Toughening of poly(lactic acid) without sacrificing stiffness and strength by melt-blending with polyamide 11 and selective localization of halloysite nanotubes

B. J. Rashmi, K. Prashantha*, M-F. Lacrampe, P. Krawczak

Mines Douai, Department of Polymers and Composites Technology and Mechanical Engineering, 941 rue Charles Bourseul, CS 10838, F-59508 Douai Cedex, France

Received 15 December 2014; accepted in revised form 25 February 2015

Abstract. This paper aims at improving the mechanical behavior of biobased brittle amorphous polylactide (PLA) by extrusion melt-blending with biobased semi-crystalline polyamide 11 (PA11) and addition of halloysite nanotubes (HNT). The morphological analysis of the PLA/PA11/HNT blends shows a strong interface between the two polymeric phases due to hydrogen bonding, and the migration of HNTs towards PA11 phase inducing their selective localization in one of the polymeric phases of the blend. A ‘salami-like’ structure is formed revealing a HNTs-rich tubular-like (fibrillar) PA11 phase. Moreover, HNTs localized in the dispersed phase act as nucleating agents for PA11. Compared to neat PLA, this leads to a remarkable improvement in tensile and impact properties (elongation at break is multiplied by a factor 43, impact strength by 2, whereas tensile strength and stiffness are almost unchanged). The toughening mechanism is discussed based on the combined effect of resistance to crack propagation and nanotubes load bearing capacity due to the existence of the fibrillar structure. Thus, blending brittle PLA with PA11 and HNT nanotubes results in tailor-made PLA-based compounds with enhanced ductility without sacrificing stiffness and strength.

Keywords: polymer blends and alloys, biopolymers, polylactide, polyamide 11, halloysite nanotubes

1. Introduction

Polylactide or poly(lactic acid) (PLA) is considered as being a promising thermoplastic polyester because of its renewable resource-based origin along with its biodegradability and its biocompatibility [1–4]. Nevertheless, its inherent brittleness is a major drawback for its large-scale commercial applications. Thus, numerous approaches have been adopted to correct this drawback [1, 2, 5], one of them being based on melt blending PLA with a more ductile engineered polymer such as polyamide (PA).

Ebadi-Dehaghani *et al.* [6] showed that the tensile behavior of PLA varies dramatically from brittle to ductile when blended with at least 15 wt% of a terpolymer of PA (PA6/PA66/PA610). The elongation

at break increases from 5% (neat PLA) to 176% (PLA with 20 wt% of PA). The two glass transition temperatures (T_g) of PLA and PA in blends shift to lower T_g than their respective original ones, sign of a partially miscible system due to the interactions led by hydrogen bonding between the molecules of PA and PLA. The spherical particles of PA are dispersed homogeneously in the PLA matrix. The strong interfacial adhesion of the two phases is beneficial for the improvement of the ductility. Unfortunately, this toughness improvement was achieved at the expense of the tensile resistance which decreases by 25% [6]. Arrieta *et al.* [7] reported a significant improvement of the unnotched Izod impact strength of PLA when blended with 50 wt% of a bio-based

*Corresponding author, e-mail: kalappa.prashantha@mines-douai.fr
© BME-PT

PA610 and 2 phr epoxy resin as reactive compatibilizer. While neat PLA shows a brittle behavior, unnotched impact strength of the compatibilized blend achieves no break level. This toughening effect was ascribed to (i) the formation of a polyester-polyamide block copolymer during blending, which acts as an efficient compatibilizing agent reducing the dispersed phase size and (ii) the reaction between epoxy resin and the terminal functional groups of both PLA and PA610 favoring adhesion between the two components. Nevertheless, the compatibilized blend did not exhibit improved mechanical properties (Young modulus, tensile and flexural strengths, elongation at break) except unnotched impact strength [7]. Derho *et al.* [8] characterized the morphology, thermal and mechanical behavior of PLA/PA11 blends over a large composition range. The good compatibility between both polymers, highlighted by the morphological analysis, induces an increase in the ductility only for PA11 content higher than 50 wt%, obtained at the expense of rigidity and yield stress. For the blend containing 20 wt% of PA11, the elongation at break remains similar to that of the neat PLA while its rigidity is reduced by approximately 38% [8]. Pai *et al.* [9] showed that such PLA/PA11 blends can be compatibilized by titanium isopropoxide catalyst through interchange reaction. However, an improvement of the ductility and toughness is observed only for high PA11 contents (>50 wt%), both Young modulus and stress at break showing a substantial decrease.

Recent literature reports suggest that, nanostructured polymer blends having a minor polymer phase with nanoscale dimensions offer much promise because of enhanced toughness in comparison to conventional polymer blends [10–12]. This method was used by Nuzzo and coworkers [13–15] to prepare PLA/PA11 blends containing small amounts of nanoparticles (organo-modified montmorillonite (OMMT), sepiolite and carbon nanotubes). Co-continuous morphologies are obtained and with fillers preferentially located inside the minor PA11 phase. These blends show improved thermal stability, their structural integrity being kept up to ~160°C, i.e., about 100°C above the PLA glass transition temperature. But no information was given on their tensile behavior and their ductility. Finally, existing literature suffers from a lack of detailed investigations on the mechanical properties and toughening mecha-

nism in particular for PLA/PA11 nanocomposites, which opens the avenues for further studies.

So, in practice, a PLA-based material having good stiffness-toughness balance along with high bio-based PLA content remains still elusive. Therefore, the present work focuses on the toughening of PLA without sacrificing stiffness and strength by melt blending with bio-sourced PA11 and by phase selective localization of natural halloysite nanotubes in PA11 phase of blends.

2. Experimental

2.1. Materials

Poly lactide (PLA) in pellets form (4032D, Natureworks, USA) has a specific gravity of 1.24 and a melt flow index around 7 g/10 min at 210°C. Polyamide 11 (PA11) is an injection molding grade (Rilsan® BMNO TLD, Arkema, France). Halloysite nanotubes (HNT) (Natural Nano, Inc, USA) have an average diameter of 80 nm, a length of about 1.2 microns, and a density of 2.5 g·cm⁻³. All materials used in this study were dried in an oven at 80°C overnight to remove any excess moisture.

