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Structure and properties of nylon 6–clay nanocomposites: effect of temperature and reprocessing

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Abstract Melt-compounding is a technique which has been commonly used for producing polymer–clay nanocomposites with enhanced mechanical, thermal, and physical properties. Twin-screw extruders have been found to effectively exfoliate the clay platelets due to their high shear intensity. However, concerns about polymer and organoclay degradation have been raised in some studies. In this investigation, a composite of nylon 6–Cloisite 30B with fully exfoliated and well-dispersed clay particles was produced using a single-screw extruder and hence with limited polymer degradation. We show that processing temperature plays an important role in enhancing dispersion and that reprocessing at a higher temperature can enhance both dispersion and exfoliation and thus can result in composites with superior properties. We attempt to elucidate how the change in melt viscosity—coupled with the change in processing temperature—affects clay exfoliation and dispersion.

Introduction

Since the pioneering work by Toyota in 1989, polymer–clay nanocomposites (PCN's) have received considerable interest from both research and industrial communities. Their improved mechanical and thermal properties as well as their increased resistance to flammability and gas permeability have been reported by many researchers [1–5]. Such improvements put PCN's forward as an attractive alternative to conventional microcomposites.

Different synthesis and processing techniques are used for obtaining PCN's. The choice of technique depends on the type of polymeric matrix used, the type of clay, as well as the required structure of the final composite [2, 6, 7]. In this respect, melt compounding techniques using conventional polymer processing techniques—especially extrusion—have been widely used because of their availability, simplicity, and low cost [1–7]. Moreover, one of the widely researched composites is that composed of smectite clays, particularly montmorillonite, with nylon 6. This is instigated by the early success of Toyota in developing montmorillonite–nylon 6 nanocomposites exhibiting greatly enhanced thermal and mechanical behavior [1–7]. For these nanocomposites, and generally for ones incorporating smectite clays, it is well documented in the literature that an exfoliated structure, where the clay layers are pushed completely apart within the polymer matrix to result in a disordered array, offers superior enhancements in behavior than an intercalated one, where the polymer intercalates the clay layers which remain stacked [2, 4, 7]. In order to improve the compatibility between the hydrophilic surfaces of the smectite clay layers and the hydrophobic polymer matrix, therefore improving exfoliation/intercalation, the clay layers are organically modified, typically with alkylammonium or alkylphosphonium cations [7]. These clays are typically referred to as organoclays.

The effect of the processing technique on the degree of exfoliation has been studied by several researchers. Many investigations compared both single- and twin-screw

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extruders. In one of the earliest reported studies, Cho and Paul [8] prepared composites of nylon 6 and different types of fillers (Cloisite Na+, organoclay, and glass fiber) by melt compounding using both twin- and single-screw extruders. Single-screw extrusion of the organoclay nanocomposite resulted in a mixture of exfoliated as well as undispersed particles. The poor exfoliation in single-screw extruded samples was attributed to the insufficient amount of shear and the short residence time. The effect of the intensity of shear and residence time on the degree of dispersion was later studied by Dennis et al. [9] who melt blended two types of organoclays (15A and 30B) with nylon 6 using four different types of screw extruders (one single and three twin with different screw configurations). Similar to the investigation by Cho, samples prepared using the single-screw extruder were found to be only partially delaminated in spite of the longer residence times used. On the other hand, a clear trend of improved delamination as residence time increases was observed for 15A clay compounded in the twin-screw extruder. The studies by Cho and Paul [8] and Dennis et al. [9] both pointed toward a desired balance between residence time and shear stress in order to achieve better delamination and dispersion of the clay layers. A similar conclusion was also made by Fornes et al. [10].

A more recent investigation by Yang and Ozisik [11] who investigated, among others, the effect of processing conditions on nylon 6 nanocomposites reported that once a critical morphology is established, longer residence times at the same shear stress level do not have any effect on dispersion. The effect of the number of extrusion cycles in both single- and twin-screw extruders on silicate nanodispersion was the focus of another recent study by Russo et al. [12]. They found that reprocessing with a single-screw extruder results in re-agglomeration of the silicate layers; attributed to a possible degradation of the organic part of the clay. Reprocessing in the twin-screw extruder, on the other hand, was found to lead to enhanced dispersion. Matrix degradation was also observed and attributed to the high shear stress in twin-screw extruders which resulted in chain scission. Thus, two opposite phenomena seem to be at play: enhanced dispersion on one hand and matrix and organoclay degradation on the other.

