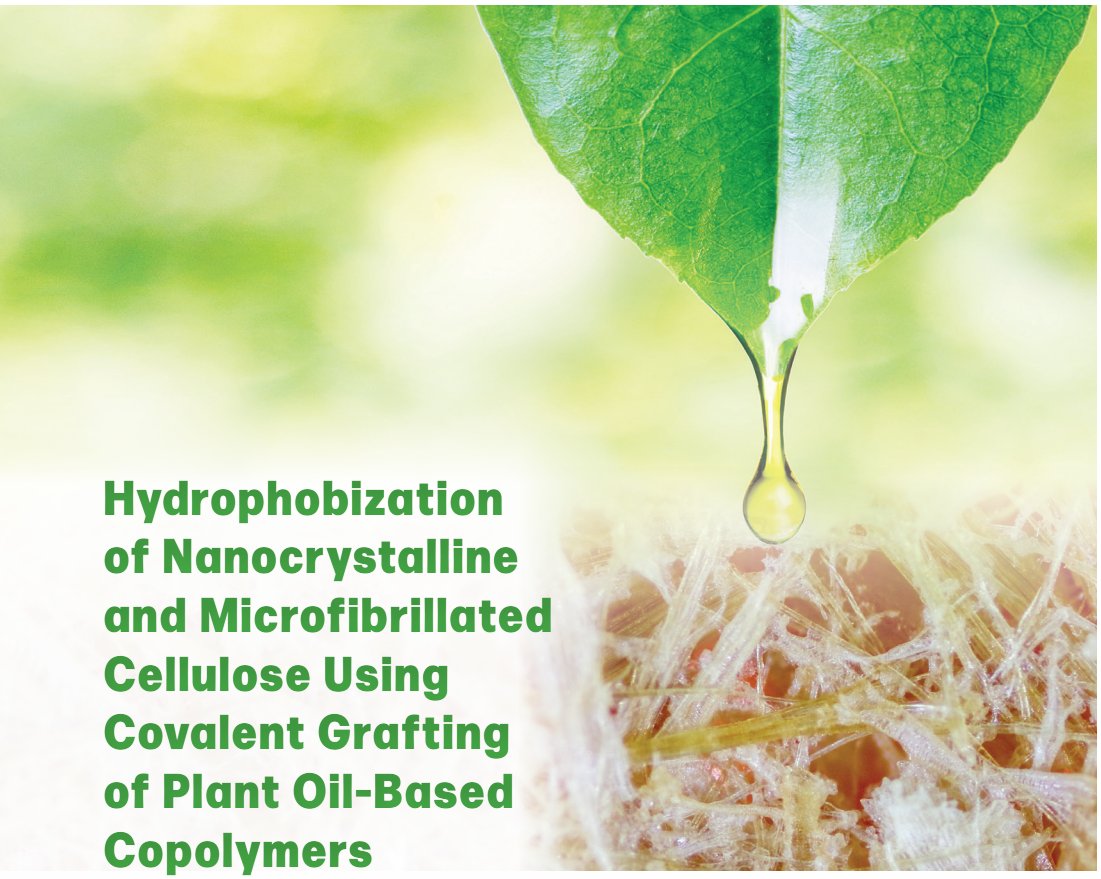

Hydrophobization of Nanocrystalline and Microfibrillated Cellulose Using Covalent Grafting of Plant Oil-Based Copolymers

By Tetiana Shevtsova, Zoriana Demchuk, Oleh Shevchuk, Sergiy Minko, and Andriy Voronov

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Cellulose, a linear polysaccharide biopolymer, has applications in various industries including food packaging, personal care products, and construction, due to its unique physico-chemical properties, as well as its biocompatibility and biodegradability. This study introduces a methodology to enhance the hydrophobicity of nanocrystalline (CNC) and microfibrillated (MFC) cellulose, using the covalent attachment (grafting) of copolymers based on plant oils.

Current methodologies for cellulose surface modification are limited in terms of hydrophobizing agents due to both their high cost and the fact that most are not renewable. This study focuses on the surface modification of CNC and MFC by graft copolymers from plant oil-based acrylic monomers (POBMs) developed by this research group.

The grafting and the properties of the resulting copolymers were determined using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) to demonstrate the presence of grafted POBMs and their impact on the characteristics of modified CNC and MFC.

