Surface Charges Control the Structure and Properties of Layered Nanocomposite of Cellulose Nanofibrils and Clay Platelets

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ABSTRACT: The interfacial bonding and structure at the nanoscale in the polymer—clay nanocomposites are essential for obtaining desirable material and structure properties. Layered nanocomposite films of cellulose nanofibrils (CNFs)/montmorillonite (MTM) were prepared from the water suspensions of either CNFs bearing quaternary ammonium cations (Q-CNF) or CNFs bearing carboxylate groups (TO-CNF) with MTM nanoplatelets carrying net surface negative charges by using vacuum filtration followed by compressive drying. The effect of the ionic interaction between cationic or anionic charged CNFs and MTM nanoplatelets on the structure, mechanical properties, and flame retardant performance of the TO-CNF/MTM and Q-CNF/MTM nanocomposite films were studied and compared. The MTM nanoplatelets were well dispersed in the network of TO-CNFs in the form of nanoscale tactoids with the MTM content in the range of 5−70 wt %, while an intercalated structure was observed in the Q-CNF/MTM nanocomposites. The resulting TO-CNF/MTM nanocomposite films had a better flame retardant performance as compared to the Q-CNF/MTM films with the same MTM content. In addition, the effective modulus of MTM for the TO-CNF/MTM nanocomposites was as high as 129.9 GPa, 3.5 times higher than that for Q-CNF/MTM (37.1 GPa). On the other hand, the Q-CNF/MTM nanocomposites showed a synergistic enhancement in the modulus and tensile strength together with strain-to-failure and demonstrated a much better toughness as compared to the TO-CNF/MTM nanocomposites.

KEYWORDS: cellulose nanofibrils, montmorillonite platelets, surface charges, nanocomposites, mechanical properties

1. INTRODUCTION

Cellulose nanofibrils (CNFs), also called as microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC), prepared from wood pulp are 3 orders of magnitude smaller than the intact wood fiber cells. The typical fibril width of wood CNFs is in the range of 3−15 nm with wide distribution of lengths from 500 nm to several micrometers. The production of CNFs-based functional and bioinspired nanocomposite materials combining lightweight, robust mechanical properties, multifunctionality, and the structural control over multiple length scales are highly desirable.1 Particularly, the interfacial interactions and properties of the hybrids from nanocellulose and 2D materials such as clay and graphene oxide have attracted an increasing attention.2−4 Montmorillonite (MTM), a smectite-type clay, is one of the most commonly used layered silicates with net negative charges located on the surface of each nanoplatelet.3 The thickness of the nanoplatelets is around 1 nm, and the lateral dimension may vary from 30 nm to several micrometers. Clays are found in nature in the form of tactoids, i.e., clusters of a few to many platelets that are parallel to each other and separated by a constant spacing of ca. 1 nm.6−7 The properties of a clay/polymer hybrid nanocomposite are believed to be related to the structure of the clay in the polymer matrix.8,9 In particular, the aspect ratios of the clays and the extent of dispersion (exfoliation) of the nanoclay within the polymer matrix have a significant impact.10−11 At low clay volume fractions, clays are often completely exfoliated and dispersed homogeneously in the polymer matrix with a random orientation, achieving better properties such as high stiffness, fire retardancy, and barrier properties.6,12 At high clay volume fractions, ordered structures mimicking the brick-and-mortar microstructure of a nacre are favored in the fabrication of high mechanical performance structural materials.13−15 Therefore, in order to engineer and manufacture high-performance CNFs/clay nanocomposites, it is essential to have not only optimal processing conditions and
clay volume fractions but also a controlled interfacial interaction between the CNF and clay and their assembly. The hybrids of CNFs with inorganic clay nanoplatelets such as the MTM have been extensively studied previously and have demonstrated an excellent mechanical performance together with other functionalities such as low oxygen permeation, thermal shielding, and fire retardancy.\textsuperscript{12–17} Our first reported multilayered CNF/MTM nanocomposite with a weight ratio of 50:50 showed a lower modulus and tensile strength as compared to the neat CNF nanopaper due to the aggregation of the native CNF and MTM.\textsuperscript{16,17} Later, CNF/MTM nanocomposites with different MTM contents (10–80 vol %) were prepared by carefully and completely exfoliating the MTM in water before mixing with the native CNF.\textsuperscript{27} The synchrotron radiation scattering analysis confirmed that the MTM platelets were well dispersed in the form of a single platelet and loose stacks of 2–3 platelets when MTM contents increased up to 35 vol %, resulting in an increase in the modulus for the nanocomposites. However, the tensile strength of the CNF/MTM nanocomposites was still lower than that for the neat CNF nanopaper due to the poor interaction between the native CNF and MTM. Furthermore, chitosan was added as the tertiary component in the CNF/MTM composites to improve the interactions of native CNFs and MTM via ionic interactions.\textsuperscript{18,28} Another method to improve the dispersion of nanoclays such as the MTM and saponite (SPN) in the CNF matrix without using an additional surfactant or charged polymers was to use 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized CNFs that are negatively charged carboxylate groups and having higher dispersibility in water. The resulting hybrid nanocomposites demonstrated a significant improvement on mechanical properties with a 5 wt % MTM or 10 wt % SPN content in the composite as compared to neat CNFs.\textsuperscript{20,21} To increase the interfacial adhesion, dopamine was conjugated to TEMPO-oxidized CNFs and formed catechol/metal ion chelation and hydrogen bonds with the MTM. The nanocomposites exhibited a superior barrier and mechanical properties as compared to the unmodified CNFs.\textsuperscript{24} Surface cationic charged CNFs have also been utilized to introduce a strong ionic interaction between CNFs and anionic clay platelets, leading to improved mechanical and barrier properties.\textsuperscript{19,20} On the other hand, positively charged aminoclay nanoparticles such as 3-aminopropyl-functionalized magnesium phyllosilicate can be also utilized. The nacre-like hybrid films of the exfoliated aminoclays and carboxylated CNFs displayed a synergistic high tensile strength and large strain-to-failure owing to the ionic bonding between anionic CNFs and cationic clay.\textsuperscript{25} Thus, both cationic and anionic surface charged CNFs have been previously used in the layered nanocomposites of CNFs/clay and demonstrated an improved mechanical performance. However, the effect of different surface charge interactions on the structure and properties of the CNFs/clay nanocomposite was not studied and systematically compared previously.

