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A comparative study of different nanoclay-reinforced cellulose nanofibril biocomposites with enhanced thermal and mechanical properties

Cheng Yong^a, Changtong Mei^a, Mingjie Guan^a, Qinglin Wu^b, Jingquan Han^a and Xiuxuan Sun^b

^aCollege of Materials Science and Engineering, Nanjing Forestry University, Nanjing, China; ^bSchool of Renewable Natural Resources, Louisiana State University, Baton Rouge, LA, USA

ABSTRACT

The objective of this research was to comprehensively compare the effects of nanoclay bentonite (BT), halloysite nanotubes (HNTs) and sulfuric acid-etched halloysite nanotubes on the surface wettability, morphological, mechanical and thermal properties of cellulose nanofibril (CNF) biocomposites. A simple and environmental safe casting-evaporation method was used to fabricate these samples, which comprised up to 10 wt% of nanoclay. The surface wettability, tensile testing and TG results showed that the biocomposites with BT exhibited greater hydrophobicity, larger modulus and strength and better thermal stability than with HNTs at low content. However, at high content, the biocomposites with HNTs exhibited larger elongation at break. The DMA results indicated that biocomposites with HNTs exhibited better molecular motion restriction than with BT. These results combined with Fourier Transform Infrared (FTIR) also indicated interfacial interactions between CNF matrix and nanoclay. Acid treatment would help promote the interfacial interactions between HNTs and CNFs, resulting in enhanced mechanical and thermal properties. This comparative study will help in the choice of appropriate nanoclay for use in functional biomaterials in industrial production applications.

F-BT biocomposite

CONTACT Changtong Mei Rei@njfu.edu.cn © 2017 Informa UK Limited, trading as Taylor & Francis Group

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Introduction

Studies on nanocomposites based on classic polymer and silicate nanoclays currently use synthetic polymers for example, polyethylene [1,2], polypropylene [3,4], polystyrene [5,6], polyimide [7,8] and polymethacrylate [9] as the matrix in most fields. However, the environmental constraints on the use of petroleum-based polymers, especially in the packaging field, have accelerated research aiming to replace these nanocomposites matrix by renewable, sustainable, biodegradable and environmentally friendly polymers [10,11].

Natural cellulose fiber is one of the most widespread and plentiful natural organic biopolymer and is also renewable and sustainable with impressive mechanical properties [12,13]. Recently, researchers have reported the use of nanocellulose as reinforcing fillers to improve polymer properties in terms of relative reactive surface and bioactivity, high specific mechanical properties [14-16]. However, few reports have described the use of nanocellulose as a continuous matrix. A fiber-matrix may exhibit different toughening mechanisms compared with traditional petroleum-based polymers. Some considerations have to be taken into account during the conception of nanocellulose biocomposites. (1) The degradation of nanocellulose is one of the most important disadvantages under exposure to environmental conditions including humidity and sunlight [17,18]. The synergistic effects of oxygen and water reduce the mechanical properties and dimensional stability of nanocellulose. (2) The application of nanocellulose is also challenging because it does not melt and is not soluble in some conventional solvents due to the factor of strong hydrogen bonds and its crystalline structure [19,20]. Therefore, it is necessary to modify nanocellulose matrices with proper fillers to form a good interfacial bonding between them. (3) It is difficult to produce or regenerate nanocellulose from natural fibers without any environmental pollution at low cost thus far [21,22], increasing the cost of the resulting nanocomposites.

