Multi-parameter in-process monitoring of clay dispersion during melt compounding with PLA

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Abstract. The time evolution of organoclay particle size and volume fraction, as well as the shear viscosity, are measured in-line for a series of Poly(lactic acid)/organoclay composites, using a rheo-optical die coupled to a prototype modular co-rotating twin screw extruder. The small angle light scattering patterns and light attenuation recorded during transient experiments indicate that clay dispersion develops through melt intercalation between the clay galleries, thereby expanding the aggregates size, and eventually leads to aggregates break-up, i.e., exfoliation. The simultaneous recording of shear viscosity also indicates that smaller viscosities promote a faster melt intercalation and exfoliation but hinder the extent of clay dispersion. The methodology used in the present study validates the well accepted mechanism for clay dispersion and can be applied straight away for the monitoring of PNC manufacturing during practical production.

Keywords: nanocomposites, industrial applications, extrusion, exfoliation, in-process monitoring

1. Introduction

The ‘nano effect’ that enhances the properties of polymer/clay nanocomposites (PNC) is intimately related with the extent of the dispersion of the layered clay tactoids in the polymer matrix via intercalation and exfoliation [1–4]. Thus, monitoring the level of clay dispersion during the manufacture of PNC is central to the production of materials with adequate performance [5, 6]. However, the characterization of PNC produced by twin screw extrusion has shown somewhat contradictory results (see e.g. [7] and references therein), probably due to the different thermomechanical histories associated with sample preparation. This is particularly relevant for the rheological testing, even if it is a well-established technique for the assessment of clay dispersion [8–11], as reagglomeration or dispersion might develop during sample preparation. In addition, the rheological study of PNC containing biodegradable matrices

such as poly(lactic acid) (PLA) might bring further difficulties due to their limited thermal stability.

Alternatively, coupling experimental techniques to compounding extruders for the in-situ characterization of PNC, i.e. in-process monitoring, is an attractive route to by-pass sample preparation and the inherent morphological changes. Light-based techniques are particularly interesting for this purpose, as they allow for in-line implementation, i.e., measurements are made in real-time and directly in the main flow channel, without interfering with the flow.

Light attenuation has been proposed to monitor clay exfoliation. It has been reported that during transient experiments where the feeding of the extruder is switched from the matrix to the PNC, or between different PNC formulations, the scattering of light by big enough particles is responsible for the time evolution of the light attenuation [12–14]. Using a modified Beer’s law for light attenuation (relating the

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transmitted light with the volume fraction of the particles [12]) and a calibration with non-exfoliated and totally exfoliated PNC, the ratio of the attenuated light intensity to the initial light intensity recorded during steady extrusion allows for the in-line tracking of the particle volume fraction in the PNC. Next, upon subtracting the particle volume fraction computed above to the total clay volume fraction set in the PNC formulation, an estimation of the extent of exfoliated clay is obtained.

However, in practice, this approach is often oversimplified, mainly because calculations are made based on particle volume fraction alone, i.e., the contributions from clay particle size to light attenuation are neglected. Indeed, under the Rayleigh-Debye-Gans approximation ($2\pi R/\lambda[n_p/n_m - 1] \ll 1$, where λ is the light wavelength, n_p and n_m are the particle and matrix refractive indexes respectively [15]), the light attenuation (or turbidity) τ by a sphere with radius R is given by Equation (1) [16]:

$$\tau = \frac{1}{D} \ln \frac{I_0}{I} = 6 \left(\frac{2\pi}{\lambda} \right)^2 \phi \left(\frac{n_p}{n_m} - 1 \right)^2 R \quad (1)$$

where D is the sample thickness, I and I_0 are the transmitted and impinging light intensities, respectively, and ϕ is the particle volume fraction. This approximation is valid for particles ranging from 100 nm to 10 microns, when visible light is used to illuminate the sample, and for nearly matching refractive indexes [16, 17]. Thus, an assessment of clay dispersion by light attenuation requires separating the effects of R and ϕ . In addition, the use of Equation (1) implies checking for the lack of flow-induced structural orientation (which leads to anisotropic light scattering) and absence of multiple scattering.

