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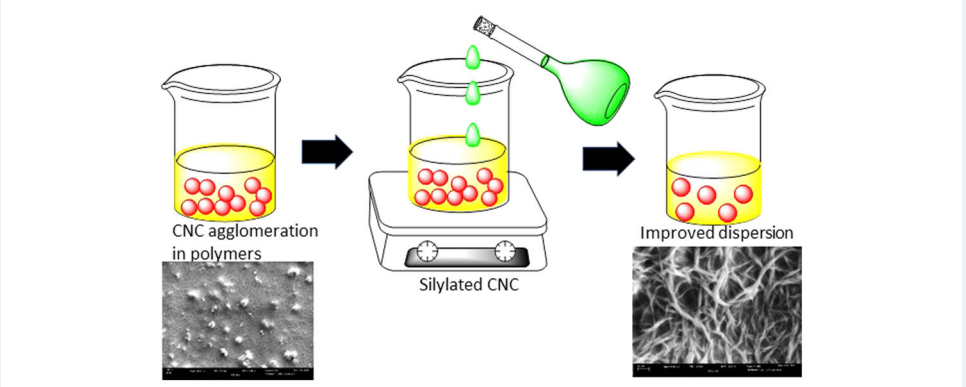
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ABSTRACT

Cellulose nanocrystal (CNC) has potential to be used as a reinforcement in polymeric nanocomposites because of their inherent biodegradability, universal accessibility, and superior mechanical properties. The most crucial challenge faced in the nanocomposite production is dispersing the nanoparticles effectively in the polymer matrix, so that the exceptional mechanical properties of the nanoparticles can be transferred to the macroscale properties to the bulk nanocomposites. In this research, a safe, effective and ecofriendly modification was used to functionalize the surface hydroxyl groups of CNC *via* silane treatment. These modified CNCs were used as reinforcements to prepare poly (ethylene oxide) (PEO)/CNC nanocomposites. The composites were prepared using solvent casting method. The composite properties were evaluated using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Thermo-Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Analysis (DMA). The SEM micrographs demonstrated that the composites incorporated with silane treated CNCs showed improvement in the dispersion behavior of the nanoparticles in the matrix. Oxidative combustion of the composites containing silane treated CNCs promoted char formation and enhanced thermal stability. The composites containing (1:1) silane treated CNCs exhibited the better crystallization ability, highest storage modulus, and lowest tan δ value compared to the other silane treated systems indicating improved dispersion of CNC. The polysiloxane network provided an efficient surface covering of the CNC molecules, imparting reduced polar surface characteristics and enhancing the overall mechanical properties of the composites.

GRAPHICAL ABSTRACT



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Cellulose nanocrystals; poly (ethylene oxide); dispersion; thermal stability; mechanical properties; self-condensation reaction

1. Introduction

Biodegradable and renewable materials have received special attention from both scientific and industrial communities due to their potential to cope with the effects of global warming and pollution. Cellulose is the most abundant bio-based polymer and has been used as a potential biodegradable and renewable material for industrial products. In the last few decades, nanostructured cellulose materials have become a new field of interest because of the specific physical and chemical properties of these materials. Nanocellulose can be

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distinguished in two main categories: 1) Cellulose nanofibrils (CNF), which is produced mainly by mechanical defibrillation, and 2) Cellulose nanocrystals (CNC), obtained by acid treatment. Both CNFs and CNCs are used for different applications because of their different properties [1]. The development of high performance/functional composites using nanofillers has become a prominent area of recent research. The selection of nanofillers has raised serious concerns for the environment and there is an immense need to introduce sustainable and bio-degradable nanofillers. Nanocellulose materials have great potential as nanofillers [2]. Amongst the nanocellulose materials, CNCs have gained special attention because of their high crystallinity (54–88%), superior mechanical properties (tensile strength $\sim$ 7 GPa, elastic moduli $\sim$ 150 GPa), light weight, transparency, relatively low cost and broad capacity to modify surface properties [1, 3–8].

In nanocomposites, the surface properties of CNCs affect the interfacial adhesion between filler and matrix, which ultimately dictates the overall properties of the composites together with the filler properties, orientation and aspect ratio. The most critical challenge in nanocomposite processing is to transfer the exceptional mechanical properties of CNCs at single fiber level to the macroscale properties of the bulk nanocomposites. This can only be achieved by enhancing the dispersion of CNCs and optimizing the filler-matrix interface [9], which is where the surface modification processes of CNCs come into play. The surface modifications are mainly conducted to introduce surface charges or functional groups, and tune the surface energy characteristics to enhance compatibility to the polymer matrices, while keeping the original morphology of CNCs intact [6]. Surface modifications not only induce surface charges or tune the surface energies of CNCs, but they also confer new properties to CNCs [10]. The surface modification techniques can be divided into two categories: 1) chemical surface modification through different chemical reactions, and 2) physical surface modification, using different physical means such as ultrasonication, electric pulses, or mechanical drawing. There are different types of chemical modifications reported to date such as polymer grafting, acetylation, esterification, acid treatment, isocyanate treatment, silanization. Amongst these methods, silanization has gained popularity because of the improvement in mechanical performance of the composites and use of a water/alcohol-based system, making this method more ecofriendly.

