Effect of polymer/organoclay composition on morphology and rheological properties of polylactide nanocomposites

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Abstract

In this work the relationships between system composition, polymer-organoclay interaction, morphology and rheological response, under shear and elongational flow, of different melt compounded PLA/organoclay nanocomposites are investigated, with the aim to properly select the better organoclay for a well specified PLA grade and processing technology. Polylactide nanocomposites are prepared using two commercial polylactide grades (PLA 4032D and PLA 2003D) and two different organomodified montmorillonites (Cloisite 30B and Nanofil SE3010). FTIR analysis evidences the occurrence of stronger polymer/organoclay interactions for the system PLA4032D+C30B, resulting in a higher clay dispersion and exfoliation levels. Moreover, rheological tests at low shear rates show that, if PLA 2003D is used as polymer matrix (differing from PLA4032D by the presence of a high molecular weight tail), a better dispersed nanomorphology can be obtained with Nanofil SE3010, characterized by a double d-spacing compared to Cloisite 30B, despite the higher polar character of this latter nanofiller. On the other hand, elongational rheological measurements evidence for NSE3010 based hybrids a marked extensional thickening, whilst the stronger polar interactions between the phases in both the polylactide grades filled with C30B, determine increments in elongational viscosity, but inhibit the strain hardening behavior.

Keywords: polylactide nanocomposites, organomodifiers, FTIR analysis, dynamic rheology, extensional rheology

1. Introduction

Polylactic acid (PLA) is one of the most promising renewable biodegradable polymers. PLA belongs to the family of aliphatic polyesters derived from α-hydroxyl acids. The building block of PLA (2-hydroxy propionic acid) can exist in optically active D- or L-enantiomers. Depending on the proportion of the enantiomers, PLA of variable material properties can be derived to yield high-molecular-weight amorphous or crystalline polymers. This allows the production of a wide spectrum of PLA polymers to match performance requirements. Properties such as high gloss and clarity, high tensile strength, good heat seal-ability, and low coefficient of friction make PLA a suitable candidate for a wide variety of applications. There are, however, some issues such as a low drawability, unsatisfactory toughness and limited gas barrier properties that should be properly overcome [1]. Moreover, commercial linear PLA grades often do not offer the processability needed for some polymer processing operations involving extensional flow (e.g., film blowing, stretch blow molding, foaming, fiber spinning, thermoforming) owing to their low melt strength and absent or weak strain hardening behavior[1-3]. Copolymerization, blending and filling techniques are generally used to prevail over these drawbacks. Recently, there have been several attempts to broaden the processability and the end-use properties of PLA by developing PLA/clay nanocomposites [4-22].

Significant progress has been made in analyzing the manifold relationships between system composition, processability and morphology of polylactide–silicate nanocomposites, however a general understanding has yet to emerge and some more theoretical and experimental studies are indispensable to be able to properly select the better organoclay for a well specified PLA grade and processing technology. Moreover, for what specifically concerns the rheological behavior of polylactide nanocomposites, scientific works have been mainly concentrated on shear measurements [6-8,17,19], while studies on elongational flow are still scarce and not always coherent on scientific attribution of the observed phenomena [22-25]. Uniaxial elongational flow is at the base of conventional stretching processes and the study of the extensional rheological response of polylactide nanocomposites can provide powerful and precious indications on nanostructural modifications induced by elongational flow and on

manufacturing capability in industrial processes such as film extrusion, thermoforming and fiber spinning. Previous studies have demonstrated that elongational flow can actually modify the nanomorphology of polymer nanocomposites, enhancing exfoliation degree and promoting orientation along stretching direction [26-28]. Applied drawing can also induce clay–clay electrostatic interactions, which can translate into three-dimensional silicate arrangements and/or aggregation of the filler [24-30]. Moreover, in an our recent work the extensional behavior of copolyamide-based nanocomposites was analyzed and correlated to bubble stability in the film blowing processing of these materials [26].