Inorganic clay minerals on the nanometer-scale are appropriate reinforcing fillers for improving the properties of nanocomposites. Most researches published recently have designed layered-silicate nanocomposites using bentonite (BT) or its organic derivative as reinforcing fillers [23-25], few investigations have compared these biomaterials with other nanoclay. The composition and structure of bentonite and other kaolin clays vary greatly in most instances, and this feature closely correlate with their use in different applications according to their characteristic features [26]. Recent studies on tubular silica-based naturally occurring halloysite nanotubes (HNTs) have attracted interest for use as reinforcing fillers. HNTs, similar to Carbon Nanotubes (CNTs), have relatively weak interactions between tubes because of their unique geometry and the presence of aluminum and hydroxide on the inner surfaces and silicate on the external surfaces. HNTs can form hydrogen bonds with polymers because of some hydroxyl groups on the outer surface of tubes; thus, HNTs disperse well in a polymer matrix without additional chemical modification [27–29]. Furthermore, the higher stiffness as well as the higher length-diameter aspect of HNTs compared with bentonite can provide a high degree of reinforcement in polymer matrices [30]. Acid treatment would help to enhance the interfacial bonding between HNTs and cellulose nanofibril (CNF) by increasing porosity and surface area and forming many acidic functional groups [31,32].

In this work, we compared the effects of BT, HNTs and sulfuric acid-etched halloysite nanotubes (s-HNTs), used as reinforcing fillers, on the tensile and thermal properties of (cellulose nanofibril) CNF biocomposites to understand the contribution of their structures,

contents and interfacial interactions to the properties of CNF biocomposites. This environmentally friendly CNF bio-based film, prepared by simple homogenization and hot pressing method may help improve the thermal properties of the composite and illustrate the surface wettability mechanism and the mechanical mechanism based on different clay structures, which may be intimately related to their ultimate CNF applications. The comparison of the effects of the nanoclays in CNF nanocomposite may show more uncertainty due to the combination of the lamellar, tube-like and entangled structure. This study presents a preliminary comparison of the effects of the nanomorphology of nanofillers on the improvement of CNF-based biocomposites, this providing a basis for the selection of nanoreinforcement biomaterials for use in industrial polymers applications.

Materials and methods

Materials

Sodium bentonite (BT) (200 mesh, dry powder) was purchased from Baroid Industrial Drilling Products Inc. (Houston, TX, U.S.A.).

HNTs with pore size volumes of 1.26-1.34 ml/g, a specific gravity of 2.53 g/cm³, a surface area of 65 m²/g and a cation exchange capacity of 8 mequiv./100 g were purchased from Sigma-Aldrich Inc. (St. Louis, MO, U.S.A.).

s-HNTs were prepared by mixing 15% sulfuric acid with HNTs at 85 °C for 1.5–2 h. The samples were then rinsed and filtered several times until neutral pH was achieved, dried in a vacuum oven at 90 °C for more than 24 h and then crushed in an agate mortar.

CNF hydrocolloid was collected from microfibrillated cellulose (Celish KY 100-S grade, 25% solid content, Japan) using nine cycles of high-pressure homogenization treatments (Microfluidizer M-110P, U.S.A.).

Preparation of biocomposite films

CNF biocomposite films reinforced by 2.5, 5.0 and 10.0 wt% nanoclay were prepared as follows: A nanoclay dispersion (0.5 wt%) containing 0.031, 0.062 or 0.125 g of nanoclay was slowly added into a CNF colloidal solution (0.5 wt%) containing 1.22, 1.19, or 1.13 g of CNF to obtain dispersed mixtures with a total volume of 250 ml each, herein termed CNF-Clay 2.5%, CNF-Clay 5% and CNF-Clay 10%, respectively. For the three nanoclay type: BT, HNTs and s-HNTs. The mixtures were homogenized using a high-pressure homogenizer for 1 h and were further dispersed by ultrasonic treatment for 1 h. Then mixture solutions were then vacuum-filtered through a filter membrane (polyvinylidene fluoride microfiltration, 0.65 µm pore size, 125 m thickness, DVPP14250, EMD Millipore, Billerica, Massachusetts, U.S.A.). Filtration time was controlled from 30 to 60 min, according to the eventual biocomposite film thickness and the nanoclay concentration. And after that, each wet biocomposite film was carefully peeled off from the filter membrane and then placed between two filter papers. Each stacked film and filter papers was then placed between two metal plates under constant pressure. Finally, biocomposite films with thicknesses from 80 to 110 µm were obtained after oven drying at 40 °C for 24 h and then vacuum dried at 70 °C for 2 h. A diagram of the preparation of the nanoclay-reinforced CNF biocomposite films is shown in Figure 1.