CNC has been reported [11–16] to blend with various polymers, such as, poly (3-hydroxybutyrate-co-3-hydroxyhexanoate (PHBH), poly (lactide), poly (vinyl alcohol), poly (propylene) and poly (caprolactone). Xu et al. [11] reported grafting of CNC with PHBH using (3-aminopropyl) triethoxysilane (APES) as a coupling agent. The experimental results showed improvement in dispersion of CNCs in PHBH matrix and enhancement in mechanical properties. In another study of Taipina et al. [12], a silane with isocyanate groups (isocyanatepropyltriethoxysilane) was used to modify the surface characteristics of CNCs. The primary goal of this study was to produce an oligomeric network of polysilsesquioxane, which can create an efficient nanocrystal covering. The modified CNCs showed less polar surface characteristics and better dispersion than the pristine ones. Qian et al. [13] used silane compatibilized (triethoxyvinylsilane, A-151) bamboo cellulose nanowhiskers (BCNW) as nanofillers for poly (lactic acid) (PLA) matrix. The mechanical properties of the silane-treated BCNWs were improved compared to the untreated ones. However, there was no clear evidence of improvement of dispersion of BCNWs in the polymer matrix. Yin et al. [14] functionalized CNC surface using □ -aminopropyltriethoxysilane and used as nanofillers for poly (lactic acid) (PLA) composites. The electron microscope images showed that the dispersion of CNCs in the polymer matrix was improved because of the change in surface characteristics while as a result thermal stability and mechanical properties are also enhanced.

Inspired by these results of silane treatment, a green and a sustainable technology for CNC functionalization was selected to improve the dispersion of CNCs in poly (ethylene oxide) (PEO) matrix and enhance the overall mechanical performance of the composites. Despite the small quantity of hydroxyl groups on the surface of the CNCs, the formation of the siloxane network provides an efficient surface covering of the CNCs (Figure 1). Moreover, this surface modification technique ends up in giving the CNCs less polar surface characteristics and makes them more compatible to hydrophobic polymer matrices. Overall, the main aim of the research was to develop a safe, effective and ecofriendly surface modification technique of CNCs to make them compatible to hydrophilic as well as hydrphobic matrices and to improve the dispersion behavior of CNCs in the matrix.

2. Experimental section

2.1. Materials

Poly (ethylene oxide) (PEO) (average M_v = 1,000,000) powder, with a melting temperature of 229 °C, purchased from Sigma Aldrich was used as polymer matrix. The CNC with dimensions of 10–15 nm width and 80–100 nm length and hence

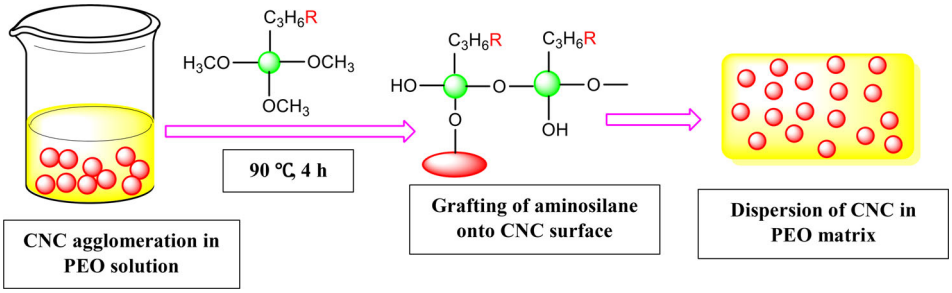


Figure 1. Reaction mechanism of silane grafting onto CNC surface.

aspect ratios of 5–10 were provided by USDA Forest Products Laboratory (Madison, WI, USA). They were extracted by the sulfuric acid hydrolysis process from softwood pulp. The CNCs were desulfated using hydrothermal treatment. The (3-aminopropyl) triethoxysilane (APES) with a purity of 98% was purchased from Sigma Aldrich. The specifications of silane were molecular weight (M_w = 221.37 g/mol), boiling point (217 °C), melting point (93 °C) and density (0.946 g/mL). Deionized (DI) water purchased from Millipore, USA was used as solvent.