2.2. Compounding and processing procedure

Masterbatches containing 15 wt% of halloysites were prepared by adding nanotubes in the melt zone of a twin-screw extruder (Haake PolyLab OS, Thermoscientific, USA) equipped with a screw of 16 mm diameter and *L/D* of 40 length to diameter ratio. The temperature profile of the extruder for the production of PA11/HNT masterbatch was set at 220°C in the feed zone, sequentially at 225, 227, 230, and 232°C in the metering zone and 235°C at the die. The screw speed and feed rate were set at 60 rpm and 1 kg·h⁻¹ respectively. In case of PLA/HNT masterbatch, the temperature profile in the extruder was set between 170 to 180°C from feed zone to die. The screw speed and feed rate were set at 40 rpm and 1 kg·h⁻¹ respectively. Extruded masterbatches were cut into small pellets in a pelletizer (SGS 25-E4, Scheer, Germany). Both masterbatch pellets were dried at 80°C in vacuum oven for overnight to remove residual water content for further utilization. The previously prepared 15 wt% halloysite nanotubes loaded PLA/HNT and PA11/HNT masterbatches were diluted with neat PLA and neat PA11 to give 2, 4 and 6 wt% HNTs in PLA/PA11 nanocomposites with a blend mixture ratio of 80:20 compounded using afore mentioned twin-screw extruder

Figure 1. Schematic illustration of compounding process

(Figure 1). The melt-compounding temperature of the barrel was in the range of 193 to 198°C at a screw speed of 100 rpm. After compounding, the extrudate strand was cut into pellets.

After pelletizing, the dried (80°C in vacuum oven for overnight) nanocomposite granules were compression-molded into 2 mm-thick plates using a hydraulic press (Dolouets, France) at 205°C during 2 min for rheological experiments. For mechanical testing, nanocomposite granules were injection-molded (Babyplast 6/10P, Spain) into standard test specimen for tensile, impact and dynamic mechanical tests. During injection molding, the temperature profile ranged from 200 to 205°C and the mold temperature was kept at 35°C. The injection molding throughput and the holding pressure were 1.25 cm³·s⁻¹, and 80 bars respectively with a cooling time of 10 seconds. As a reference, neat PLA/PA11 in the same proportion was also similarly extruded and then injection-molded for rheological and mechanical studies.

2.3. Characterization methods

2.3.1. Scanning and transmission electron microscopy

Scanning electron microscopy (SEM) was used to analyse morphology (S-4300 SE/N, Hitachi, Japan). Injection-molded samples were cryofractured both in transversal and longitudinal directions. Then, samples were coated with a thin gold layer (Polaron E5100 series II, Watford) to observe the morphology under high vacuum at 5 kV.

Additionally, for transmission electron microscopy (TEM), injection-molded samples were cut using a cryo-diamond knife on a microtome (Leica ultracut, LEICA, Germany) to give sections with a nominal

thickness of 150 nm. These sections were transferred to Cu grids of 400 meshes. Bright-field TEM images of nanocomposites were obtained at 200 kV under low dose conditions with an electron microscope (Philips CM30 Zaventem, Belgium), using a CCD camera (Gatan, USA).

2.3.2. Differential scanning calorimetry (DSC)

Thermal transitions of the materials were examined by differential scanning calorimetry (DSC 7 Perkin-Elmer, USA) under nitrogen flow (20 mL·min⁻¹). Samples were crimple-sealed in aluminum pans and heated from 30 to 220°C at a heating rate of 10°C·min⁻¹ (first heating scan), equilibrated at 220°C for 2 min, cooled at 10°C·min⁻¹ to 30°C, equilibrated at 30°C for 2 min, and then heated again to 220°C at 10°C·min⁻¹ (second heating scan).

2.3.3. Rheology

Oscillatory shear measurements were performed using an advanced rheometric system (HAAKE MARS, TA Instruments, Germany). The measurements were performed at 205°C using plate and plate geometry (diameter, 35 mm). Deformation in the linear viscoelastic region was found to be 2% and then chosen for all subsequent frequency sweep tests. Samples were equilibrated at 205°C before testing. The frequency was varied from 0.1 to 100 rad·s⁻¹.

2.3.4. Dynamic mechanical analysis (DMA)

The viscoelastic behavior was studied in tension by dynamic mechanical analysis (DMA+150, Metravib, France). Dynamic strain sweep was first performed to determine the linear viscoelastic range of the materials. The tests were then performed at a strain

amplitude of 2% and a frequency of 1 Hz. Data were collected from -50 to 120°C at a scanning rate of 3°C·min⁻¹. Rectangular DMA specimens (nominal dimensions, (4±0.2)×(10±0.5)×30 mm³) were cut from injection-molded impact bar samples.

2.3.5. Mechanical behavior testing

The mechanical properties were evaluated from injection-molded specimens. Tensile strength and elongation at break were measured at a crosshead rate of 5 mm·min⁻¹ and modulus at 1 mm·min⁻¹, using a tensile machine (Lloyd LR 50 K, USA) at 25°C and 50% RH according to ISO 527 standard. Charpy notched and un-notched impact tests were carried out as per ISO 179-1 standard by using a pendulum impact machine (Model 5101, Zwick, Germany) at 25°C and 50% RH. All the reported values were calculated as averages over five and ten specimens for tensile and impact test respectively.

3. Results and discussion

3.1. HNTs selective localization in PLA/PA11 blend

The selective localization of nanofillers in a specific polymer phase of an immiscible polymer blend is generally governed by thermodynamic factors. Wetting coefficient ω_a is proposed to deduce the selective localization of nanofiller according to Equation (1) [16]:

$$\omega_a = \frac{\gamma_{\text{nanofiller-polymer}_1} - \gamma_{\text{nanofiller-polymer}_2}}{\gamma_{\text{polymer}_1,2}} \quad (1)$$

where, $\gamma_{\text{nanofiller-polymer}_1}$, $\gamma_{\text{nanofiller-polymer}_2}$, and $\gamma_{\text{polymer}_1,2}$ are the interfacial energies between nanofiller and polymer₁, between nanofiller and polymer₂, and between the two polymer phases. In the present work PLA represents polymer₁ and PA11 represents polymer₂. If $\omega_a > 1$, nanofiller preferentially locates in polymer₂; if $\omega_a < -1$, nanofiller preferentially locates in polymer₁, and if $-1 < \omega_a < 1$, nanofiller locates at the interface.

