomposites (~20 g), the reaction was scaled-up 10x using a sonicator bath.

3.3.1 Preparation of CAN Oxidized CNCs

As a control, CNCs were oxidized with CAN using the same reaction profile as above, but without the monomer, methyl methacrylate. Oxidized CNCs were extensively purified by dialysis and ultrafiltration to remove residual CAN and degraded polysaccharides.

3.4 Preparation and Characterization of CNC/PMMA Nanocomposites

A series of four samples with 0.25 wt. %, 0.5 wt. %, 1 wt. %, and 2 wt.% nanocrystal loadings with respect to PMMA for ball milled and melt mixed PMMA-*g*-CNC/PMMA and CNC/PMMA nanocomposites, for a total of 16 nanocomposites. This is in addition to ball milled and melt mixed PMMA as a control. Small test samples that were ball milled with 4 wt. % and 8 wt. % were made initially and characterized by SEM.

3.4.1 Nanocomposites by Ball Milling

Freeze dried CNCs were sonicated into MEK for 10 minutes, while PMMA-*g*-CNCs were never freeze dried and were already present in MEK. The ball-milling

preparation method is the same for each set of samples: 1 wt. % solutions of CNCs and PMMA-*g*-CNCs in MEK were added to plastic Nalgene bottles with approximately 50 g of PMMA and 250 mL MEK to form a series of nanocomposites with 0.25, 0.5, 1 and 2 wt. % CNCs with respect to PMMA mass. Metal balls (0.8 mm diameter) were added to each container at approximately half the liquid volume. The containers were put on rollers (175 RPM) to rotate for 24 hours. Then, the mixture was poured into a large container to facilitate MEK evaporation inside the fume hood. Once evaporated, the solid composite was mechanically broken up using a household blender (BL10450HB, Black and Decker, New Britain, CT), transferred into an open container and put in a vacuum oven at 60 °C for one week to remove remaining MEK. Following this, the composite was melt pressed at 160 °C, 7000 lbs (Carver Benhtop Standard Auto Series Carver Inc., Wabash, IN) to remove any MEK and to homogenize the material.

3.4.2 Nanocomposites by Melt Mixing

Freeze dried CNCs and PMMA-*g*-CNCs were mixed with approximately 50 g PMMA to form a series of nanocomposites with 0.25, 0.5, 1 and 2 wt. % CNCs with respect to PMMA. Samples were slowly added to a Haake melt mixer (Haake Rheomix, Thermo Scientific, Waltham, MA) at 160 °C and allowed to mix for 10 minutes at 60 RPM. Following this, the composite was melt pressed at 160 °C (Carver Benhtop Standard Auto Series Carver Inc., Wabash, IN) to remove any MEK and to homogenize the material.

3.5 Characterization Techniques

3.5.1 Fourier-Transform Infrared Spectroscopy

Freeze dried CNCs and PMMA-*g*-CNCs were incorporated into KBr pellets at approximately 1 wt. %, as was done for a neat PMMA sample. FTIR spectra were recorded in transmission mode on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific).

3.5.2 Atomic Force Microscopy (AFM)

Polished silicon wafers (Grinm Semiconductor Materials Co. Ltd, Beijing, China) were cut into 1 cm × 1 cm squares and dipped into a 0.1 wt. % PAH solution for 1 hour and rinsed in purified water to adsorb a cationic precursor layer on the substrate. The silicon wafers were then dropped with either 0.001 wt. % CNC or PMMA-*g*-CNC suspensions and spun at 400 RPM on a spin coater (Chemat Technology KW-4A, Northridge, CA). The cellulose-coated silicon wafers were imaged by AFM using a Nanoscope IIIa Multimode Scanning Probe Microscope with an E scanner (Bruker AXS, Santa Barbara, CA). The tapping mode images were collected in air with silicon cantilevers (AC 160TS, Olympus Canada Inc, Richmond Hill, ON, Canada).

3.5.3 Electrophoretic Mobility

The electrophoretic mobility was measured using a Zeta Potential ZetaPlus Analyzer (Brookhaven, Holtsville, NY). All samples were measured at 0.25 wt. % CNC concentrations, with 5 mM NaCl at 25 °C.

3.5.4 Dynamic Light Scattering (DLS)

DLS experiments were carried out with a Malvern Zetasizer Nano-S instrument (Malvern, Worcestershire, UK) with a detection angle of 173°. Suspensions of CNC

and PMMA-*g*-CNC were filtered through a Millipore Millex-FH nylon syringe filter (0.45 μ m) prior to the measurements, which were obtained at 0.05 wt. % CNC concentrations and 25 °C.

3.5.5 Rheology

Shear viscosity measurements of CNC and PMMA-*g*-CNC/PMMA composites were carried out on an ARES Rheometer at 170, 180 and 200 °C on disks (7 mm diameter, 1-2 mm thickness). The individual strain rate for each sample was found by performing a strain sweep test. Strain rates near the center of the linear region were taken as the strain rate for each sample. Frequency sweep tests were performed at each sample's strain rate. All data reported is an average of 3 test samples.