In the present study, the evolution of R and ϕ , as well as of the shear viscosity, are measured in-line for a PLA/organoclay system, using a rheo-optical die designed to record simultaneously small angle light scattering (SALS) patterns and flow curves, coupled to a prototype modular co-rotating twin screw extruder [18, 19]. The tool box presented in earlier works [18–20] is here augmented with an in-line light attenuation measurement. This new set-up allows for the independent in-process measurement of R and ϕ . The data presented here thus contribute to a better assessment of clay dispersion, as they do not rely on the assumptions mentioned above. As a result, all rheological and structural parameters are assessed in-line during extrusion, thereby by-passing

all experimental issues associated with thermosensitive materials such as biodegradable PNC.

2. Experimental

An extrusion grade poly(lactic acid) powder (Ingeo™ Biopolymer 4043D from NatureWorks, USA) was obtained from Resinex, Belgium. This grade was delivered with the following specifications: melt flow rate (MFR) of 6 g/10 min (210 °C, 2.16 kg), density of 1.24 g/cm³ and melting point of 145–160 °C. The nanoclay was a montmorillonite, modified by dimethyl-dihydrogenated tallow ammonium, Dellite 72T, supplied by Laviosa Chimica Mineraria, Italy. In spite of the thermal degradation of the surfactant triggering the degradation of the polymer matrix [21], Dellite 72T was selected as the organic modification of the clay allows for the expansion of the clay interlayer spacing, giving way to the intercalation of polymer chains into the clay galleries and thus enhancing the dispersion of the filler [1, 3, 7, 9, 12, 21]. Before processing, PLA and clay were dried under vacuum at a temperature of 90 °C for two hours and at 120 °C overnight, respectively.

The experimental set-up used for the in-line tracking of PNC dispersion is presented in Figure 1. An in-line rheo-optical double slit die was coupled to a prototype modular intermeshing co-rotating twin screw extruder (with a screw diameter of 13 mm and a length to diameter ratio (L/D) of 27) and mini-gear pump (MS0525-C-230-CCW-S Xaloy Europe GmbH, Germany), which was used to minimize possible surging. In all experiments, the screw speed and temperature profile were kept constant at 40 rpm and 190 °C, respectively, whereas the mini-gear pump was operated at 9 rpm. Under these conditions, the shear rates developed are of the same order of magnitude of those found in larger machines operating under normal conditions. Also, the screws contain mixing sections consisting of staggered kneading disks that are efficient in promoting dispersion.

The design, construction and rheological validation of the double slit die have been reported elsewhere [19]. In short, the die consists of 2 slits allowing for the independent rheo-optical measurement and production of rectangular tapes, respectively, while maintaining constant extrusion conditions (feed rate and screw speed). The flow rate in the measuring slit is varied by a valve positioned at its entrance, whereas a second valve balances the flow rate in the tape production slit to keep a constant pressure at the

Figure 1. a) Photograph of the experimental set-up. 1: volumetric feeder (the second feeder is not pictured for the seek of clarity). 2: twin screw extruder. 3: mini gear pump. 4: double slit rheo-optical slit die. 5: pressure transducer to monitor the pressure at the exit of the gear pump. 6: pressure transducers for the rheo-optical channel. 7: He-Ne laser. 8: pinhole. 9: CCD camera. 10: screen to collect SALS patterns. 11: photo detector for turbidity measurements. 12: beam splitter. b) Schematic diagram of the experimental set-up. Numbers have the same meaning as in a).

extruder/gear pump outlet. Consequently, changes in shear rate in the measuring channel can be achieved under constant thermomechanical conditions in the extruder. The rheo-optical slit is equipped with 2 melt pressure transducers (to compute a pressure drop for each flow rate) and 2 optical windows (for laser light transmission or optical microscopy). The optical train for SALS has been described elsewhere [18], and is here augmented with a beam splitter and a photodetector (DET-100-002 Hinds instruments, USA) placed at 45° with respect to the light path for the simultaneous recording of turbidity (see Figure 1).