2.2. Surface modification of CNC in PEO solution

The surface modification of CNCs using APES was done using the procedure as reported in literature [11]. The first step involved dissolving CNCs in deionized water at room temperature under continuous stirring. One gram of dry mass of CNC was dissolved in 100 mL of DI water separately in four beakers for four formulations. In the second step, 1 g of PEO was dissolved in each beaker at room temperature. In the third step, APES were dissolved in each beaker, in different concentrations. The weight ratios of CNC:APES were 1:1, 1:2.5 and 1:5, respectively in three formulations. In the fourth formulation, no silane was added. The fourth formulation was intended to check the reinforcment effect of CNC to the matrix and to perform the comparative studies of the effect of silane treatment on the dispersion behavior of CNC and mechanical properties of the resultant composites. All the solutions containing silane were kept under continuous stirring for 30 min. The solution without silane was stirred continuously until the CNC and PEO dissolved completely in water. In the fourth step, all the three solutions containing silane, were heated to 90 °C for 4 h to trigger silanization in the surface hydroxyl groups of the CNCs. Finally, a control sample solution was also prepared dissolving only 1 g of PEO in 100 mL of DI water, at room temperature. All the characterizations and the property comparison of the resultant composites were done with reference to this control sample of PEO. The formulation of each sample is shown in Table 1.

Table 1. Formulation of nanocomposite samples.

Sample	PEO (%)	CNC (%)	CNC: Silane (weight ratio)
PEO	1	0	–
1PEO/1CNC	1	1	–
1PEO/1CNC/1Silane	1	1	1:1
1PEO/1CNC/2.5Silane	1	1	1:2.5
1PEO/1CNC/5Silane	1	1	1:5

2.3. Nanocomposite film sample preparation

The PEO/CNC nanocomposite films were prepared using the film casting method [17, 18]. All the three formulations containing silane, were cooled to the room temperature. Then 20 mL from each of the five formulations (including the control and the no-silane one) were taken and poured very slowly in Teflon (PTFE) petri-dishes to make films, and to minimize the formation of air bubbles. The solutions were left for 24–48 h until the films were completely solidified. Two films were prepared for each formulation.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR) spectroscopy

The samples were analyzed using FTIR spectroscopy (Nicolet i550, Thermo Fisher Scientific, USA) in an attenuated total reflection (ATR) mode. The final spectrum of each sample was an average of 32 scans at a resolution of 4 cm^{-1}, in the wavenumber range of 400-4000 cm^{-1}.

2.4.2. Scanning electron microscopy (SEM)

The morphology of the film surface and dispersion of CNC in PEO matrix was analyzed using SEM. Images of surface morphology were taken at three magnifications (20 K, 40 K and 60 K) using field emission scanning electron microscope (Supra 55VP, Zeiss, Thornwood, NY, USA), operating at an accelerating voltage of 1.0 kV, in the Image and Chemical Analysis Laboratory (ICAL) at Montana State University. The samples were coated with a thin film of Iridium for 30 s for conductivity before capturing the images.

2.4.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a TA Instruments Thermogravimetric Analyzer (TGA Q500, New Castle, USA) in North Dakota State University. The samples were tested in thermal degradation mode, under a flowing nitrogen atmosphere with a flow rate of 60 ml/min, from 25 °C to 500 °C, at a heating rate of 10 °C/min.

2.4.4. Differential scanning calorimetry (DSC)

The thermal properties of the samples were measured by using DSC (Q2000, New Castle, USA) under a nitrogen atmosphere in North Dakota State University. The samples of about 4-5 mg were taken and scanned over a temperature range from 20 °C to 100 °C at a heating rate of 10 °C/min.

2.4.5. Dynamic mechanical analysis (DMA)

Dynamic mechanical analyzer (DMA Q800, New Castle, USA) was used to understand the dynamic storage and loss modulus of the samples. The viscoelastic properties of the samples were also studied through tan δ curve. Selected samples with dimensions of approximately (15 mm × 8 mm × 0.6 mm) were tested using the film tension mode at a constant frequency of 1 Hz and a strain amplitude of 15 µm. The test was performed in the temperature range of 30 °C to 110 °C and the heating rate was set at 5 °C/min. For each formulation, two replicates were tested, and the mean values were reported.

