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Synthesis of Montmorillonite Nanoclay Reinforced Chitin-cellulose Nanocomposite Film

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Abstract. Montmorillonite (MMT) nanoclay reinforced chitin-cellulose nanocomposite is a biodegradable polymer that has potential as a food packaging material. In this study, it was synthesized using 1 and 5 wt% MMT (1NC and 5NC) via solution casting. Good miscibility of chitin and cellulose was interpreted by the presence of cylindrical particles revealed in the SEM image, and the XRD peak at $\sim 19^\circ$ and shoulder at $\sim 23^\circ$. Peaks were also observed at 2.62 and 2.27° for 1NC and 5NC, respectively, that corresponded to 16.87 and 19.47 Å interlayer spacings, both of which were higher than that of pristine MMT which is 12.57 Å. This suggested that chitin-cellulose penetrated MMT and that 5NC had a lower degree of intercalates, which was confirmed by EDX mapping. This better MMT dispersion was speculated to be due to the nematic state of 5NC gel. With molecules sliding off easily in the gel, polymer penetration in the interlayer spacing was easier. This was verified by its lower apparent viscosity. Finally, this better MMT dispersion resulted to a good stress transfer and, maybe, introduced a more torturous crack path for 5NC. These improved its toughness (2.22 J/mm³) and Young's modulus (6.25 GPa).

1. Introduction

The world has generated of at least 6.3 billion metric tons of plastic waste in which $\sim 79\%$ of it is accumulated in landfills or natural environment. Without action, an increase to 12 billion metric tons of landfill plastic waste is expected by 2050 [1]. This huge amount of plastic waste is highly-contributed by single-used plastic, or throwaway. This includes food packages.

To address this, various environmental sustainability practices have already been implemented or promoted by the government. One of these is the usage of paper-based containers as a substitute to petrochemical-based polymeric counterparts. However, this seemingly good alternative is, in fact, further threatens the sustainability of the environment. This is because of: (1) virgin paper pulp mass production that promotes tree felling; and (2) the polyethylene film, which is used for inside proofing, is non-recyclable and takes years to degrade. For these reasons, fabrication of food packaging material that utilizes biodegradable polymer is a topic of research nowadays.

Chitin-cellulose film is a biodegradable polymer that has potential to be used as a food packaging material [2]–[3]. However, its water vapor permeability (WVP) is still high to be used for such application. For this reason, montmorillonite (MMT) nanoclay was added to it, which resulted to a decrease of WVP [4]. But, the film became brittle in the process due to the incorporation of immense amount of MMT. Therefore, for this study, MMT nanoclay was added in smaller amounts to enhance the mechanical integrity of this film.



2. Methodology

2.1. Materials

Chitin flakes (C9213), cellulose medium fibers (C6288), montmorillonite nanoclay (Nanomer 1.34MN, 682640) and N,N-dimethylacetamide (185884) were obtained from Sigma-Aldrich. Lithium chloride (Dried, Unilab 292-500) was procured from Ajax Fine Chem. Methanol and isopropanol were acquired from Pharmco-Aaper and Macron, respectively.

2.2. Fabrication of nanocomposite film

Chitin was dissolved in lithium chloride-dimethylacetamide solution (LiCl-DMAc). MMT was then added to it and sonicated. The resulting slurry was stirred to improve the homogenization. Two different concentrations of MMT, 1 wt% and 5 wt%, were used. Cellulose was swelled using deionized water (DI), methanol and DMAc. After, it was also dissolved in LiCl- DMAc.

The MMT-chitin mixture and cellulose solution was combined and sonicated, and then casted into a glass tray forming a gel. The gel was soaked in isopropanol then methanol. Excess solvent was removed. After soaking, it was cold-pressed and then oven dried. This resulted to a nanocomposite film with average thickness of 0.022 mm.

2.3. Determination of microstructure of nanocomposite film

Microstructure of the nanocomposite films were observed via a field emission scanning electron microscope (FESEM, Hitachi SU-8230) with an accelerating voltage of 4 kV. Magnifications of 500, 10kx and 20 kx were used. Samples were sputter coated with Pt for 60 sec prior to the test. Image J was utilized to measure the dimension of the chitin-cellulose particles.