The experimental procedure followed here replicated the transient extrusion experiments adopted in earlier studies [12–14]. PLA was fed at a flow rate of 120 g/h into the extruder using a miniaturized volumetric feeder (DMV 18 V, Moretto, Italy). When viscosity readings in the double slit die reached steady state, PLA feeding was stopped and a polymer/clay premix with a preset clay concentration (0.5, 1, 2.5 or 5 wt%) was immediately fed at the same flow rate (120 g/h) using a second volumetric feeder (Piovan MDP1). This defined the start of the experiment. The initial clay volume fraction ϕ_i is given by Equation (2):

$$\phi_i = \frac{w}{w + \frac{\rho_C}{\rho_{PLA}}(1 - w)} \quad (2)$$

where w the preset clay weight fraction in the PNC, ρ_{PLA} and ρ_C the density of PLA and clay, respectively. During the procedure, turbidity τ and pressure

drop ΔP were continuously measured and SALS patterns were captured every minute. Intensity profiles extracted from the circular average of the isotropic SALS patterns were analyzed with the Debye-Anderson-Brumberger (DAB) Equation (3) [25]:

$$I_q = \frac{A}{(1 + (qR)^2)^2} \quad (3)$$

where A is a constant and q is the scattering vector that relates to the scattering angle θ through $q = (4\pi n \sin(\theta/2))/\lambda$, where n is the refractive index of the PNC. The values of R and τ are then inserted in Equation (1) to compute the volume fraction of particles ϕ at all times. The initial clay volume fraction is then used to calculate the percentage of dispersed clay at 40 minutes using the following relationship: $E = (\phi_i - \phi(40 \text{ minutes}))/\phi_i \cdot 100$.

To support the interpretation of the in-line data, PNC extrudates (rectangular tapes) were further characterized by off-line testing. Rotational rheometry (ARG2, TA instruments, USA) was carried out at 190°C to quantify the PNC thermal degradation, by performing time sweep experiments with a small amplitude oscillatory shear of 5% at a frequency of 1 Hz. Extrudate samples were loaded between the preheated plates (25 mm diameter) and 2 minutes were left for thermal equilibrium and sample relaxation at the set gap (1 mm) before starting the time sweep experiments. Melt intercalation was assessed by wide angle X-ray diffraction (WAXD), using a Bruker D8

Discover diffractometer (lambda source of 0.154 nm), with a scanning range from $2\theta = 1.5$ to 5° with 0.04° steps. X-ray analysis was performed at room temperature for Dellite 72T powder, PLA and PNC extrudates collected at different times. The spatial distribution of nanoclay in the matrix was assessed using scanning electron microscopy (SEM). The cross section of PNC extrudates fractured in liquid nitrogen was imaged with a scanning electron microscope (Quanta 200 ESEM, FEI, Hillsboro, Oregon USA), using an accelerating voltage of 9.00 kV and secondary electron imaging mode.

3. Results and discussion

Figure 2 shows the time evolution of the pressure drop ΔP , transmitted light intensity I and SALS patterns acquired from the instant a polymer/clay pre-mix was fed into the mini-extrusion line. The data are scaled with respect to the signals recorded for neat PLA (ΔP_{PLA} , I_0). After a time lag of 10 minutes corresponding to the average residence time of the material in the extruder (4 minutes) and gear pump (6 minutes), both $\Delta P/\Delta P_{\text{PLA}}$ and I/I_0 signals drop. The descent is steeper and more pronounced as more clay is incorporated in the PNC. Viscosity enhancement by the presence of solid fillers is usually expected [22], but several phenomena, including wall slip or the well-known thermal degradation of PLA [23, 24] favored by the addition of clay, may be put forward to rationalize the decrease in $\Delta P/\Delta P_{\text{PLA}}$ with increased clay content. These will be discussed below, taking on board results from optical data and off-line rheometry. All SALS patterns in Figure 2 show

isotropic features, thus suggesting the absence of flow-induced structural orientation of clay and thereby validating the use of Equation (1) in the following analysis.

