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Overview of Carbon Nanocrystals (CNCs) and CNC Polymer Composites

Gaelen Clayton

Introduction

Carbon nanocrystals (CNCs) are a biodegradable, sustainable, high strength material with many potential applications. One of the main areas of study is their use as fillers in polymer matrices to improve mechanical and film properties of these materials. This report will cover the methods used to synthesize CNCs from hardwood pulp, and to prepare soy protein isolate (SPI) and CNC composite films. It will also provide a survey of contemporary literature on CNCs, and discuss the current theories and research being conducted on CNCs and CNC composite films.

Methods

Materials:

- Paper pulp
- 64% Sulfuric acid
- Deionized water
- SPI powder
- Glycerol
- NaOH solution

Synthesis of CNCs via Sulfuric Acid Hydrolysis

Around 10g of pulp (scaled as needed) was measured into a 500 mL Erlenmeyer flask using a funnel. The scale was tared without the weight of the funnel to ensure that the measurement did not include pulp stuck to the sides of the funnel. 10x the amount of pulp (~100mL) of 64% sulfuric acid was added to the flask and stirred using a glass rod until no white flakes of pulp were visible. The mixture was placed in a 45°C oil bath, a stir bar was added and turned to ~40 rpm. The speed was increased to up to ~150 rpm as the cellulose broke down and the mixture liquified. The solution was kept in the bath until it started to turn slightly black, around 30 min. Then the solution was removed, immersed in ice, and diluted 10 fold using ~900 mL of deionized water to quench the reaction.

The solution was then transferred to four 50mL centrifuge tubes. Around 35mL was added to the first tube, then the others were filled so that the weights were ± 0.05 g from the weight of the first tube. The tubes were then centrifuged for 30 min at 4300 rpm. The supernatant fluid was drained, and the tubes were refilled up to 35mL. The tubes were placed back in the centrifuge for another 30 min. This process was repeated until all the solution had been centrifuged.

A dialysis bag was prepared by soaking in water and clamping one end. The solid CNCs were suspended using minimal water and the resulting solution was added to the dialysis bag. The other side of the bag was clamped and the bag was allowed to dialyze for a minimum of 2-3 days. Finally, the CNCs were removed and freeze-dried using liquid nitrogen for 2-3 days.

Preparation of SPI-CNC-nanocomposite films

5g of SPI powder and 2.5g of glycerol were added to 95 mL of deionized water in a 500mL Erlenmeyer flask. The glycerol was measured first, and the SPI powder was then weighed to be exactly twice the weight of the glycerol. The water was then added in order to have a ratio between SPI and water of 1:19, for a final ratio of glycerol/SPI/water of 0.5:1:19. NaOH solution was then added until the pH of the mixture was 9.0 ± 0.2 . A stir bar was added and the mixture was stirred at 85°C for 30 min in an oil bath. To find the amount of CNC to add to the solution in order to form a film with a certain percent of CNC, the following equation was used.

$$CNC (g) = Solution (g) \cdot \frac{SPI (g) + Glycerol (g)}{SPI (g) + Glycerol (g) + H_2O (g)} \cdot \frac{CNC \text{ in composite } (\%)}{SPI (g) + Glycerol (g)}$$

The CNCs were added to the mixture as according to the formula above, and the mixture was divided into 50 mL aliquots and sonicated for 5 min with 1 min processing time intervals with 15 s pulse time at 100% power. The solution was placed in ice in the sonicator to prevent overheating. The sonicated mixture was then degassed by transferring the solution to a vacuum flask and connecting a vacuum for 10 min. The vacuum was released slowly from the side and the mixture was ready for casting.

The casting apparatus was set up by placing plastic molds in the shape of a dog-bone on a metal plate, and weighing them down. 0.8 mL of mixture was added to each mold, with care taken to ensure that the mixture was uniformly distributed, especially in the center of the dog-bone. The molds were then placed in a controlled chamber at 25°C and 53% humidity for 48 h for the films to dry before testing. The films were then removed from the plate by removing the molds from the plate and then using razors to separate the film from the metal. The removed films were stored in the controlled chamber until mechanical testing.