MMT dispersion was verified using energy dispersive X-ray spectrometer (EDX) with an accelerating voltage of 5 kV to measure the Si-K α signal. X-ray diffractometer (XRD, Rigaku SmartLab) was also employed using a Cu-K α target with a scan rate of 2 °/min.

2.4. Mechanical integrity of film

Following ASTM D882-12, tensile test was conducted using a Universal Testing Machine (UTM, Shimadzu Autograph-IC) with 1 kN load cell to measure Young's modulus. Origin Pro8 was utilized to determine the toughness of the films via area integration of the stress-strain curves obtained from the tensile test.

2.5. Supplementary tests

Using the same parameters, SEM and XRD were conducted to verify the miscibility of chitin and cellulose. Moreover, using Brookfield DV-II + Pro with spindle no. 63, viscosities of the MMT-chitin-cellulose mixtures were measured to validate the MMT dispersion result.

3. Results and discussion

The chitin-cellulose films with 1 wt% and 5wt% montmorillonite (MMT) nanoclay (1NC and 5NC, respectively) were transparent as shown from Figure 1. This was attributed to the amount of MMT incorporated into the film. In contrast, [4] produced a brown-colored and opaque film, because of the large incorporation of MMT, that was 180 wt%.

It was also observed that folds were present at the sides for both films, as indicated by the arrows in Figure 1. These folds were caused by the shrinkage of the films during the removal of lithium chloride-dimethylacetamide (LiCl-DMAc) in the soaking phase [3]. The hydroxyl proton of cellulose (and also maybe chitin) is bonded with the Cl⁻ in which is accompanied by the Li⁺ that is solvated by the DMAc molecules [5]. When the gel was soaked with isopropanol and methanol, DMAc was dissolved to these alcohols. This would have disrupted the bonding of chloride of LiCl and hydroxyl proton of cellulose (and also maybe chitin), leaving only the hydrogen-bonded chitin-cellulose [6].

Finally, few small dots that were non-uniformly dispersed were also noticed in both films, see red circles in Figure 1. These could be the remnants of few undissolved chitin and/or cellulose. Nanoclay being the small visible dots was not plausible, because of its very low concentration and uniform

dispersion in the chitin-cellulose matrix, as represented by the uniformly-dispersed Si atoms shown in Figure 3c and d.

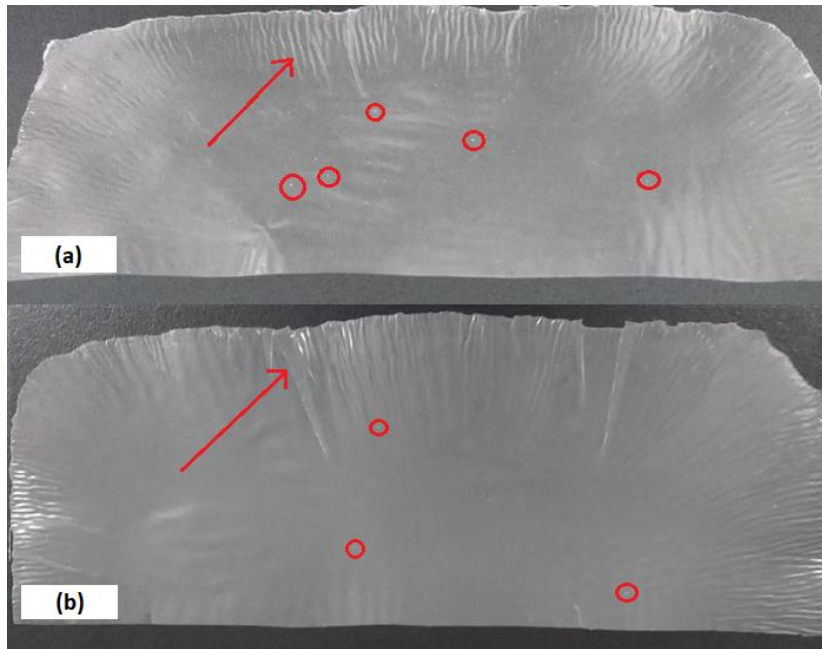


Figure 1. Visual observation of (a) 1 wt% and (b) 5 wt% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

3.1. Microstructure of the nanocomposite film

As shown in the micrographs of Figure 2a and b, mounds and fibrous-like structures were present at the surface of both 1 and 5NC films. The latter could be attributed to cellulose because of its fiber form [3]. However, the former could be inferred as chitin. These microheterogeneities of chitin-cellulose blend is expected, because of the negative Flory-Huggins parameters which were calculated at cellulose content greater than 2.5wt%, and, in this study, 20% was used [7]. Nevertheless, accumulation of these structures at certain sites of the films could have resulted to the appearance of small dots in Figure 1.