The interfacial energy between nanofiller and polymer can be adjusted in different degrees by different surface modifications of nanofiller and/or the modification of polymer matrix. The interfacial energy can be calculated according to the harmonic-mean (Equation (2)) and geometric-mean (Equation (3)) [17]:

Table 1. Surface energy data of the ternary system components

Material	Surface energy [mN·m ⁻¹]			References
	γ_i^{total}	γ_i^{d}	γ_i^{p}	
PLA	47.0	35.9	11.1	[18]
PA11	45.0	40.0	5.0	[19]
HNT	28.4	26.9	1.5	[20]

Table 2. Calculated interfacial energy

Material	Interfacial energy [mN·m ⁻¹]	
	Harmonic-mean equation	Geometric-mean equation
PLA/PA11	2.5	1.3
PLA/HNT	8.7	5.0
PA11/HNT	4.5	2.3

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^{\text{d}} \gamma_2^{\text{d}}}{\gamma_1^{\text{d}} + \gamma_2^{\text{d}}} + \frac{\gamma_1^{\text{p}} \gamma_2^{\text{p}}}{\gamma_1^{\text{d}} + \gamma_2^{\text{d}}} \right) \quad (2)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - (\sqrt{\gamma_1^{\text{d}} \gamma_2^{\text{d}}} + \sqrt{\gamma_1^{\text{p}} \gamma_2^{\text{p}}}) \quad (3)$$

In this work, surface energy values of PLA, PA11 and HNTs are taken from the literature [18–20] (Table 1) and those values are used to calculate interfacial energy (Table 2). Based on interfacial energies, the wetting coefficient (ω_a) was calculated according to Equation (1). Its value is 1.69 and 2.11 using harmonic-mean Equation (2) and geometric-mean Equation (3), respectively. Therefore, the theoretical calculation indicates that HNTs preferentially locate in the PA11 phase during the melt-blending processing.

3.2. Morphology

Figure 2 shows representative SEM images of the cryo-fractured PLA/PA11 blends with and without HNTs in both transversal (perpendicular to injection molding) and longitudinal (along the injection molding) directions. It is well known that the mechanical properties of blends are strongly dependent on their morphology and the control of the morphology is crucial for the final properties of the product [21–23]. In case of neat blends, PA11 is dispersed in PLA matrix. The transversal images (Figure 2a) show a ‘sea–island’ morphology of the blends, where the continuous phase is PLA and the spherical dis-

Figure 2. SEM images of PLA/PA11/HNT systems in transversal (a, b, c, d) and in longitudinal (a', b', c' and d') directions. (a, a') Neat blend; (b, b') with 2 wt% HNTs; (c, c') with 4 wt% HNTs; (d, d') with 6 wt% HNTs.

persed phase represents PA11. In the longitudinal direction (Figure 2a'), an heterogeneous discontinuous fibrillar morphology is observed which is attributed to the viscosity difference between the PLA and PA11 [24]. Whatever the observation direction, the interface between PA11 and PLA seems to be weak, a clear gap between the PLA matrix and the PA11 domains being clearly observed. This means that PLA and PA11 are not totally miscible.

The incorporation of HNTs leads to a totally different phase structure. The droplet size increases slightly (Figure 2b). This is due to the fact that, when added to PLA/PA11, all HNTs migrate into PA11 phase due to their affinity towards PA11 and remain trapped inside the PA11 phase, thereby increasing the droplets size. Also, increase in HNTs content enhances the droplets viscosity (see section 3.4) and their resistance to breakup, leading to enlarged dispersed phase.

Also, longitudinal section shows that irregular cylindrical structures of PA11 in flow direction turned out to regular fibrillar structures upon addition of 2 wt% HNTs (Figure 2b') compared to the binary PLA/PA11 blend. However, with increase in HNT concentration to 4 and 6 wt% (c, c' and d, d'), discontinuous fibrillar structure is observed, which is similar to that of the neat blends.

Figure 3 shows the SEM images of neat blends and 6 wt% HNTs-filled blend with higher magnification. HNTs are hardly visible in the PLA matrix, confirming that during processing migration of HNTs from PLA/HNT masterbatch to PA11 matrix has happened, and that HNTs are largely localized in PA11 domain forming interesting 'salami-like' structure

(Figure 3b). In general, the localization of nanofillers in polymer blends should be linked to the balance of interactions between the surface of the nanofillers and the polymer components and wettability factor [25]. As predicted earlier, HNTs are selectively localized inside PA11 (shown in Figure 3a and 3b) and at the interface. This is attributed to HNTs affinity towards PA11 which is higher than that towards PLA. Further morphological observations show that, the interface between neat PLA and PA11 is not sharp, indicating the partial compatibility or weak interaction between PLA and PA11 components (Figure 2a), but with the addition of HNTs this interface quality tends to improve. The difference compared to PLA/PA11 blends without HNTs is that, the PA11 phase holds tightly with the PLA phase, indicating that the interface between the PLA and PA11 phases with the addition of HNT is much stronger than for the binary blend without HNTs.

The selective confinement of HNTs in the PA11 phase is further proved by characterizing the samples using transmission electron microscopy (TEM). The cross-section of PLA/PA11 blend exhibits regular drop-matrix morphology with micro-sized PA11 domains in the continuous PLA matrix (Figure 4a). Upon addition of 2 wt% HNTs into the blends, HNTs appear selectively confined inside the PA11 phase (Figure 4b), while almost no nanotubes can be noticed within the PLA phase. Interestingly, only ultra-micron-sized PA11 droplets are unfilled, which is not surprising, as the length/size of PA11 droplets should be greater than that of HNTs in order to accommodate nanotubes in their domain. Further, upon addition of 4 wt% HNTs, the size of the HNTs-

Figure 3. SEM images in transversal direction: (a) PLA/PA11 with weak interface and (b) PLA/P11/6 wt% HNT systems showing a good interface with salami like structure

Figure 4. TEM images in transversal direction: (a) PLA/PA11, (b) PLA/PA11/2 wt% HNT, (c) PLA/PA11/4 wt% HNT and (d) PLA/PA11/6 wt% HNTs

filled PA11 droplets slightly increases while the number of unfilled PA11 droplets substantially decreases (Figure 4c). Finally, for 6 wt% HNTs, the size of the HNTs-filled PA11 droplets further increases while only traces of unfilled PA11 droplets are observed (Figure 4d). These observations clearly indicate that the presence of the HNTs in the PLA/PA11 blends creates a regular morphology, which still depends on the halloysite content. Also, at higher loading, HNTs form a network structure in the nanocomposites.