In this work, nanocomposite films of the MTM with different contents (1–70 wt %) in the matrix of either anionic charged TEMPO-oxidized CNFs (TO-CNF) or cationic charged CNFs bearing quaternary ammonium cations (Q-CNF) were prepared by vacuum filtration of the corresponding colloidal water suspensions of CNFs and MTM and dried in an oven. The objective was to understand the effect of the dispersion and interaction of the MTM and CNFs on the structure, mechanical, and flame retardant properties of the CNFs/MTM nanocomposites. The dispersion of the MTM in the nanocomposite was characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The modulus of the filler MTM in the TO-CNF and Q-CNF matrices determined from the composite modulus and the volume fractions of MTM allowed us to evaluate the effect of the dispersion and surface interaction on mechanical properties. The effects of the dispersion and intercalation structure of the MTM in the CNF matrix on flame retardant properties were also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. A commercial never-dried softwood sulphite pulp was provided by Nordic Paper and used as the starting cellulose fibers. Sodium montmorillonite (MTM, Cloisite Na+, a natural bentonite) with a stated density of 2.86 g/cm\textsuperscript{3} and a cation exchange capacity (CEC) of 92.6 mequiv/100 g clay was supplied by BYK Additives & Instruments (former Rockwood Additives and Southern Clay Products Inc.). TEMPO, glycidyltrimethylammonium chloride, sodium hydroxide, silver nitrate, and all other chemicals were purchased from Sigma-Aldrich and used without further purification.

2.2. Preparation of TO-CNF and Q-CNF. TO-CNF was prepared by the chemical modification of wood pulp fibers using the NaClO/NaBr/TEMPO system at pH 10, followed by mechanical homogenization as described in our previous work.\textsuperscript{24,29} The carboxylate content of TO-CNF was measured by the conductometric titration method reported previously.\textsuperscript{29} Q-CNF was prepared by a cationization reaction of wood pulp fibers as described in our previous work.\textsuperscript{26} The obtained slurry of quaternized pulp fibers were dispersed in water at a concentration of 0.5 wt % and disintegrated by a high-speed kitchen blender (Vita-Prep 3 model, Vita-Mix Corp., USA) for 8 min to produce a Q-CNF sample. The content of the quaternary ammonium cation group was measured by conductometric titration. Typically, 100 mg (dry weight) of Q-CNF suspended in Mill-Q water was titrated with 8 mM of AgNO\textsubscript{3} solution by adding 0.2 mL in 60 s intervals.