Figure 1. Sketch of the preparation process of CNF-Clay.

Characterization of the biocomposite films

Transmission electron microscopy

The microstructure of the nanoclays was recorded using a transmission electron microscope (Tecnai G2 20 STWIN, FEI, U.S.A.) at an accelerating voltage of 200 kV. Prior to observation, the 0.1 wt% nanoclay suspensions were previously dropped onto a copper grid coated with a perforated carbon support film (Agar Scientific, U.K.).

Surface wettability

Water contact angle experiments were measured using an FTA 1000 analyzer (First Ten Angstroms, U.S.A.) with the static method. A drop of 4 μ L of deionized water was carefully dropped on the top surface of the film. The water contact angels based on five samples were measured until no obvious change was found on both sides for symmetry at an accuracy 0.01° using a CCD camera.

FTIR spectroscopy test

FTIR spectra of films were recorded using a Bruker FTIR analyzer (Tensor-27, Germany). Each sample was placed onto the ZnSe ATR crystal cell. Data were recorded using averaging over 32 scans, over a range of $4000-500 \text{ cm}^{-1}$ at room temperature.

Scanning electron microscopy

The microstructure of the biocomposite films was inspected by scanning electron microscopy (SEM) (Hitachi, S-3400 N, Japan) with an accelerating voltage at 15 kV. Prior to observation, the samples were frozen in liquid nitrogen, and the surfaces were subjected to brittle fracture. Cross-section and surface were sputtered with gold-palladium alloy and then transferred to the SEM observation.

Tensile testing

The tensile properties of the biocomposite films were determined with an Instron 5582 testing machine (Instron Co, U.S.A.) according to the ASTM D638-10 standard at a cross-head speed of 5 mm/min at room temperature. Specimens of 40 mm in length, 10 mm in width and 80–110 μ m in thickness were obtained for measurement. The tensile strength and tensile modulus were determined from the strain-stress curves based on five samples.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) were measured using a thermo-gravimetric analyzer TGA (TA Q50, U.S.A.) to study the thermal stability of biocomposite films. Samples were tested from 30 to 600 °C. The heating rate was 10 °C/min and the nitrogen flow rate was 40 ml/min. To eliminate small amounts of residual water in samples, samples were preheated in a vacuum oven at 50 °C for more than 24 h.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) tests of biocomposites were performed using a dynamic mechanical analyzer (Q800, U.S.A.) in tensile mode at a frequency of 1 Hz and a strain amplitude of 0.1% to determine biocomposite thermomechanical properties. The dimensions of the film were 80–110 μ m (thickness), 20 mm (length) and 5 mm (width). Samples were carried out with a temperature from 30 to 220 °C at a heating rate of 2 °C/min.

Results and discussion

Microstructure of the nanoclays

Figure 2 presents the transmission electron microscopy (TEM) micrographs of BT, HNTs and s-HNTs. The natural bentonite sample exhibited the presence of micro-aggregations of silicate layers. These silicate layers comprised crystaline particles with smooth, flat surfaces. The natural halloysite samples exhibited a tube-like structure, among which some exhibited alumite plates. The HNTs were 400–1200 nm in length, and their inner and outer diameters were 10–80 and 100–150 nm, respectively. After acid treatment, some HNTs started to bend



Figure 2. TEM micrographs of (a) BT, (b) HNTs, and (c) s-HNTs.

and break down due to dehydration, as depicted in Figure 2(c). Because sulfuric acid can dissolve halloysite at both the outer and inner surfaces, the outer surface began to peel, and the inner surface decomposed into amorphous silica [32,33], leading to thinning of tubes from inside. The inner Lameller and tube-like structures may be useful for different reinforcement applications, as will be discussed subsequently.