3.3. Thermal behavior

Thermal behavior of PLA/PA11 blend and its nanocomposites was investigated by DSC. The heating and cooling thermograms are shown in Figure 5 and corresponding data are summarized in Table 3. In heating endotherm (Figure 5a), one can see one exotherm corresponding to cold crystallization of PLA (T_{cc}). Comparing the thermograms (Figure 5a) and calorimetric parameters (Table 3), the influence of HNTs on the cold crystallization of the PLA in PLA/PA11 hybrid blends is clearly visible. When HNTs

are added, the T_{cc} of the PLA decreases from 105 to 97°C. The crystallization enthalpies also decrease in the nanocomposites. The decrease of the T_{cc} in the neat blend may be explained as follows. Presence of amorphous PA11 chains could activate the chain mobility of PLA, thereby advancing the cold crystallization of PLA. Furthermore, the surface of the dispersed PA11 domains might also act as nucleating centers and thereby enhance the crystallization of the PLA in the blends, which is accordance with the reported literature [26]. Then, decrease in T_{cc} in ternary nanocomposites is due to characteristic changes of PA11 phase related to migration of HNTs to PA11 matrix bringing further decrease in T_{cc} of PLA phase. Two peaks appearing at about ~52 and ~60°C correspond to the glass transition temperatures (T_g) of PA11 and PLA phases respectively. Addition of HNT has no profound effect on the T_g of the blends. However a marginal increase was observed at high HNT content (~54°C for PA11 and 61.5°C for PLA). This is probably due to the indirect nucleation effect exerted by HNTs. Two endotherms corresponding to melting temperature (T_m) of PLA

Figure 5. DSC thermograms (a) second heating scan and (b) cooling curves for PLA/PA11/HNT systems with different HNT concentrations

(~168°C) and PA11 (~189°C) are visible. The melting temperature remains unaltered with increasing filler concentration. The appearance of shoulder peak in PA11 is attributed to the melting of preferentially oriented PA11 macromolecules. This preferential orientation is inhibited in presence of PLA showing a single peak in PLA/PA11. But, upon addition of HNTs, preferential orientation reappears, which is in accordance with the literature [27]. The intensity of

shoulder peak increases with increasing filler concentration.

During cooling (Figure 5b), the neat PLA/PA11 blend shows two peaks, one big at ~98°C and another small one at around 165°C indicating the fractionated crystallization of PA11. Crystallization at the higher temperature corresponds to bulk crystallization of PA11, which takes place due to effective heterogeneity in the PA11 phase, and crystallization at the lower temperature corresponds to crystallization of PA11 droplets, which needs much larger supercooling [13, 27]. The fractionated crystallization process becomes less evident when the HNTs are added with a reduced peak at 98°C indicating a lower number of fine droplets as observed in TEM image (Figure 4), while peak at 165°C increases drastically. This change in crystalline structure is very important as it governs the mechanical performances of polymer systems. Addition of filler not only alters blend microstructure, but also affects the crystallization behavior of the polymer phases. This further indicates that, HNTs are selectively localized in PA11 matrix as observed in Figures 2 and 4. For neat PLA, no crystallization exothermic peak can be seen as PLA is completely amorphous, due to its slow crystallization kinetics [6, 28, 29]. Addition of filler does not induce any crystallization in PLA phase.

3.4. Rheological behavior

Figure 6 shows the storage modulus (G') and the complex viscosity (η^*) as a function of frequency for PLA/PA11 blends with and without HNTs. Upon addition of 2 and 4 wt% HNTs, G' does not change apparently (Figure 6a), whereas it largely increases at relatively lower frequency for 6 wt% HNTs. A plateau is observed in that case at low frequency, indicating the formation of a percolated network structure of the HNTs in the melt. These inconsistent variations of storage modulus with increasing content

Table 3. Thermal properties of PLA/PA11/ HNT ternary systems

Material	Second heating [°C]						Cooling [°C]			
	$T_{M(PLA)}$	$T_{M(PA)}$	T_{cc}	$\Delta H_{cc(PLA)}$	$T_{g(PA)}$	$T_{g(PLA)}$	$T_{C1(PA)}$	$T_{C2(PA)}$	$\Delta H_{C1(PA)}$	$\Delta H_{C2(PA)}$
PLA	168	—	106	—	—	60	—	—	—	—
PA11	—	190	—	—	54	—	—	159	—	39
PLA/PA11	168	189	105	15	52	60	98	165	13.2	0.4
PLA/PA11/2 wt% HNT	168	189	103	10	53.4	61	96	167	0.3	5.1
PLA/PA11/4 wt% HNT	167.7	189.7	102	10.2	53.5	61	93	168	0.2	5.2
PLA/PA11/6 wt% HNT	168	190	97	13.7	53.8	61.5	92	168	0.2	5.5

ΔH_{cc} cold crystallization enthalpy of PLA, ΔH_{C1} & ΔH_{C2} crystallization enthalpy of PA11

Figure 6. Storage modulus (G') (a) and complex viscosity (η^*) (b) of PLA/PA11/HNT systems with frequency sweep as a function of HNT content at 205°C

of the HNTs may be explained as follows. The original aspect ratio of HNTs is very low (between 10 and 30) and very high loading is necessary to see substantial increase in the storage modulus at low frequency [30]. Therefore, in spite of good distribution of PA11 in PLA phase (Figure 2) and uniform dispersion of HNTs in PA11 at 2 and 4 wt% HNTs contents, the effect of the HNTs on the rheological properties of nanocomposites is not visible and hence in this case, rheological properties of the material are mainly governed by PLA matrix. At 6 wt% HNTs, the presence of a large number of HNTs in PA11 phase induces the formation of percolated network structure and the rheological properties of material are determined by both PLA and HNTs-filled PA11 components. Consequently, pseudo-solid-like behavior is observed in 6 wt% HNTs-filled PLA/PA11 blend only.