Figure 3 shows examples of fits of Equation (3) to intensity profiles measured at steady state for all studied PNC. Besides the good quality of the fits resulting in less than 1.5% error in the determination of R , Figure 3 indicates that the PNC containing 5 wt% clay scatters as much light as the PNC containing 2.5 wt%. Multiple scattering by the clay particles could explain the saturation in light intensity for all

Figure 3. SALS intensity profiles measured at steady state condition for PNC with 0.5 wt% (squares), 1 wt% (circles), 2.5 wt% (up triangles) and 5 wt% (diamonds) clay content. Lines are fits of Equation (3) to the data. Inset: scattered intensity measured at $q = 2 \mu\text{m}^{-1}$ as a function of the clay content in wt%. The line is a guide to the eyes.

Figure 2. Time evolution of the pressure drop ΔP normalized by the pressure drop measured with neat PLA, ΔP_{PLA} (a) and of the transmitted light intensity I normalized by the light intensity transmitted by neat PLA, I_0 (b). Time zero corresponds to the instant when PNC is fed in lieu of PLA. SALS patterns recorded at 1 min (corresponding to neat PLA light scattering pattern), at $I/I_0 = 0.5$ and at steady pressure drop reading are also reported in (b).

q . The inset to Figure 3 confirms this scenario as departure from a linear relationship between the clay content and the light intensity scattered at $q = 2 \mu\text{m}^{-1}$ is evident beyond 2.5 wt%. Thus, R values measured for 5 wt% clay are only qualitative as multiple scattering causes a deceptive reduction in particle size [15, 20].

Figure 4 offers a comparison between the time evolution of the turbidity τ and the average clay particle size R . After 10 minutes, τ shows a monotonic increase with time, which corresponds to a progressive increase in R . This probably corresponds to polymer chains intercalating via diffusion within the individual platelets of the clay tactoids. Subsequently, R decreases before reaching a stationary value at longer times, which coincides with a slower increase in τ followed by a steady state plateau. The transients are accelerated when more clay is added to the PLA matrix, as more and larger particles (R varies between 0.73 ± 0.02 micron for 0.5 wt% clay and nearly 0.9 micron at larger clay contents) reach the rheo-optical die. As a result of the faster transient, the initial increase in R is barely probed for samples formulated with 2.5 and 5 wt% clay. In addition, as discussed above, SALS data for the latter are subjected to multiple scattering (see inset to Figure 3), which results in a spurious reduction of 0.05 micron in the stationary value of R . Overall, data in Figure 4 suggest that faster $\Delta P/\Delta P_{\text{PLA}}$ and I/I_0 transients seen in Figure 2 relate to faster time evolutions in average particle size and to larger particles. A faster PLA chain diffusion into clay galleries favored by a

Figure 4. Time evolution of turbidity τ (lines) and particle size R (symbols) for PNC with 0.5 wt% (squares, solid line), 1 wt% (circles, dashed line), 2.5 wt% (up triangles, dotted line) and 5 wt% (diamonds, dashed-dotted line) clay content.

reduced viscosity could explain the data reported in Figures 2 and 4.