2.3. Preparation of CNF/MTM Nanocomposite Films. The MTM powder was uniformly dispersed in deionized water at a concentration of 0.5 wt % with magnetic stirring for one week. A desired amount of 0.5 wt % MTM water dispersion was slowly added to a 0.1 wt % Q-CNF or 0.1 wt % TO-CNF water suspension. After being thoroughly mixed with Ultra-Turrax (IKA T25) and degassed, the TO-CNF/MTM and Q-CNF/MTM suspensions were vacuum filtered to form a hydrogel using a 0.22 μm Durapore membrane filter. The hydrogel was subsequently placed between metal sheets and dried in an oven at 50 °C under a load of ca. 300 N. The obtained TO-CNF/MTM and Q-CNF/MTM nanocomposite films with MTM:CNF weight ratios of 1:99, 5:95, 10:90, 25:75, 40:60, 50:50, and 70:30 were coded as TM1, TM5, TM10, TM25, TM40, TM50, TM70, and QM1, QM5, QM10, QM25, QM40, QM50, and QM70, respectively. The neat films of the TO-CNF and Q-CNF samples were prepared using the same procedure. The thickness of the films was around 40 μm.

2.4. Characterizations. Atomic force microscopy (AFM) topographic height images were recorded in air, using a ScanAsyst mode on a MultiMode 8 atomic force microscopy system (Bruker, Santa Barbara, CA, USA). The samples were dried on a silica substrate and scanned using a cantilever having a resonance frequency of 70 kHz, a spring constant of 0.4 N/m, and a nominal tip radius of 2 nm (ScanAsyst-AIR, Bruker, Camarillo, CA, USA). The conductometric titration was performed with a conductometric station (SevenCompact, Mettler-Toledo). The FT-IR spectra were obtained by using a PerkinElmer Spectrum 2000 instrument equipped with an MCT(A) Golden Gate Single Reflection ATR system (Specac Ltd., UK) in a spectral range of 600–4000 cm\textsuperscript{-1} with a resolution of 4 cm\textsuperscript{-1}. The zeta (ζ) potentials of the holocellulose fibers were measured using a Zetasizer Nano ZS instrument (Malvern, Worcestershire, UK) at 25 °C.
°C following the Smoluchowski method. For the measurements, the samples were suspended in distilled water at a final concentration of 0.1 wt %. The UV spectra were obtained using a Varian Cary 50 Bio UV−visible spectrophotometer at room temperature. The XRD diffractograms were recorded using a Philips X′Pert Pro diffractometer (model PW 3040/60) in the reflection mode (2.5−13° 2θ angular range for neat MTM and the composites, 10−30° for the cellulose nanofibrils and wood pulp). The Cu Kα radiation (λ = 1.5418 Å) was generated at 45 kV and 40 mA and monochromatized using a 20 μm Ni filter. Diffractograms were recorded from rotating specimens using a position-sensitive detector. The tensile mechanical properties of the nanocomposites were measured using a universal material testing machine (Instron 5944, UK). The samples were conditioned at a relative humidity (RH) of 50% for at least 2 days. The modulus was determined from the slope of the initial low strain region of the stress−strain curve. Toughness, defined as work of fracture, was calculated as the area under the stress−strain curve. The FESEM of the tensile fractured surfaces of the nanocomposites was observed using a Hitachi S-4800 FESEM, which was operated at 1 kV. Self-extinguishing flammability tests were performed using the nanocomposite films with a dimension of 4 × 1 cm². The specimen was mounted in a holder at a 45° angle and exposed to a flame for 1 s. After the ignition, the flame was removed. For vertical flame tests, a gas flame was kept at the bottom of the specimens for a duration of 5 s, and the height of the burned area was monitored using a video camera. The porosities of the CNF/MTM nanocomposite films were estimated based on their bulk density calculated from the measured dry weight and apparent volume (geometry), and their theoretical composite density was calculated by known weight fractions, assuming 1.5 g cm⁻³ as the density for CNF and 2.86 g cm⁻³ for the MTM.