In the present paper polylactide nanocomposites, reinforced with commercially available organoclays, were prepared using a melt intercalation technique. The resins, used as polymer matrices, were two grades of semi-crystalline polylactide acid, PLA 4032D and PLA 2003D, characterized by different amounts of D-isomer and specifically designed by the supplier for different processing operations. The layered silicates, selected as nanofillers, were two montmorillonites, Cloisite 30B (C30B) and Nanofil SE3010 (NSE3010), characterized by different organic modifiers, which provide a more pronounced polar character in the case of C30B and an higher basal interlayer spacing for NSE3010.

A morphological characterization, by TEM and FTIR investigations, was conducted in this study to point out the influence of composition (polylactide grade and type of organic modifier) on the nanostructure of the produced hybrid systems. All the samples were also submitted to rheological measurements, both in shear and elongational mode. The rheological response of the hybrid systems was correlated to the obtained nanostructure and the different polymer-clay affinity.

2. Experimental

2.1 Materials and melt compounding

The polymeric matrices were two grades of semi-crystalline polylactic acid produced by NatureWorks with the commercial names of PLA 4032D and PLA 2003D and characterized by different amounts of D-isomer (respectively 1.5% and 4%).

Two montmorillonites, organically modified with different ammonium salts (Cloisite 30B and Nanofil SE3010), were used as nanofillers. Cloisite 30B (by Southern Clay Products, Inc.), modified by methyl, tallow, bis-2- hydroxyethyl, and quaternary ammonium chloride, has a basal interlayer spacing d_{001}=18.5 Å, whilst Nanofil SE3010 (by Süd-Chemie Company) presents a d-spacing d_{001}=36.0 Å and its basic surface treatment is a dimethyl, di(hydrogenated tallow)alkyl ammonium salt. The chemical structure of the organic modifier for each organoclay is listed in Table 1, according to the data provided by the supplier.

The compounding was conducted using a twin-screw extruder (Dr. Collin GmbH - ZK 25-48D) with co-rotating intermeshing screws (D_{screw}=25 mm, L/D=42). A screw speed of 150 rpm and a temperature profile of 200-200-185-185°C (from hopper to die) were used. Prior to processing, the materials (both the polymers and the nanoclays) were dried in a vacuum oven at 80°C for 18 hours, to avoid bubble formation and polymer degradation during processing.

The hybrids were produced at 4wt % of silicate content by making use of a volumetric feeder. The strand of the extruded material was cooled in a water bath at approx. 15°C and a strand pelletizer (Dr. Collin GmbH CSG 171/2) allowed to produce pellets of suitable size for the characterization.

The effective level of organoclay into each extruded sample was determined by thermogravimetric analysis, which was carried out with a TGAQ500 (TA Instruments), from 25 to 600°C at a thermal scan rate of 10°C/min in nitrogen atmosphere, according to ASTM E1131–03. The amount of residue was corrected for the loss of organic component present, respectively in Cloisite 30B and Nanofil SE3010. Each determination was repeated on five specimens to obtain statistical silicate loading values.

2.2 Characterization

Mel flow index tests were carried out using a CEAST Melt Indexer at 210°C and with a

weight of 2.16 Kg, according to ASTM D1238.

The molecular weights and the molecular mass distributions of polymer samples were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000 - 1,000,000 Å).

Transmission electron microscopy (TEM) analyses were conducted at different magnification levels on the melt-compounded pellets. The images were captured on sections located normal to the extrusion direction, prepared by microtoming of ultra-thin specimens with a Leica Utracut UCT microtome. The morphological parameters (number of silicate platelets per stack, distance between clay particles, etc.) of the nanocomposite samples were evaluated by following the method proposed by Vermogen et al. [31]. Images were taken at different magnifications in order to include in the analysis different types of clay platelets (individual sheets, thinner tactoids, thicker tactoids and agglomerates) to provide a good statistics of the distribution of the filler in the matrix. Around 300 tactoids/platelets were considered for each measurement.