3.5.6 Scanning Electron Microscopy (SEM)

A Hitachi SU8000 STEM (Hitachi, Tokyo, Japan) was used to image nanocomposite samples. Ball milled nanocomposite samples were spin coated (4000 RPM) onto cleaned silicon wafers, which were fractured to view the cross section of the nanocomposite samples. Melt mixed sampled from broken Instron dogbones were imaged at the break point. SEM microtome images were obtained using a Lieca Ultra Cut-E Microtome fitted with a Diamond knife.

3.5.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis measurements were performed using a thermoanalyzer (Q5000, TA Instruments, New Castle, DE). 20-25 mg of freeze-dried CNCs and PMMA-g-CNCs were heated to 900 °C with a heating rate of 10 °C/min.

3.5.8 Tensile Testing

Nanocomposite samples were molded into dogbone shapes consistent with ASTM

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D638 (gage length 31.8 mm, width 4.4-4.6 mm, thickness 2-3 mm) for tensile testing using a 5 kN load cell, 1mm/min cross speed. Measurements were done using a table mounted Instron Universal tensile tester Model 3366 (Instron Corp., Norwood, MA).

3.5.9 X-Ray Diffraction (XRD)

X-Ray diffraction was performed on freeze-dried CNCs, oxidized CNCs, and PMMA-*g*-CNCs using a Bruker D8 Discover (Bruker Corp., Billerica, MA) with a cobalt sealed tube (λ_{avg} = 1.79026 Å), 35 kV, 45 mA and 0.5 mm micro slit. The sample was placed on top of a piece of Silicon wafer for the data collection. Two frames were collected to obtain a 20 range of 8-44°. Frames were also obtained for a blank Si wafer, which were subtracted from the sample frames. To determine the percent crystallinity of the sample, peaks were manually inserted to all the observed crystalline peaks, and a fixed amorphous peak was kept at 24.1°.

3.5.10 Optical Microscopy

A Keyence VHX 2000 Digital Microscope (Keyence Corp., Osaka, Japan) was used to optical image nanocomposite samples that were spin coated (4000 RPM) on to glass slides.

Chapter 4: Hydrophobic Modification and Characterization of Cellulose Nanocrystals

4.1 Surface Modification Reaction

PMMA-*g*-CNCs were prepared using a ceric ammonium nitrate-initiated "grafting from" polymerization reaction. The aqueous, one-pot synthesis is shown schematically in Figure 10. The PMMA-*g*-CNCs were purified by ultrafiltration with a stirred cell using water and methyl ethyl ketone to remove all excess acid, initiator and PMMA homopolymer. The worked-up suspensions showed limited stability in water, ethanol, methyl ethyl ketone and acetone, where they slowly sedimented to the bottom of their vials.



Figure 10: Schematic diagram of the "grafting from" polymerization of PMMA onto cellulose nanocrystals with CAN redox initiator.

When the grafting reaction was carried out at, or above, room temperature, the reaction mixture began to solidify with the increasing presence of PMMA homopolymer. Methyl methacrylate homopolymerizes at ambient temperatures with an initiator and is insoluble in water; this can be considered a competing reaction to the grafting of PMMA from the CNC surface. As such, the amount of PMMA grafted to CNCs is inferred to be small, however, quantitative characterization of the PMMA degree of polymerization or degree of functionalization on CNCs was not undertaken. In total, to prepare the nanocomposites described in Chapter 5, 20 g of PMMA-*g*-CNCs were synthesized.

4.2 Characterization of Modified Cellulose Nanocrystals

The presence of PMMA on the surface of the nanocrystals was confirmed by FTIR spectroscopy. The spectra of PMMA, CNCs, and PMMA-g-CNCs were compared, and are shown in Figure 11. The transmittance bands at 2990 and 1730 cm⁻¹ correspond to characteristic C-H and C=O PMMA stretches, respectively. PMMA-g-CNCs also show the same bands as unmodified CNCs. Though this result provides evidence for the presence of PMMA on the surface of CNCs, it cannot distinguish between PMMA that is covalently bound to the CNCs versus PMMA that is closely associated with the CNCs. Due to our previous experience grafting vinyl monomers to CNCs with this polymerization method, the extensive characterization carried out in that work [21], and the exhaustive purification used to remove PMMA homopolymer, we believe that PMMA is likely bound to the CNC surface. The aforementioned grafting reaction found that there was approximately 4300 units of polymer per CNC particle, one for every three surface anhydroglucose units [21]. The ideal amount of polymer grafted to the surface would be enough that the surface energy was lowered between the matrix and the nanoparticle, but that the particles could still form networks through interparticle interactions. The

significance between polymer-grafted and polymer-coated CNCs is unknown at this stage, but should be explored further.



Figure 11: FTIR spectra of PMMA (red), CNCs (blue), and PMMA-g-CNCs (black).

To verify that the size, morphology and degree of aggregation of CNCs were not significantly changed during the grafting reaction, the samples were characterized with AFM and DLS. AFM height images are presented in Figure 12 and show that PMMA-*g*-CNCs are similar in size to unmodified CNCs, but that small homopolymer particles (dots in Figure 12b) are apparent. For this specific PMMA-*g*-CNC sample, ultrafiltration purification was not undertaken which explains the presence of PMMA particles. The AFM images show that PMMA-*g*-CNCs are slightly more aggregated than unmodified CNCs. This result is unsurprising, given the tendency of the nanoparticles to come close together during the reaction at low pH and to possibly experience polymer bridging, and their visible flocculation in suspension after the reaction. Despite the appearance of some aggregates, individualized nanocrystals are also visible.

