

Halloysite nanotube reinforced polylactic acid composite

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Abstract:

Poly(lactic acid) (PLA) has long history in medical applications, and reinforced PLA has the potential to be used in the medical applications that require high mechanical strength such as coronary stents and bone fixation devices. Halloysite nanotube (HNT) has received considerable attention recently due to its tubular structure, high aspect ratio, high mechanical strength, thermal stability, biocompatibility and sustained drug releasing property. Halloysite has been investigated in compounding with many polymers. However, the research in compounding halloysite with biodegradable materials for use in biological applications is sparse. In this study various weight fractions of HNT was compounded with the biodegradable polymer PLA using a melt compounding method. Tensile test, fourier infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), contact angle test, scanning electron microscopy (SEM), void content and thermogravimetric analysis (TGA) were carried out to study the PLA/HNT composite. Tensile test results indicated that Young's modulus and stiffness of PLA were enhanced with the addition of HNT; FTIR spectra showed the interaction between the PLA and HNT; whereas contact angle measurements indicated that the wettability of the PLA/HNT composite was not affected by the addition of HNT. However, the thermal stability of PLA was adversely effected by the addition of HNT which may be related to the presence of voids between the polymer and matrix. Nevertheless, the reinforced PLA/HNT composite, that maintains the surface characteristics, may prove beneficial for use in biological applications.

1. Introduction

Poly(lactic acid) (PLA) is a type of biodegradable thermoplastic aliphatic polyester that derived from renewable resources. PLA attracts a lot of research attention due to its renewability, biodegradability, biocompatibility, and good mechanical properties [1]. PLA has a long safety history in medical field [2] and a variety of medical implants made from PLA have been developed, such as sutures, stents, and bone fixation devices, such as screws, pins, rods and plates. PLA has also been involved in controlled slow drug releasing systems due to its relatively slow biodegradation rate. However, the drawbacks of brittleness and poor thermal stability limit the manufacture process and application of PLA [1, 3].

The incorporation of various fillers into the PLA based polymer is a useful approach for enhancing its thermal stability, mechanical properties and hydrolysis resistance [4]. Fillers utilized for this purpose include silica, carbon nanotubes, natural fibers and nanoclays. Georgiopoulou *et al.* reported that silica nanoparticles accelerated the degradation of PLA but yielded a composite which had enhanced mechanical properties [5]. It was also reported that the silica fillers increased tensile strength, Young's modulus, thermal stability, and hydrolysis resistance of PLA/silica composite [6]. Carbon nanotubes and PLA composite were studied by Wu & Liao, who reported that 1wt% loading of carbon nanotubes dramatically enhanced the thermal and mechanical properties of PLA [7]. Tokoro *et al.* reported that the addition of bamboo fibers (BF) improved thermal properties and heat resistance of PLA/BF composite due to the constraint of deformation of PLA in conjunction with crystallinity promoted by annealing treatment [8]. Kasuga *et al.* reported that the addition of a small amount of hydroxyapatite fibres (HAF) improved the modulus of elasticity of the PLA/HAF composite [9]. Montmorillonite was also reported to be effective filler for PLA in term of improved thermal stability and reduced flammability [10].

Halloysite nanotubes (HNTs) are a type of clay that has received considerable attention lately due to its environmental friendliness, biocompatibility, and natural abundance which make it an important nanomaterial for biomedical applications [11, 12]. It has being reported that HNTs show good cytocompatibility with a variety of cells both alone [11] and in combination with polymer matrices [13]. HNTs are similar to kaolin clay, having an empirical chemical formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$ [11]. HNTs have a tubular structure with a high aspect ratio, the length of HNT particles ranges from 0.2 to 2 μm , and the inner and outer diameters of the tube range from 10 to 40nm and 40 to 70nm respectively [12] with a length of 1000-2000nm [13]. The high aspect ratio of HNTs helps to reinforce polymers in composites by optimizing the load transfer from the polymer matrix to the nanotubes. The reported HNTs reinforced polymers include epoxy [14] and Poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) [15]. Furthermore, the addition of HNTs has resulted in improved thermal stability of polymers such as polypropylene [16], and poly (glycerol sebacate) [17]. The mechanism of the improvement in thermal stability was found to be related to three HNT aspects, i.e. 1). HNTs have a much higher thermal stability than the polymers (HNTs begins to degrade at approximately 400°C). 2). Well-dispersed HNTs exert a barrier effect toward both mass and heat transports, improving the thermal stability of the nanocomposites. 3). The polymer chains and degradation products can enter the lumens of the HNTs, delaying mass transport and significantly improving the thermal stability [12]. However, the overall effect of HNTs on biodegradable polymers such as PLA is sparsely reported [1]. Hence the current study was designed to investigate the effect of HNT on the surface wettability, thermal and mechanical properties of PLA.