3. RESULTS AND DISCUSSION

3.1. Dispersion of the MTM in the Nanocomposites.

The MTM was exfoliated into an individual single-layer nanoplatelet with an average thickness of 1.0 ± 0.1 nm in deionized water, as revealed by the AFM analysis (Figure 1a). The average size of the MTM platelets was 245 ± 85 nm (Figure 1d). The surface of MTM nanoplatelets has permanent negative charges, which facilitated the colloidal stability of the MTM in water after exfoliation. Both TO-CNF and Q-CNF showed an individualized cellulose nanofibril structure with a fibril length up to several micrometers (Figure 1b,c). The TO-CNF with negatively charged carboxylates (1.21 mmol/g) on the nanofibril surface had an average width of 3.9 ± 0.8 nm.
(Figure 1e), while the Q-CNF with a quaternary ammonium cation (0.72 mmol/g) on the nanofibril surface had an average width of 2.6 ± 0.9 nm (Figure 1f), similar to those prepared with the same conditions in our previous work.\textsuperscript{23,30} The successful preparation of TO-CNF and Q-CNF from the native wood pulp fibers was also confirmed by FT-IR spectroscopy (Figure 2a). Compared to the wood pulp fibers, the spectrum of TO-CNF showed a new band at 1600 cm\textsuperscript{-1}, corresponding to the C=O stretching frequency of carbonyl groups in their salt form. On the other hand, the spectrum of Q-CNF showed of a new band at 1480 cm\textsuperscript{-1}, corresponding to the trimethyl groups of the quaternized ammonium. Both TO-CNF and Q-CNF showed a typical diffraction pattern of cellulose I, the same as the native wood pulp fibers (Figure 2b). The two peaks centered at about 14.8 and 16.8° in the X-ray diffraction patterns were separated by curve fitting using the pseudo-Voigt function. The crystal sizes of the corresponding planes were calculated from full widths at half heights of the diffraction peaks by the Scherrer’s equation.\textsuperscript{31} The average crystal size of TO-CNF was 4.2 nm, similar to that for the native wood pulp fiber (4.4 nm). The average crystal size of Q-CNF was lower (3.1 nm), probably due to delamination of cellulose microfibrils during the chemical modification. These average crystal size values for TO-CNF and Q-CNF are compatible with the microfibril width values measured by AFM. The surface charges of TO-CNF, Q-CNF, and MTM were also confirmed by the ζ-potential measurements. The ζ-potential values for TO-CNF, Q-CNF, and MTM were $-105.6 \pm 11.8$, $87.3 \pm 9.8$, and $-42.0 \pm 0.9$ mV, respectively. The AFM height images for dilute suspensions of Q-CNF/MTM and TO-CNF/MTM mixtures dried on a silica substrate are shown in Figure 2. Although the MTM plateaues possess a permanent negative surface charge, the edge surfaces can be protonated and exert a positive charge. As expected, the cationic-charged cellulose nanofibrils (Q-CNF) were preferably adsorbed on the surface of the MTM nanoplatelets (Figure 2c), while the anionic-charged cellulose nanofibrils (TO-CNF) were preferably adsorbed on the edges of the MTM nanoplatelets (Figure 2d).

As the TO-CNF was mixed with the MTM in water, colloidal stable and transparent suspensions were obtained with the MTM content ranging from 1 wt % up to as high as 70 wt % (Figure 3a), owing to the electrostatic repulsion between MTM and TO-CNF. When the MTM content was 25 wt % or lower, the dilute TO-CNF/MTM water suspensions (0.1 wt %) exhibited a light transmittance of above 90% at 400–800 nm, similar to that for the neat TO-CNF suspension (Figure 3b). As the MTM content was increased to 70 wt %,
the TO-CNF/MTM water suspension still showed a high light transmittance of 80−90% at 500−800 nm, higher than that for the neat MTM suspension. This indicates that TO-CNF and MTM can be mixed at any ratio in water to produce a homogeneous dispersion of nanoscale particles owing to their surface negative charges.