3. Results and discussion

3.1. Spectroscopy analysis of the composite films

The FT-IR spectra of the PEO and all the composites containing CNC (untreated and silane treated) are shown in Figure 2. In the PEO spectra, three -C-O-C- peaks appeared at 1145 cm^{-1}, 1112 cm^{-1} and 1062 cm^{-1}. The characteristic C-H stretching band was also observed between 3000 cm^{-1} and 2800 cm^{-1} [19]. For the PEO-CNC samples, the peaks at 3340 cm^{-1} and 1380 cm^{-1} represented the stretching and bending vibrations of O-H groups, indicating the incorporation of CNC in the matrix [20]. In case of the silane treated CNC composite samples, the characteristic band at 1580 cm^{-1} corresponding to the NH_2 band, shifted to 1560 cm^{-1} because the formation of an amide band [11]. This confirms grafting of silane onto the surface of the CNC.

3.2. Morphological study of the composite films

Figure 3 shows the SEM images of PEO-CNC composite films, both silane treated and untreated. The untreated CNCs showed a poor dispersion behavior

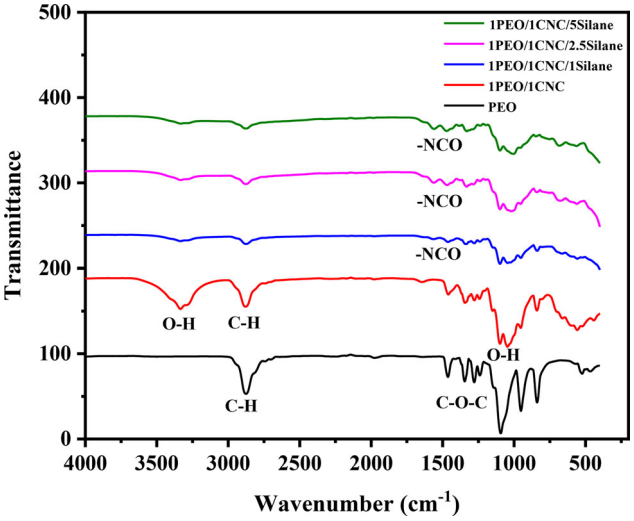


Figure 2. Transmission spectra of PEO, untreated CNC incorporated PEO, (1:1) silane treated, (1:2.5) silane treated and (1:5) silane treated CNC incorporated samples measured using FTIR.

in PEO matrix. The slow evaporation rate of the solvent pushed the nanocrystals to closer proximity and favored the formation of large agglomerates. But, the 1PEO/1CNC/1Silane and 1PEO/1CNC/2.5Silane samples exhibited improved dispersion behavior. In 1PEO/1CNC/1Silane sample, there were still bundles of CNCs clogging together present in the polymer matrix. In case of 1PEO/1CNC/2.5Silane, individual CNC crystals can be observed in some areas and clogging of bundled CNC in other areas. Again, the 1PEO/1CNC/5Silane samples showed very poor dispersion behavior. This may be due to the excess of silane present in the system. The reaction of silane and CNC surface groups reached the saturation point in case of 1PEO/1CNC/2.5Silane, and started adversely affecting the dispersion behavior of CNC when more silane was added to the system.

3.3. Thermogravimetric property analysis of the composite films

The effect of CNC incorporation and the silane treatment on the thermal properties of the PEO matrix were examined using thermogravimetric measurement and represented in Figures 4 and 5 and Table 2. The degradation of PEO started at ~340 °C and the polymer was sharply decomposed in a single step leaving almost no residue above 490 °C. After the incorporation of CNC, the onset point was decreased to ~270 °C, but the rate of mass loss was also decreased and the residue was still 6.7% above 490 °C. The surface sulfate groups present in the CNC caused the decrease in the onset degradation temperature because of the catalytic nature of the sulfate esters. In this two-step