2. Materials and methods

2.1 Materials

PLA was obtained from NatureWorks LLC, Ingeo biopolymer 7032D. Halloysite nanotube (HNT) was supplied by Applied Minerals; DRAGONITE-HP. All materials were used as received.

2.2 Blends synthesis

The PLA/HNT composites with mass fractions of 100/0, 98/2, 95/5, 90/10, 85/15 wt% were prepared by melt compounding using an APV (Model MP19TC (35:1)) twin screw compounder with 19mm diameter screws, at temperature profile of 170/190/180/170/160/110/50°C, and a screw speed of 35rpm. Prior to compounding PLA was dried at 80°C for 4 hours and HNT was dried at 100°C for 3 hours. The excluded compound was pelletized and dried at 40°C overnight. Subsequently, the dried compound was compression molded into thin sheets at 190 °C and 75 bar pressure with the holding period of 20 seconds using a Daniel's compression molder. Thus, test specimens were prepared from these sheets using a physical punching process to punch out standard tensile test specimens [18].

2.3 Differential scanning calorimetry

Differential scanning Calorimetry (DSC) was carried out using a DSC 2920 Modulated DSC (TA Instruments) with a nitrogen flow rate of 20ml/min to prevent oxidation. Calibration of the instrument was performed using indium as standard. All the samples were dried at 60°C for 8 hours prior to testing. Test specimens weighed between 8 and 12 mg were measured on a Sartorius scales (MC 210 P), capable of being read to five decimal places. Samples were crimped in non-perforated aluminum pans, with an empty crimped aluminum pan used as the reference. The thermal history was removed by heating samples from 20°C to 220°C at the rate of 30°C/min, and then held isothermally at 220°C for 10 min. The samples were then cooled down from 220°C to 20°C at 30°C/min. Finally, the thermal properties of the samples were recorded by heating the samples from 20°C to 220°C at the rate of 10°C/min. Crystallinity, glass transition temperature and melting temperature of each sample were analyzed.

2.4 Fourier transfer infrared spectroscopy (FTIR)

Attenuated total reflectance Fourier transform infrared spectroscopy (FTIR) was carried out on a Perkin Elmer Spectrum One fitted with a universal ATR sampling accessory. All data were recorded at 21°C in the spectral range of 4000–650cm⁻¹, utilizing a 4 scan per sample cycle and a fixed universal compression force of 70-80 N. Subsequent analysis was carried out using Spectrum software.

2.5 Morphology

SEM was performed using a Mira XMU SEM in back scattered electron mode to determine the shape and distribution of halloysite in the polymeric matrix. Energy Dispersive X-ray (EDX) was performed using an Oxford Instruments detector to determine the elemental composition of halloysite and composites of PLA and halloysite. The accelerating voltage utilized was 10KV for raw halloysite nanotubes and 20Kv for composite materials. Prior to analysis, test samples were placed on an aluminum stub, and the samples were sputtered with a gold using Baltec SCD 005 for 110 s at 0.1 mbar vacuum before testing.

2.6 Surface wettability

The surface wettability of the composites was assessed using a First ten angstroms, FTA32 goniometer. In this test the Sessile Drop contact angle technique was utilized with distilled water as the probe liquid. Five contact angle readings (n=5) were recorded for each sample.

2.7 Mechanical testing

The mechanical properties of the PLA/HNT composites were characterized by tensile testing each different blend. Tensile testing was carried out on a Lloyd Lr10k tensometer using a 2.5kN load cell on ASTM standard test specimens at a strain rate of 50mm/min. Data was recorded using Nexygen™ software. The tensile tests were carried out in adherence to ASTM D 882. Five individual test specimens were analyzed per group and prior to testing the thickness of each sample was measured. The percentage strain at maximum load, stress at maximum load, stiffness and Young's Modulus of each sample were recorded.