FTIR measurements were carried out on neat matrices and nanocomposites in the range of 4000–650 cm^{-1}, using a Nexus ThermoNicolet spectrometer equipped with a SmartPerformer accessory for ATR analyses. The spectra were collected at 2 cm^{-1} spectral resolution and 64 scans were co-added.

Rheological experiments were conducted with a Rheometric Scientific rotational rheometer, ARES (Advanced Scientific Expansion System) under a nitrogen atmosphere and after drying the samples at 80°C for 18 hours in a vacuum oven in order to prevent moisture induced degradation phenomena. Rheological measurements in oscillatory mode were performed at 190°C in an angular frequency range from 0.1 to 100 rad/s, using 25 mm diameter parallel plates. The deformation of 5% of strain amplitude was determined from strain sweep measurements in order to ensure linear viscoelasticity of the dynamic tests. In order to measure the first normal stress difference (N$_1$), steady shear viscosity tests were also conducted at 170°C from 1 to 10 s^{-1}, using a cone-plate geometry. The diameter of both the

upper cone (cone angle=0.1 radians) and the bottom plate was equal to 25 mm and a gap of 0.0533 mm was set. When the polymer melt is squeezed between the cone-plate geometry, normal stresses will be introduced. Therefore, after material loading a 10 minutes delay was set, before the measurement starts, to relax all the stresses in the sample.

Rheological tests in elongational mode were performed by using a Sentmanat Extensional Rheometer (SER) [32, 33]. This instrument (model SER-HV-A01, manufactured by Xpansion Instruments) was designed for use as a detachable tool on ARES. Samples for testing were prepared by compression molding, using a preheated hydraulic press, and cut into small rectangles with the following dimensions: thickness, width and length of 0.8 mm × 6 mm × 15 mm, respectively, which were specifically chosen within the recommended ranges of sample dimensions for optimum instrument performance [32]. The elongational tests were performed at 180°C and different Hencky strain rates (0.5, 1, and 10 s^{-1}), until the maximum achievable Hencky strain (equal to 3.8).

3. Results and Discussion

The resins, used as polymer matrices in this study, were two grades of semi-crystalline polylactide acid, PLA 4032D and PLA 2003D, characterized by different amounts of D-isomer (respectively $\cong 1,5\%$ and $\cong 4\%$). In particular, PLA 2003D is a general purpose extrusion grade suitable for thermoforming, whilst PLA 4032D is specifically designed to be converted into biaxially oriented films, accordingly to the data provided by the supplier. The layered silicates, selected in this work as nanofillers, were two montmorillonites (C30B and NSE3010) characterized by different organic modifiers (Table 1), which provide a more pronounced polar character in the case of Closite 30B and a higher basal interlayer spacing for Nanofil SE3010.

The proper selection of the more suitable organoclay (C30B or NSE3010) for each PLA grade (PLA 4032D and PLA2003D) represents a key issue in order to enhance processability and/or the performances of the neat polylactide resins. To this purpose a deep investigation of the molecular characteristics of the neat polylactide resins was firstly performed.

Melt flow index (MI) and gel permeation chromatography (GPC) measurements were carried out on both the polylactide grades. The results, reported in Table 2, did not evidence significant differences between the two resins, even if all the moments of the GPC curves for PLA 2003D are slightly higher than those of PLA 4032D.

On this point it is worthy to highlight that, when the differences in the molecular weights and molecular weight distributions (for example by the presence of high molecular weight fractions or branching) are enough small, they can be undetectable by conventional GPC methods or MI measurements, but can be sufficient to affect the elasticity of a polymer melt [34]. In this case, first normal stress difference measurements (N_1) might be necessary to reveal these occurrences, since they are very sensitive to molecular structure parameters and micro-structural changes caused by flow, such as for example large scale disentangling of chains.

In Figure 1 the shear viscosities and the first normal stress differences (N_1) for both the polylactide resins are reported as a function of the shear rate.