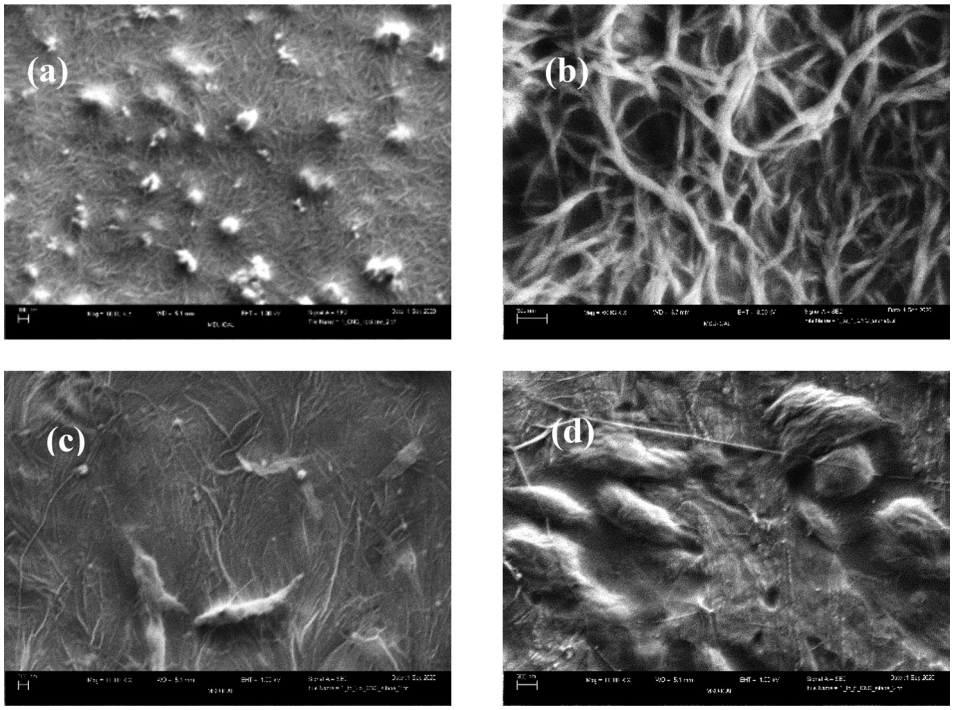


Figure 3. SEM images of PEO-CNC composite films: (a) 1PEO/1CNC, (b) 1PEO/1CNC/1Silane, (c) 1PEO/1CNC/2.5Silane and (d) 1PEO/1CNC/5Silane samples.

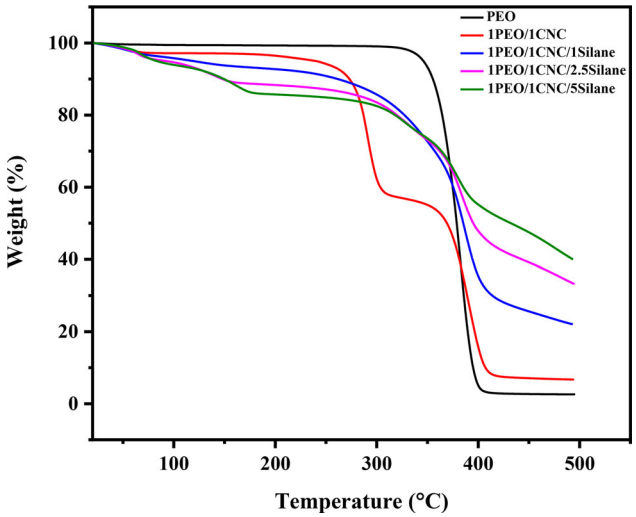


Figure 4. TGA thermogram of PEO, untreated CNC incorporated PEO, (1:1) silane treated, (1:2.5) silane treated and (1:5) silane treated CNC incorporated samples.

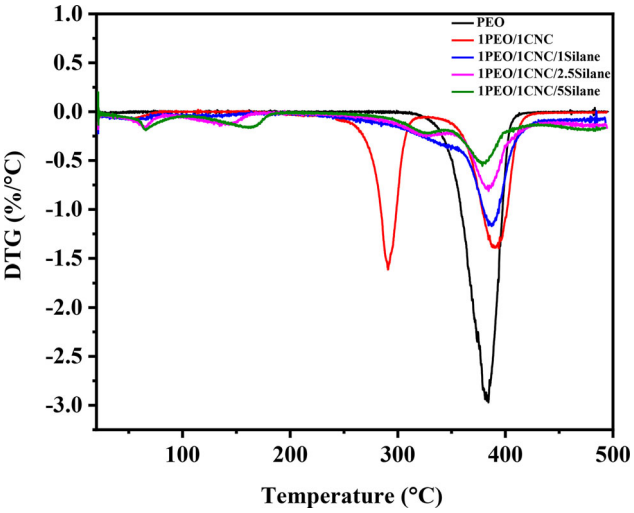


Figure 5. Derivative thermogravimetric (DTG) curves of PEO, untreated CNC incorporated PEO, (1:1) silane treated, (1:2.5) silane treated and (1:5) silane treated CNC incorporated samples.

degradation process, the first step was caused by the degradation of the amorphous regions of CNC. The second step indicated the degradation of the crystalline part of CNC. Therefore, there is a slight decrease in thermal stability with the incorporation of CNC in the matrix. When the (1:1) silane grafted CNCs were incorporated in the PEO matrix (1PEO/1CNC/1Silane samples), the onset point was improved to ~310 °C, and the char formation was increased leaving almost 22% residue. As the amount of silane was increased, the amount of residue also increased, reaching 33.6% and 40.4% for 1PEO/1CNC/2.5Silane and 1PEO/1CNC/5Silane samples, respectively. In all the silane treated composite films, the mass loss was much lower than the pristine CNC treated ones. The incorporation of silane treated CNCs increased the thermal stability of the composite films as inferred from the above data. This increase in thermal stability of the nanocomposites can be attributed to the shielding effect of the three dimensional polysiloxane network grafted onto the surface of the modified CNC. Therefore, the degree of grafting of silane onto CNC was calculated using the following equation:

$$\text{Graftingdegree} = (W_a - W_0) \times 100 / W_a \quad (1)$$

Table 2. Grafting degree of each formulation from TGA.