The frequency dependency of the complex viscosity (η^*), for all samples is shown in Figure 6b. Upon introduction of HNTs, viscosity of the blend increases

and the shear-thinning behavior is intensified with increase in the nanotubes concentration. Higher viscosity of nanocomposites arises from the network structure of HNT-rich PA11 phase as observed from the morphological images of the nanocomposites (section 3.2). Another possible reason for increased viscosity of nanocomposites is the higher flow resistance of macromolecules due to the interaction between HNTs and the polymer [27]. Both storage modulus and complex viscosity are the highest for 6 wt% HNTs. The increase in the storage modulus (G') and the complex viscosity (η^*) is ascribed to the interfacial interactions between polymer chains and filler surface [30, 31].

3.5. Viscoelastic properties

During dynamic mechanical analysis (DMA) (Figure 7), storage modulus (E') of all the samples logically decreases with increasing temperature and a more rapid drop occurs at glass transition region of PLA. Addition of HNTs to the PLA/PA11 blend increases the storage modulus in the glassy region (Figure 7a) and increase in HNTs concentration further increases the storage modulus of the blends, which can be attributed to the mobility restriction of the polymer chains. Due to selective positioning of HNTs in PA11 matrix coupled with their nucleating action, HNTs not only reinforce the polymers blend but also increases the size of the PA11 phase in PLA matrix.

The temperature dependence of $\tan \delta$ of PLA/PA11 blend and ternary nanocomposites are presented in Figure 7b. The $\tan \delta$ curves show two dynamic relaxation peaks. The peak observed at 65–68°C is often interpreted as the T_g of PLA. This peak does not shift upon HNTs addition, indicating that the presence of the HNTs does not affect significantly the T_g of PLA, which is slightly higher than that obtained from DSC data (Table 3). However, addition of HNTs considerably lowers the intensity of the $\tan \delta$ peak (Figure 7b); the higher the HNTs content, the lower is the peak intensity. The damping behavior of the material is reduced, because the presence of well dispersed HNTs localized in PA11 fibrils retards the segmental motions of the polymer matrix during the transition, thus resulting in the reduction of sharpness and height of the $\tan \delta$ peak [32, 33]. This is in agreement with the significant increase in the elastic component due to the presence of the HNTs in the blends [34].

Figure 7. Storage modulus (a) and $\tan \delta$ (b) versus temperature for PLA/PA11/HNT systems

The other peak appearing at 105°C for the PLA/PA11 blend is due to the cold crystallisation of the PLA. Its intensity also decreases with increase in HNTs content. This confirms the previous DSC analysis indicating that HNTs act as a nucleating agent for the crystallisation of PLA. The fact that HNTs act as both reinforcing filler and indirect nucleating agent for crystallisation of PLA is quite interesting, considering the fact that HNTs localize only in PA11 domain as observed by SEM and TEM.

3.6. Mechanical behavior

The mechanical behavior of injection-molded PLA/PA11 (80/20) blends and nanocomposites was

assessed using tensile and impact tests. The mechanical properties (tensile strength, Young's modulus, strain-at-break, and impact resistance) of the materials are shown in Table 4.

Tensile behavior

The typical tensile stress–strain curves of the PLA/PA11 blends and its nanocomposites are shown in Figure 8. During tensile tests, all the samples showed distinct yielding and stable neck growth with characteristics of a ductile fracture. The neat PLA is a brittle polymer with poor ductility (3.96%) and high strength (54 MPa) (Table 4). When PLA is blended with PA11 the ductility increases up to 79% without significant change in the tensile strength and with only a slight (about 10%) reduction in the modulus. Derho *et al.* [8] reported the brittle fracture for PLA/PA11 (80:20) blends, with decrease in elongation at break due to the presence of micron-sized PA11 nodules in PLA matrix. On the contrary and interestingly in the present work, the PA11 phase appears in elongated/stretched structure (quasi-fibrillar) (Figure 2). Therefore, mixing PLA with PA11 at 80:20 ratio changes the brittle fracture of neat PLA to the ductile fracture of the PLA/PA11 blend.

Also, the tensile behavior of the nanocomposite blends varies significantly with different HNT load-

Figure 8. Tensile stress–strain curves of PLA/PA11/HNT systems

Table 4. Mechanical properties of PLA/PA11/ HNT ternary systems

Sample	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]	Notched impact resistance [$\text{kJ}\cdot\text{m}^{-2}$]	Un-notched impact resistance [$\text{kJ}\cdot\text{m}^{-2}$]
PLA	54.5±1.6	3.6±0.2	2923±14	3.1±0.3	16.4±2
PA11	43.7±2.5	254±7	1220±12	—	—
PLA/PA11 (80:20)	53.5±2.5	79±7	2569±12	3.4±0.4	19.0±2
PLA/PA11/2 wt% HNT	54.5±1.5	155±8	2782±11	5.6±0.4	37.0±2
PLA/PA11/4 wt% HNT	53.6±2.6	145±4	2879±21	4.8±0.6	29.2±3
PLA/PA11/6 wt% HNT	54.2±1.1	139±4	2974±14	4.4±0.6	27.8±3

ings. Upon HNTs addition into PLA/PA11 blend, ductility of the material increases dramatically. Compared to neat blend, the elongation at break for the 2 wt% HNTs-filled PLA/PA11 samples almost doubles, increasing from 79 to 155 %, and the modulus increases by ~8% without change in tensile strength. This is due to the fact that, HNTs induced almost uniform PA11 fibrillation in PLA matrix (Figure 2b'). On further increase in HNTs content, a slight decrease in elongation at break is noticed, hardly significant i.e. 145% for 4 wt% HNTs and 139% for 6 wt% HNTs-filled PLA/PA11 blends. This could be due to overloading of HNTs that may induce formation of aggregates or cause damage to PA11 fibrils leading to early fracture of samples. However, decrease in ductility is not eminent; elongation at break remains higher than that of the neat blend. The Young's modulus of the PLA/PA11 blend further increases with increase in HNTs content without altering tensile strength displaying a positive combination of yield stress and strain at break resulting in an optimum filler content (~2 wt%) to achieve balanced tensile properties.