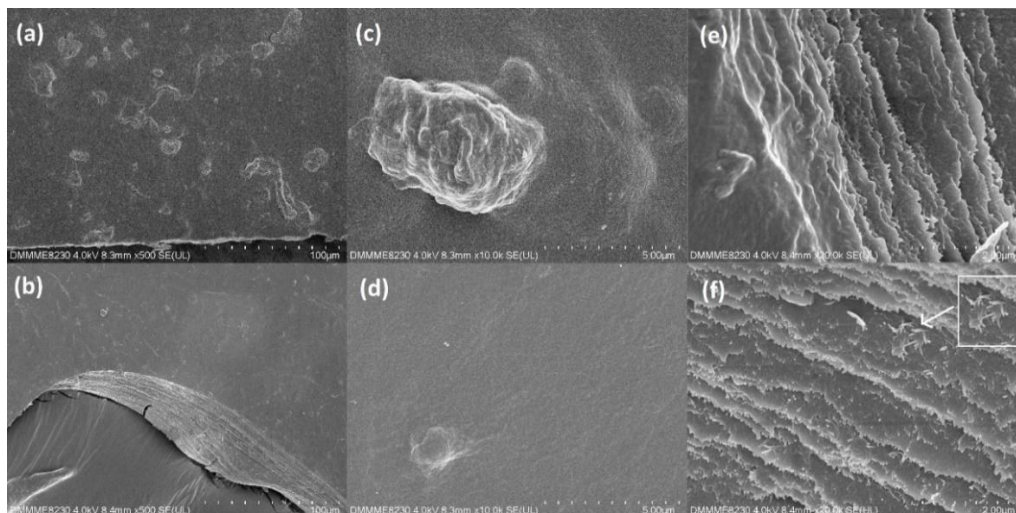


Figure 2. Comparison of surface, surface mounds, and cross-section of 1 wt% (a, c, e) and 5 wt% (b, d, f) montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

It should be noted that a comparison of the degree of surface roughness induced by the said microheterogeneities for 1 and 5NC would be difficult to imply for this study. The seemingly “smooth” surface shown for 5NC in the Figure 2d micrograph is only applicable for certain areas. It is because 5NC had also large mounds with size comparable to that of 1NC (not shown). Furthermore, the surface of both films as shown by the micrographs generated by SEM-EDX, see Figure 3a and b, showed equivalent qualitative roughness.

For the cross-sections of the films, layers were observed for both films. This was also the case for the study of Zhang for chitin-cellulose in 2002 [8]. However, it should not be inferred that this is an inherent structure of chitin-cellulose. It is because the structure could be the effect of cold-pressing. Moreover, if focused in the Figure 2f inset, cylindrical particles of diameter of 37.2 nm appeared as the components of each layer. These were the chitin-cellulose particles [6]. This was validated by the peak at $\sim 19^\circ$ with a shoulder at $\sim 23^\circ$ present in the diffractograms of both 1 and 5NC films shown in Figure 5. This indicated a good miscibility of cellulose and chitin [9].

In terms of nanoclay distribution in the chitin-cellulose film, SEM-EDX mapping was conducted. Silicon atoms of MMT was used as the determining atoms to describe distribution, because: (1) oxygen atoms of MMT would be impossible to pinpoint due to the fact that both cellulose and chitin have also oxygen, and (2) the number of aluminum atoms is only a half of that of silicon, which, if chosen as the determining atom, would be more difficult to magnify the nanoclay presence, due to the low nanoclay content of the films.