Survey of Literature

Cellulose nanocrystals (CNCs), also known as cellulose nanofibrils or nanowhiskers, are microscopic crystals derived from raw cellulose. CNCs are a biodegradable, sustainable, high strength material and as such a significant amount of research has gone into their potential applications, such as their use as a filler in a polymer matrix. Raw cellulose is found in many organic substances, such as bacteria and plant cell walls. Composed of long chains of beta-cellulose monomers, these long chains pack together to form microfibrils, which are further assembled into cellulose fibers (Habibi, 2010). The structure of cellulose varies greatly, with six polymorphs of cellulose having been identified. The most prevalent type, Cellulose I, has two suballomorphs, Cellulose I- α and I- β , which differ in their hydrogen-bonding patterns (Habibi, 2010). Cellulose is composed of both crystalline and amorphous regions. To create a useful material, the amorphous regions must be removed.

The crystalline regions of cellulose have an extremely high tensile strength, theoretically stronger than steel (Habibi, 2010). In order to form CNCs, the amorphous regions, which contain materials such as starch, lignin, and hemicellulose, must be removed (Lu, 2013). This is often achieved by acid hydrolysis. Acids such as HCl or sulfuric acid can be used to hydrolyze the cellulose, removing the amorphous regions and breaking the long chains into smaller, nano-sized particles, which are called CNCs. XRD analysis shows a significant increase in crystallinity from raw cellulose to cellulose nanocrystals (Lu, 2013). These CNCs usually have a high aspect ratio (Xiao, 2021), and sulfuric acid hydrolysis also leaves

sulfate groups on the surface of the CNCs, which can increase electronegativity and hydrogen bonding potential.

While CNCs have admirable qualities, their applications on their own are limited. Instead, research has focused on their use as reinforcing fillers in polymer matrices. When added to such a matrix, CNCs can improve qualities, such as tensile strength, elastic modulus, moisture uptake, and swelling. However, these benefits are limited by the dispersion of CNCs in a matrix. While CNC/hydrophilic polymer composites are easily prepared, the hydrophilicity of the composite creates unsatisfactory moisture properties and are of little use. Dispersion of CNCs into hydrophobic polymers has proven a challenge. This lack of dispersion can cause aggregations, where CNCs clump together instead of evenly distributing themselves throughout the matrix. This happens when hydrogen bonding overpowers negative surface charges on the CNCs, causing attraction, and is exacerbated when the CNCs are dried (Agustin, 2013). Aggregation creates an uneven surface and worsens qualities such as tensile strength and swelling. Sulfuric acid hydrolysis leaves sulfate groups on the surface of the CNCs, which can increase electronegativity and hydrogen bonding potential (Xiao, 2021), promoting better dispersion of CNCs into the polymer. As discussed below, modifications to the surface of CNCs, such as polydopamine coatings, may promote better dispersion as well.

CNCs increase the tensile strength of polymer matrices by creating percolation networks between the particles. When the concentration of CNCs passes the percolation threshold, the CNC particles begin to interact with each other and produce nanoeffects that strengthen the matrix beyond the increases of strength resulting from the simple mixture rule at lower concentrations. This network creates a homogenous and ordered microstructure, compared to the disordered matrix before the addition of CNCs (Xiao, 2021). A few things can increase the tensile strength of a composite. The first is the amount of hydrogen bonding, which increases interactions between CNCs and promotes dispersion of the CNCs into the matrix, preventing aggregations (Wang, 2020). Secondly, the amount of interfacial interactions is important. The more interactions between the CNCs and the matrix, the greater the increase of tensile strength in the composite (Wang, 2020). Interfacial interactions prevent defects such as cracks and pores in the materials, which cause failure of the composite, lowering tensile strength. As the concentration of CNCs in a composite increases, the strength also increases, to a point. The greater the concentration of CNCs, the greater the number of interfacial interactions and hence greater strength (Han, 2018 & Xiao, 2021). However, once the concentration of CNCs gets too high, aggregations begin to appear and the strength of the material begins to decrease (Han, 2018).

