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Revolutionizing polymethyl methacrylate toughness: Achieving 190% improvement with nanocellulose reinforcement while maintaining optical clarity

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Abstract: Polymethyl methacrylate (PMMA) is widely used in applications requiring high transparency and durability, such as optical lenses and protective coatings. However, its inherent brittleness limits its application in high-impact environments. This study investigates the incorporation of cellulose nanocrystals (CNCs) into PMMA to significantly enhance its toughness without compromising its optical clarity. By reinforcing PMMA with CNCs, the nanocomposites exhibited a remarkable 190% increase in toughness while maintaining 90% optical transparency. The innovation lies in achieving a balance between toughness and transparency through controlled CNC dispersion within the PMMA matrix, which minimizes excessive bonding that could lead to brittleness. Proper CNC dispersion was achieved through in-situ polymerization, allowing the nanocrystals to interact with the polymer matrix through van der Waals forces rather than covalent bonds. This approach reduces stress concentration and mitigates the formation of defects in the polymer matrix, ultimately leading to a tougher, more flexible material. In addition to enhancing mechanical properties, this study underscores the importance of controlling CNC content to preserve the intrinsic optical transparency of PMMA. These findings open new possibilities for CNC-reinforced PMMA in advanced applications that demand high mechanical performance coupled with excellent optical properties, extending its use in fields such as medical devices, protective coatings, and transparent structural materials.

Keywords: PMMA; Cellulose; Toughness; CNC; Transparency

1. Introduction

Polymethyl methacrylate (PMMA), a glassy amorphous polymer at room temperature, has a transparency of approximately 92%, making it the highest transparency polymer material currently available (Mbarek et al., 2018). It has a Young's modulus of around 3 GPa and a tensile strength of 60-70 MPa. Compared to glass, PMMA offers superior light transmission, higher impact resistance, and weighs only half as much (Ali Sabri et al., 2021; Ash et al., 2001). These properties allow it to be used in diverse applications, such as LED light covers, LCD light guide panels, aquarium windows, artificial dentures, large tanks, and aircraft windows. Known as "organic glass," PMMA is often used as a glass substitute. However, due to its lack of toughness and limited ductility, PMMA is prone to cracking, which reduces its lifespan in many applications, limiting its usability. The goal of this study is to enhance the mechanical properties of PMMA, specifically its toughness and flexibility, without compromising its transparency. Previous studies on PMMA composites primarily focused on improving stiffness; however, enhancing ductility remains a challenge due to

PMMA's brittle nature. In this study, we introduce cellulose nanocrystals (CNCs) derived from natural nanocellulose, which serve as a reinforcing filler to improve PMMA's ductility and toughness. Our innovation lies in achieving this balance without diminishing optical clarity, by carefully controlling CNC dispersion and interaction within the PMMA matrix.

Various studies have calculated the axial stiffness of cellulose through theoretical approaches. Mariano et al. (2014) summarized research on the axial stiffness of cellulose, noting that when hydrogen bonding is considered, the Young's modulus of cellulose I crystals averages 132 GPa. Without hydrogen bonding, the modulus drops to an average of 92 GPa. Iwamoto et al. (2009) conducted three-point bending tests using AFM on CNCs, revealing that CNCs exhibit a much higher Young's modulus than metal materials. Additionally, CNCs have a low coefficient of thermal expansion, are easily chemically modified, have a low density, are non-toxic, and produce highly transparent films. They are renewable and biodegradable, making them suitable as nanocomposite fillers and for applications in drug delivery, textiles, displays, and filtration membranes.

In recent years, the nanonization of fillers has been a prominent focus in composite material research. When nanofillers are ideally dispersed, they create many interface regions within the matrix, where these regions' properties significantly affect the composite's overall characteristics. Nanocellulose is particularly appealing due to its excellent mechanical properties, biodegradability, and renewability, making it a popular subject in nanocomposite studies (Akbar et al., 2024; Fujisawa et al., 2014; Makruf et al., 2024; Nurdin et al., 2023; Oktaviani et al., 2023; S.-C. Shi, Hsieh, et al., 2024). However, nanocellulose, due to its nanoscale size and hydrophilic functional groups, exhibits high surface energy, which leads to a greater tendency for aggregation compared to other nanofillers. As a result, most research on nanocellulose composites has focused on using hydrophilic matrices (such as PVA or PEG), which show more pronounced mechanical improvements.