Sample	Residue wt. (%)	Grafting degree (%)
PEO	2.5	–
1PEO/1CNC	6.7	–
1PEO/1CNC/1Silane	22.1	26.4
1PEO/1CNC/2.5Silane	33.6	49.6
1PEO/1CNC/5Silane	40.4	77.9

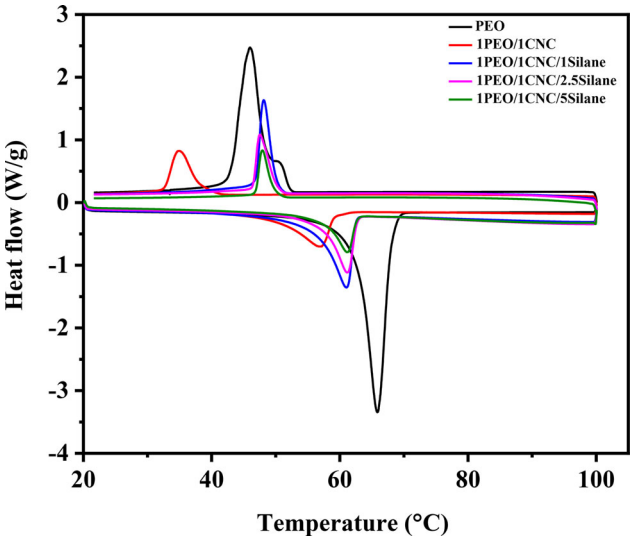


Figure 6. DSC thermograms of PEO, untreated CNC incorporated PEO, (1:1) silane treated, (1:2.5) silane treated and (1:5) silane treated CNC incorporated samples.

Table 3. Crystallization behavior of each formulation from DSC.

Sample	T_c	T_m	Crystallinity (%) (X_c)
PEO	45.9 °C	65.8 °C	61.7
1PEO/1CNC	35.1 °C	56.9 °C	26.2
1PEO/1CNC/1Silane	48.1 °C	60.9 °C	55.1
1PEO/1CNC/2.5Silane	47.2 °C	61 °C	41.5
1PEO/1CNC/5Silane	47.8 °C	61.2 °C	24.1

where W_a is the residue weight of composite after grafting and W_0 is the residue weight of composite before grafting. The degree of grafting was maximum in case of 1PEO/1CNC/5Silane samples, around 70%, followed by the 1PEO/1CNC/2.5Silane and 1PEO/1CNC/1Silane ones.

3.4. Crystallization behavior of the composite films

The non-isothermal crystallization behavior of the PEO-CNC composites was studied using DSC. The DSC results were shown in Figure 6 and Table 3. The crystallinity (X_c) was determined by the following equation:

$$X_c(\%) = \Delta H_m \times 100 / \Delta H_m^{\,0} \times (1 - x) \qquad (2)$$

where ΔH_m is the melting enthalpy, $\Delta H_m^{\,0}$ is the theoretical enthalpy of 100% crystalline PEO (197 J g^{-1}), and x is the weight fraction of filler (CNC).

In case of pure PEO, the crystallinity (%) was 61.7%, but the glass transition temperature (T_g) was not detected, as it was significantly lower (-67 °C) than room temperature. In contrast to pure PEO, all the CNC incorporated samples, both silane treated and untreated, showed a decrease in crystallinity. The 1PEO/1CNC sample showed a decrease in crystallization temperature (T_c) and melting temperature (T_m) and crystallinity (%) compared to pure PEO, indicating the nucleating effect of CNCs. A heterogeneous nucleation mechanism was induced by the nanofillers which in turn decreased the free energy barrier and accelerated the crystallization process. The PEO polymer chains surrounded the crystal nucleus and created an energy barrier to hinder the macromolecular chains to enter the lattice, favoring the formation of disordered and metastable crystal structures [21]. The confinement effect of nanocrystals hindered the chain diffusion and folding at the crystal growth front and formed thinner spherulites [22]. The 1PEO/1CNC/1Silane samples showed an improvement in crystallization ability (X_c = 55.1%) compared to the 1PEO/1CNC and other silane treated samples. Also, the highest crystallization temperature (T_c) (48.1 °C) was observed in case of 1PEO/1CNC/1Silane samples. In general, the higher the T_c observed upon cooling, the faster the crystallization rate of the polymers. Therefore, the crystallization ability of PEO was the best in the case of (1:1) silane treated CNC incorporation. The T_c and crystallinity of 1PEO/1CNC/1Silane samples were increased because of the restricted mobility of the polymer chains, indicating a better interfacial interaction between the modified filler (silane treated CNC) and the matrix. Silane acted as a compatibilizer which facilitated the dispersion and penetration of CNCs within the polymer matrix [23].