Introduction

Cellulose, one of the most abundant natural polymers, boasts remarkable strength, stiffness, and sustainability. However, there are challenges in applying cellulose to materials fabrication which include high hydrophilicity and, therefore, poor compatibility with most polymer matrices.[1] Modification of cellulose to improve the material's water resistance and compatibility with specific polymer matrices remains a challenge among researchers due to cellulose's complex chemical structure and extensive hydrogen bonding between macromolecules.

The need for cellulose modification arises mainly from the desire to overcome extensive hydrophilicity to unlock the full potential presented in this abundant biopolymer. The modification process needs to tailor cellulose properties to specific applications to make material applicable in diverse industrial applications. For instance, the hydrophobization of cellulose is important when aiming to create water-resistant materials with improved chemical and mechanical properties.[2, 3]

In this study, emulsion polymerization was utilized as a versatile and highly effective methodology for hydrophobizing cellulose.[4] The approach brings several advantages, including minimized environmental impact, scalability, and the utilization of biobased resources.[5]

Cellulose nanocrystals (CNCs) and microfibrillated cellulose (MFC) already play important roles in biomaterials, providing versatility for sustainable innovations.[6] Modifying the CNCs and MFC with plant oil-based polymers can be a significant undertaking, offering opportunities to tailor properties for specific applications. This article explores the importance of hydrophobizing these cellulosic

materials and highlighting their promising properties to be applied as sustainable biomaterials.

Methods

To determine the surface energy and the contact angle of modified cellulose, water and diiodomethane contact angle measurements were carried out by a contact angle/surface tension analyzer using a drop shape analyzer (DSA 100, KRÜSS, Hamburg, Germany). Reported values were an average of 5 droplets.

The morphology of modified cellulose was observed on a tungsten filament 100 kV transmission electron microscope (TEM) JEOL JEM-100CX II, (JEOL, Peabody, MA). For the TEM measurements, a small amount of modified cellulose diluted with ethanol was placed onto a copper mesh covered with a thin carbon film. The samples were characterized after drying.

Fourier transform infrared spectra were recorded with a Nicolet 8700 FTIR spectrometer (Thermo Scientific) equipped with a Smart iTR attenuated total reflectance (ATR) sampling accessory. FTIR spectra in the range of 400–4000 cm^{-1} of modified CNC and MFC samples were recorded in reflectance mode, with 64 scans per sample. The analysis of the obtained FTIR spectra was conducted by identifying the chemical bonds in the molecule's chemical structure according to standardized absorption peaks of functional groups.

The thermogravimetric analysis (TGA) investigated the thermal degradation of CNC and MFC samples. Employing a Discovery TGA 550 thermogravimetric analyzer (TA Instruments), the samples (ranging from 5 to 15 mg) underwent heating from 20 to 650 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere.

The surface elemental composition of modified CNC and MFC materials was analyzed using a Thermo Scientific™ K-Alpha™ X-ray photoelectron spectroscopy (XPS) instrument. The equipment featured a monochromatic Al Kα (1486.68 eV) X-ray source and an Ar+ ion source (up to 4000 eV). To ensure accurate results, all samples went through an argon ion cleaning process to minimize trace contaminants, such as oxygen and carbon, prior to analysis. The argon cleaning was applied to a 2 mm × 2 mm area of each sample by sputtering with an Ar+ ion cluster beam set to 4000 eV for 120 seconds using the MAGCIS® cluster gun. The XPS survey scan focused on the observation of photoemission lines for C1s, O1s, and N1s. The survey scan was an average of 10 scans with a Pass Energy of 200 eV, Dwell Time of 10 ms, and an Energy Step size of 1.0 eV. Spectra were collected at a 90° angle normal to the surface within a 400-µm area. To maintain optimal conditions, the chamber pressure was kept below 1.5 × 10–7 Torr, and the analysis was conducted at ambient temperature. The instrument's software, Avantage, was employed for the quantification of atomic concentrations.