Composite reinforcement has long been a common method for enhancing polymer strength and toughness. Initially, micro-sized fillers were used in polymer matrices, but achieving the desired toughening effect required high-volume percentages of these fillers. For toughening brittle polymers, several key conditions must be met: the filler size must be small, the dispersion in the matrix must be uniform, and the size distribution of the fillers must be minimized. The interparticle distance (ID) should fall within an optimal range ($ID_{min} < ID < ID_{max}$) (Kausch & Michler, 2007). Additionally, the bonding strength between the matrix and fillers should not be too muscular, allowing localized debonding under stress and contributing to toughening behavior.

Research related to nanocomposite has surged in recent years. Under ideal dispersion, nanofillers significantly increase contact surface area with the matrix and reduce the interparticle distance, even at low filler content. This enhances the importance of the interphase zone, whose properties are shaped by adhesion between the filler and matrix. Modifying the filler surface can control adhesion, impacting polymer chain mobility. The aspect ratio of the filler also affects nanocomposite properties; higher aspect ratios provide more surface area and promote debonding, improving toughness. B. Benjamin, based on S. Wu's theory, studied how poor filler-matrix compatibility influences mechanical behavior. Using 17 nm and 38 nm aluminum oxide nanoparticles in PMMA, they found that only 2.2 wt% of the 38 nm particles improved toughness. They proposed that interfacial cavities increase chain mobility, aiding local yielding, with stress for cavity growth inversely proportional to cavity radius. Smaller nanoparticles or higher compatibility prevent cavity formation. When chain mobility changes and interparticle distance drops below a critical threshold, local yielding occurs, leading to significant changes in composite properties (Ash et al., 2004; Fauza et al., 2023).

Modifying nanofiller surface properties controls filler-matrix compatibility. Nanocellulose is naturally hydrophilic, while most plastics are hydrophobic, making surface modification essential in nanocellulose-reinforced plastics. Two methods are common: using amphiphilic surfactants for physical adsorption, or chemical surface modification. The first is simpler but harder to control; the second improves hydrophobicity but risks weakening mechanical properties if overdone. Heux et al. (2000) used BNA surfactants to modify CNCs, improving dispersion in nonpolar solvents. Oksman et al. (2006) enhanced PLA/CNC composite toughness by adding PEG 150. Fujisawa et al. (2014) used PEG(48)-NH2 to improve CNF dispersion and compatibility in PLLA matrices. CNCs offer excellent mechanical properties, biodegradability, and renewability, ideal as nanocomposite fillers. However, most studies focus on hydrophilic matrices due to their hydrophilic nature. This study aims to increase CNCs' versatility and improve PMMA’s mechanical properties using in-situ polymerization to enhance CNC dispersion in hydrophobic matrices. Surfactants were added to study how filler-matrix compatibility affects overall nanocomposite performance. Enhancing PMMA's toughness with CNCs while maintaining optical properties could expand CNC and PMMA applications.

2. Methods

Preparation of CNC and CNCs/PMMA composites

The CNC used in this study was lab-made, sourced from agricultural waste—rice straw. The extraction followed green production standards, utilizing a chlorine-free UV bleaching process based on our previous work (S.-C. Shi, Cheng, et al., 2024). This optimized process increased efficiency and improved yield (S.-C. Shi & Liu, 2021). The CNCs/PMMA composites were prepared using in-situ polymerization (S. C. Shi et al., 2022). MMA monomer and 0.0333 wt% BPO initiator were mixed in a pre-polymerization flask and sonicated for 1 minute. The flask was placed in a 90°C water bath for 20 minutes, then cooled in room-temperature water for 20 minutes. CNCs and dispersants (PEG 2000 & PEG 6000) were added, followed by sonication using a 1000 W ultrasonic processor (UP-1200, LINKO, Australia) in pulses. The flask was returned to the 90°C water bath for 30 minutes and shaken every 5 minutes for 10 seconds. The water bath temperature was then set to 70°C. The slurry was poured into a mold and cured at 70°C for 3 hours, then baked at 90°C for 1 hour to complete the composite preparation.