As the CEC of MTM is 92.6 mequiv/100 g and the cationic charge density of Q-CNF is 0.72 mmol/g, the surface of MTM nanosheets can be completely adsorbed with Q-CNF when the weight content of the MTM is lower than 42.7 wt % in the Q-CNF/MTM mixture. Thus, the negative charges on the surface of MTM nanosheets are shielded by Q-CNF bearing cationic charges. Such an ionic interaction facilitates the dispersion of exfoliated MTM nanosheets in the water suspension of Q-CNF. Indeed, when the MTM water suspension was dropped into the water suspension of Q-CNF, the formation of fibril aggregates as white flocculants in water was observed immediately by the naked eye due to the ionic interaction between the oppositely-charged MTM and Q-CNF nanoparticles. Stable nanoscale colloidal suspensions of Q-CNF/MTM in water could be obtained after thorough mixing with Ultra-Turrax and a brief sonication using a Branson Sonifier 250 instrument (Branson Ultrasonics Corp., USA) when the MTM content was 40 wt % or lower. This was indicated by the appearance of the suspensions (Figure 3a) and their higher light transmittance at 400−800 nm as compared to the neat MTM suspension (Figure 3c). However, when the MTM content was 50 wt % or higher, the visible white flocculants could not be disintegrated into nanoparticles although the suspension appeared homogeneous and stable without precipitation (Figure 3a). Consequently, the optical transmittance of the Q-CNF/MTM water suspension at 400−800 nm was significantly decreased as compared to that for the neat MTM suspension when the MTM content was higher than 50 wt % (Figure 3c), due to the light scattering caused by the flocculants.

The nanocomposite films were successfully prepared from the CNF/MTM water suspension by using vacuum filtration followed by drying in an oven under pressure, akin to the procedure of papermaking. The structures of the nanocomposites were studied by XRD and FESEM. The X-ray diffraction patterns of the Q-CNF/MTM and TO-CNF/MTM nanocomposites are shown in Figure 4a and 4b, respectively. For the Q-CNF/MTM nanocomposites, the primary diffraction peak was shifted significantly to smaller angles compared to the neat MTM (Figure 4a), corresponding to d-spacing of 1.5 to 2.3 nm with the decreasing MTM content as calculated by using the Bragg’s law (Figure 4c). The d-spacing of the neat MTM was 1.2 nm as the diffraction peak appeared at 7.4°. The expansion of the gallery space of the MTM upon increasing the content of Q-CNF nanofibrils in the nanocomposites indicates a more regular intercalated arrangement of MTM nanosheets in the nanocomposites. The d-spacing was above 2 nm when the MTM content was 50 wt % or lower, which is similar to the average width (2.6 ± 0.9 nm) of electropositive Q-CNF nanofibrils as measured by AFM (Figure 1f). This indicates that a large amount of the surface cationic charged cellulose nanofibrils have successfully entered the gallery space between the MTM nanosheets. A similar type of the intercalation structure was also observed in nanocomposites of the MTM with chitin nanofibers, which have a high degree of deacetylation.32 The rather broad diffraction peaks for the QM50 and QM70 samples suggested that a large content of MTM nanoplatelets were aggregated in the nanocomposites, which was consistent with the significant decrease in light transmittances of their water suspensions (Figure 3c). For the QM10, QM25, and QM40 samples, there was also a second minor diffraction peak at the same position for neat MTM, indicating that a very small content of the MTM platelets were still in the form of tactoids in these samples. When the MTM content was 1 wt %, no diffraction peak was detected in the QM1 sample (Figure 4a) as the MTM nanoplatelets were completely exfoliated in the nanocomposites.