Film surface wettability

The contact angle method is used to investigate the hydrophilicity of the film surface based on the level of interaction between the CNF film and their biocomposites with water. The content of 10 wt% was chosen for study due to its remarkable effect on surface wettability in relation to its low content. As depicted in Figure 3, the contact angle of the CNF film was $36.1 \pm 5.1^{\circ}$ after 60 s due to its hydrophilicity, while the corresponding value was $60.3 \pm 7.0^{\circ}$ with 10 wt% BT, this value decreased to $23.5 \pm 3.5^{\circ}$ and $19.2 \pm 3.0^{\circ}$ for 10 wt% HNTs and s-HNTs, respectively, after 60 s.

Clay type has an important role in changing a material's surface energy to favoring hydrophilicity or hydrophobicity. For better understanding the effect of clay type on biocomposite surface wettability, we set up two models combining the TEM results to illustrate the difference between the interactions of CNF with BT or HNTs from the perspective of the clay structures, as depicted in Figure 4. Bentonite is a hydrophilic clay mineral comprising octahedral sheets and an interlayer region comprising Na⁺. Overlapped layers of BT are constrained by van der Waals interaction between each layer. The CNFs form a fibrous cross-linked structure encapsulating the layers because the intact cellulose nanofibers cannot interact with bentonite sufficiently. HNTs are multi-walled hollow nanotubes, that contain octahedrally and tetrahedrally ions in a 1:1 stoichiometric ratio [27]. This directed and porous structure may exhibit greater mechanical enhancement and provide more functions in CNF biocomposites than in bentonite. Obviously, tube-like HNTs exhibits fewer hydroxyl groups compared with lamellar-structured BT.

The increased contact angle at 10 wt% BT was due to the formation of a nacre-like structure within the LBL self-assembly alternating multilayer [34] and a strong interfacial



Figure 3. Static water contact angle of CNF film and its biocomposites with 10 wt% BT, HNTs and s-HNTs.



Figure 4. Schematic models of structure of BT (a) and HNTs and (b) reinforced CNF biocomposites and clay structures.

adhesion between BT and CNFs. In the vertical direction, the entangled CNF surface was coated by lamellar-structured BT, and the voids in the networked CNF matrix was blocked by the platelets with hydrogen bonding. The decreased contact angle for the 10 wt% HNTs resulted from the spontaneous migration of hydrophilic particles to the film/water surface to reduce the interfacial energy [35], and the moisture flow in the channel was not hindered by HNTs that contained vertical tube-like structures through siphon effect. Small gaps caused by weak interfacial bonding between HNTs and CNFs might be another reason. A further reduction of contact angle as the acidified HNTs demonstrated that the surface area and pore volume of the HNTs were enlarged by sulfuric acid treatment, thus allowing more water to be absorbed.

FTIR analysis

The CNF biocomposite films were characterized using FTIR spectroscopy. The content of 10 wt% was chosen for its remarkable effect on molecular interactions compared with

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lower content. Figure 5(a) shows the main infrared spectral differences for peaks that are characteristic of CNF, BT, HNTs and s-HNTs. For the HNTs and s-HNTs, slight deviations were observed. The stretching bands for –OH (3692–3694 cm⁻¹ and 3621–3623 cm⁻¹) and Si–O–Si (1002–1011 cm⁻¹) and the bending bands for adsorbed water (1640–1645 cm⁻¹), –OH (906–917 cm⁻¹), Al–OH (748–751 cm⁻¹), and Si–O–Si (447–457 cm⁻¹) were shifted to lower values due to crystallinity changes [36]. Compared with BT, the peak observed at 1118 cm⁻¹ for the HNTs and s-HNTs is probably associated with silicon-rich nanoparticles [33], while the peak observed at 795 cm⁻¹ for BT was assigned to the plate-like form of disordered tridymite [37].