Composite material property testing

The optical clarity of the composites was analyzed using an Ultraviolet-Visible-Near Infrared Reflectance Spectrophotometer (UV-Vis-NIR, U4100, HITACHI, Japan). To assess dispersion quality and CNC integration in the PMMA matrix, surface morphology was examined using a High-Resolution Field Emission Gun Transmission Electron Microscope (HRFE-TEM, SU-500, HITACHI, Japan). Mechanical properties, specifically toughness and flexibility were evaluated according to ASTM D638 standards using a Material Testing System (MTS-810, MTS Systems Corporation, USA) for tensile testing. Nominal stress and strain were calculated, and the material’s toughness was determined by integrating the area under the stress-strain curve. Each condition was tested with at least five repeated tensile trials.

3. Results and discussion

Surface morphology and optical properties of composites

When the CNC content was below 0.1 wt%, transmittance remained around 90%, nearly identical to pure PMMA, indicating uniform dispersion of CNCs in the matrix. However, with CNC content above 0.3 wt%, transmittance significantly decreased, suggesting the presence of large CNC particles in the composite, as observed in optical microscopy (OM) images (Figure 1). The black spots represent CNC aggregates, ranging from 20 to 40 μm in size, with more severe aggregation as the CNC content increases. Transmittance is a crucial property of PMMA, and the effect of varying CNC content on transmittance was measured using UV-Vis, as shown in Figure 2. All sample thicknesses were 1.5 ±0.1 mm. The high tendency of CNCs to aggregate is due to the large number of surface atoms with unsatisfied coordination and hydroxyl functional groups in their chemical structure.

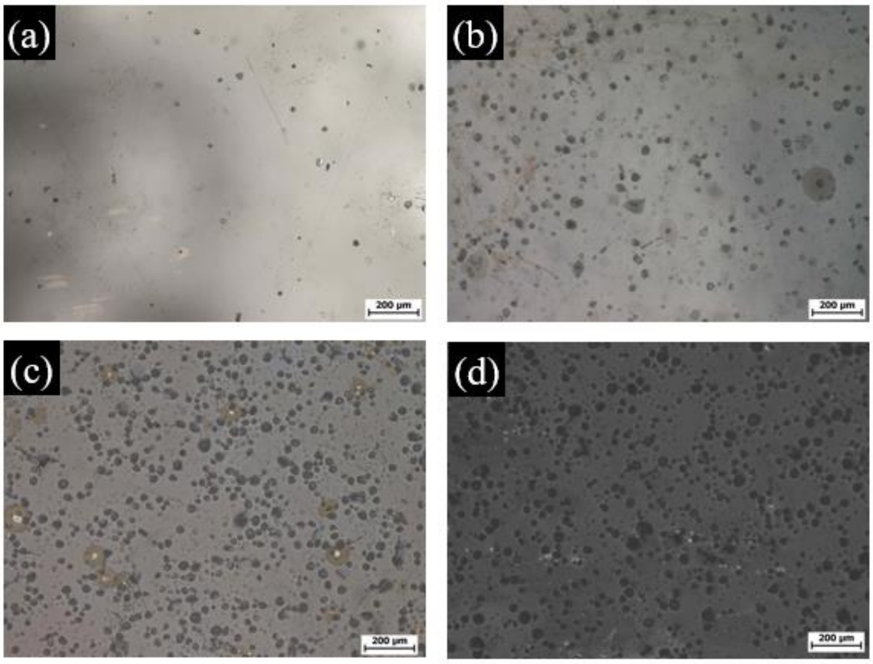

Figure 1. Optical microscopy (OM) images of CNCs/PMMA nanocomposites with (a) 0.01 wt%, (b) 0.3 wt%, (c) 0.7 wt%, and (d) 1 wt% CNCs