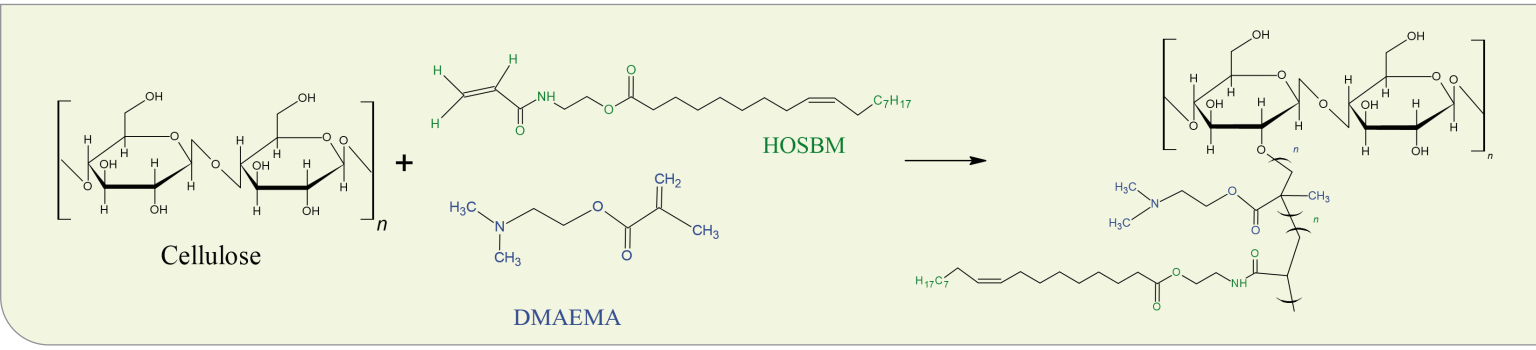
For elemental analysis, a Leco 932 CHNS combustion analyzer was used to determine percentages of carbon, nitrogen, and hydrogen in all samples. Samples of each material were weighed to a target weight of approximately 2 mg. A series of three calibration standard samples were run in the machine followed by the actual test samples. The actual process was as follows:

1. Samples were removed from sample containers and poured into foil sample capsules.
2. The capsules were weighed individually, and these weights were programmed into the machine.
3. The machine then dropped the appropriate sample into its furnace where the sample combusted.
4. After combustion, the percentages of each element were calculated.

Results and Discussion

Hydrophobized cellulosic materials can be considered for different applications such as polymer composites reinforcement, biocompatible medical devices, water-resistant coatings, sustainable textiles, eco-friendly packaging materials, drug delivery, and more. Modifying both CNC and MFC can provide a comprehensive knowledge of how these materials can meet specific industrial applications requirements. Size and structure of produced by acid hydrolysis CNC (characterized by nanoscale crystalline particles), and MFC made of larger microfibrils obtained through mechanical processes is different. **Scheme 1** shows the copolymerization scheme applied for hydrophobization of CNC and MFC using acrylic monomer derived from high oleic soybean oil (HOSBM). This monomer was synthesized via a one-step transesterification reaction developed and characterized as reported in our prior studies.[7]

SCHEME 1
Grafting of HOSBM-DMAEMA copolymers onto cellulose.



CNC and MFC were modified by the grafting of HOSBM copolymers using the emulsion polymerization at varied ratio between HOSBM and CNC/MFC such as 0.34:1, 1:1, and 1:0.34 wt/wt. To enhance the solubility of HOSBM in aqueous media, 20 wt % of 2-(Dimethylamino)ethyl methacrylate (DMAEMA) was added to the monomer mixture. To initiate the grafting reaction on the cellulosic substrate surface, a thermal initiator, ammonium persulfate, was used (7.5 wt %). The grafting reaction was carried out at 70 °C for 6 hours in the glycerol bath with continuous stirring.

The resulting emulsions with a solid content of 2-7.5% were purified to remove the unreacted monomer and ungrafted polymer by precipitation in tetrahydrofuran and following redispersion in water. The films from modified CNC/MFC were prepared by applying 5 g of emulsion on the glass substrate and curing at 70 °C for 1 hour. It is assumed that DMAEMA acts as a reactive solubilizing agent/comonomer that helps to increase HOSBM availability in grafting.

The FTIR spectrum **(Figure 1A)** compares CNC/MFC before and after grafting. Notably, the emergence of a robust peak at 3451 cm^{-1} and another at 2899 cm^{-1} in spectra recorded for both modified materials signify the presence of O-H and C-H groups, respectively, in the grafted CNC/MFC to confirm modification.

Within the HOSBM-g-CNC and HOSBM-g-MFC spectra, the N-H absorption band, spanning the 3200-3400 cm^{-1} range, overlaps with the O-H absorption band of CNC/MFC, rendering separate detection challenging. Nevertheless, the distinct peak at 3010 cm^{-1}, corresponding to double bonds in fatty acid fragments within the grafted HOSBM chains, serves as an evidence of successful grafting.