While no differences in the shear viscosity of the resins can be observed, at lower shear rates,

PLA 2003D shows significant higher values of N_1 compared to PLA 4032D, that might imply the presence in the first resin of a high molecular weight tail [34].

Shear rheological measurements, in oscillatory mode, were also performed on the neat PLA matrices and the corresponding nanocomposites, in order to investigate the bulk nanostructure of the hybrid systems. In fact, the presence of organoclays in polymeric matrices significantly affects their dynamic rheological behavior as a function of the nanoscale structure and polymer-clay interfacial characteristics.

Figure 2 compares the plots of complex viscosity vs angular frequency for the neat PLA resins and their nanocomposites based on both C30B and NSE3010 organoclays.

While the neat polylactides display a similar dynamic rheological behavior, characterized by a pseudo-Newtonian trend at low angular frequencies, all the nanocomposite samples show an increase of the complex viscosity and a shear thinning behavior that can be related to a good silicate dispersion inside the polymer matrices [35-38]. However, interesting differences among the rheological response of the nanocomposite samples can be put in evidence comparing the curves for the same matrix and for the same nanoclay. In particular, comparing the effect of the different types of organoclay on the dynamic shear viscosity of a fixed matrix, it can be observed that, in the case of the PLA 4032D-based hybrid systems, the C30B nanoclay gives higher increases of η^* and a more pronounced shear thinning behavior, in the whole range of frequencies analyzed. Beside, in the case of the PLA 2003D-based hybrid systems, the NSE3010 gives a stronger shear thinning behavior at low ω, respect to the C30B. Moreover, comparing the effect of the different matrices on the dynamic shear viscosity of nanocomposites filled with a fixed nanoclay, it can be observed that, when the filler is the NSE3010, the PLA2003D-based nanocomposite shows slightly higher η^* values respect to the PLA4032D-based one. On the contrary, when the filler is the C30B, the PLA4032D-based nanocomposite shows markedly higher η^* values respect to the PLA2003D-based one.

Similar observations can be made comparing the behavior of the dynamic storage modulus vs angular frequency for the neat PLA matrices and their nanocomposites, reported in Figure 3. At low frequencies, the G' frequency-dependence of the nanocomposites strongly decreases compared to the neat polymers, suggesting that the addition of both the organoclays

significantly modifies the long-time relaxation of the hybrids, increasing their relaxation times due to the formation of a silicate network. In particular, in agreement with the complex viscosity, the system based on PLA 4032D and C30B is characterized by the highest G' values and a more pronounced pseudo-solid behavior. This can be seen from the lowest G' slope at low angular frequencies, compared to the neat matrices and the others nanocomposites, as reported in Table 3.

The rheological results can be explained considering that the presence of two hydroxyl groups in C30B structure promotes affinity with the C=O bonds present in the PLA backbone, by increasing polar interactions between the phases and favoring the polymer intercalation in the organo-galleries. On the other hand, the presence of a high molecular weight tail in the PLA 2003D resin, as evidenced by the first normal stress difference measurements (Figure 1), could reasonable cause a reduction of the diffusion of the macromolecular chains between the silicate layers. This effect becomes mainly evident using nanofillers with low initial d-spacing. Considering the fillers used in this study, Cloisite 30B is characterized by a half d-spacing compared to Nanofil SE3010 (Table 2), so it clearly comes out that the intercalation of PLA 2003D chains inside the layers of C30B is more difficult respect to NSE3010. This result explains why in the dynamic tests we found a stronger shear thinning trend and a more pronounced solid-like behavior at low frequency range by compounding PLA 2003D grade with NSE3010 instead of C30B (Figures 2 and 3). Whilst no significant differences in the resulting dynamic shear behavior (Figures 2 and 3) can be observed for both the nanocomposite systems based on NSE3010.

In order to directly investigate the silicate distribution/dispersion inside the hybrids in relation to the system composition, TEM microscopy was also carried out on all the melt compounded samples.