The *apparent* particle size of CNCs ($119 \pm 9 \text{ nm}$), PMMA-*g*-CNCs ($120 \pm 5 \text{ nm}$), and oxidized CNCs ($113 \pm 6 \text{ nm}$) suspended in water was measured using DLS. (The term *apparent* is used in recognition that DLS gives an average hydrodynamic diameter assuming spherical particles as calculated from the Stokes-Einstein equation and the CNCs or CNC aggregates are not spherical, thus these numbers are only used in comparison and should not be taken as absolute.) The particle sizes are within range of each other, and similar to other CNC batches measured in our lab. Oxidized CNCs (i.e., CNCs submitted to the same polymerization reaction conditions but without MMA monomer) are not significantly different in size from the starting CNCs. DLS also implies limited aggregation in the PMMA-*g*-CNC sample.



Figure 12: AFM height images of (a) CNCs and (b) PMMA-*g*-CNCs spin coated from 0.001 wt. % suspensions onto a PAH coated Si wafer, showing similar nanocrystals size and no aggregation.

Enhanced thermal stability up to ~300 °C was observed for PMMA-*g*-CNCs by thermogravimetric analysis (Figure 13b). This is further evidence that there is PMMA either covalently bound to the surface, or coated on the CNCs. The presence of two large peaks indicates that there could be two distinct components in the freeze-dried PMMA-*g*-CNCs, including PMMA homopolymer, which is consistent with polymer-coated CNCs or PMMA-*g*-CNCs. The onset of the major thermal degradation has shifted from 250 °C for unmodified CNCs to around 300 °C in PMMA-*g*-CNCs. This is consistent with the expectation that the thermal stability of PMMA-*g*-CNCs will lie between CNCs and PMMA, which begins to degrade around 350 °C when heated with the same 10 °C/min profile [65].

The X-ray diffraction was performed on samples of modified, oxidized, and unmodified CNCs to determine whether the grafting reaction has an effect on the crystallinity. Since the ceric initiator cleaves part of the cellulose backbone, it is expected that CNCs that have undergone the reaction will have a lower crystallinity than unmodified CNCs. Further, we anticipate that PMMA-*g*-CNCs will have a lower crystallinity compared with oxidized CNCs due to the presence of amorphous polymer on the surface. As expected, unmodified had the highest crystallinity at 90%, which is consistent with reported values [4]. Oxidized CNCs are slightly less crystalline at 89%, while PMMA-*g*-CNCs are 87% crystalline.

4.1 Summary

PMMA was polymerized with CNCs using a one-pot, aqueous reaction with CAN as the initiator. Characterization of this new material provided evidence that the grafting was effective. PMMA-*g*-CNCs do not form stable colloidal suspensions in

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solvents (as do unmodified CNCs in water), and are less crystalline, but they are similar in size and more thermally stable.



Figure 13: Thermal gravimetric analysis of (a) CNCs and (b) PMMA-*g*-CNCs heated at 10 °C/min showing both mass loss (green) and derivative weight loss (blue).TGA analyses performed by Analytical Services at Xerox Research Centre of Canada.

Chapter 5: Preparation and Characterization of CNC/PMMA Nanocomposites

5.1 Observations

CNC/PMMA nanocomposites were prepared by melt mixing (MM) with a Haake mixer at 160 °C for 10 min and by ball milling (BM) in MEK for 24 hours. Both unmodified CNCs and modified PMMA-*g*-CNCs were incorporated into bulk PMMA at loadings of 0.25, 0.5, 1 and 2 wt. %. Ball milled samples were not mixed at high temperature, but in order to make samples for mechanical testing, all nanocomposites were melt pressed at 160 °C. Some general observations are described below.

5.1.1 Foaming

Ball milled samples had residual MEK trapped within the nanocomposite (confirmed by NMR of ball milled samples which showed peaks which were not present for the melt mixed PMMA samples), which evaporated during hot pressing and created a white foam structure. After repeated pressing, the foam structure was eliminated in some samples but persisted in others. Melt mixed samples did not experience any foaming.

5.1.2 Color

Processing conditions and nanocrystal loading had an effect on the appearance of the nanocomposites, as pictured in Figure 14. Overall, the ball milled composites retained the optical properties and clarity of PMMA, which was clear and colorless. This optical transparency gives evidence that the bubbles from foaming are absent, or very small, and that trapped solvent may still be present if it

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did not react. Low loadings of ball milled composites with PMMA-*g*-CNCs had a slight orange tint compared with similar loadings of unmodified CNCs. Surprisingly the composite with the highest loading of ball milled PMMA-*g*-CNCs was a much darker shade of orange. This may occur from the interaction of the solvent, MEK, with the oxidation of the cellulose backbone.



Figure 14: Photographs of CNC/PMMA nanocomposites showing the different colors obtained from meltmixed and ball milled compounding methods.