2.8 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of PLA/HNT composites. Tests were conducted using Perkin Elmer TGA 7 Thermogravimetric Analyzer, coupled with a Perkin Elmer Thermal Analysis controller TAC7/DX under nitrogen atmosphere. The tests were run from 30°C to 600°C, at a heating rate of 10°C/min.

2.9 Void content measurement

The void content in PLA/HNT composites was calculated to assess the undesired space inside the composites. The samples used for void content test were dumbbell-shaped standard tensile test samples with smooth surface and were not granules, hence interparticle voids were not considered in this case. The densities of provided PLA (ρ_{PLA}) and HNT (ρ_{HNT}) are 1240 and 2530 kg/m³ respectively. 5 samples of each composite blend (n=5) were weighed and immersed into water in 10ml cylinder, the volume that was occupied by the composite samples was recorded. Subsequently, the density of composite ($\rho_{Measured\ composite}$) was calculated from formula 1. The volume fraction of PLA (V_{PLA}) and HNT (V_{HNT}) can be calculated using formula 2. The theoretical density of composite ($\rho_{Theoretical\ composite}$) can be calculated from formula 3. Thus, the void content of PLA/HNT composites can be calculated from formula 4 [19].

$$\rho_{Measured\ composite} = \frac{Mass_{composite}}{Volume_{composite}} \quad \text{Formula 1}$$

$$V_{PLA} = \frac{Volume_{PLA}}{Volume_{PLA} + Volume_{HNT}} = \frac{\frac{Mass_{PLA}}{\rho_{PLA}}}{\frac{Mass_{PLA}}{\rho_{PLA}} + \frac{Mass_{HNT}}{\rho_{HNT}}} \quad \text{Formula 2}$$

$$\rho_{Theoretical\ Composite} = \rho_{PLA}V_{PLA} + \rho_{HNT}V_{HNT} \quad \text{Formula 3}$$

$$Void = \frac{\rho_{Theoretical\ composite} - \rho_{Measured\ composite}}{\rho_{Theoretical\ composite}} \quad \text{Formula 4}$$

2.10 Statistical analysis

Statistical analysis of the tensile and contact angle data between composites with different halloysite content were performed using one way analysis of variance (ANOVA) with a Tukey Post hoc test to determine differences between specific halloysite loadings.

Differences were considered significant when $p \leq 0.05$. The software used to perform statistical analysis was SPSS (IBM Version 22) for Windows.

3. Results

3.1 Compounding

The PLA/HNT composite was melt extruded followed by compression molding, and the composite was processed without difficulty. The extrudate changed in color from transparent for virgin PLA to opaque with the inclusion of halloysite. This was also observed by Liu *et al.* with injection molded composite of PLA and HNT [20].

3.2 Differential scanning calorimetry (DSC)

DSC was carried out to investigate the thermal characteristics of PLA/HNT composites. The resultant thermograms are presented in Figure 1. The glass transition temperature (T_g) of PLA reduced slightly with the addition of HNTs (Table 1). The T_g of PLA/HNT 15wt% composite was 63.6 °C, reduced from 66.6°C of virgin PLA, whereas the melting temperature of PLA/HNT composites remained consistent at approximately 172°C. The degree of crystallinity of PLA was reduced slightly with the addition of HNTs from 37.46% for virgin PLA to 34.89% for PLA/HNT 15wt%. The cold crystallization temperature (T_{cc}) reduced from 114.23°C for virgin PLA to 110.29 to 111.62°C for PLA/HNT composites.

3.2 Fourier transfer infrared spectroscopy (FTIR)

The chemical bonding and interaction between PLA and HNTs were analysed using FTIR (Figure 2). The FTIR spectrum of PLA displayed characteristic peak located at 3571 cm^{-1} corresponding to –OH stretch [21], peaks located at 2995 cm^{-1} and 2946.34 cm^{-1} which are attributed to CH stretch, and the peaks located at 1750 cm^{-1} correspond to stretching of the –C = O carbonyl group [22]. The spectrum of HNTs exhibited peaks at 3693.26 cm^{-1} and 3623.39 cm^{-1} , which were assigned to the O - H group vibration. The peaks at 1119.52 cm^{-1} and 1000 cm^{-1} were attributed to Si - O stretching, and the peaks at 906.81 cm^{-1} was assigned to Al - OH groups [23].