For the TO-CNF/MTM nanocomposites, only a slight shift of the diffraction peak to the lower angles was observed (Figure 4b). The corresponding d-spacing value only increased from 1.2 to 1.4 nm with the decreasing content of the MTM in the nanocomposites (Figure 4c). This small spacing is due to the electrostatic repulsion between the anionic charged TO-CNF and MTM, which also contributed to the formation of small MTM tactoids in the nanocomposites. The full exfoliation of MTM in the TO-CNF/MTM nanocomposites was also achieved when the MTM content was 1 wt %. These results are similar to those reported for the hybrid films of TOCN/MTM that were fabricated using a solution casting method.20

Figure 5 shows the SEM images for the cross sections of the neat Q-CNF and TO-CNF films and the Q-CNF/MTM and TO-CNF/MTM nanocomposites films prepared by the tensile
fracture. The Q-CNF (Figure 5a) and TO-CNF (Figure 5e) films showed a typical layered structure as nanofibrils were deposited flatly during vacuum filtration, and the fibrillar nature of films was also apparent.33 At a low MTM content, the nanofibrillar structure was more distinct for the QM10 sample owing to the intercalation structure (Figure 5b) as compared to TM10 (Figure 5f), which exhibited a layered nanosheet structure due to the well dispersion of MTM tactoids. At higher MTM contents, the SEM images of the cross sections of QM40 (Figure 5c), TM40 (Figure 5g), and TM70 (Figure 5h) all exhibited closely packed nanosheets and fairly uniform and regular layered microstructure, resembling the brick-and-mortar structure of a nacre. This indicates (1) the small content of MTM tactoids in the QM10 and QM40 samples as revealed by the XRD analysis that has no impact on the formation of a layered structure from the intercalated MTM with Q-CNF, and (2) a good dispersion of small tactoids of the MTM in the TO-CNF/MTM nanocomposites with different MTM contents. Such a layered structure has been reported previously in clay/polymer nanocomposite materials.14,34 The in-plane orientation of both the clay and CNF is very high (small out-of-plane deviation) in the layered structure, which is positive for the mechanical properties. The tensile fractured surface of the QM70 sample also showed a layered microstructure but with an obvious pull out of MTM aggregates or tactoids (Figure 5d). This is due to the reason that the Q-CNF/MTM nanocomposites contained both an intercalated structure and a large content of MTM aggregates when the MTM content was higher than 50 wt %, as revealed by the light transmittance of the dilute suspension (Figure 3c) and XRD analysis of the nanocomposite film (Figure 4a).

3.2. Mechanical Properties. The effects of the dispersion of the MTM and structure of the nanocomposites on their mechanical properties were investigated by the tensile test. The

Figure 5. Cross-sectional SEM images of the neat (a) Q-CNF and (e) TO-CNF films and the Q-CNF/MTM, (b) QM10, (c) QM40, and (d) QM70 and the TO-CNF/MTM, (f) TM10, (g) TM40, and (h) TM70 nanocomposite films.

Figure 6. Typical stress–strain curves of (a) Q-CNF/MTM and (b) TO-CNF/MTM nanocomposite films. Dependence of the modulus and tensile strength of the (c) Q-CNF/MTM and (d) TO-CNF/MTM nanocomposites on the weight and volume content of the MTM.
nanocomposite samples are summarized in Table 1. The volume fraction of MTM, density, and porosity of all strain-to-failure, modulus, and work of fracture, together with the mechanical property data including the tensile strength, tensile modulus, and work of fracture for Q-CNF/MTM and TO-CNF/MTM nanocomposites are shown in Figure 6a and 6b, respectively. The mechanical property data including the tensile strength, strain-to-failure, modulus, and work of fracture, together with the volume fraction of MTM, density, and porosity of all nanocomposite samples are summarized in Table 1. The tensile strength of both Q-CNF/MTM and TO-CNF/MTM nanocomposites increased first when the MTM content was increased from 5 to 10 wt % and then decreased with further increasing the MTM content. This is comparable with the nanocomposite films of the TEMPO-oxidized CNF and MTM or SPN reported in the literature.27 The effect of the MTM content on the modulus of Q-CNF/MTM nanocomposites (Figure 6c) is completely different from that for TO-CNF/MTM nanocomposites (Figure 6d). The linear increase region was observed in the range from 0 to 40 wt % MTM in which the modulus of Q-CNF/MTM nanocomposite films increased from 11.6 ± 0.5 GPa for the neat Q-CNF film to 19.6 ± 3.3 GPa for the QM40 sample (Table 1). In the range of 40–70 wt % MTM, the modulus decreased sharply to 9.8 ± 1.1 GPa for the QM70 sample. This is due to the increasing amount of MTM aggregates in the intercalated QCNF/MTM structure and the increased porosity of the composites at a higher MTM content, similar to the modulus for nanocomposites of the MTM with the native CNFs.27 For the TO-CNF/MTM nanocomposite films, the modulus increased linearly with the increasing MTM content up to 10 wt % (Figure 6d) and then reached a plateau of around 22.0 GPa as the MTM content was in the range of 25–70 wt %. This suggests a homogeneous and good dispersion of the MTM in the TO-CNF/MTM nanocomposites owing to the electrostatic repulsion, as indicated also by the XRD and FESEM analysis.