Furthermore, the presence of absorption bands at 2930 and 1540 cm^{-1}, corresponding to CH_2 groups in fatty acid fragments and the N-H amide II group in the HOSBM structure, confirms the covalent attachment of HOSBM chains to the CNC/MFC surface.

Further, grafting of HOSBM-based copolymer was confirmed using XPS analysis. Within the XPS analysis, a distinct peak at 400 eV (N1s) provides strong evidence of the plant oil-based copolymer grafting. This peak serves as an indicator of the presence of grafted fragments on the surfaces of both CNC and MFC **(Figure 2)**.

Thermogravimetric analysis was conducted for pristine and modified CNC and MFC to evaluate the percentage of the grafted amount. **Figure 3** represents thermogravimetric plots, providing information about thermal stability of the modified materials. The calculation of the grafted amount conducted using TGA involves assessing the disparity in weight loss between pristine and modified CNC/MFC at 500 and 550 °C.

At 500 °C, pristine CNC is mostly decomposed (2.3 %), while the modified material shows 35.3% weight remaining. The percentage of grafted HOSBM-based copolymers to CNC surface can be calculated using the following equation **(1)**:

$$\%\ \text{HOSBM-DMAEMA grafted} = \frac{W(cellulose)}{100-W(cellulose)} = \frac{W(grafted)-X}{100-W(grafted)} \quad (1)$$

$$\%\ \text{HOSBM-DMAEMA grafted} = 33.8\ \%$$

The amount of analyzed material was 31.3 mg, where 10.6 mg corresponds to grafted material fraction and 20.2 mg corresponds to the CNC fraction. Using **(2)** where 1 g of CNC has 700 m^2 area, the surface area of 20.2 mg CNC is:

$$\frac{20.2 \cdot 700}{1000} = 14.1\ m^2 \quad (2)$$

The grafted amount for CNC is 0.8 mg/m^2.

At the same time, pristine MFC mostly decomposing at 550 °C (2.2%), stands in contrast to the grafted MFC, which retains 27.7% of its weight; repeating the previous calculation for MFC yields of grafted copolymer is 26.1%, with the grafted amount on MFC estimated at 0.2 mg/m^2.

The increased remaining weight in the modified CNC and MFC implies an enhancement in thermal stability compared to its pristine counterparts.

The computed percentages of grafted copolymer on the CNC/MFC surfaces yield important information showing the efficacy of the grafting. The determined surface area of the modified materials, along with the corresponding grafted amounts, provides valuable insights into the efficient utilization of the CNC/MFC surface. Understanding grafting density is essential for tailoring materials with specific functionalities, such as enhancing adhesion or compatibility with other substances.

Another way in the determination of the grafting extent of HOSBM-based copolymer to the CNC/MFC was explored by the elemental analysis. The elemental analysis results for CNC and the grafted CNC can be found in **Table 1**.

The emulsion polymerization process involves grafting n moles of HOSBM (MW=379 g/mol) and DMAEMA (MW=157.2 g/mol) onto 1 g of CNC. The weight ratio between HOSBM and DMAEMA is 80:20 % wt, which is equal to 62.4:37.6 % mol. The average molecular weight of monomer mixture was calculated and is equal to 295.4 g/mol, then the weight of the product (grafted CNC) can be calculated as (1+n·295.4) g. The increasing nitrogen content in the final product is determined by HOSBM fragments presence; thus, the final nitrogen content can be derived as **(3)**:

$$\%\ N = \frac{1 \cdot 0.02\ \% + 14 \cdot n}{1 + n \cdot 295.4} = 1.8\ \% \quad (3)$$

which is equal to the number obtained in elemental analysis.

Therefore, the grafted amount is 2.0 mmol monomer/g of CNC, which is equal 0.6 g monomer/g CNC.

Weight percentage of HOSBM and DMAEMA grafted to CNC surface **(4)**:

$$\%\ W = \frac{0.6}{1+0.6} = 37.5\ \% \quad (4)$$

Assuming a 50:50 wt % ratio between CNC and monomers mixture in the feed (5 g:5 g), 3 g of monomers were used for grafting onto the CNC surface. The remaining monomers are likely polymerized in the reaction medium and removed by purification using THF after synthesis. Based on these calculations, the grafted amount is 0.9 mg/m^2.