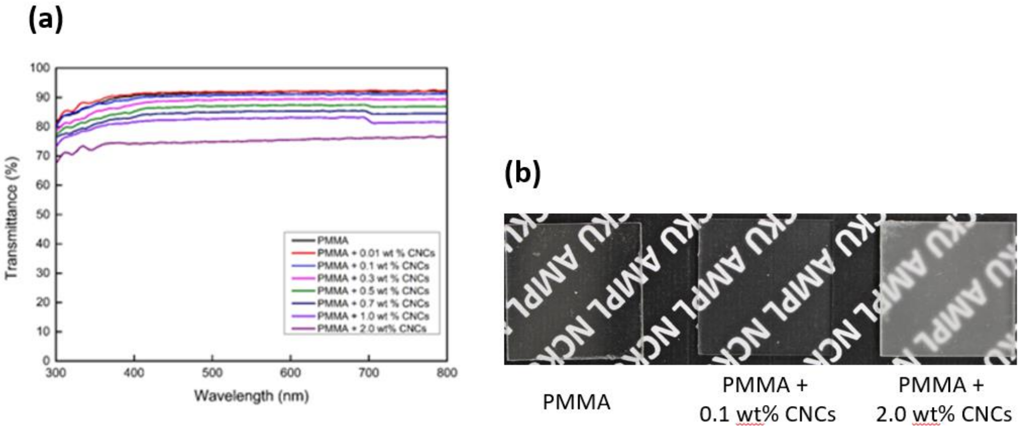

Figure 2. Transmittance test results of CNCs/PMMA nanocomposites

Mechanical properties of CNCs/PMMA nanocomposites

PMMA has a Young's modulus of 2.86 ± 0.03 GPa and a tensile strength of 69.07 ± 0.85 MPa. Before fracture, it can only withstand 5% strain, showing typical brittle fracture behavior (Figure 3). Adding 0.01 wt% CNCs resulted in no significant change in mechanical properties due to insufficient dispersion to affect the material's behavior. When CNC content was between 0.3 and 1.0 wt%, the nanocomposite exhibited similar mechanical properties to PMMA, with brittle fracture occurring at low strain and slightly reduced toughness. At 2 wt%, the material fractured at low strain, with Young's modulus and tensile strength dropping by approximately 10% and 20%, respectively, indicating severe internal defects in the PMMA matrix. However, at 0.1 wt% CNCs, necking occurred before fracture, as shown in Figures 3b and 3c (lower samples). While Young's modulus and tensile strength decreased by 10% and 20%, respectively, toughness increased by nearly 190% compared to pure PMMA (Table 1). This suggests that at 0.1 wt%, CNCs are effectively dispersed, reducing interparticle distance and allowing local yielding in PMMA under stress, leading to significant toughening effects in the nanocomposite (Ash et al., 2001).

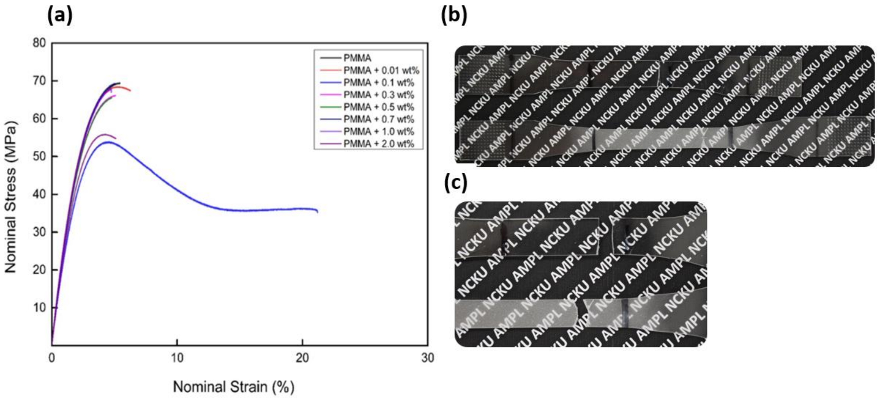

Figure 3. (a) Stress-strain curve of CNCs/PMMA nanocomposites, (b) Tensile test fracture specimens, top—pure PMMA, bottom—PMMA + 0.1 wt% CNCs, (c) Fracture surface of specimens, top—pure PMMA, bottom—PMMA + 0.1 wt% CNCs