In addition to clay exfoliation and dispersion, different techniques were used to study clay orientation within the polymer matrix. For example, Loo and Gleason [13] used a combination of Fourier transform infrared (FTIR) and transmission electron microscopy (TEM) analysis to analyze the clay orientation distribution in thin films of nylon 6–5 wt% MMT produced by spin casting. In another study, Shen et al. [14] used nanoindentation techniques to evaluate the mechanical properties of injection-molded nylon 6–clay nanocomposites parallel and perpendicular to the injection direction and observed superior mechanical properties in the flow direction which was attributed to processing-induced orientation of the clay and the crystallinity of the polymer.

This study aims at complementing this body of work. In this respect, it investigates the effect of processing temperature and reprocessing on the structure and properties of the nanocomposite of an organo-montmorillonite clay (Cloisite 30B) and nylon 6, prepared by melt blending in a single-screw extruder. The morphology and properties of the nanocomposite were studied by X-ray diffraction (XRD) analysis, TEM, nanoindentation, and melt flow index (MFI) determination.

Experimental

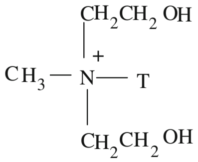
Materials used

Nylon 6 (3 mm pellets) was obtained from Sigma-Aldrich. Organically modified sodium-based montmorillonite with an average particle size of 7 µm (Cloisite 30B) was purchased from Southern Clay Products, Inc., USA. Table 1 presents the specifications of the Cloisite 30B used.

Sample preparation

Nylon 6 pellets and clay powders were first dried under vacuum for 24 h at 90 °C in order to reduce moisture

Table 1 Clay mineral specifications

	Compatibilizer	Gallery d-spacing d_{001} (Å)	Organic content (mass%)
Cloisite 30B	 **T = ~ 65% C_{18}, ~ 30% C_{16}, ~ 5% C_{14}**	18.5	28

content and thus avoid bubble formation during processing. Composite samples of 5 wt% Cloisite 30B were first prepared by hand mixing the clay and the nylon followed by melt processing in a single-screw extrusion (The J.Clytel MFG. Cleveland Ohio: screw length = 40 cm, diameter = 2 cm) at a constant rotational speed of 40 rpm, and a residence time of 4 min. Powders were fully fed into the hopper, and two different compounding temperatures were used: 230 and 250 °C. Pure nylon samples were also prepared under the same conditions and used as control samples. To avoid processing-induced clay orientations and thus anisotropic properties in the samples, as observed by Shen et al. [14], extrudates were then crushed and molded at 240 °C under a pressure of 55 bars held for 1 min. This resulted in samples PA6/230 and PA6-30B/230, as well as PA6/250 and PA6-30B/250 processed at compounding temperatures of 230 and 250 °C, respectively, in addition to samples PA6/230/250 and PA6-30B/230/250 processed at a compounding temperature of 230 °C then reprocessed at a compounding temperature of 250 °C.

X-ray diffraction

XRD patterns were collected using Cu K_α ($\lambda = 0.1542$ nm) in a D8 Bruker X-ray diffractometer, operated at 40 kV and 30 mA.

Nanoindentation

A Nanoindenter XP (MTS, USA) was used for nanoindentation testing. The molded samples were sectioned and indentations carried out in the middle of the sections at three different locations, with 25 indentations per location. A 3-sided pyramid (Berkovich) tip was used under the continuous stiffness module. The test started with loading the indenter into the sample until a depth of 5000 nm was reached. The load was then held at its maximum value for 60 s allowing creep displacement to dissipate. A constant strain rate of 0.05 s^{-1} was maintained throughout the test. The distance between adjacent indentations was set to 100 μm to avoid the effect of interaction. Thermal drift effects were minimized by starting the test once thermal drift values stabilized below 0.05 nm/s. Moreover, the test was carried out overnight after leaving the samples for 3 h inside the nanoindenter to thermally equilibrate. Minimum and maximum calculation depths were set to 2000 and 4000 nm, respectively.