To assess the extent of hydrophobization of CNC and MFC, water contact angles (WCA) were determined and surface energy calculated. The water contact angle values corresponding to different ratios of HOSBM

FIGURE 1
FTIR spectrum of pristine and modified HOSBM-g-CNC(0.34:1) (A) and HOSBM-g-MFC (1:1) (B).

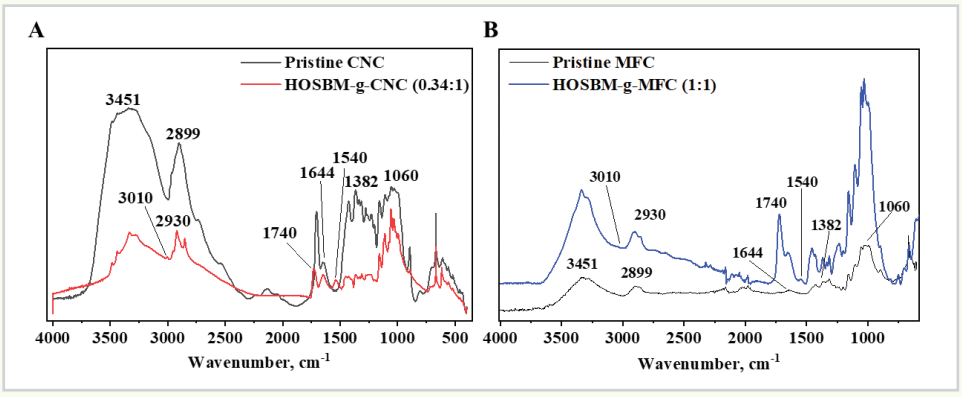


FIGURE 2
XPS analysis of pristine and modified CNC (A), MFC (B), and high-resolution spectra in N1s region for modified CNC (C).

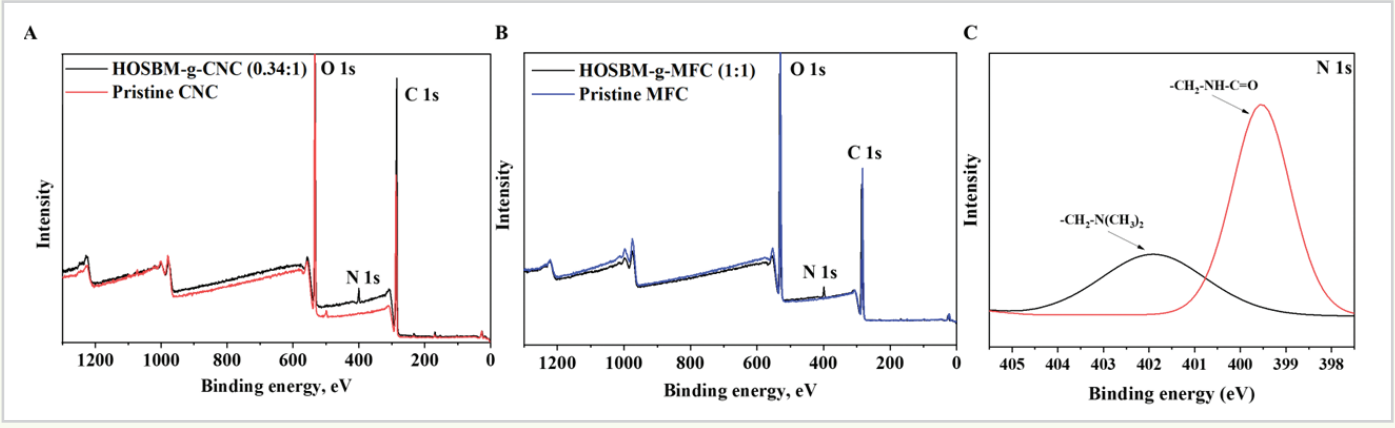
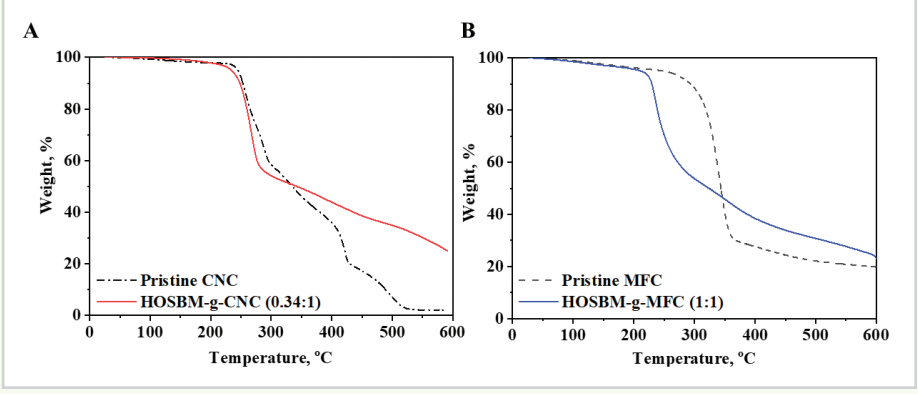