The characteristic absorption bands of both PLA and HNTs were displayed in the FTIR spectrums of PLA/HNT composites as expected. The appearance of peak at 3696.39 cm^{-1} corresponding to O – H group of HNT in PLA/HNT 15wt% composite confirmed the presence of HNTs in the PLA matrix. The peak at 906.81 cm^{-1} on the HNT spectra corresponds to the Al - OH groups of HNT, and this peak was observed in composites materials containing 10 and 15 wt% HNT at 913.07 cm^{-1} and 911.44 cm^{-1} respectively.

3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy images indicated that halloysite nanotubes utilized in the current study were indeed rod-like in structure with the diameter of the rods in the nanorange (Figure 3). Furthermore, the elemental composition of the HNTs was found to contain aluminum and silicone at an elemental ratio of approximately 1:1, where aluminum represented $14.26 \pm 2.4\%$ and silicone represented $14.59 \pm 3.1\%$ of the total composition. This corresponds to the elemental composition of HNT which is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$ [11]. Ubiquitous carbon and oxygen were also observed. Trace amounts of calcium were observed but this was likely contamination.

The structure of PLA was uniform and its elemental composition was recorded as carbon and oxygen only. When HNTs were incorporated into PLA, BSE images indicated the presence of higher density materials within the polymer matrix as evidenced by bright spots in the

photomicrograph (Figure 4). However, high magnification of the halloysite was not possible due to decomposition of the polymer matrix at higher magnifications. Nevertheless, HNT particles were visible and a good dispersion appeared to have been achieved, although aggregated HNT remained visible. Additionally, intimate contact between the HNT and the matrix did not always occur as evidenced by spaces between the particles and the matrix. The elemental composition of this material was similar to that of HNTs, but in this instance aluminum accounted for 0.4 ± 0.15 and $3.7 \pm 1.8\%$ for 2wt% and 15wt% HNT respectively. Similarly, silicone accounted for 0.6 ± 0.3 and 3.6 ± 2.5 for 2wt% and 15wt% HNT respectively.

3.4 Surface wettability

Contact angle measurements indicated that the incorporation of 2-15wt% HNT did not have a statistically significant effect on the surface wettability of PLA ($p = 0.269$) and the contact angle remained at $72.12 \pm 3.7^\circ$.

3.5 Mechanical testing

Mechanical testing was performed to assess the effect of halloysite incorporation on percent strain at maximum load, stress at maximum load, Young's Modulus and stiffness of PLA (Table 2). Statistical analysis of the data indicated that halloysite did not have a significant effect on the percentage strain at maximum load ($p = 0.224$) or stress at maximum load ($p = 0.439$) observed for PLA. However, halloysite did have a significant effect on PLA in terms of stiffness and Young's modulus ($p \leq 0.002$ for both comparisons). From post hoc analysis of the data for comparison of percentage halloysite loading, it was found that composites containing 2 and 5wt% halloysite had significantly higher stiffness values than virgin PLA ($p \leq 0.018$ for both comparisons). Furthermore the addition of 15wt% halloysite resulted in significantly lower stiffness compared to samples containing 5wt% halloysite ($p = 0.006$). No further significant differences were observed in terms of stiffness values for PLA/HNT composites ($p \geq 0.07$ for all comparisons). Conversely, the modulus of PLA composites containing 15wt% halloysite was significantly higher than that of virgin PLA, and composites containing 2 and 5wt% halloysite ($p \leq 0.028$, for all comparisons). No further differences were detected in terms of modulus for PLA/HNT composites ($p \geq 0.193$ for all comparisons).

3.6 Thermogravimetric analysis (TGA)

Neat PLA degraded completely, while the PLA/HNT composite degraded with forming residue. This residue can be assigned to the HNT content of the sample, and it can be noticed that there was a gradual reduction in weight loss in PLA/HNT composite between 350 and 450°C, which corresponds to the fact that HNT starts degradation at approximately 400°C. The onset weight loss temperature for PLA was 392.898°C, which reduced to 306.662°C for PLA/ HNT 2wt%, 303.164°C for PLA/ HNT 10wt%, and 300.87°C for PLA/ HNT 15wt% (Figure 5). As the onset weight loss temperature of the PLA/HNT composites decreased with the increase addition of HNT, this indicated that the thermal stability of PLA/HNT composites was reduced comparing with that of the neat PLA.