The composite modulus \( E_{\text{comp}} \), describing the reinforcement achieved from a high-modulus inorganic filler into a low modulus polymer matrix, can be predicted by the classical “rule of mixtures”25,26:

\[
E_{\text{comp}} = E_{\text{MTM}}V_{\text{MTM}} + E_{\text{CNF}}V_{\text{CNF}}
\]

where \( E_{\text{MTM}} \) is the modulus of the filler MTM, and \( V_{\text{MTM}} \) is its volume fraction. \( E_{\text{CNF}} \) is the modulus of the matrix TO-CNF or Q-CNF, and \( V_{\text{CNF}} \) is the corresponding volume fraction. The moduli of the filler MTM \( E_{\text{MTM}} \) for the Q-CNF/MTM and TO-CNF/MTM nanocomposites were determined from the plot of \( E_{\text{comp}} \) versus \( V_{\text{MTM}} \) in Figure 6c and 6d, respectively. For the Q-CNF/MTM nanocomposites, the effective \( E_{\text{MTM}} \) was 37.1 GPa as determined from the slope of a linear fit in the 0–21.6 vol % MTM range (Figure 6c) using eq 1. Using the same method, the effective \( E_{\text{MTM}} \) for the TO-CNF/MTM nanocomposites was determined to be 129.9 GPa from the slope of a linear fit in the 0–4.9 vol % MTM range (Figure 6d). As expected, both effective \( E_{\text{MTM}} \) values were lower than the theoretical estimate of the MTM in-plane modulus which was predicted to be 170–270 GPa from molecular dynamics simulations and first-principles calculations37 and 178–265 GPa from density/modulus relationships of analogous minerals.37 Interestingly, the effective \( E_{\text{MTM}} \) value (129.9 GPa) for TO-CNF/MTM nanocomposites was in the same order of magnitude as the theoretically estimated value and 3.5 times higher than that for Q-CNF/MTM nanocomposites. This indicates that the good dispersion of clay nanoplatelets in the TO-CNF nanocellulose network through electrostatic repulsion demonstrated a better reinforcing effect in the nanocomposites as compared to the intercalated structure achieved via the interfacial interaction between Q-CNF and clay platelets.

The Q-CNF/MTM nanocomposites showed an increase in strain-to-failure as compared to the neat Q-CNF nanopaper at a 5 wt % MTM while the strain-to-failure of the TO-CNF/MTM nanocomposites were all lower than the neat TO-CNF nanopaper (Table 1). The synergistic enhancement in the modulus and tensile strength together with strain-to-failure for the QM5 sample was ascribed to the interfacial interaction between Q-CNF and clay platelets. This is in contrast to the modulus and tensile strength together with strain-to-failure of the QM5 sample was ascribed to the interfacial interaction between Q-CNF and clay platelets. This is in contrast to the modulus and tensile strength together with strain-to-failure of the QM5 sample was ascribed to the interfacial interaction between Q-CNF and clay platelets. This is in contrast to the modulus and tensile strength together with strain-to-failure of the QM5 sample was ascribed to the interfacial interaction between Q-CNF and clay platelets.
nanoclay and bacterial cellulose prepared by an in situ biosynthesis, which showed a toughness of 17.71 MJ/m². On the other hand, the toughness of the TO-CNF/MTM nanocomposites at 5 wt % MTM was 10 ± 0.4 MJ/m², only 9% higher than that for the neat TO-CNF nanopaper, although it showed a higher strength and modulus owing to the strong reinforcing effect of homogeneous dispersed MTM tactoids in the composite as compared to the Q-CNF/MTM film. The reduced interfacial sliding between TO-CNF and MTM tactoids in the TO-CNF/MTM films during failure resulted in the decreased strain-to-failure.