As depicted in Figure 4(b), the peak intensities for the inner-surface hydroxyl groups and inner hydroxyl groups of the CNF/s-HNT biocomposites was stronger than those of the CNF–HNT biocomposites due to their high density of –OH groups [34]. The intensity of hydrogen-bond interaction in CNF biocomposites was reduced and shifted to higher frequency (from 3326 to 3331 cm⁻¹ and from 906 to 917 cm⁻¹ with the help of peak-fit processing) compared with neat CNF film. This confirmed that interfibrillar hydrogen bonding was reduced by the presence of clays and by the new hydrogen bonding between the CNF and the clays.

Film tensile properties

The tensile properties of CNF films and their biocomposites with different clay content are shown in Table 1. The addition of 2.5 wt% nanoclay into the CNF matrix improved the Young's Modulus and tensile strength of the biocomposites for two reasons: first, small amount of clays disperse well in the CNF matrix, and this may restrict the mobility of CNF chains under loading; second, correct hydroxyl bonding between the CNF and the clays may ensure that no debonding occurs or that no voids exist between them [38]. However, the Young's Modulus and tensile strength decreased obviously with excessive proportions of nanoclays due to their agglomeration; this might create stress concentrations in the CNF matrix. Furthermore, elongation at break also decreased at excessive proportions of nanoclays.



Figure 5. FTIR transmittance spectra of (a) CNF, BT, HNTs and s-HNTs, and (b) CNF film and its biocomposites with 10 wt% clays.

System	Clay content (wt %)	Young's modulus (GPa)	Tensile strength (MPa)	Strain at break (%) 11.3 ± 1.2	
CNF	-	9.1 ± 1.8	114.1 ± 13.3		
CNF-BT	2.5	11.2 ± 2.1	122.3 ± 15.1	11.9 ± 1.8	
	5.0	12.1 ± 1.4	130.0 ± 16.0	9.3 ± 1.0	
	10.0	9.5 ± 0.7	101.3 ± 11.5	8.6 ± 0.6	
CNF-HNTs	2.5	10.9 ± 1.9	118.3 ± 13.8	11.5 ± 1.8	
	5.0	9.6 ± 0.9	115.5 ± 22.9	12.2 ± 1.0	
	10.0	9.9 ± 1.9	106.7 ± 14.5	10.1 ± 2.6	
CNF-s-HNTs	2.5	10.5 ± 1.7	120.9 ± 24.2	11.9 ± 2.6	
	5.0	11.6 ± 2.5	125.1 ± 14.9	12.2 ± 2.0	
	10.0	11.4 ± 1.8	115.3 ± 21.7	11.6 ± 1.9	

Table 1. Tensile property of CNF films and their biocomposites with different clays.

The Young's Modulus and tensile strength of the CNF-BT biocomposites were stronger than those of CNF-HNT biocomposites at low clay contents. Compared with the BT clay, the fewer hydroxyl groups on the HNTs outer surfaces resulted in insufficient interaction with CNF as mentioned in Figure 2. Furthermore, the tube-like morphologies did not generate enough opportunities for large-area contacts compared with the BT platelets [27]. However, the Young's Modulus and tensile strength of the CNF biocomposites containing 10 wt% BT decreased by as much as 15.7 and 17.2%, respectively, compared to the other two CNF-HNTs biocomposites. For this reason, we obtained SEM micrographs (Figure 6) of the fractured surfaces of CNF biocomposites including 10 wt% BT or HNTs at room temperature. The 10 wt% BT clays exhibited plate-like structures that generated larger coatings over the CNF surface and had irregular, larger pores, while the tube-like HNTs were inserted into an entangled CNF matrix, thus creating smaller microvoids. Therefore, it was possible for smaller particles to act as crack arrestors under loading by inducing deformation; furthermore, compared with bigger voids, the formation of large number of smaller voids probably contributes more to adsorbing energy, thus maintaining the sample strength [30]. The analysis of strain at break also confirmed that adding 10 wt% BT reduced the biocomposite elongation by 24%, while the use of an additional 10 wt % HNTs decreased the elongation by 10.93%. For the CNF-s-HNT biocomposites, stronger interfacial adhesion was obtained due to the improvement in mechanical properties that resulted from the increased number of hydroxyl groups after acid treatment; this result corroborated the FTIR results, and led to higher intrinsic stiffness.