At this stage, it is important to characterize the morphology of the PNC, in order to confirm the generally accepted mechanism for clay dispersion in model systems, involving intercalation and exfoliation [26, 27], and correlate the latter with the data in Figure 4. For clay contents below 2.5 wt%, X-ray spectra of PNC extrudates sampled at different times were featureless. Full clay exfoliation could explain such results. However, SEM pictures of PNC extrudates with 0.5 wt% clay reveal the presence of particles larger than 1 micron, as shown in Figure 5. Thus, the detection limit of the diffractometer seems to be the source for the absence of peaks in WAXD spectra of PNC at lower clay contents. For more concentrated PNC, WAXD spectra indicate that melt intercalation occurs continuously until a steady nanostructure is reached. This is illustrated in Figure 6 for PLA compounded with 2.5 wt% clay, where the d_{001} reflection is seen to shift to smaller angles with processing time. The shift to smaller angles in Figure 6 relates to an increase in the clay interlayer distance d . Similar results were found for PNC extrudates containing 5 wt% clay (see Figure 7), demonstrating the progressive increase in clay interlayer distance d from 2.9 nm at shorter times (which is roughly the value measured for the clay powder received, see the horizontal line in Figure 7) to 3.6 nm at longer times. Thus, polymer diffusion within the clay galleries develops progressively, leading to melt intercalation and the first increase in clay particle size evidenced in Figure 4. As suggested in Figure 7 by the progressive narrowing of the width of the d_{001} reflections with time (the narrower the width, the smaller the number of platelets in a clay stack [27]), clay stacks containing a smaller number of platelets are formed at longer times. These are probably formed due to partial delamination or exfoliation of melt intercalated layers, thereby explaining the reduction in R seen in Figure 4.

Since both R and τ data have been acquired separately (see Figure 4), they can now be inserted in Equation (1) to compute the time evolution of the particle volume fraction $\phi(t)$ given in Figure 8. Figure 8 embodies the in-process monitoring of clay dispersion, as it offers a direct and simultaneous information about $\phi(t)$ and the apparent shear viscosity $\eta_{\text{app}} = \Delta P/Q$ measured at an apparent shear rate of 23 s^{-1}

Figure 5. SEM pictures of the cross section of PNC extrudates with 0.5 wt% clay (a) and with 2.5 wt% clay b). Scale bar is 10 µm. The inset in b) is a zoom of the SEM picture (scale bar indicates 2 microns) where white arrows point to delaminated stacks within a clay particle.

for all PNC except for 5 wt% clay, as multiple scattering hinders the use of Equation (1) for this system. The drop in η_{app} with time seems to be related to the continuous increase in particle volume fraction. Thus, one might try to correlate the corresponding steady state values of both parameters at longer time, as to examine the effect of clay content on the relative drop in shear viscosity $\Delta\eta_{app} = \eta_{app}(10 \text{ minutes}) - \eta_{app}(40 \text{ minutes})$ and on the percentage of dispersed clay E . E is not to be identified with a specific degree of clay exfoliation [13], as particles with sizes below the detection limit of SALS (roughly 100 nm in the

present case [17]) contribute to this percentage together with fully exfoliated clay platelets. It is worth noting here that the surface fraction of clay particles (with areas larger than $0.12 \mu\text{m}^2$ corresponding to particles with R larger than 100 nm) represents $0.66 \pm 0.1\%$ of the analyzed area in sections of extrudates of PNC with 2.5 wt% clay (a total of 10 SEM images similar to those displayed in Figure 5 were analyzed). This corresponds to $73.3 \pm 3.9\%$ of dispersed clay. A similar SEM analysis of extrudates from the PNC containing 0.5 wt% clay returns a percentage of dispersed clay of $79.3 \pm 1.9\%$. These values are in

Figure 6. WAXD spectra of PNC extrudates with 2.5 wt% clay collected at 11 minutes (open circles), 17 minutes (open diamonds), 27 minutes (open triangles) and 39 minutes (open squares); filled circles present the WAXD spectrum of clay powder.

Figure 7. Time dependence of the inter lamellae distance d (triangles) and of half height width HHV of the d_{001} reflection peak (squares) in PNC with 2.5 wt% clay (solid symbols) and 5 wt% clay (open symbols).