FIGURE 3
TGA analysis of pristine and modified CNC (A) and MFC (B).



and DMAEMA in the monomer feed indicate the hydrophobization of CNC after grafting. Composition of 85 wt % HOSBM and 15 wt % DMAEMA results in WCA of 66.1° (±1.2), while for a composition of 80 wt % HOSBM and 20 wt % DMAEMA higher WCA of 86.7° (±2.6). Thus, it was confirmed that the monomer ratio of HOSBM:DMAEMA of 80:20 % wt/wt serves as an optimum ratio of monomers to allow successful grafting to CNC surface.

Table 2 shows WCAs and calculated surface energy for various experimental surface/volume ratios for MFC. For the obtained experimental data, the 0.34:1 ratio chosen for CNC results in higher WCA indicating the successful grafting of HOSBM to CNC surface compared to MFC.

TABLE 1
Elemental Analysis Result for CNC and Grafted CNC

	% C	% H	% N
CNC	42.34	6.00	0.02
Grafted CNC	46.04	6.71	1.75

TABLE 2
Water Contact Angle and Surface Energy of Different Formulation

Ratio (MFC:MM)	Surf Energy mN/m	Water Contact Angle, °
1:0.34	39.3±3.5	76.3 (±3.0)
1:1	36.2±2.2	86.2 (±3.1)
0.34:1	37.1±2.2	108.3 (±8.4)

Due to their hydrophilic nature, CNCs can be dispersed in water but face challenges when being placed in non-polar dispersion medium. The results from TGA and WCA analyses conclusively demonstrate that CNC exhibits superior dispersibility, boasting a higher grafting percentage. This superiority directly translates to a more elevated water contact angle at the same ratio when compared to MFC.

Grafted HOSBM-based copolymers introduced onto the CNC surface significantly enhance the hydrophobicity of the CNCs, influencing their interaction with water. If the modification is partial or balanced, some hydrophilic character may still be retained, allowing for a stable suspension.

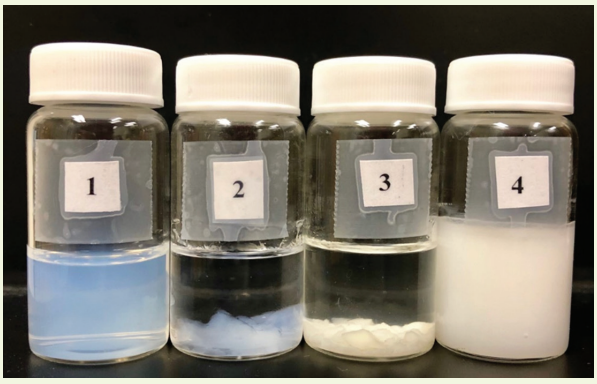
The grafted polymer layer is important for increasing the hydrophobicity of CNCs, thus making this material more compatible with hydrophobic counterparts. This hydrophobic nature facilitates the dispersion of grafted CNCs in hexane, resulting in a stable colloidal system **(Figure 4)**.

The morphology of CNCs and modified CNCs was compared using transmission electron microscopy (TEM) **(Figure 5)**. It is clearly seen that morphological changes occur upon modification. Aggregated structures are observed forming bundles comprised of several modified nanocrystals. This shows that inherent structural characteristics of modified CNCs are different in comparison to pristine material.

Next, the theoretical thickness of the absorbed (grafted) layer, based on HOSBM onto CNC surface, was calculated assuming that HOSBM molecule is spherical as well as all of the monomer molecules are consumed in grafting reaction.