Melt flow index

The effects of clay addition and of processing parameters on the melt viscosity of neat nylon and of composite samples were analyzed using MFI. MFI was measured in g/10 min according to ASTM standard D1238 using a RAY-RAN Melt Flow Indexer (Ray-Ran Test Equipment Ltd.). The test conditions used entailed a temperature of 235 °C and a load of 2.16 kg. The samples were cut into small pieces, then introduced in the heated die, extruded, and collected during a specified interval of time (1 min). Once this extrudate cooled, its mass was recorded. The test was conducted thrice for each sample. Flow rate consistency was ensured by discarding any void-containing samples and by purging the material before starting the timer.

Transmission electron microscopy

Samples were covered with a protective sputter coating of Au–Pd, then subjected to focused ion beam milling using the lift-out method to obtain electron-thin foil sections. TEM analysis was conducted on a Tecnai F20 (200 kV) TEM.

Fourier transform infrared

In order to assess the impact of the processing temperatures on the organic modifier in the used montmorillonite organoclay, infrared studies were conducted using a Nicolet 380 FTIR. Cloisite 30B samples heated for 2 h at 250 °C, conditions representing the highest processing temperature employed and the maximum processing time used, were prepared in the form of KBr pellets. 2 mg of the sample was mixed with 200 mg of KBr (spectroscopic grade) and then subjected to 1400 kPa.

Results and discussion

X-ray diffraction

XRD analysis revealed that basal reflection for Cloisite 30B (basal spacing 18.5 Å) significantly decreased in the sample subjected to melt compounding at 230 °C and disappeared in the sample subjected to melt compounding at 250 °C, as well as the reprocessed sample, as shown in Fig. 1. The decrease in intensity of the basal reflection XRD peak is indicative of the separation of the clay layers, and its disappearance is widely taken as an indication of the clay exfoliation [2, 3, 5, 7].

Nanoindentation

Figures 2 and 3 present the nanoindentation characterization results for the different nanocomposite and neat polymer samples. They demonstrate enhanced mechanical

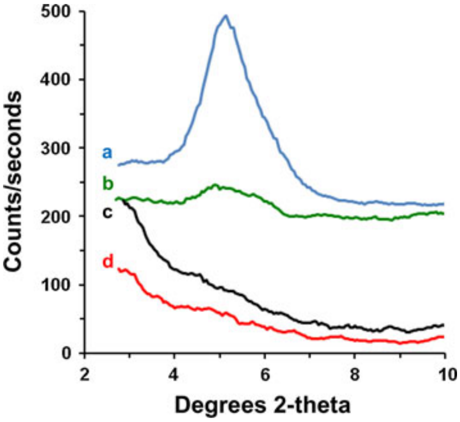


Fig. 1 XRD diffraction patterns for (*a*) Cloisite 30B, (*b*) PA6-30B/230, (*c*) PA6-30B/230/250, and (*d*) PA6-30B/250