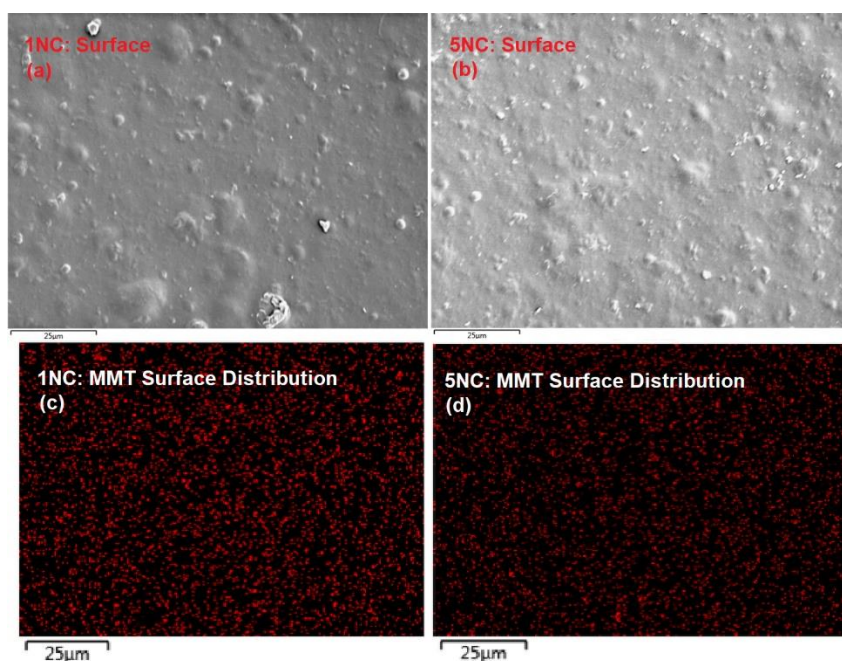


Figure 3. SEM-EDX mapping of monmorillonite nanoclay surface distribution in 1 wt% and 5 wt% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

Seen in Figure 3c and d, both films had areas of agglomeration, as shown by the red patches, which implied that intercalates, or, maybe, tactoids, were the abundant nanoclay dispersed structures [10]. Comparing the two films, 1NC was more agglomerated than 5NC. Agglomeration could have resulted, because the sonication and mechanical stirring were not enough to break the clay-clay surface interactions [11]. This was verified by the left shift from 2.62 to 2.27° peak for the MMT signal of 5NC, see Figure 5, which, using Bragg's equation, would be the interlayer spacing increase from 16.87 to 19.47 Å. Both were higher than the interlayer spacing of pristine MMT that was 12.57 Å, which would mean a successful penetration of chitin-cellulose into the MMT. Additionally, this polymer penetration could have decreased the intra-chain bonding of chitin, which corresponded to the lowered intensity of its (013) plane for 5NC.

Better dispersion of MMT in the chitin-cellulose matrix in 5NC may be due to the nematic state degree of its gel. In this study, pristine chitin/LiCl-DMAc solution was already in this state, because it

exhibited a glittering light yellow visual [12]. With this, it was speculated that addition of 5 wt% MMT further favored the solution to become more nematic. Since molecules slide off with each other the easiest in this state [12], polymer penetration to the interlayer spacing was easier for 5NC. This was verified by its lower apparent viscosity value as shown in Figure 4.

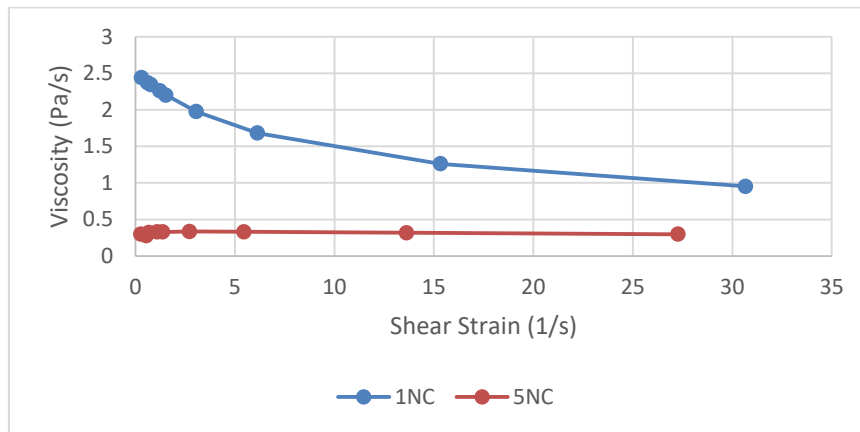


Figure 4. Viscosity measurements of 1 wt% and 5 wt% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films in increasing shear rate.