Composites that were melt mixed had a much wider array of colors due to the higher temperatures experienced for longer times in the Haake mixer. Contrary to earlier tests, in which the unmodified CNCs caused significant discoloration compared with modified CNCs, the unmodified CNCs experienced less discoloration and had a more uniform color distribution over all samples. Generally, higher loadings of PMMA-*g*-CNC led to darker nanocomposites. The presence of water in the Haake mixer also led to darker colored nanocomposites (not shown).

We do not believe that the CNCs are fully degrading during melt mixing but that surface polysaccharides begin to caramelize under the experimental conditions used. This is consistent with the caramelization temperature of glucose, which is 160 °C. Caramelization occurs when glucose heated and loses water in a pyrolysis reaction, creating a variety of smaller molecules. There could also be differences in CNC thermal stability from the rate of temperature change. The TGA temperature is ramped at 10 °C/min giving a thermal degradation onset above 170 °C for both kinds of CNCs, while the addition of nanocrystals into the melted PMMA at 160 °C represents an almost instantaneous temperature increase to near the degradation temperature. Furthermore, the temperature profile within the Haake mixer is not uniform, implying that some CNCs are subjected to even higher temperatures. Alternatively, the discoloration may arise from the hydrolysis of cellulose by free sulfuric acid, which is from sulfate esters which are cleaved from the surface of CNCs. This discoloration is non-ideal as PMMA is often used for its optical properties, however, it is possible that the melt mixing conditions and degree of PMMA grafting from CNCs may possibly be tailored to give nanocomposites with better transparency.

5.2 Morphology of Nanocomposites

5.2.1 Scanning Electron Microscopy

The morphology of CNC and PMMA-*g*-CNC/PMMA nanocomposites was examined using SEM. Initially, high loadings of PMMA-*g*-CNCs that were ball milled for 24 hours were examined using SEM to view the threshold at which CNCs form networks (Figure 15). This experiment was performed with PMMA-*g*-CNCs that had not been subjected to the ultrafiltration stirred cell work up, so it is likely that there was still homopolymer in the PMMA-*g*-CNC sample and the real nanocrystals loadings are actually lower than stated. Clearly visible networks of PMMA-*g*-CNCs can be seen in the 8 wt. % loading sample. The lower loadings appear to have good distribution of small, white areas consistent with CNC size and confirmed in the literature. Since the 2 wt. % PMMA-*g*-CNC/PMMA nanocomposite showed good distribution and dispersion of the nanoparticles, we elected to use it as the highest loading for future experiments.



Figure 15: SEM images of a) 2%, b) 4%, and c) 8% loadings of PMMA-*g*-CNC in ball milled PMMA nanocomposites.,showing good nanoparticle (white) dispersion and distribution within he PMMA matrix (grey). SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

SEM images for ball milled nanocomposites with the lower experimental loadings of PMMA-*g*-CNCs are shown in Figure 16. Though the SEM samples are cross sectioned in the same way, there will always be inherent differences in the

way the nanocomposite will break, and so the images will have inconsistencies in composition. In addition, these nanocomposites were not heat processed and so are not completely analogous to the samples that have undergone mechanical testing. The lowest loadings of modified CNCs show very small white, round, regions of CNCs bound by PMMA with no obvious aggregates, which gives evidence that there the nanoparticles have been successfully dispersed form one another. Some of these white CNC regions are circled in the SEM images in red. Overall, the nanocrystals do not appear to be well distributed within the matrix, so ball milling with evaporation at these conditions may not be an ideal method to create uniform nanocomposites. At loadings above 1 wt. %, the light colored PMMA-g-CNC regions are more prevalent and are a clear part of the nanocomposite. In the 2 wt. % sample, the PMMA-g-CNC areas appear to be close to forming a particle network. The SEM images give evidence that there are PMMA-g-CNCs present in the matrix and that the amount of CNC region is affected by the loading. Given the preparation of the material, it is also possible that these regions, which appear to have good PMMA-g-CNC distribution, are actually composed entirely of aggregated nanocrystals. Since those types of large aggregates will disturb the cohesive polymer matrix, the material is more likely break in those places. This will be explored further with SEM microtomes of the samples.



0.5 wt. %, (C) 1 wt. %, (D) 2 wt. % PMMA-*g*-CNC in PMMA on silicon wafers, showing nanoparticle dispersion and distribution within the matrix. SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

SEM images of ball milled CNC/PMMA composites appear in Figure 17. The highest loading (2 wt. %) was not completed in time for the preparation of this Chapter. The trend for CNCs in PMMA is less clear than with the PMMA-*g*-CNC/PMMA composites. In the 0.25 wt. % CNC loaded nanocomposite, there are large regions of polymer (grey) with no nanocrystals at the bottom right corner of the image, and regions with high CNC concentrations (white) in the top of the image, especially the top right corner. These regions are circled in red. Similarly, the nanocomposite with 1 wt. % CNC loading has bands of regions that show CNCs in the top left corner and the center, as well as some CNCs at the bottom right corner. Other regions appear to have no CNCs. By contrast, the 0.5 wt. % CNC loading has almost no clear polymer regions without CNCs. It is therefore likely that other areas

of the 0.5 wt. % would show large regions of unreinforced polymer. From these images alone, it appears that for ball milled samples, CNCs aggregate more in the PMMA matrix than PMMA-*g*-CNCs, as expected. However, given that the sample is more likely to break at areas with agglomerates, this could instead give evidence that CNCs have smaller agglomerates than PMMA-*g*-CNCs. The outer bounds of the agglomerated areas are visible at this magnification, which gives evidence that at least some of the agglomerates are smaller than $2x2 \ \mu m^2$, which would not be the case for samples with PMMA-*g*-CNCs, if the SEM images only show agglomerates.