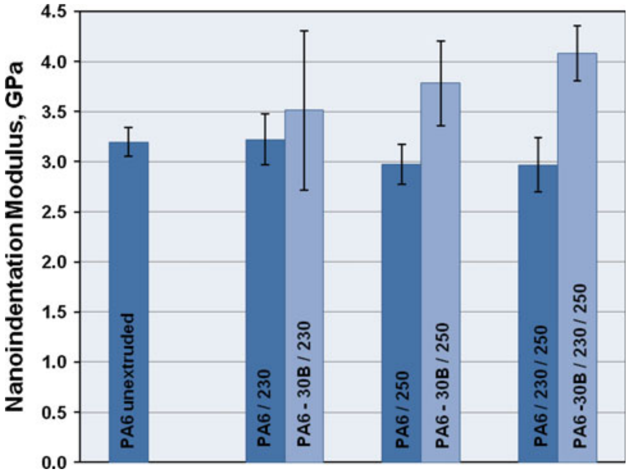


Fig. 2 Average nanoindentation modulus of the different samples

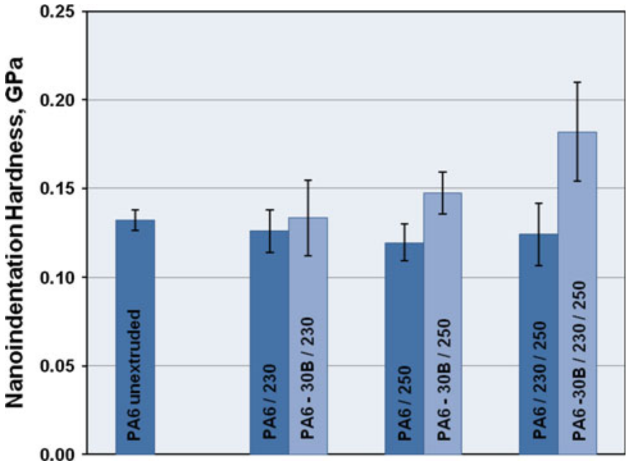


Fig. 3 Average nanoindentation hardness of the different samples

properties (nanoindentation hardness and modulus) for the nanocomposite in comparison to the neat polymer. Moreover, increasing the processing temperature from 230 to 250 °C further enhanced the mechanical properties. This was further accentuated by reprocessing at 250 °C. However, it is seen that higher processing temperatures, as well as reprocessing, result in a slight deterioration in the mechanical behavior (nanoindentation hardness and modulus) of the neat polymer. This could be attributed to possible thermal degradation with increased processing temperatures, and, possibly, to shear thinning for the reprocessed samples. It is noteworthy that the modulus values obtained for the composite samples in this investigation are higher than that of reported by other researchers [8, 12, 14] who prepared composites of nylon 6 and about 5 wt% Cloisite 30B using twin-screw extruders and in one case [12] after two reprocessing cycles. Dennis et al. [9], on the other hand, obtained a slightly higher tensile modulus of 4.4 GPa for similar composites, processed by twin-screw extruder.

Table 2 summarizes the percent enhancement for the composite samples prepared at the different conditions.

Melt flow index

Following other studies which investigated the relationship between viscosity and exfoliation in single-screw extruders, for example Russo et al. [12] who observed reduced complex viscosity after two reprocessing cycles and attributed this to the re-agglomeration of the silicate layers, MFI is used in this study to explore the change in melt viscosity of the prepared samples and to correlate the change to the degree of dispersion of the clay layers in the nylon matrix. As shown in Fig. 4, composite samples processed at 230 °C (PA6-30B/230) were found to have the highest MFI, i.e., the lowest melt viscosity. This can be related to poor exfoliation and non-uniform dispersion of the silicate layers. When increasing the processing temperature to 250 °C, the melt viscosity of the composite sample (PA6-30B/250) was found to increase which can be attributed to better exfoliation and dispersion. The reprocessed nanocomposite (PA6-30B/230/250) showed the highest viscosity which is attributed to full exfoliation and uniform dispersion of the silicate layers.

The MFI values for the neat polymer show an interesting trend. Compared to the neat polymer processed at 230 °C, processing at a higher compounding temperature of 250 °C increases MFI, whereas reprocessing significantly reduces MFI. Two factors seem to be coming into play: processing at higher compounding temperatures, as reported elsewhere [12, 15], results in thermal degradation due to chain scission leading to a decrease in melt viscosity. On the other hand, reprocessing of the polymer could have resulted in increased cross-linking, as suggested in [16], leading to an increase in melt viscosity. In the case of the composite samples, the presence of the silicate layers in the polymer matrix seems to prevail over these two effects with the

Table 2 Nanoindentation modulus and hardness values for the different composite samples

	Modulus enhancement		Hardness enhancement	
	Observed[a] (%)	Corrected[b] (%)	Observed[a] (%)	Corrected[b] (%)
PA6-30B/230	9	9	6	6
PA6-30B/250	27	29	23	25
PA6-30B/230/250	38	40	48	50

[a] Percent enhancement values determined relative to the neat un-extruded polymer

[b] Percent enhancement values determined relative to the neat un-extruded polymer, and corrected for the effect of deterioration of the neat polymer as a result of processing under the same conditions as each of the respective composite sample