TEM images of PLA 4032D nanocomposites filled with C30B and NSE3010 nanoclay are reported in Figure 4.

Both the hybrids were characterized by a mixed intercalated-exfoliated nanostructure. However, a higher degree of silicate dispersion with smaller stacks of intercalated filler was observed for the nanocomposite system with C30B. In particular, TEM micrographs of the

hybrids at higher magnification level (Figure 4 c-d) well evidence in C30B based nanocomposites the presence of intercalated stacks constituted by about 3 silicate layers, whilst NSE3010 hybrids show a significantly higher number of platelets per intercalated tactoids (approximately 12 per stack, calculated as specified in the experimental section). Moreover, a distance of about 500 nm exists between silicate particles (exfoliated platelets and/or intercalated stacks) in NSE3010 hybrids, while for C30B nanocomposites this distance is reduced by half, evidencing in this latter case a better dispersion of the organoclay on nanoscale, accordingly to the dynamic shear reological results (Figures 2 and 3).

TEM images of PLA2003D hybrids, loaded with C30B and NSE3010 nanoclay, are reported in Figure 5.

Both the hybrid systems show a nanoscale morphology comprised of intercalated stacks surrounded by a distribution of exfoliated layers. In particular, slight differences between the samples are evident from the micrographs, with a more uniform size distribution of the silicate particles for the system PLA2003D+NSE3010. This result is in accordance with the rheological behavior of the corresponding nanocomposites (Figures 3 and 4).

A deep investigation of the interactions between the two grades of PLA and the different organoclays was carried out by means of ATR-FTIR analysis. The peak assignments are listed in Table 4, accordingly to the literature [39, 40]. The FTIR spectra of the neat PLA 4032D and its nanocomposites are reported in Figure 6.

Comparing the spectra, it can be observed that typical absorption bands of the montmorillonite (Si-O-Si stretching in the region 1080-950 cm^{-1}) are covered by the saturation of the PLA bands, as expectable [41]. The other signals of the neat PLA remain essentially unaltered in the FTIR spectrum of both the nanocomposites, except for the strong CO band, which is sensitive to the polymer morphology and conformation.

In the case of the PLA 4032D+C30B system this band is shifted toward higher wavenumber, from 1747 to 1751 cm^{-1}. This result may be explained hypothesizing that the confinement of the polymeric chains inside the silicate galleries results in a lowering of their mobility and in a disordering of the polymer chains arrangement, which can account for the decrease (weakening) of the polymer-polymer hydrogen bonding and the consequent strengthening of

the covalent C=O bonds in the nanocomposite, causing them to vibrate at higher frequencies [42].

In the case of the PLA 4032D+NSE3010 system, instead, the CO band is splitted in two signals, one of which remains at the original vibration wavenumber, the other is shifted about 4 cm^{-1} higher. This suggests that only a part of the polymer chains are confined inside the silicate galleries, as a result of a lower degree of polymer-organoclay interaction in this system. These results are coherent with the obtainment of better dispersed PLA 4032D-based nanocomposites using as filler the Cloisite 30B instead of Nanofil SE3010, as well evidenced by rheological and TEM characterization of these hybrids (Figures 2, 3 and 4).

FTIR spectra of PLA 2003D neat matrix and its nanocomposites are compared in Figure 7.

Similarly to what was already found in the case of PLA 4032D-based systems, all the samples exhibit the same absorption bands with no change in their shape and no shift in position except for the CO one. In particular, for both the PLA 2003D+C30B and PLA 2003D+NSE3010 nanocomposites the CO band is splitted in two signals, one of which remains at the original vibration wavenumber, the other is shifted about 4 cm^{-1} higher. This finding is coherent with the similar nanomorphology obtained for both the PLA 2003D based systems, as evidenced by the results of the morphological characterization of the samples reported in Figure 5.

The effect of system composition (PLA grade and organoclay type) on the rheological response of the nanocomposites was further analyzed by performing elongational flow tests.