In order to understand further the effect of elongated/stretched PA11 phase with and without HNTs on tensile properties of the blends, the necked down region of the tensile specimen was cryo-fractured longitudinally and morphologies were character-

ized using SEM (Figure 9). Neat blends during the tensile test showed a fracture surface with stretched PA11 phase. Debonding of the PA11 from the PLA matrix under tensile stress is clearly observed. As explained earlier (section 3.2), the original fibrillar structure is not uniform and it remains the same even after stretching. PLA/ PA11 blends with 2 wt% HNT have the highest elongation at break, and HNTs-filled PA11 phase experiences tremendous plastic deformation in the loading direction. All the PA11 fibrils show a uniform stretching without any debonding between PA11 and PLA. No HNTs are visible on the surface of PA11 fibrils, which confirms the greater affinity of HNTs towards PA11. This effectively facilitates the bridging of necking zone by continuous stretching of PA11 with HNTs alignment as the deformation zone propagates along the triaxial deformation. This phenomenon provides a continuous stretching and orientation in the deformation zone, which greatly enhances the ductile characteristics of the PLA/PA11 blends. In case of 4 wt% HNTs and 6 wt% HNTs-filled PLA/PA11 blends, the fractured morphology is quite similar, which is a reflection of their tensile properties (Table 4). In both cases, diameters of the fibrils are much bigger due to overloading of HNTs and there exist a mismatch between the stretching of PA11 and HNTs alignment during the tensile deforma-

Figure 9. Fracture mechanism of longitudinally cryo-fractured tensile failed samples-right: deformation of PA11 phase in PLA (a) PLA/PA11 (80:20)-left: deformation of HNTs localized in PA11 dispersed in PLA (b) PLA/PA11/2 wt% HNT, (c) PLA/PA11/4 wt% HNT and (d) PLA/PA11/6 wt% HNT

tion, which eventually causes an early failure of the sample.

Impact properties

Table 4 shows the notched and un-notched Charpy impact strength of PLA/PA11 blend and its nanocomposites. PLA is known for its brittle characteristics; therefore, toughening agents are widely used to enhance the PLA impact strength [35–37]. Considering the tensile elongation at break results, PA11 may be expected to be a good candidate for blending with PLA to increase the PLA toughness. Nevertheless, both notched and un-notched Charpy impact strength of unfilled blend are not as good as

expected (3.4 and 19 kJ·m⁻² in notched and un-notched specimens respectively), only slightly higher than neat PLA. By introducing 2 wt% HNTs to PLA/PA11 blends, the notched impact strength increases by + 67% and the un-notched impact strength by + 95%. HNTs effectively toughen the matrix through the stretching of PA11 phase. Further increasing the concentration of the HNTs does not increase the impact strength. Slight decrease in the impact strength (both notched and un-notched) of 4 and 6 wt% HNTs-filled PLA/PA11 blends may be attributed to the excessive localization of HNTs in PA11 phase, as discussed earlier in the tensile properties section. The elongation at break for the blend con-

Figure 10. Fracture mechanism of impact failed samples – deformation of phase of PA11 in PLA: (a) PLA/PA11 (80:20), (b) PLA/PA11/2 wt% HNT, (c) PLA/PA11/4 wt% HNT and (d) PLA/PA11/6 wt% HNT

taining 4 and 6 wt% HNTs showed similar trend as that of the impact strength. These results are in accordance with those obtained for the clay filled poly(L-lactide)/polypropylene blends [4].

The fracture surface was observed in the vicinity of the notch under SEM (Figure 10). The neat blend shows a fracture surface with multiple-sized elongated PA11 fibrils. The toughening effect in this case remains moderate due to the lower compatibility between the phases. Some voids due to pullout of dispersed PA11 domain are clearly observed, which suggests a poor interfacial adhesion between PLA and PA11 phases. In comparison to neat blend, the compound containing 2 wt% HNTs shows numerous fibrils which are stretched on the fracture. No obvious interface between the different phases is observed between the PLA and the HNTs-filled PA11 phases. In case of 4 wt% HNTs and 6 wt% HNTs-filled PLA/PA11 blends, the fractured morphology is similar (Figure 10) to that of tensile failed samples. In both the cases, although good adhesion between fibrils and matrix was observed, stretching of fibrils was limited due to high filler content.

4. Conclusions

A fully bio-based blend with PLA as the dominant component with improved ductility and impact strength and unaltered tensile strength and stiffness was produced by blending amorphous brittle PLA with semi-crystalline PA11 and natural halloysite nanotubes (HNTs). Blending PLA and PA11 at 80:20 ratio leads to the formation of an irregular fibrillar structure due to the viscosity ratio of the two thermoplastics. PLA ductility increases (tensile elongation at break being multiplied by a factor 20), however at the slight expense of strength and stiffness. This fibrillar structure of the PLA/PA11 blend is kept upon addition of HNTs, but the morphology becomes interestingly more regular at 2 wt% HNTs. As predicted by thermodynamics rules, microscopic observations confirm that HNTs are selectively located in the PA11 phase. Such a regular fibrillar structure associated with the polymers interface improvement leads to significantly enhanced toughness of the brittle neat PLA. Elongation at break in tension increases from 3.6% (neat PLA) to 155% (PLA/PA11 + 2wt% HNT) without sacrificing tensile strength or Young modulus. In the same time, impact resistance is multiplied by 2. So, proper selection of bio-based PLA and PA11 blend composition and

addition of naturally available HNTs, which positively alter the microstructure of blend, may effectively result in ‘engineered’ materials with significantly enhanced mechanical properties.

Acknowledgements

Authors would like to thank International Campus on Safety and Intermodality in Transportation (CISIT), Nord-Pas-de-Calais Region and European Community (FEDER). The authors sincerely acknowledge Dr. Rajashekhara Shabadi, Unité Matériaux et Transformations, Université Lille1 (France), for his precious help in TEM observations.