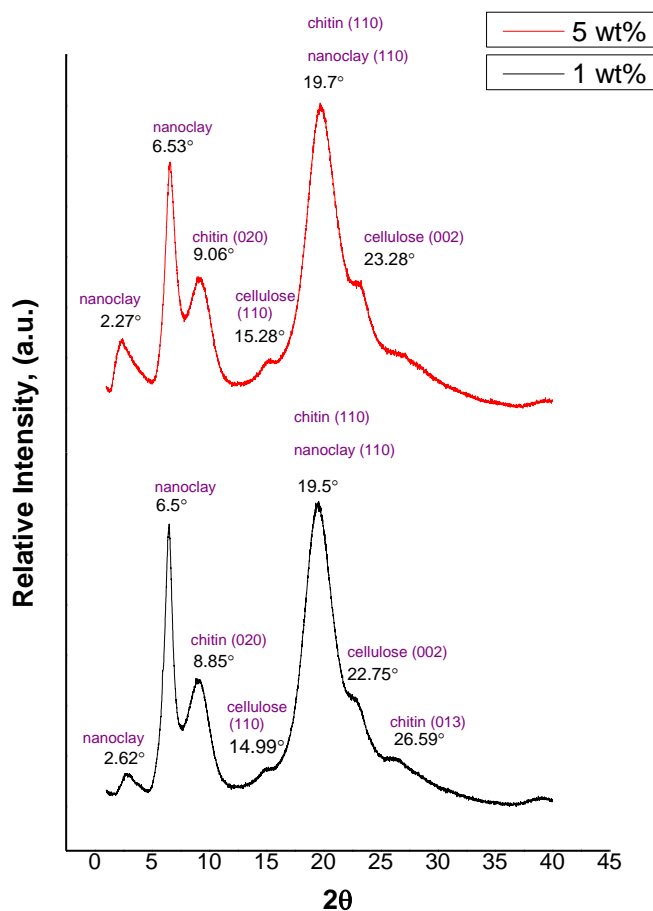


Figure 5. X-ray diffractograms of 1 wt% and 5 wt% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

3.2. Mechanical strength of nanocomposite film

Nanoclay with an exfoliated dispersion structure in a polymer matrix would result to a composite with higher mechanical properties than with an intercalated counterpart [13], [14]. This enhancement is caused by: (1) the high aspect ratio that enables high nanoclay surface area to interact with the polymer matrix, and (2) the better nanoclay dispersion and distribution in the said matrix, which results to a uniform matrix-to-reinforcement stress and strain transfer throughout the composite [14]. Since complete exfoliation seems impossible in real practice, a combination of phase-separated, intercalated, and exfoliated nanoclay is usually observed in which the degree of the latter is maximized to achieve the aforementioned property enhancement [15]. A low incorporated nanoclay concentration usually would result to this said maximization [16]–[18]. For this reason, between 1NC and 5NC, it is expected that the former would have better mechanical properties, i.e. Young's modulus and toughness. However, the results in table 1 and Figure 6 began to differ.