Figure 8. Time dependence of the volume fraction in clay particles ϕ (b) and of the apparent shear viscosity η_{app} (a) for PNC containing 0.5 (squares), 1 (circles) and 2.5 (triangles) wt% clay. The inset in (b) presents the relative drop in apparent viscosity $\Delta\eta_{app}$ (squares) and the degree of clay dispersion E (triangles), both measured at steady state, as a function of the initial clay volume fraction ϕ_i .

fair agreement with E values computed from SALS data and reported in the inset to Figure 8b. This plot shows that the relative drop in shear viscosity $\Delta\eta_{app}$ increases with ϕ_i but does not correlate with the non-monotonic dependence of E with ϕ_i . Therefore, for this biodegradable PNC, in-line measurement of

pressure drop cannot be simply used to assess the extent of clay dispersion and exfoliation.

As far as the decrease of η_{app} with clay content is concerned, three tentative explanations can be put forward. First, a lubrication effect of the clay caused by the migration of particles towards the walls of the

Figure 9. SEM pictures of extrudates of PNC with 2.5 wt% clay imaging areas near the die wall (a) and in the bulk of the extrudate (b). Scale bar 5 μm .

slit can contribute to a reduced apparent viscosity [28]. However, a statistical analysis of SEM images taken at different locations within extrudates cross sections (see examples of such images in Figure 9 for the PNC formulated with 2.5 wt% clay) does not seem to indicate such particle migration. Second, PLA confinement between clay particles could lead to local shear rate enhancement in the polymer matrix. Such enhancement, combined with the shear thinning viscosity of a PNC melt, could result in an effective reduction in the steady shear viscosity measured at a single flow rate. Yet, flow curves measured in-line, and presented in Figure 10 for neat PLA and PLA formulated with 1 wt% clay, show that PNC are essentially Newtonian fluids for the range of shear rates and clay contents studied. This behavior is in harmony with the absence of flow-induced clay orientation documented by isotropic SALS patterns in Figure 2, and rules out this hypothesis. Third, PLA degradation, possibly accelerated by the degradation of surfactants used to modify the clay [21], could result in chain scission and thus loss of viscosity. Indeed, results from rotational rheometry shown in the inset to Figure 10 and performed on PNC extrudates, do indicate that the thermal degradation of the PLA matrix is faster when more clay is added to the PNC. Therefore, the in-process determination of η_{app} allows monitoring the PNC degradation, as clay

exfoliation does not simply relate to PNC rheology (see inset to Figure 8b) for this specific bionanocomposite. The accelerated PLA degradation in the presence of clay surfactant also explains the faster decrease in R for larger clay content, as smaller PLA chains diffuse more easily within clay aggregates and galleries,

4. Conclusions

The use of a rheo-optical die coupled to a prototype twin screw extrusion line allowed for the first time the in-process monitoring of flow curves and extent of clay dispersion in a set of Poly(lactic acid)/organoclay composites. The separation of effects from clay particle size and volume fraction is performed by analyzing the SALS patterns measured in-situ together with light attenuation. As a result, the true volume fraction of clay aggregates can be computed during transient experiments performed with PNC with less than 5 wt% clay to avoid multiple scattering.

The time evolution of the multiple parameters acquired during the melt processing of these thermomechanically sensitive PNC confirms the well accepted dispersion mechanism involving intercalation and exfoliation [23, 24]. The in-process monitoring of shear viscosity confirmed that faster diffusion of smaller polymer chain (due to PLA thermomechanical degradation) promotes a faster clay dispersion. However, the concomitant reduction in melt viscosity does not favor clay exfoliation and thus does not improve the level of clay dispersion.

Overall, the methodology validated in the present study with transient experiments can be applied straight away for the monitoring of PNC manufacturing during practical production.

Figure 10. Flow curves measured in-line for the neat PLA (solid squares) and the PNC formulated with 1 wt% clay (open squares). Inset: time dependence of the reduction in the complex dynamic viscosity $\eta_{red} = |\eta^*(t)|/(|\eta^*(t=0)|)$, measured at 1 Hz with a 5% sinusoidal deformation. PNC with 0.5 wt% (squares), 1 wt% (circles), 2.5 wt% (up triangles) and 5 wt% (diamonds) clay content.

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