References

- [1] Soulestin J., Prashantha K., Lacrampe M. F., Krawczak P.: Bioplastics based nanocomposites for packaging applications. in ‘Handbook of bioplastics and biocomposites engineering applications’ (Ed.: Pilla S.) Wiley, New York, 76–119 (2011)
DOI: [10.1002/9781118203699.ch4](https://doi.org/10.1002/9781118203699.ch4)
- [2] Rusu D., Boyer S. A. E., Lacrampe M. F., Krawczak P.: Bioplastics and vegetal fiber reinforced bioplastics for automotive applications. in ‘Handbook of bioplastics and biocomposites engineering applications’ (Ed.: Pilla S.) Wiley, New York, 397–449 (2011).
DOI: [10.1002/9781118203699.ch15](https://doi.org/10.1002/9781118203699.ch15)
- [3] Nijenhuis A. J., Colstee E., Grijpma D. W., Pennings A. J.: High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: Thermal characterization and physical properties. *Polymer*, **37**, 5849–5857 (1996).
DOI: [10.1016/S0032-3861\(96\)00455-7](https://doi.org/10.1016/S0032-3861(96)00455-7)
- [4] Pulapura S., Kohn J.: Trends in the development of bioresorbable polymers for medical applications. *Journal of Biomaterials Applications*, **6**, 216–250 (1992).
DOI: [10.1177/088532829200600303](https://doi.org/10.1177/088532829200600303)
- [5] Zhang L., Gon S. H., Lee S. Y.: Miscibility and crystallization behaviour of poly(L-lactide)/poly(*p*-vinylphenol) blends. *Polymer*, **39**, 4841–4847 (1998).
DOI: [10.1016/S0032-3861\(97\)10167-7](https://doi.org/10.1016/S0032-3861(97)10167-7)
- [6] Ebadi-Dehaghani H., Khonakdar H. A., Barikani M., Jafari S. H.: Experimental and theoretical analyses of mechanical properties of PP/PLA/clay nanocomposites. *Composites Part B: Engineering*, **69**, 133–144 (2015).
DOI: [10.1016/j.compositesb.2014.09.006](https://doi.org/10.1016/j.compositesb.2014.09.006)
- [7] Arrieta M. P., Fortunati E., Dominici F., Rayón E., López J., Kenny J. M.: Multifunctional PLA–PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohydrate Polymers*, **107**, 16–24 (2014).
DOI: [10.1016/j.carbpol.2014.02.044](https://doi.org/10.1016/j.carbpol.2014.02.044)
- [8] Derho J., Soulestin J., Krawczak P.: Structural evolution of poly(lactic acid)/poly(ethylene oxide)/unmodified clay upon ambient ageing. *Journal of Applied Polymer Science*, **131**, 40426/1–40426/8 (2014).
DOI: [10.1002/APP.40426](https://doi.org/10.1002/APP.40426)