Thermal stability

The TGA-DTG results obtained for the CNF films and their biocomposites containing 10 wt% clays are presented in Figure 7, and the weight loss at different temperatures are summarized in Table 2. The content of 10 wt% was chosen for its remarkable effect on the thermal properties compared with lower contents. All biocomposite films exhibited a slight weight loss in low temperature region due to the runoff of adsorbed water. As a general trend, weight loss results for CNF biocomposites containing 10 wt% clays showed a considerable decrease of the characteristic temperature and maximum weight loss rate (WLR), indicating that thermal degradation occurred first at low temperature with the addition of clays. The thermal degradation of samples containing clays occurred at lower temperature possibly due to the catalytic action of clays and adsorbed water [39]. The WLR of CNF biocomposite containing BT decreased remarkably compared with pure CNF film due to





Figure 6. SEM micrographs of the fractured surface of CNF biocomposites with 10 wt% BT at low magnification (a), at high magnification (b) and with 10 wt% HNTs at low magnification (c), at high magnification (d).



Figure 7. TGA (a) and DTG (b) curves of CNF film and its biocomposites with 10 wt% clays.

the barrier effect created by lamellar structure. Physically adsorbed water between layers shown in Figure 4(b) might be released over a longer period. The weight loss of raw HNTs at this temperature (weight loss 10%) was higher than that of acid-treated HNTs, which can be attributed to the dehydration and the destruction of s-HNTs during the sulfuric acid treatment [32,40]. The residue content at 600 °C is summarized in Table 2. The residue of

Table 2. Weight loss temperature of 10 wt% ($T_{10\%}$) and 50 wt% ($T_{50\%}$) as well as Maximum thermal degradation temperature (T_{max}) and maximum weight loss rate (WLR) for the TGA of CNF films and their biocomposites.

Samples	T _{10%} (°C)	Т _{50%} (°С)	T _{max} (°C)	WLR _{max} (%/min)	Residue at 600 °C (%)
CNF	305.6	348.6	348.1	1.59	20.3
CNF-BT 10%	276.9	342.4	328.3	1.05	32.2
CNF-HNTs 10%	313.2	351.6	343.3	1.46	28.6
CNF-s-HNTs 10%	315.6	352.4	345.1	1.59	28.7

the pure CNF film was approximately 20%, and the inorganic contents of the nanoclays were similar to their theoretical clay contents, demonstrating the homogeneity of the clay distribution in the CNFs.

The corresponding DTG curves for the CNF films and their biocomposites are consistent with the TGA results. As presented in Figure 7(b), the maximum degradation rates of CNF biocomposites were lower than that of the pure CNF film. The lower degradation rate can be attributed to the protective barrier layer formed by the clays as they dispersed into the CNF matrix towards the CNF thermal degradation products as mentioned above for the surface wettability analysis. Therefore, this thick and effective inorganic layer may be able to slow the rate of degradation and improve the thermal stability of the biocomposites [30]. Among these nanoclays, the thermal stability of the CNF nanocomposites containing BT clays clearly presented a better performance around the temperature corresponding to the lowest degradation rate as due to their special structure.