Figure 17: SEM cross-section of spin-coated ball milled (A) 0.25 wt. %, (B) 0.5 wt. %, and (C) 1 wt. % CNC/PMMA nanocomposite samples on silicon wafers that shows poor distribution of nanocrystals (white) in the matrix (grey). SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

Melt mixed samples taken from broken Instron dogbones. The loadings of 0.25 wt. % and 2 wt. % of CNCs and PMMA-*g*-CNCs were investigated for CNC dispersion and are shown in Figure 18. Similarly to the ball milled nanocomposites, higher loadings of CNCs appear as small white particles within the PMMA matrix (grey). By contrast, the 2 wt. % loading of PMMA-g-CNCs show no clear difference from PMMA. This indicates that the PMMA-g-CNC/PMMA composites have a lot of unreinforced polymer from nanoparticle aggregation. Lower loadings of modified and unmodified nanocrystals do not clearly shows the presence of nanocrystals within the matrix. This is likely because there is not enough material.



Figure 18: SEM images of broken dogbone edges used for tensile testing of (A) PMMA, (A) 0.25 wt. % CNCs, (A) 2 wt. % CNCs, (D) 0.25 wt. % PMMA-*g*-CNCs, (E) 2 wt. % PMMA-*g*-CNCs. SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

To get a better understanding of how modified and unmodified CNCs are distributed in the melt mixed nanocomposite dogbones, the 2 wt. % loadings were microtomed and examined using the SEM. Agglomerates were visible in both CNCand PMMA-*g*-CNC-containing samples, and samples of unreinforced PMMA showed no particle agglomerates (Figure 19). The distribution of particles was different for each sample; PMMA-*g*-CNCs were present in large (>50 um) agglomerations that were unevenly distributed throughout the polymer matrix, while unmodified CNCs had much smaller, more evenly distributed regions. This result is consistent with the alternate explanation of the previous SEM images, which was that the PMMA-*g*-CNC/PMMA composite images only showed agglomerates, while CNC/PMMA composite images showed both agglomerates and PMMA matrix. This is further evidence that PMMA-*g*-CNCs have inferior distribution in PMMA after melt mixing and ball-milling compared with unmodified CNCs, and form larger agglomerates at these processing conditions.



B) Microtome of melt mixed CNC/PMMA dogbone

C) Microtome of melt mixed PMMA-g-CNC/PMMA dogbone



Figure 19: SEM images of microtome melt mixed (A): PMMA, (B) 2 wt. % CNC/PMMA, and (C) 2 wt. % PMMA-g-CNC/PMMA nanocomposites from dogbone samples, showing agglomeration of the nanoparticles. SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

Images of the agglomerated nanoparticles at higher magnification are shown in Figure 20. The CNC/PMMA sample shows a nanocrystals with a different morphology than in the PMMA-*g*-CNC/PMMA sample, as the nanoparticles appear in a linear ridge mixed partially with smooth PMMA. By contrast, the PMMA-*g*-CNC/PMMA sample shows jagged particles with no smooth PMMA regions. Again, this gives evidence that CNCs are better dispersed and less agglomerated in the PMMA matrix than PMMA-*g*-CNCs.



Figure 20: SEM images of microtome melt mixed (A) 2 wt. % CNC/PMMA and (B) 2 wt. % PMMA-*g*-CNC/PMMA nanocomposites from dogbone samples, showing a close up of agglomerated particles. SEM images prepared by Sandra Gardner at Xerox Research Centre of Canada.

5.2.2 Optical Microscopy and Atomic Force Microscopy

Nanocomposites of ball milled PMMA-*g*-CNCs and PMMA were studied using optical microscopy and AFM. The ball milled samples were spin coated on to clean glass slides without any other preparation. Under the optical microscope, high loadings of PMMA-*g*-CNCs in the nanocomposite are correlated with large circular areas with diameters under 100 µm on the surface (Figure 21). Initially, these areas appeared to be aggregates of PMMA-*g*-CNCs, but AFM images (Figure 22) confirmed that they were open pores on the nanocomposite surface. The exact reason for these pores is unknown, but it is clearly related to the amount of nanoparticles in the matrix. One possible explanation is that there is water or solvent bound to the PMMA-*g*-CNC surface and it removed or evaporates more slowly than MEK. We do not suspect that this is caused by phase separation in the material or particle aggregation, and it may be related to the foaming of the ball milled nanocomposites when they are heated. Further study into this phenomenon is necessary.



Figure 21: Optical microscopy images of A) 0.25 wt. %, B) 0.5 wt. %, C) 1 wt. %, and D) 2 wt. % ball milled PMMA-g-CNC/PMMA nanocomposites spin coated onto a glass slide. Large holes begin to appear on the surface of the nanocomposites with increasing PMMA-g-CNC content.