- [9] Pai F.-C., Lai S.-M., Chu H.-H.: Characterization and properties of reactive poly(lactic acid)/polyamide 610 biomass blends. *Journal of Applied Polymer Science*, **130**, 2563–2571 (2013).
DOI: [10.1002/app.39473](https://doi.org/10.1002/app.39473)
- [10] Feng F., Lin Y.: Structure and property of polylactide/polyamide blends. *Journal of Macromolecular Science Part B: Physics*, **49**, 1117–1127 (2010).
DOI: [10.1080/00222341003609179](https://doi.org/10.1080/00222341003609179)
- [11] Stoclet G., Seguela R., Lefebvre J.-M.: Morphology, thermal behavior and mechanical properties of binary blends of compatible biosourced polymers: Polylactide/polyamide11. *Polymer*, **52**, 1417–1425 (2011).
DOI: [10.1016/j.polymer.2011.02.002](https://doi.org/10.1016/j.polymer.2011.02.002)
- [12] Patel R., Ruehle D. A., Dorgan J. R., Halley P., Martin D.: Biorenewable blends of polyamide-11 and polylactide. *Polymer Engineering and Science*, **54**, 1523–1532 (2014).
DOI: [10.1002/pen.23692](https://doi.org/10.1002/pen.23692)
- [13] Nuzzo A., Coiai S., Carroccio S. C., Dintcheva N. T., Gambarotti C., Filippone G.: Heat-resistant fully bio-based nanocomposite blends based on poly(lactic acid). *Macromolecular Materials and Engineering*, **299**, 31–40 (2014).
DOI: [10.1002/mame.201300051](https://doi.org/10.1002/mame.201300051)
- [14] Nuzzo A., Acierno D., Filippone G.: Clay-filled bio-based blends of poly(lactic acid) and polyamide 11. *AIP Conference Proceedings*, **1459**, 208–210 (2012).
DOI: [10.1063/1.4738445](https://doi.org/10.1063/1.4738445)
- [15] Nuzzo A., Bilotti E., Peijs T., Acierno D., Filippone G.: Nanoparticle-induced co-continuity in immiscible polymer blends – A comparative study on bio-based PLA-PA11 blends filled with organoclay, sepiolite, and carbon nanotubes. *Polymer*, **55**, 4908–4919 (2014).
DOI: [10.1016/j.polymer.2014.07.036](https://doi.org/10.1016/j.polymer.2014.07.036)
- [16] Sumita M., Sakata K., Asai S., Miyasaka K., Nakagawa H.: Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black. *Polymer Bulletin*, **25**, 265–261 (1991).
DOI: [10.1007/BF00310802](https://doi.org/10.1007/BF00310802)
- [17] Wu S.: *Polymer interface and adhesion*. Marcel Dekker, New York (1982).
- [18] Molinaro S.: *Bio-based food packaging films: Influence of formulation and processing on functional properties*. PhD Thesis, University of Udine (2013).
- [19] Lennon P., Espuche E., Sage D., Gauthier H., Sautereau H., Valot E.: Comparison of the wetting behaviour of polyamides presented as particles and films – Influence of a plasma microwave treatment. *Journal of Materials Science*, **35**, 49–55 (2000).
DOI: [10.1023/A:1004728229418](https://doi.org/10.1023/A:1004728229418)
- [20] Wu H., Watanabe H., Ma W., Fujimoto A., Higuchi T., Uesugi K., Takeuchi A., Suzuki Y., Jinnai H., Takahara A.: Robust liquid marbles stabilized with surface-modified halloysite nanotubes. *Langmuir*, **29**, 14971–14975 (2013).
DOI: [10.1021/la4041858](https://doi.org/10.1021/la4041858)
- [21] Dave V., Tamagno M., Focher B., Marsano E.: Hyaluronic acid-(hydroxypropyl)cellulose blends: A solution and solid state study. *Macromolecules*, **28**, 3531–3539 (1995).
DOI: [10.1021/ma00114a006](https://doi.org/10.1021/ma00114a006)
- [22] Nam S. Y., Lee Y. M.: Pervaporation and properties of chitosan-poly(acrylic acid) complex membranes. *Journal of Membrane Science*, **135**, 161–168 (1997).
DOI: [10.1016/S0376-7388\(97\)00144-0](https://doi.org/10.1016/S0376-7388(97)00144-0)
- [23] Yousfi M., Soulestin J., Vergnes B., Lacrampe M.-F., Krawczak P.: Compatibilization of immiscible polymer blends by organoclay: Effect of nanofiller or organo-modifier? *Macromolecular Materials and Engineering*, **298**, 757–770 (2013).
DOI: [10.1002/mame.201200138](https://doi.org/10.1002/mame.201200138)
- [24] Chomat D., Soulestin J., Lacrampe M. F., Sclavons M., Krawczak P.: *In situ* fibrillation of polypropylene/polyamide 6 blends: Effect of organoclay addition. *Journal of Applied Polymer Science*, **132**, 41680/1–41680/13 (2015).
DOI: [10.1002/APP.41680](https://doi.org/10.1002/APP.41680)
- [25] Frieberg B., Kim J., Narayanan S., Green P. F.: Surface dynamics of miscible polymer blend nanocomposites. *ACS Nano*, **8**, 607–613 (2014).
DOI: [10.1021/nn405233a](https://doi.org/10.1021/nn405233a)
- [26] Zhang K., Mohanty A. K., Misra M.: Fully biodegradable and biorenewable ternary blends from polylactide, poly(3-hydroxybutyrate-co-hydroxyvalerate) and poly(butylene succinate) with balanced properties. *ACS Applied Materials and Interfaces*, **4**, 3091–3101 (2012).
DOI: [10.1021/am3004522](https://doi.org/10.1021/am3004522)
- [27] Prashantha K., Lacrampe M.-F., Krawczak P.: Highly dispersed polyamide-11/halloysite nanocomposites: Thermal, rheological, optical, dielectric, and mechanical properties. *Journal of Applied Polymer Science*, **130**, 313–321 (2013).
DOI: [10.1002/app.39160](https://doi.org/10.1002/app.39160)
- [28] Garlotta D.: A literature review of poly(lactic acid). *Journal of Polymers and the Environment*, **9**, 63–84 (2001).
DOI: [10.1023/A:1020200822435](https://doi.org/10.1023/A:1020200822435)
- [29] Lim L.-T., Auras R., Rubino M.: Processing technologies for poly(lactic acid). *Progress in Polymer Science*, **33**, 820–852 (2008).
DOI: [10.1016/j.progpolymsci.2008.05.004](https://doi.org/10.1016/j.progpolymsci.2008.05.004)
- [30] Prashantha K., Lacrampe M. F., Krawczak P.: Processing and characterization of halloysite nanotubes filled polypropylene nanocomposites based on a masterbatch route: Effect of halloysites treatment on structural and mechanical properties. *Express Polymer Letters*, **5**, 295–307 (2011).
DOI: [10.3144/expresspolymlett.2011.30](https://doi.org/10.3144/expresspolymlett.2011.30)
- [31] Schmitt H., Prashantha K., Soulestin J., Lacrampe M. F., Krawczak P.: Preparation and properties of novel melt-blended halloysite nanotubes/wheat starch nanocomposites. *Carbohydrate Polymers*, **89**, 920–927 (2012).
DOI: [10.1016/j.carbpol.2012.04.037](https://doi.org/10.1016/j.carbpol.2012.04.037)

- [32] Liu X., Dever M., Fair N., Benson R. S.: Thermal and mechanical properties of poly(lactic acid) and poly(ethylene/butylene succinate) blends. *Journal of Environmental Polymer Degradation*, **5**, 225–235 (1997). DOI: [10.1007/BF02763666](https://doi.org/10.1007/BF02763666)
- [33] Pothan L. A., Oommen Z., Thomas S.: Dynamic mechanical analysis of banana fiber reinforced polyester composites. *Composites Science and Technology*, **63**, 283–293 (2003). DOI: [10.1016/S0266-3538\(02\)00254-3](https://doi.org/10.1016/S0266-3538(02)00254-3)
- [34] Elwathig H., You W., He J., Yu M.: Dynamic mechanical properties and thermal stability of poly(lactic acid) and poly(butylene succinate) blends composites. *Journal of Fiber Bioengineering and Informatics*, **6**, 85–94 (2013). DOI: [10.3993/jfbi03201308](https://doi.org/10.3993/jfbi03201308)
- [35] Zhang K., Nagarajan V., Misra M., Mohanty A. K.: Supertoughened renewable PLA reactive multiphase blends system: Phase morphology and performance. *ACS Applied Materials and Interfaces*, **6**, 12436–12448 (2014). DOI: [10.1021/am502337u](https://doi.org/10.1021/am502337u)
- [36] Jiang L., Wolcott M. P., Zhang J.: Study of biodegradable polylactide/poly(butylene adipate-co-terephthalate) blends. *Biomacromolecules*, **7**, 199–207 (2006). DOI: [10.1021/bm050581q](https://doi.org/10.1021/bm050581q)
- [37] Ishida S., Nagasaki R., Chino K., Dong T., Inoue Y.: Toughening of poly(L-lactide) by melt blending with rubbers. *Journal of Applied Polymer Science*, **113**, 558–566 (2009). DOI: [10.1002/app.30134](https://doi.org/10.1002/app.30134)