Dynamic mechanical behavior

The storage modulus and $\tan \delta$ of the CNF films and their biocomposites containing 5 wt% BT, HNT and s-HNT clays are shown in Figure 8 as a function of temperature. The content of 5 wt% was chosen due to its remarkably better in mechanical properties, as shown in Table 1.

As depicted in Figure 8(a), the storage modulus of the CNF films and their biocomposites with 5 wt% clays decreased gradually as the temperature increased. The curve for CNF-Clay trended less steeply downward than that for the pure CNF film due to the structural



Figure 8. Storage modulus (a) and mechanical damping $tan\delta$ (b) of CNF film and its biocomposites with 5 wt% clays.

organization and intrinsic properties of the nanosized clays and to the mechanically crosslinked structure together with the formation of new hydrogen bond [41]. Among these three naonclays, the storage modulus curve of CNF-BT 5% decreased the least (33.7%); this value compares with that of CNF-HNTs 5% (53.4%). These values are in accordance with the TG results showing that the BT clay was the most thermally stable clay. The storage modulus of CNF containing the acidified HNTs was stronger than that of raw HNTs, as shown for the tensile properties, due to the enhanced interfacial bonding between the clays and the CNF matrix.

The interfacial interaction between the clays and the CNF matrix can also be studied based on mechanical damping value, $tan\delta$. Energy is mainly consumed at the interface between the reinforcement and the matrix. If frictional energy is adsorbed under loading, the molecular motion will be constrained, and $\tan \delta$ will also be small. In Figure 8(b), all curves showed a peak temperature of approximately 200 °C, corresponding to the main stress relaxation based on the glass-rubber transition [38]. The damping values, $tan\delta$, of the CNF biocomposites containing 5 wt% clays were noticeably smaller than that of the pure CNF film due to the strong interfacial adhesion between the CNF and the nanoclay, which restrained the motion of the CNF network. However, from 30 °C to 220 °C, the damping values, $tan\delta$, of the CNF biocomposites containing 5 wt% clay increased more remarkably than that of the pure CNF film, and this result was similar to that obtained by other researchers [38]. In the CNF-Clay biocomposites, the clays might reduce the intermolecular interactions among the CNF chains and at high temperature some nanoclays would be forced to agglomerate, possibly creating new stress concentrations. The weakened interface and stress concentrations would not sufficiently prevent molecular chain slipping [34], leading to a rapid increase of the damping value, $\tan \delta$. The effect of molecular motion limitation containing HNTs decreased more remarkably with temperature increasing due to the worse interfacial bonding. The acid treatment would help to reinforce the CNF matrix due to new hydrogen bonds, as demonstrated previously.

Conclusions

The results showed that the combination of CNF and clays exhibited different variation in surface wettability due to their different clay structures, but achieved the same noticeable reinforcement when using small amounts due to the good dispersion and interfacial hydrogen bonding. However, the mechanical properties disimproved as the amount of clay increased due to the agglomeration of excessive clay. The thermal degradation temperatures rates of the CNF biocomposites were also lower for the nanoclays due to the formation of thermal protective layers. The interfacial hydrogen bonding also had an important effect on storage modulus and the damping values, tan δ , due to the restraint it placed on molecular motion.

For CNF biocomposites containing BT, HNTs and s-HNTs, the unique structures and chemical modifications of these compounds were the primary reasons underlying their mechanical and thermal distinctions. CNF–BT biocomposites exhibited greater hydrophobicity, larger modulus and strength and better thermal stability due to strong interfacial adhesion and thick protective layer. However, at high content, the biocomposites with HNTs exhibited larger elongation at break. The DMA results indicated that biocomposites with HNTs exhibited better molecular motion restriction than with BT. These results combined with FTIR also indicated interfacial interactions between CNF matrix and nanoclay. More hydroxyl groups are created by acid treatment which improves the surface area and pore volume, thus reinforcing the thermal stability and mechanical properties of the CNF biocomposites.

Disclosure statement

No potential conflict of interest was reported by the authors.

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