3.3. Flame Retardancy. Flame retardancy is an important measure of the performance for the cellulosic nanofibers and MTM-based inorganic–organic hybrid biocomposites. The role of MTM platelets in flame retardancy was investigated by cone calorimetry in a previous study. The oriented MTM platelets have several beneficial effects: heat shielding, oxygen barrier function, delayed evaporation of combustive gases from cellulose degradation, and increased charring of cellulose due to oxygen depletion. To study effect of the structures of Q-CNF/MTM and TO-CNF/MTM nanocomposites on their flame retardancy behavior, the self-extinguishing characteristics of the nanocomposite films (size 4 × 1 cm²) were measured using a 45° flammability test. The neat Q-CNF and TO-CNF films and the nanocomposite films with MTM contents lower than 5 wt % were completely burned into ashes within 3 s after exposure to a flame for 1 s. In Figure 7a, photographs of the Q-CNF/MTM and TO-CNF/MTM nanocomposite films with MTM contents of 10–50 wt % are presented after the test. The TO-CNF/MTM films showed self-extinguishing characteristics upon removal of the flame even at a 10 wt % MTM content, much better than the Q-CNF/MTM films. Even though the Q-CNF/MTM film with a 10 wt % MTM content was completely burned, it maintained its shape and integrity after burning. When the MTM content was 50 wt %, the Q-CNF/MTM also showed self-extinguishing characteristics.

To further compare the difference between the QM50 and TM50 nanocomposite films, we used a bench-scale vertical flame test. Both film samples were exposed to a gas flame at the bottom of the specimen for a duration of about 5 s, and the height of the burned area was monitored by a video camera. Figure 7b shows photographs of the TM50 and QM50 nanocomposite samples at times indicated during the vertical flame tests. Clearly, the TM50 film showed better flame retardancy with a delayed initial ignition time and a reduced relative burned height as compared to the QM50 sample. As revealed by the XRD analysis, the Q-CNF nanofibrils were intercalated between the exfoliated single MTM nanoplatelets in the Q-CNF/MTM nanocomposite, while the MTM tactoids were well dispersed in the TO-CNF/MTM nanocomposite and formed a continuous “wall” structure of brick-and-mortar. The structure of TO-CNF/MTM nanocomposites has obvious advantages in hindering the transport of oxygen and diffusion of decomposition products, which lead to the resistance of the material against burning even if the MTM content is as low as 10 wt %.

4. CONCLUSIONS
Layered nanocomposite films of CNFs and MTM nanoplatelets with different MTM contents (1–70 wt %) were successfully prepared by using either anionic charged or cationic charged CNFs without any tertiary component. The anionic charged TO-CNF facilitated the good dispersion of the MTM in the nanocomposite, and MTM platelets were in the form of nanoscale tactoids that were well assembled in the layered composite as the MTM contents were in the range from 5 to as high as 70 wt %. The reinforcing effect of the MTM that was extremely high as the effective MTM modulus for the TO-CNF/MTM was determined to be 129.9 GPa. Cationic charged Q-CNF demonstrated a strong interaction with the anionic charged MTM platelets, and a rather homogeneous intercalation structure was formed in the layered nanocomposites as the MTM contents were in the range from 5 to 40 wt %. Although the effective MTM modulus (37.1 GPa) for the Q-CNF/MTM was lower than that for the TO-CNF/MTM nanocomposites, the Q-CNF/MTM nanocomposites showed a synergistic enhancement in the tensile strength, modulus, and strain-to-failure owing to the interfacial ionic interaction, which was not achieved by improving the interfacial bonding reported previously. In addition, the brick-and-mortar structure formed by the assembly of nanoscale MTM tactoids with TO-CNF showed better fire retardant properties as compared to the intercalation structure from Q-CNF and exfoliated MTM single platelets. Thus, by controlling the interfacial interaction between CNFs and clay nanoplatelets and volume fraction of MTM, we have achieved an excellent nanostructure control in CNFs/clay nanocomposites.
which enables an interesting combination of stiffness, strength, toughness, and flame retardant properties.

## Author Contributions

All authors have given approval to the final version of the manuscript.

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