Table 1. Mechanical properties of CNCs/PMMA nanocomposites with different CNC content

Sample	Young's Modulus (GPa)	Tensile Strength (MPa)	Strain at reak (%)	Toughness (J/m^2)
PMMA	2.86±0.03	69.07±0.85	5.43±0.66	2.65±0.45
PMMA + 0.01 wt% CNCs	2.92±0.01	68.30±0.49	6.50±1.58	3.37±1.06
PMMA + 0.1 wt% CNCs	2.50±0.08	53.40±2.37	19.21±2.96	7.70±0.96
PMMA + 0.3 wt% CNCs	2.76±0.02	64.97±0.86	5.30±0.67	2.45±0.43
PMMA + 0.5 wt% CNCs	2.75±0.01	64.49±0.97	4.99±0.54	2.22±0.38
PMMA + 0.7 wt% CNCs	2.88±0.01	68.32±0.72	4.77±0.37	2.24±0.26
PMMA + 1.0 wt% CNCs	2.88±0.02	66.34±2.03	4.27±0.57	1.85±0.38
PMMA + 2.0 wt% CNCs	2.59±0.04	54.00±1.31	5.86±1.61	2.41±0.75

To further investigate the effect of interfacial property changes between CNCs and PMMA on the nanocomposite, 0.01 wt% and 0.025 wt% of PEG 2000 and PEG 6000 were added to 0.1 wt% CNCs/PMMA composites. The tensile test results of these composites are shown in Figure 4 and Table 2. First, comparing the effect of surfactant addition, both surfactants exhibited the same trend. At 0.01 wt%, the Young's modulus and tensile strength slightly exceeded those of the original PMMA + 0.1 wt% CNC composite, and strain before fracture increased. However, the high standard deviation suggests uneven surfactant adsorption on the CNC surface, causing localized toughening in some areas, leading to inconsistent material quality. At 0.025 wt%, the tensile strength and Young's modulus returned to values similar to pure PMMA, indicating that both PEG 2000 and PEG 6000 improved compatibility between PMMA and CNCs, but the toughening effect disappeared. This is likely because uniform adsorption of surfactant restricted the mobility of PMMA chains around CNCs, preventing local toughening.

Next, comparing the effect of surfactant molecular weight, the results showed that at the same concentration, composites with PEG 6000 had slightly lower Young's modulus and tensile strength than those with PEG 2000. This is attributed to the inverse relationship between surfactant adsorption and molecular weight—PEG 6000 adsorbed less on CNCs, leading to reduced mechanical properties.