Figure 22: AFM images of A) 0.25 wt. %, B) 0.5 wt. %, C) 1 wt. %, and D) 2 wt. % ball milled PMMA-g-CNC/PMMA nanocomposites spin coated onto a glass slide. Large holes begin to appear on the surface of the nanocomposites with increasing PMMA-g-CNC content.

5.3 Rheology of Nanocomposites

5.3.1 Shear Viscosity (η)

The average shear viscosity of ball milled and melt mixed PMMA at 200 °C was compared with the viscosities of the nanocomposite samples with 2 wt. % CNC and PMMA-a-CNC loadings, and with each other. Melt mixed PMMA had a 44% higher viscosity than ball milled PMMA (Figure 23), which suggests that the processing method has changed the way the polymer chains interact with one another, though it is possible that this is due to residual solvent or impurities in the ball milled samples. The difference is not likely to be from thermal degradation (including crosslinking) of PMMA, which occurs past 300 °C, but instead from either the effects of removing the solvent, MEK, or from trapped solvent. MEK plasticizes PMMA, and the polymer chains will expand in volume and create many polymer-MEK contacts. Upon rapid heating and pressure at 160 °C (i.e., during hot pressing), the MEK quickly evaporates and forces the polymer chains together quickly, potentially creating polymer globules [66]. Due to the presence of either tightly coiled polymer chains or solvent, there are fewer polymer chain interactions and viscosity decreases. It is expected that all ball milled samples will have lower viscosity than the melt mixed samples, however only the highest nanoparticle loading (2 wt. %) was tested at 200 °C. Loadings of 0.25 wt. % nanocomposites were tested at 170 and 180 °C, but showed no discernable difference to PMMA or to 2 wt. % nanocomposites because the temperature too close to the melting temperature of PMMA (160 °C) and the samples still had some solid character.



Figure 23: Average viscosity of melt mixed (MM) and ball milled (BM) PMMA at 200 °C.

For ball milled samples, the composite with CNCs had a higher viscosity than both the control, PMMA, and the modified CNCs (Figure 24a). This gives evidence that the CNCs, having been reasonably well dispersed into the matrix, are forming networks with the polymer chains and with other CNCs to create a stronger network structure than PMMA alone. By contrast, samples with PMMA-*g*-CNCs had a lower viscosity than the control. The surface PMMA groups on the PMMA-*g*-CNCs would undergo the same rapid coiling as the PMMA chains and may cause more steric effects by taking up more space, preventing the PMMA chains from forming good interactions with the nanocrystals. Alternatively, more MEK could have been absorbed by the modified nanocrystals.

For melt mixed samples, the PMMA control sample had the highest average viscosity (Figure 24b), which suggests that the addition of both CNCs and PMMA-*g*-CNCs had a negative impact on the interconnected PMMA structure by poor

dispersion. This is consistent with the SEM images that show large agglomerates of the nanoparticles, particular the PMMA-*g*-CNCs. The modified CNCs again gave the composite a lower viscosity than the unmodified CNCs. Degradation by scission is also a possibility for the increase in the polymer viscosity.



Figure 24: Viscosity of (A) ball milled (B) melt mixed 2 wt. % loadings of CNC/PMMA composites and PMMA at 200 °C.

5.3.2 Shear Modulus (G')

The shear modulus (G') of the nanocomposites showed similar trends to the viscosity. Melt mixed PMMA has a higher G' than ball milled PMMA (Figure 25), indicating that the PMMA chains have less chain interaction when solvent is removed. This can again be attributed to the formation of PMMA "globules" during heating due to solvent evaporation, or from solvent trapping.



Figure 25: Storage modulus of melt mixed (MM) and ball milled (BM) PMMA with no CNCs.

The graph showing melt mixed samples shows that unreinforced PMMA had the highest storage modulus, followed by unmodified CNCs and tghen PMMA-*g*-CNCs, indicating that both nanocrystals had a negative impact on the strength of the matrix. This is likely due to poor dispersion of the nanocrystals in the nanocomposite, as well as caramelization. During processing, PMMA-*g*-CNC/PMMA nanocomposites experienced more degradation and appeared dark brown as shown in Figure 26. Degradation of the CNCs may impact their crystallinity and strength, which could explain why those composites had both a lower viscosity and storage modulus compared to the PMMA control.

In ball milled samples, again the nanocomposites with CNCs had values that indicated better reinforcement than both PMMA and PMMA-*g*-CNC/PMMA. This is good evidence that the CNCs are somewhat dispersed in the matrix and have started to create some networks within the molten polymer, which is weaker than melt mixed polymer and therefore easier to reinforce. Conversely, samples with modified CNCs had a lower modulus. The PMMA-*g*-CNCs are not forming particle networks, and are instead interfering with the relatively strong chain interactions of PMMA. Again, this could be from the collapse of surface PMMA groups on CNCs, which would have poor interaction with the matrix PMMA.


Figure 26: Storage modulus of (A) melt mixed (MM) and (B) ball milled (BM) nanocomposites.