On the other hand material response to extensional deformations is of particular interest in many important polymer processing operations.

Figure 8 a-b report the elongational viscosity curves as a function of time and at different Hencky strain rates for PLA 4032D and PLA 2003D respectively. In particular, the uniaxial elongational tests were performed at strain rates $\geq$0.5 s^{-1}.

For both the systems, the extensional viscosity in the linear region increases with time and it isn't affected by the Hencky strain rate. The results of the elongational tests for pure PLA 4032D show no strain hardening in the entire range of applied strain rates (Figure 8a). The linear structure of PLA 4032D is responsible for its no strain hardening behavior under

uniaxial extensional flow. Beside, in Figure 8b pure PLA 2003D shows a strain hardening behavior. In particular, by comparing the η_E^+ plots for the neat matrices, it emerges that, in the linear region, the extensional viscosity of PLA 2003D is comparable with PLA 4032D, in agreement with the shear viscosity behavior (Figure 1). Moreover, it is interesting to note that, at Hencky strain of about 1.5, the elongational viscosity of PLA 2003D rapidly increases, implying the occurrence of strain hardening. In literature it is well known that extension thickening is exhibited when the rate of deformation considerably exceeds the rate of molecular relaxation. In the case of the resin PLA2003D, its strain hardening behavior can be reasonably attributed to the presence of a high molecular weight fraction, as already evidenced in this work by N_1 measurements (Figure 1) and also supported by other findings in literature [43, 44].

In Figure 9 a,b the elongational viscosity curves, at an Hencky strain rate of 0.5 s^{-1}, for polylactide nanocomposites based on PLA 4032D and PLA 2003D are reported, respectively. NSE3010 based hybrids show viscosity similar to the neat matrices in the linear region and a strain hardening behavior in the region at long times. This peculiar extensional thickening behavior can be related to the presence of silicate platelets, which build up three-dimensional arrangements, hindering extensional flow similarly to branches of macromolecular chains. In other words, in hybrid systems characterized by a low polymer-clay affinity, such as NSE3010-based nanocomposites, uniaxial elongational flow seems to promote edge-to-face-electrostatic interactions between silicate platelets, as also observed in other systems [ref].

Conversely, the nanocomposites with C30B exhibit extensional viscosity values higher than the neat polymers and no strain hardening behavior. In this case, the strong polymer-clay affinity of C30B with the polylactide resins shields the electrostatic clay-clay interactions, responsible for the strain hardening phenomenon, favoring at high Hencky strains the alignment of silicate layers toward the stretching direction as consequence of polymer chains alignment.

4. Conclusions

The results of this work evidenced that even small differences in the molecular structure of the polylactide resin, affect the developed nanomorphology and processability as a function of the specific characteristics of the selected organoclay. In particular, nanocomposites at a constant silicate loading were produced by melt compounding using two commercial polylactide grades (PLA 4032D and PLA 2003D) and two different organo-montmorillonites (Cloisite 30B and Nanofil SE3010). FTIR analysis evidenced the strongest polymer/organoclay interactions for the system PLA4032D+C30B, resulting in a higher clay dispersion, as revealed by the morphological characterization of the hybrids in both solid and melt state. However, if PLA 2003D is used as polymer matrix, a better dispersed nanomorphology can be obtained with Nanofil SE3010, characterized by a double d-spacing compared to Cloisite 30B, despite the higher polar character of this latter nanofiller.

On the other hand, the structural modifications, induced by stretching, in the polylactide based nanocomposites analyzed in this study, were proved to strongly influence properties such as extensional viscosity, and strain hardening behavior that are fundamental for assessing their performances in processing operations where extensional flow is mainly involved. The entity of these modifications was highly dependent on the polymer–clay affinity. In particular, NSE3010-hybrids evidenced a marked extensional thickening, whilst the stronger polar interactions between the phases in both the polylactide grades filled with C30B, determined increments in elongational viscosity, but inhibited the strain hardening behavior.

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