The addition of these CNCs also impacts the rigidity of the composites. The elongation at break was found to decrease when CNCs were added to an SPI composite (Han, 2018, Xiao, 2021, & González, 2019). This decrease in flexibility can possibly be attributed to a more rigid and continuous microstructure, which restricts the movement of matrix polymers. This rigidity could be both beneficial or undesirable, depending on the application of the composite.

These aggregations can be seen using SEM images of the fracture surface of the composite, as seen in Figure 1 below (Xiao, 2021).

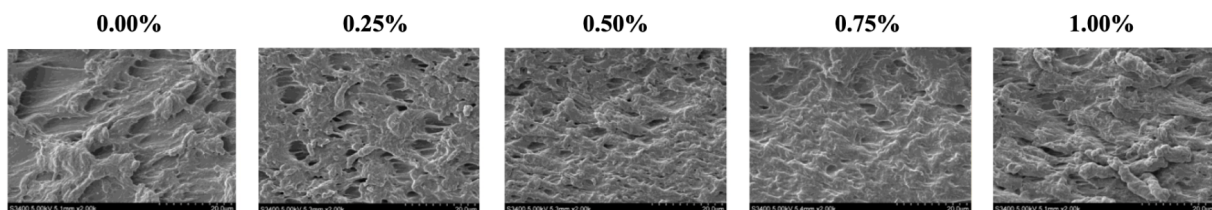


Figure 1: SEM Images of SPI-CNC composite surfaces at 0.00% to 1.00% CNC concentration

The pure SPI film shown in this image is disordered. As CNC content increases from 0.25% to 0.75%, the structure becomes more compact, organized, and homogenous. However, when the CNC content reached 1.00%, the surface became rougher and the aggregation of CNCs is evident. This study also found that the tensile strength of the composite was slightly lower at the 1.00% composition, further supporting the conclusion that strength is inversely related to CNC aggregation.

Increasing CNC content also impacts properties such as hydrophobicity, moisture content, and swelling. SPI is a moderately hydrophobic polymer. When combined with SPI films, the film surface becomes more hydrophobic (González, 2019 & Han, 2018). The hydrophilic groups of the polymer were attracted to the negatively charged surfaces of the CNC components, exposing the hydrophobic groups to the surface. However, Yaqing et. al. found that composite becomes more hydrophilic with added CNCs, and theorizes that this is due to the ability of hydroxyl groups on the CNC surfaces to form hydrogen bonds. Yizhuo et. al. and Baoxia et. al. also found an increase in hydrophilicity when CNCs were added to PLA and EPSFMA polymer matrices respectively, likely due to the same effects of hydroxyl groups. Swelling and moisture uptake also decreased as CNC content increased, until aggregation occurred (González, 2019 & Han, 2018). Adding CNCs reduced the affinity the matrix had for water, and the addition of CNCs reduced the size and prevalence of pores in the matrix, both of which reduced the amount of water that could be absorbed by the composites (González, 2019 & Agustin, 2013). This reduced moisture uptake is beneficial when considering applications such as food preservation and packaging (González, 2019), as the integrity of the film is less affected by wet products.

Surface modifications to the surfaces of CNCs can help facilitate the dispersion of CNCs into hydrophobic polymers. One such method is to coat the surface of CNCs in polydopamine (PDA) molecules. Dopamine self-polymerizes in mild alkaline environments, so by dispersing CNCs in an alkaline solution of dopamine, PDA spheres can be grafted onto the surface of the CNCs, without impacting the crystallinity of the cellulose itself (Xu, 2022). The PDA coating has very strong adhesion, which increases the interfacial interactions between the PDA-CNCs and the PLA matrix. When added to PLA, the addition of these modified CNCs increases tensile strength to a greater degree than unmodified CNCs (Xu, 2022).

Conclusion

Carbon nanocrystals are a material with significant potential applications. Polymer matrices reinforced with CNCs have been found to have improved mechanical properties like tensile strength, and decreased hydrophilicity and moisture uptake. Surface modification such as grafting of polydopamine onto the surfaces of CNCs has proven to improve dispersion of CNCs into hydrophobic polymers, increasing tensile strength in those composites. While much research has been done, there are still significant opportunities for research and discovery in this field.

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