5.4 Summary of Rheology

The rheological data presented here show that there are only small differences in the nanocomposites, which is to be expected because each sample is at least ~98 wt. % PMMA. However there were notable differences in both the processing methods and the degree of CNC modification. Ball milled samples had a

lower viscosity and storage modulus compared with their counterpart melt mixed samples. Nanocomposites with CNCs had higher mechanical properties than PMMA*g*-CNCs in all cases, and ball milled nanocomposites with CNCs had higher rheological properties than ball milled PMMA. This gives evidence that the ballmilling, and specifically the addition and removal of solvent, creates weaker composites at these processing conditions due to the coiling of the individual PMMA polymer chains. The rheological trends agree with the SEM microtome images of the samples, which showed worse dispersion with PMMA-*g*-CNC/PMMA nanocomposites.

5.5 CNC/PMMA Nanocomposite Performance

Tensile tests were performed on each sample and the Young's modulus was calculated. Figures 27 and 28 compare two groups of samples in four ways; (i) melt mixed and ball milled CNC/PMMA nanocomposites (Figure 27a), (ii) melt mixed and balled milled PMMA-*g*-CNC/PMMA nanocomposites (Figure 27b) (iii) melt mixed CNC and PMMA-*g*-CNC/PMMA nanocomposites (Figure 28a) and (iv) ball milled CNC and PMMA-*g*-CNC/PMMA nanocomposites (Figure 28b). The data sets for each pair of complimentary samples, shown adjacent to one another in the graphs, were statistically analyzed using a t-test assuming unequal variance with p<0.05. The significance that the populations were from different groups was reported with statistical standards for p values and shown at the top of each pair. All values for the Young's modulus of these nanocomposites are significantly below the calculated theoretical Young's modulus from 2 wt. % CNC addition, which was 4.77 GPa (as shown in section 2.5.1).

Melt mixed CNC/PMMA composites generally had increased modulus values as more CNCs were added, and the highest loading statistically outperformed unreinforced PMMA. This result is somewhat disappointing, but shows that the strength of CNCs can overcome some thermal degradation and contribute to the reinforcement of the polymer at higher loadings. Ball milled CNC/PMMA nanocomposites statistically performed the same regardless of CNC content, indicating that the nanoparticles had no net effect on the reinforcement of PMMA.

Melt mixed PMMA-*g*-CNC/PMMA composites at all loadings were statistically identical to each another, though samples with PMMA-*g*-CNC had a larger sample spread. This indicates that PMMA-*g*-CNCs provide no statistical reinforcement on the PMMA matrix, but can cause larger discrepancies within the samples. Similarly, ball milled PMMA-*g*-CNC/PMMA nanocomposites showed no statistical differences from one another, including unreinforced PMMA.

This data agrees with the rheology data in that ball milled samples mechanically underperform compared to melt mixed samples in almost all cases. The only samples in which ball milled and melt mixed samples had the same performance was at the lowest loadings of CNCs, 0.25 and 0.5 wt. %, which were the same melt mixed samples that also had the most thermal degradation discoloration.





Comparing the effects of melt mixed CNC and PMMA-*g*-CNC/PMMA nanocomposites (Figure 28), we found that PMMA-*g*-CNCs showed more consistency with respect to loading than nanocomposites with unmodified CNCs after both melt mixing and ball milling. Again, this is consistent with SEM and rheology data, as PMMA-g-CNCs form large agglomerations in the matrix, which hinders nanocomposite performance in those areas. For melt mixed CNCs, the trend for the Young's modulus is more correlated with nanoparticle loading, which is also expected based on the smaller agglomerate sizes, and therefore a larger reinforced nanocomposite volume.

The toughness was also calculated from the Instron tensile testing and all composites were found have the same toughness within error (ca. 0.8 MPa) as shown in Figure 29.



Figure 28: Comparison of the Young's modulus for (A) melt mixed and (B) ball milled PMMA nancomposites with CNCs and PMMA-*g*-CNCs (PCNCs), loadings are indicated along the x axis in wt. %. ns not significant at p < 0.05; * significant at p < 0.05; ** significant and p < 0.01; *** significant at p < 0.001; **** significant at p < 0.001



Figure 29: Comparison of the toughness for (A) melt mixed and (B) ball milled PMMA nancomposites with CNCs and PMMA-g-CNCs (PCNCs), loadings are indicated along the x axis in wt. %.

Chapter 6: Conclusions and Recommendations

Harnessing the unique properties of nanomaterials for improving composites has become a popular area of research in the past decade. Cellulose nanocrystals have the added advantages of being low cost, biodegradable, and mechanically strong with tunable surface chemistry. Using CNCs as reinforcing agents for nanocomposites may be a major area of development in the coming years.

In this thesis, we have presented (1) the surface modification of cellulose nanocrystals with PMMA, (2) the effect of modified and unmodified CNC loading in nanocomposites, and (3) the differences in rheological and mechanical properties of melt mixed and ball milled CNC/PMMA nanocomposites. This work is a good first step towards better fundamental knowledge of CNC-containing products for future academic and industrial projects.