3.5. Dynamic mechanical property analysis of the composite films

Dynamic viscoelastic properties such as storage modulus (E′), loss modulus (E″) and loss factor (damping parameter, tan δ) were studied through dynamic mechanical analysis. The variation in storage modulus of pure PEO and corresponding composites as a function of composition and temperature while the samples were subjected to elevated temperature at a constant rate is shown in Figure 7 and the values are tabulated in Table 4.

For pure PEO, the storage modulus is approximately 206 MPa. The addition of untreated cellulose nanocrystals (1PEO/1CNC) led to a significant increase in storage modulus (3034 MPa), which further increased when silane treated CNCs (1PEO/1CNC/1Silane) were incorporated in the matrix

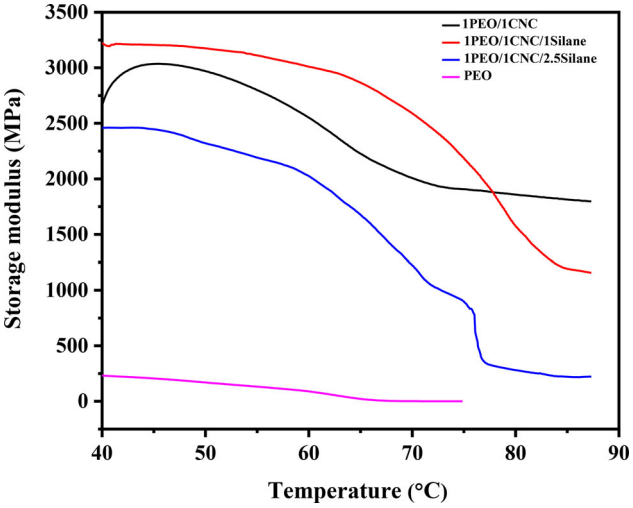


Figure 7. Representative curve of storage modulus as a function of temperature of PEO, untreated CNC incorporated PEO, (1:1) silane treated and (1:2.5) silane treated CNC incorporated samples.

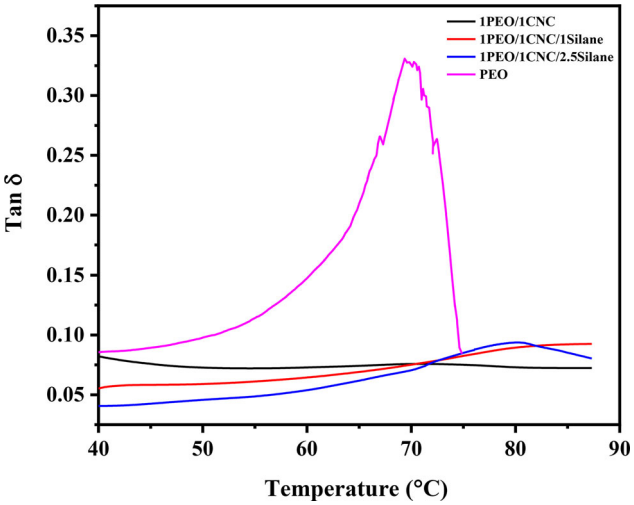


Figure 8. Tan δ curves as a function of temperature for PEO, untreated CNC incorporated PEO, (1:1) silane treated and (1:2.5) silane treated CNC incorporated samples.

Table 4. Mechanical properties of each formulation from DMA.

Sample	Peak tan δ	Storage modulus (MPa)	
		45 °C	85 °C
PEO	0.3264	206	–
1PEO/1CNC	0.0758	3034	1814
1PEO/1CNC/1Silane	0.0911	3147	1087
1PEO/1CNC/2.5Silane	0.0935	2258	251
1PEO/1CNC/5Silane	–	–	–

(3147 MPa). However, as the concentration of silane is increased from (1:1) to (1:2.5), the storage modulus sharply decreases (2258 MPa) due to the plasticizing effect of silane. Over the temperature range in this study, the formulation 1PEO/1CNC/1Silane exhibited the highest storage modulus value. This indicates that the grafted CNCs can form strong interaction networks that can facilitate stress transfer better than the ungrafted CNCs. The 1PEO/1CNC/5Silane formulation could not be tested for storage modulus as it was too brittle to withstand any amount of tensile force.