3.7 Void content measurement

A void is undesired space remained in a composite material. The measurement of void content was used to assess the space between PLA and HNT in this current study. The void content in the composite was relatively high (Table 3), which consisted of not only the space between PLA and HNT, but also air trapped in the composite during processing which contributed to this high void content, as evidenced by the void content measurement of PLA alone (7.26%). The presence of these void spaces may have resulted in the reduction in

thermal stability of the PLA/HNT composite as they have acted as a focal point for degradation to begin. It is interesting to notice that the void content measurement increased with the addition of HNT, from 10.9% for PLA/ HNT 2wt% to 13.2% for PLA/ HNT 5wt%, 16.8% for PLA/ HNT 10wt% and 27.2% for PLA/ HNT 15wt%.

4. Discussion

PLA has been widely used in medical field since it undergoes hydrolytic degradation which eliminates the need for a secondary surgery to remove the implant. In applications of biodegradable surgical sutures, bone fixation devices and stents, PLA or PLA based materials are often applied. PLA is recognized for being a strong biodegradable material with elastic modulus of 3000-4000MPa and tensile strength of 50-70MPa [3]. But to be suitable for high loading applications such as bone fixation devices and artery stents, PLA still needs to be reinforced.

The current study employed raw HNT for this purpose. From analysis of the resultant data, it was found that the incorporation of HNT into the PLA matrix caused a slight but noticeable reduction in T_g (range 1.7 to 3°C) and T_m (range 0.8 to 1.3°C). As T_g is a measure of the stiffness of the polymeric backbone chain, the reduction in T_g indicates that there was a slight increase in the flexibility of the polymer chain. This decrease in T_g corresponded in general to a decrease in crystallinity. As such, it can be postulated that the decrease in the ordered structure of the crystalline regions led to increased flexibility with the incorporation of HNT. Similar scale reductions in degree of crystallinity were reported by Haroosh *et al.* in investigations of electrospun PLA/ Polycaprolactone/HNT composites [23]. Additionally, Liu *et al.* reported that HNT acted as a nucleating agent resulting in lower cold crystallization temperature as was found in the current study where the reduction in T_{cc} was found to be in the range of 110.29°C to 111.62°C, which corresponds to values published by Liu *et al* [20]. However, Liu *et al.* also reported an increased degree of crystallinity for PLA/HNT composites. However these samples were prepared using an injection molding process which has controlled cooling which encourages crystal growth whereas in the current study crystallinity may have been retarded by quench cooling which followed the compression molding of polymer films.

Chemical analysis of the structure of the base materials using FTIR indicated that both PLA and HNTs contained functional groups as reported in the literature [21, 22, 24]. As there are no absorption peaks for HNTs in the region of 3300 – 1300 cm⁻¹, when blends of PLA and HNTs were prepared, the addition of HNTs did not affect the characteristic absorption peaks of PLA in this region. The peak at 906.81 cm⁻¹ on the HNT spectra which corresponds to the Al - OH groups of HNT, was observed in the higher HNT loaded PLA/HNT composites. However, in the FTIR spectra of the composite materials this peak exhibited a positive shift to 913.07 cm⁻¹ and 911.44 cm⁻¹ for 10 and 15 wt% loading of HNT respectively. Devine & Higginbotham found that increases in intramolecular bonding between polymer components resulted in a negative shift in the absorbance values of the peaks involved in intramolecular bonding [25]. Conversely, the increase in the absorbance value of the Al-OH peak in the current study indicates a reduction in intramolecular bonding between the HNTs particles which was caused by dispersion of the HNT in the polymer melt. However, morphological analysis carried out using SEM indicates that complete intercalation did not occur as large microrange particles are clearly visible in the photomicrograph (Figure 4). This could be down to mixing as HNTs have a net negative charge on exterior surface, which promotes a good dispersion. However the formation of these relatively large particles in the composite does indicate that the HNTs have an affinity to form agglomerates, which might be responsible for the reduction in thermal stability of PLA/HNT composites detected by TGA.