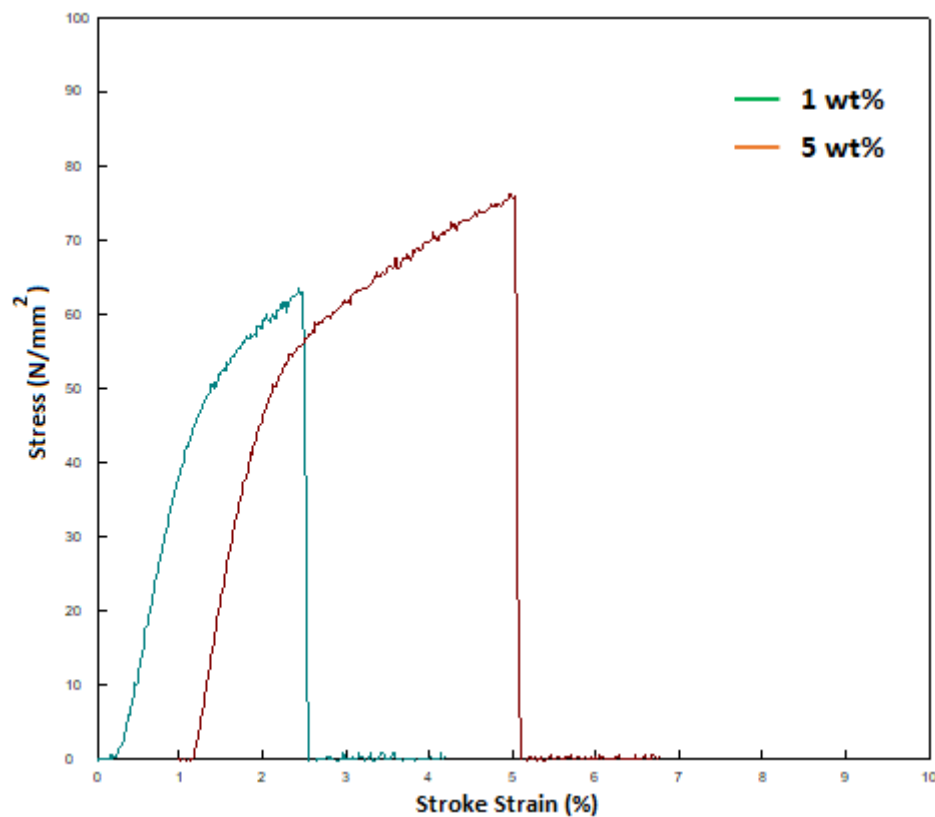


Figure 6. Stress-strain curve of 1 wt% and 5 wt% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

Table 1. Young's moduli of 1 wt%, 5 wt%, and 1 (w/v)% montmorillonite nanoclay reinforced chitin-cellulose nanocomposite films.

Nanoclay Concentration	Young's Modulus (GPa)	Toughness (J/mm ³)
1 wt%	5.67	0.96
5 wt%	6.25	2.22
1 (w/v)%	0.03 ^a	--

^a [3]

Increase of clay concentration should have incorporated brittleness, because it is a ceramic. However, it was determined through integration of the stress-strain curves in Figure 6 that 5NC was 43.24% tougher than 1NC. It should be noted that, because of the increase in interlayer spacing shown in Figure 5, nanoclay was better distributed in 5NC as verified by the lower amount of agglomerates shown in the EDX maps in Figure 3. This better nanoclay distribution might have introduced a torturous path for crack propagation which resulted to a tougher 5NC [13], [16]. On the other hand, 1NC was less tough, because its larger amount of agglomerates could have acted as stress concentrators resulting to a premature film breakage, instead of crack inhibitors [13], [17]. Meanwhile, for the Young's moduli of 1NC and 5NC, it was determined that the latter had the larger value. Evidently, it should have the higher value, because it had a wider interlayer spacing. And, as mentioned, wider interlayer spacing would result to a well dispersed and distributed nanoclay in the film that would result to a better stress (or strain) transfer between the chitin-cellulose matrix and the nanoclay reinforcement, consequently, caused a higher Young's modulus. However, in contrast to the toughness values difference, the difference of Young's moduli between the films was only 8.97%. This could have resulted from the small interlayer spacing difference of these films [12]. Furthermore, using the data of [3], it is observed that increasing the nanoclay concentration further to 1 (w/v)% resulted to a drop of the said modulus [3], [12]. This might have caused by the 30.97% decrease of the interlayer spacing at the said nanoclay content, which could have signified higher degree of agglomeration. By integrating this Young's Modulus-interlayer spacing relationship, it could be inferred that, maybe, with a better dispersion-distribution technique, the nanoclay content that could result to the highest degree of exfoliation, if not 5wt%, would be near to that concentration.

4. Conclusion

Montmorillonite (MMT) nanoclay reinforced chitin-cellulose nanocomposite film (NC) was successfully fabricated using 1 and 5wt% of MMT. It was determined that the latter was tougher (2.22 vs. 0.96 J/mm³) and stiffer (Young's modulus: 6.25 vs. 5.67 GPa) than that of 1 wt%. This was due to the lower nanoclay agglomeration experienced by the said film, as shown via EDX mapping, which was further proven by the increase of nanoclay interlayer spacing from 16.87 to 19.47 Å. It is suggested that low agglomeration of the latter film was caused by the nematic state of its gel, which made the molecules in it to slide off easily with each other. This was verified by its lower viscosity. Moreover, good miscibility of chitin and cellulose solution was proven through the 19.7° chitin peak with a 23.28° cellulose shoulder shown in the X-ray diffractograms. Thus, even if surface mounds were present in both films, it could be stated that microheterogeneity of chitin and cellulose was only at a lower extent as to not mask the said peak associated with the said miscibility.

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