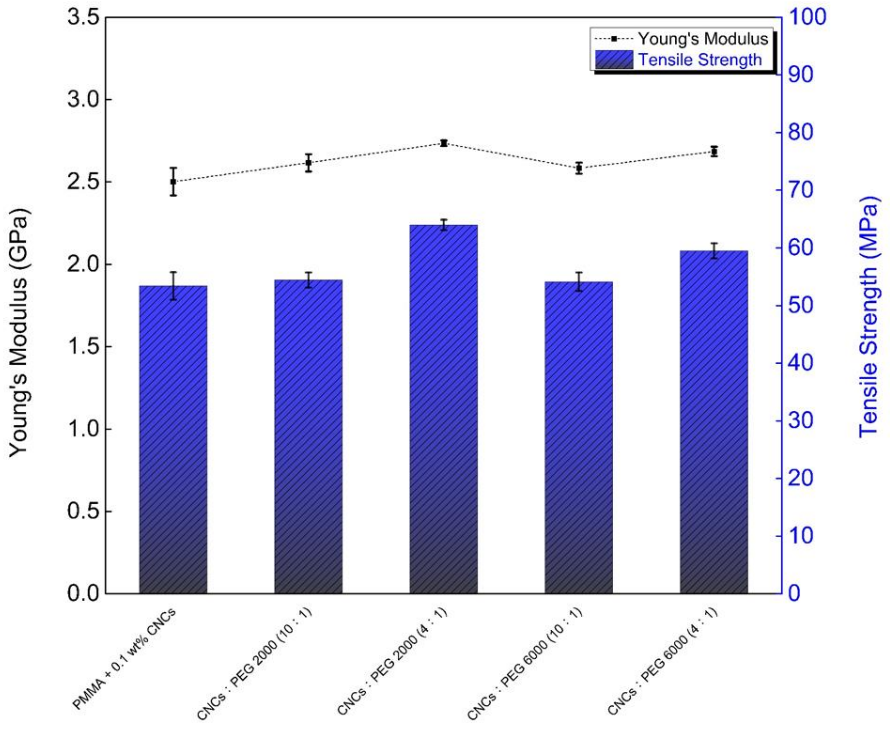

Figure 4. Comparison of Young's modulus and tensile strength for surfactant/0.1 wt% CNCs/PMMA nanocomposites with different surfactant contents

Tensile test results indicated that when the CNCs content was as low as 0.01 wt%, the mechanical properties remained almost identical to pure PMMA. This is because the small clusters formed were too few to affect the overall properties of PMMA significantly. As the CNCs content increased, minor agglomeration resulted in larger particles, and micro-scale cracks developed around them. These cracks caused localized stress concentration, leading to crack propagation under load. When the CNCs concentration reached 2.0 wt.%, severe aggregation occurred, with large particles forming throughout the matrix. This caused significant stress concentration during loading, which failed to improve toughness and reduced Young's modulus and tensile strength.

Table 2. Comparison of mechanical properties for surfactant/0.1 wt% CNCs/PMMA nanocomposites with different surfactant contents

Sample	Young's Modulus (GPa)	Tensile Strength (MPa)	Strain at break (%)	Toughness (J/m^2)
PMMA	2.86±0.03	69.07±0.85	5.43±0.66	2.65±0.45
PMMA + 0.1 wt% CNCs	2.50±0.08	53.40±2.37	19.21±2.96	7.70±0.96
PMMA + 0.1 wt% CNCs + 0.01 wt% PEG 2000	2.62±0.05	54.42±1.34	29.41±13.65	11.74±4.92
PMMA + 0.1 wt% CNCs + 0.025 wt% PEG 2000	2.74±0.02	63.96±0.92	5.63±0.61	2.52±0.30
PMMA + 0.1 wt% CNCs + 0.01 wt% PEG 6000	2.58±0.03	54.12±1.61	26.41±5.31	10.57±2.02
PMMA + 0.1 wt% CNCs + 0.025 wt% PEG 6000	2.69±0.03	59.48±1.31	6.33±0.44	2.92±0.26

In summary, significant property changes in the nanocomposite only occur when there is no strong bonding between the filler and matrix and no irreparable defects form within the matrix. Sufficient CNCs must be uniformly dispersed to exploit the nanoscale effect, where CNCs are connected to PMMA via van der Waals forces. In this experiment, these conditions were met at a CNCs concentration of 0.1 wt%, enabling PMMA to exhibit ductile behavior, with clear necking observed during tensile testing.

4. Conclusion

In the CNCs/PMMA nanocomposites study, a significant 190% improvement in toughness and enhanced ductility were achieved compared to pure PMMA while maintaining 90% optical transparency. This enhancement increases the manufacturing flexibility of PMMA and reduces brittleness in applications such as acrylic dentures and automotive light covers. The key to improving both toughness and ductility in CNCs/PMMA nanocomposites lies in achieving optimal compatibility between the filler and the matrix—avoiding overly strong bonding between them. Additionally, CNCs must be uniformly dispersed within the matrix to utilize the nanoscale effect fully. In this state, the CNCs interact with PMMA via van der Waals forces, preventing the formation of irreparable defects in the matrix. This approach enables the toughening of the glass polymer.

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Declarations

Author contribution

Guan-Ting Liu: Formal analysis, investigation, visualization, data curation. Shih-Chen Shi: Conceptualization, supervision, methodology, funding acquisition, writing - original draft. Dieter Rahmadiawan: Validation, writing - review & editing

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Conflict of interest

There are no conflicts of interest in this research.

Ethical Clearance

There are no human or animal subjects in this manuscript and informed consent is not applicable.

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