As observed from the graph, the 1PEO/1CNC/1Silane samples, exhibited higher modulus than the other samples. When the amount of silane was increased in the reaction system, the storage modulus gradually decreased. This may be due to the formation of increased self-condensation reaction to form polysiloxane network on the CNC surface. Since in the other systems most of the silane linkages were engaged in the formation of siloxane bridges, this phenomenon severely influenced the grafting of CNCs and in turn the mechanical properties of the samples [24].

The tan δ is the ratio of the loss modulus to storage modulus indicating the damping characteristics of polymers. A low tan δ intensity indicates that the material is more elastic than viscous [25]. According to that, all the nanocomposite samples indicated a more elastic response, as shown in Figure 8. However, with the incorporation of silane in the composites, the tan δ values increased, exhibiting more viscous behavior compared to the no silane containing samples. As the concentration of silane was increased, the tan δ values gradually increased. The nanocomposite samples exhibiting higher peaks in tan δ curves and lower storage modulus, indicated more viscoelastic behavior.

The relatively simple Cox-Krenchel model was used to calculate the moduli of the composites and their results were compared with the experimental values [26]. The rule of mixture type relationship for the randomly oriented short fiber composites is:

$$E = \eta_0 \eta_L E_f v_f + (1 - v_f) E_m \quad (3)$$

where E is the elastic modulus of the composite, E_f and E_m are fiber and matrix moduli, respectively, v_f is the fiber volume fraction, η_0 is fiber orientation factor and η_L is fiber length efficiency factor. Neglecting transverse deformations, η_0 for random 3-D fiber orientation = 1/5, η_L was assumed as 1, fiber volume fraction was of 50%. The modulus of PEO (E_m) was 206 MPa based on the experimental results. The modulus of CNC varies considerably between 50-200 GPa, based on the methods used to measure the tensile properties, types of cellulose (cellulose I or II) and the ratio between two celluloses. In the current study, a value of 145 GPa for CNC (E_f) was used for theoretical modeling [22].

Therefore, the theoretical modulus of composite was

$$E = 1/5 \times 1 \times 145 \times 0.5 + 0.5 \times 0.206 = 14.6 \text{GPa}$$

The experimental modulus was only 3 GPa. This indicated that the CNC was highly agglomerated in

Table 5. Storage modulus of other CNC composites with similar filler loadings.

Composite	Storage modulus (MPa)	Ref.
PEO/CNC	820	[22]
PHBH/CNC	1385	[11]
PLA/CNC	1992	[14]
PLA/CNC	2642	[28]
PLA/CNC	2490	[29]

the PEO matrix because of the high viscosity of the polymer solution and weaker hydrogen bonding with the nanocystals. Moreover, the mechanical dispersion step used to mix PEO and CNC could influence the size of CNC. The low aspect ratio of CNC (5-10) also plays a pivotal role in reducing the length efficiency factor from 1(100%) about 0.2 (20%) [22, 27]. Table 5 represents the storage modulus values of other CNC composites with similar filler loadings. From the following data, it is clearly evident that silane treatment of CNC significantly improved the mechanical properties of the composites.

4. Conclusion

The dispersion of nanofillers in the polymer matrix is the most crucial challenge in the process of nanocomposite production. In this study, PEO was successfully grafted onto the surface of CNC *via* aminosilane in a typical silane treatment. The grafting mechanism was carefully studied and confirmed by the FT-IR spectra. The scanning electron micrographs showed improvement in dispersion behavior of the silane treated CNCs in the matrix as compared to the untreated ones. Incorporation of silane treated CNC increased the amount of char formation, compared to the untreated CNC composites and control samples. The (1:1) silane treated CNC incorporated samples showed the highest degree of crystallization (X_c = 55.1%) and the highest crystallization temperature (T_c = 48.1 °C), compared to the other silane treated samples. The addition of (1:1) silane treated CNC led to a significant increase in the storage modulus of the nanocomposites. However, a further increase in concentration of silane resulted in a decrease in storage modulus, increase in tan δ and lowering of onset degradation temperature. This indicated an optimal concentration of silane in the composite samples, as a result of an increase in the self-condensation reaction of the silane linkages to form the polysiloxane network. As a result, only a small amount of silane linkages were available to react with the surface hydroxyl groups of CNC. It can be concluded from this research, that the (1:1) silane treated CNC incorporated composites exhibited the best overall performance in terms of thermal and physical and mechanical properties. Thus this surface silane treatment of CNC can prove to be a successful path to disperse CNCs in polymer matrices, and also enhanced compatibility between the matrix and the fillers, reducing the polar characteristics of the fillers.

Disclosure statement

No potential conflict of interest was reported by the authors.

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