In the CNC surface modification section (Chapter 4), to the best of our knowledge, we have presented the first example CNCs with grafted PMMA. This novel result adds to the many surface modifications of CNCs. Our method is straightforward and industrially feasible, and extends previous work in the Cranston group whereby other (more hydrophilic) vinyl monomers were grafted to CNCs using ceric ammonium nitrate as the free radical polymerization initiator. The PMMA-*g*-CNCs had the same size, morphology, and crystallinity as unmodified CNCs, and the FTIR spectra provided evidence that there was PMMA associated with the CNC surface.

In the CNC/PMMA nanocomposite section (Chapter 5), we have presented new nanocomposites with modified and unmodified CNCs within a PMMA matrix by wet ball milling and melt mixing. Our expectation was that CNCs modified with PMMA would have better compatibility and lower surface energy within the PMMA matrix, which would lead to better dispersion and better mechanical properties. Contrary to our expectations, the PMMA-*g*-CNCs samples showed lower dispersion in the matrix and lower viscosity, shear modulus, and Young's modulus values compared with unmodified CNCs.

Grafting polymers to the CNC surface may weaken the physical CNC interface, and while the chemical compatibility with PMMA may be enhanced, the degree of grafting may be too low to cause any effects in the bulk material properties. While SEM, AFM and optical microscopy were used to assess CNC dispersion within the polymer matrix, the full set of samples was not measured and it is therefore difficult to make absolute conclusions about differences in dispersion. Overall, large agglomerates of modified and unmodified CNCs were observed in the SEM microtome images, and the distribution of PMMA-*g*-CNC samples was less uniform than for unmodified CNCs.

Nanocomposites prepared both ways, i.e., by both ball milling and melt mixing, did not show significant improvement in mechanical properties over PMMA control samples. Ball milled composites, including PMMA, performed significantly worse than melt mixed samples, making these processing conditions undesirable for future composites. We suspect that the ball milled samples are inferior overall due

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to either trapped solvent, or the relatively fast removal of solvent from the system (during both evaporation and heating), which causes the polymer chains to coil. Both theories would support a reduced polymer chain interaction and a weaker material overall. This behaviour has a stronger effect on weakening the composite than the nanocrystals do in strengthening it, which could be why the ball milled samples are statistically identical to each other, and do not have the same mechanical properties as melt mixed samples.

For melt mixed CNC/PMMA nanocomposites, improvements in the mechanical strength came with increased loading, as expected. The more reinforcing agent present in the system, the more likely that it will reinforce the matrix, in the absence of aggregation. For PMMA-g-CNC/PMMA nanocomposites, all samples had the same Young's modulus, statistically. This result can be explained in different ways. First, that the increasing reinforcement from adding nanocrystals is counteracted by thermal degradation, which was prominent in samples with high PMMA-g-CNC loading. Alternatively, large agglomerates in the material could counteract the reinforcement from adding nanocrystals, which was observed more prominently for samples with PMMA-g-CNCs. Finally PMMA-g-CNCs may not be effective reinforcing agents at all. Most likely, the lack of reinforcement at high loadings comes from thermal degradation and particle agglomeration, since PMMAg-CNCs are similar in size, morphology, and crystallinity to unmodified CNCs. Though PMMA-g-CNCs exhibit elevated thermal stability below 300 °C, the heating during TGA is slow and step-wise, while the addition of CNCs to the melt mixer at 160 °C is rapid.

Future work on this project should include a quantitative characterization of the grafted nanocrystals to determine average polymer chain length and average number of grafts on each CNC. This may be accomplished using mass spectrometry and/or enzymatic degradation of the cellulose backbone to liberate the grafted PMMA chains. Next, optimizing the grafting reaction to maximize the number and chain length of PMMA grafts, should be undertaken. This can be done by using previous techniques to characterize grafting reactions with different times, initiator concentration, or monomer concentration. More controlled polymerization techniques (i.e., ATRP) may be needed to get the full range of surface modifications needed to elucidate the effect of polymer surface grafting on composite properties.

Further characterization of the nanocomposites is also necessary, including completing the SEM series with images of ball milled samples from broken dogbones. Dispersion of CNCs in the composites could also be assessed with modulus mapping by AFM. Changing the processing method, polymer matrix, and surface groups on the CNCs are also areas of interest for future work. Applying similar modification chemistry with the general processing approaches presented here but with softer hydrophobic polymers will likely produce nanocomposites where the effect of adding unmodified or modified CNCs is more enhanced. Adding high shear mixing with extrusion may allow for alignment of the nanoparticles, which would strengthen the composite. Finally, reducing the amount of sulfur surface esters may give better CNC thermal stability and reduce discoloration in melt mixed samples. In summary, the surface grafting of PMMA onto cellulose nanocrystals was done to improve the surface compatibility of CNCs with a PMMA nanocomposite matrix. Our work focused specifically on the modification with CAN because it is a quick, aqueous based reaction with minimal purification, and can be scaled industrially. Mechanical testing on CNC/PMMA and PMMA-*g*-CNC/PMMA nanocomposites made by melt mixing and ball milling was done to examine the effects of the both the mixing method and the surface modification on the properties of the new material. There are further challenges in tuning surface chemistry of CNCs for polymer matrix compatibility; this work is one step towards tailored nanomaterials that take advantage of CNC strength and tunability to enhance the properties of polymer nanocomposites.

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