Liu et al. reported that compared to pure PLA improved thermal stability of PLA/HNT composites was achieved with high content of HNT, and the uniformly dispersed HNT in the polymer matrix attributed to the increase of thermal stability of the clay polymer nanocomposite (CPN) by developing a barrier effect against the volatile pyrolyzed products of PLA and retarding thermal degradation of the CPN [20]. However, a high content of HNT in PLA/HNT composite is not ideal for biodegradable medical applications, and the reduction in thermal stability observed in the current study may indicate that the space between PLA and HNT allowed the volatile pyrolyzed products of PLA to accumulate, thereby accelerating degradation. This is further supported by the lack of intimate contact between HNTs and PLA in SEM and this indicates that surface treatment of the HNT may be necessary prior to incorporation into a PLA matrix for fabrication using extrusion processes. In terms of surface treatments of HNTs, positive results were reported by Prashantha *et al.*, who investigated unmodified HNTs and quaternary ammonium salt treated (QM-HNTs) compounded with polypropylene, and found that a better dispersion in the case of QM-HNTs compared to unmodified HNTs [26]. Haroosh *et al.* also reported that a better dispersion was obtained in the case of 3-aminopropyltriethoxysilane modified HNTs compared to unmodified HNT in compounding with PLA/Polycaprolactone compound [23]. Deng *et al.* modified HNTs with potassium acetate and reported improved mechanical properties in HNT/epoxy composite compared to neat epoxy [14]. It is also reported that sulphuric acid treated HNTs were potential carriers for enzyme, drug and sensors, since the sulphuric acid destroyed the crystal structure of HNTs and resulted in fixed micropore and controllable mesopore size distributions [27].

Wettability plays an important role in drug releasing industry, because drug release is to a large extent influenced by penetration of a dissolution liquid into a polymer matrix, if an aqueous medium does not wet a matrix, its penetration into the polymer bulk and the resulting drug extraction would be considerably hindered [28]. PLA is recognized as hydrophobic and HNTs is relatively hydrophobic [4, 12]. Hence, the addition of HNTs did not affect the wettability of PLA.

Semicrystalline PLA has a reported tensile strength of 50-70MPa, Young's Modulus of 3-4 GPa and elongation at break of 2-10% [3]. In the current study corresponding values were found to be 52.33 ± 16.89 MPa, 1898 ± 56.95 MPa and $2.88 \pm 1.06\%$ respectively. Mechanical test results indicated that HNTs exhibited a reinforcing effect on PLA where the incorporation of HNT resulted in a significant increase in stiffness and Young's Modulus. Despite the lack of statistical significance, the tensile strength of the composites did increase with HNT, where 5wt% HNT loading yielded the highest result with a value of 62.7MPa. This value approximates values reported by Raquez *et al.* and Wu & Liao who reported tensile strength values of 70MPa for a 6wt% loading of HNTs and 65 MPa for 3wt% loading of multi-walled carbon nanotubes respectively for injection molded samples [1, 7]. However, it should be noted that due to the high pressures involved in injection molding it is likely that this process would eliminate at least some of the voids encountered in the current study. Liu *et al.* also assessed the tensile strength of HNT/PLA composites, and reported an increase in tensile strength up to 30wt% loading of HNT which resulted in a tensile strength of 74 MPa [20]. However, little difference was observed in HNT loadings between 5 and 20wt% HNT loading which resulted in tensile strengths of circa 65 MPa which again corresponds to results in the current study. The evident reinforcing effect of HNT can be attributed to the size of the HNTs being smaller than the critical crack length that typically initiates failure in a composite, therefore improve the strength of the composite [29]. The reinforcing effect is influenced by the structural characteristics of the reinforcing fillers, dispersion state, and interfacial interactions [20]. Hence due to the high aspect ratio of HNTs, the strength,

modulus, stiffness and impact resistance of polymers can be increased simultaneously by HNTs. Furthermore, since the interfacial interaction between HNTs and polymers strongly influences the mechanical improvement, the mechanical properties of the composite can be tailored by modifying HNTs using chemical and physical approaches [12].

5. Conclusion

This study focused on the effect of low volumes of HNTs on mechanical and thermal properties of extruded PLA films. PLA/HNT composites were prepared by melt compounding. The introduction of HNTs into PLA matrix created flexible mobility of PLA chains and resulted in slightly lower glass transition temperature. The presence of voids partly as a result of poor contact between the HNT and the PLA matrix caused a decrease in the thermal stability of the PLA/HNT composites. However, mechanical tests indicated that the addition of HNTs significantly improved Young's modulus and stiffness of PLA, while the percentage strain at maximum load and stress at maximum load of PLA were not affected. Hence the reinforced PLA/HNT composites could be potentially used in biological applications that require high strength, such as coronary stents and bone fixation devices.

Disclosures

The authors declare that there is no conflict of interests regarding the publication of this article, this manuscript has not been published elsewhere and it has not been submitted simultaneously for publication elsewhere.

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