Assuming, the 1:1 (wt/wt) ratio of CNC and HOSBM/DMAEMA (80% and 20%, respectively), average surface area of CNC whiskers 450 m^2/g, and 5 g of CNC used in the experiment, the total calculates surface area is 2250 m^2.

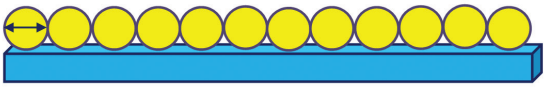
FIGURE 4
Dispersions of unmodified CNCs in water (1), and hexane (2), and the grafted-CNCs in water (3), and hexane (4).



If 0.017 moles of moles of HOSBM/DMAEMA mixture is applied in the experiment (νHOSBM=m/MW(HOSBM)=(4/379)+ν(DMAEMA)=m/MW(DMAEMA)=1/156) and HOSBM molecule is spherical ($S=\frac{4}{3}\pi r^3$), the radius of the molecule would be:

$$R=7.4\cdot 10^{-9}\sqrt[3]{\frac{M}{\rho}}=7.4\cdot 10^{-9}\sqrt[3]{\frac{379}{0.945}}=5.457\cdot 10^{-8}\ \text{m} \quad (5)$$

The diameter of the HOSBM molecule is $1.091 \cdot 10^{-7}$ m.



The surface cross-area of HOSBM molecule is:

$$S=\pi\cdot R^2=3.14\cdot(5.457\cdot 10^{-8})^2=93.505\cdot 10^{-16}\ \text{m}^2 \quad (6)$$

Number of HOSBM molecules required to cover 1m^2 of CNC surface forming a monolayer:

$$N=1/93.505\cdot 10^{-16}\ \text{m}^2=1.07\cdot 10^{18} \quad (7)$$

Number of moles of HOSBM molecules used to cover 1m^2 of CNC:

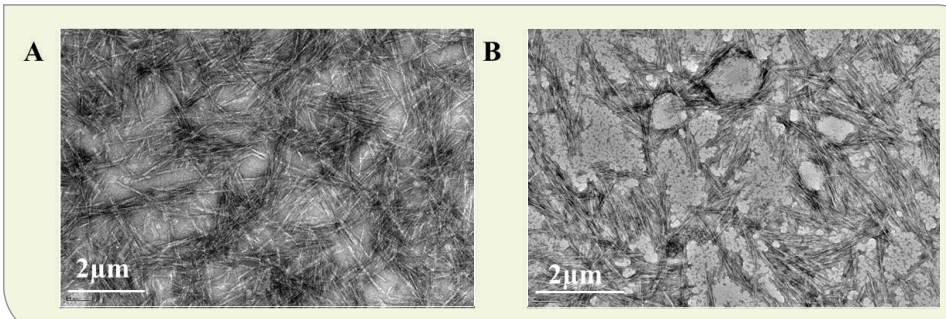
$$\vartheta=\frac{N_A}{N}=\frac{1.07\cdot}{6.022\cdot}\frac{10^{18}}{10^{23}}=1.778\cdot 10^{-6}\text{mol} \quad (8)$$

Amount of HOSBM required to cover 1m^2 of CNC:

$$m=379\cdot 1.778\cdot 10^{-6}=6.74\cdot 10^{-4}\ \text{g} \quad (9)$$

For 5 g of CNC, the average surface area is around 2250 m^2, therefore for the grafting process we should use $6.74 \cdot 10^{-4} \cdot 2250 = 1.52$ g of HOSBM. In our study, we used the excess amount of HOSBM (5 g) to allow the full grafting of HOSBM to active sites on CNC surface considering that some HOSBM molecules can take part in emulsion polymerization in the media forming homopolymers.

FIGURE 5
TEM images of the unmodified (A) and grafted CNC (0.34:1) (B).



Summary

In summary, this study introduces grafting of plant oil-based acrylic chains on CNC and MFC to customize the materials for specific industrial applications. A higher grafted amount is achieved for CNC. The grafting induces changes in surface energy with a potential for tuning the hydrophilicity of cellulose based on the grafted amount. This shift in hydrophobicity directly influences the cellulose's interaction with different disperse media thus providing opportunities for utilization of modified materials in various polymer matrixes and solvent environments. Synthetic conditions, so far, facilitated a more efficient modification procedure for CNC (as confirmed by thermal analysis). The developed methodology can be extended to the other cellulosic biopolymers modification. ❊

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