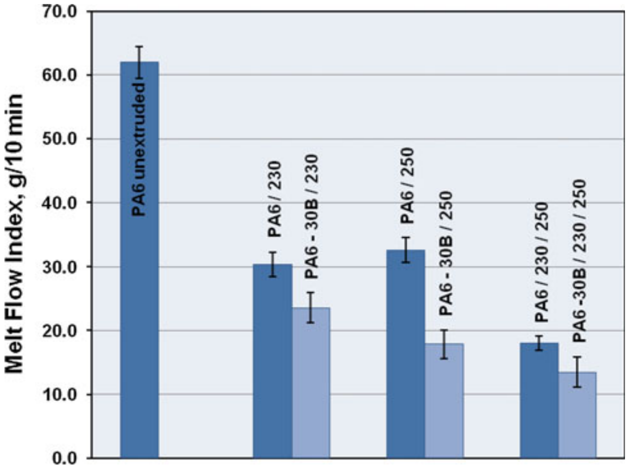


Fig. 4 MFI values for the different samples

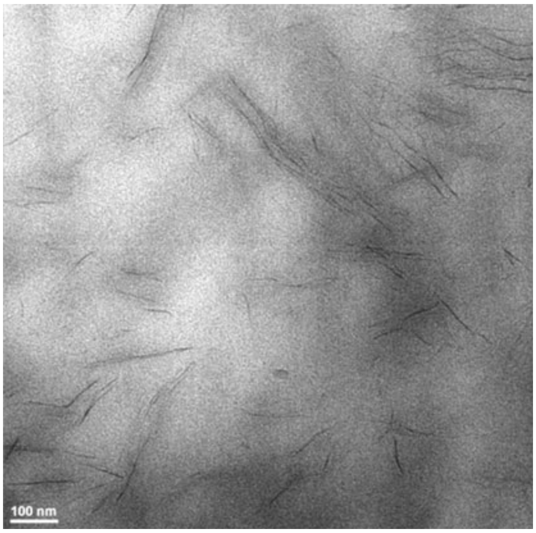


Fig. 5 TEM image of composite sample PA6-30B/230 showing varying clay density with individual layers as well as stacks and tactoids

observed trend of decrease in melt viscosity with higher compounding temperature and or reprocessing due to better exfoliation and dispersion.

Transmission electron microscopy

Figure 5 shows a TEM image of sample PA6-30B/230. Tactoids of stacked clay layers with an average thickness of around 14 nm can be noticed. Varying densities of clay tactoids can be observed within the matrix, which indicates non-uniform dispersion of clay tactoids. When increasing the processing temperature to 250 °C, the nanocomposite sample, PA6-30B/250, shows enhanced dispersion, as shown in Fig. 6, indicated by the existence of uniformly dispersed individual layers. Figure 7 shows superior dispersion and full exfoliation of clay layers for the reprocessed sample PA6-30B/230/250. The reported TEM results are in agreement with the nanoindentation analysis, presented earlier, in which the reprocessed samples displayed the highest enhancements in both modulus and hardness. In accord with our observations, Russo et al. [12] observed enhanced dispersion of the clay layers in samples produced by melt compounding in a twin-screw extruder and then subjected to reprocessing in the same extruder. However, the effect of change in the reprocessing temperature was not investigated in their case.

Fourier transform infrared

The FTIR spectra of the original (as-received) Cloisite 30B, the one heated at 250 °C for 2 h, are presented in Fig. 8. Bands at ~3630 and ~3400 cm^{-1} are associated with the stretching modes of Si–OH and –OH groups of interlayer water; bands at ~1120 and ~1050 cm^{-1} correspond to the Si–O bending and stretching modes, respectively; bands at ~530 and ~470 cm^{-1} correspond to the stretching modes of Al–O and Mg–O, respectively. In addition, bands at ~2920 and ~2850 cm^{-1} are attributed to the $–CH_2$ asymmetric and symmetric stretches, respectively, and the ~1470 cm^{-1} band is attributed to the $–CH_2$ bending vibration [17–19]. It is important to note that the ~2920, ~2850, and ~1470 cm^{-1} bands were still observed after heat treatment, indicating that the alkylammonium ions in Cloisite 30B were still present. These observations are in accordance with those reported by

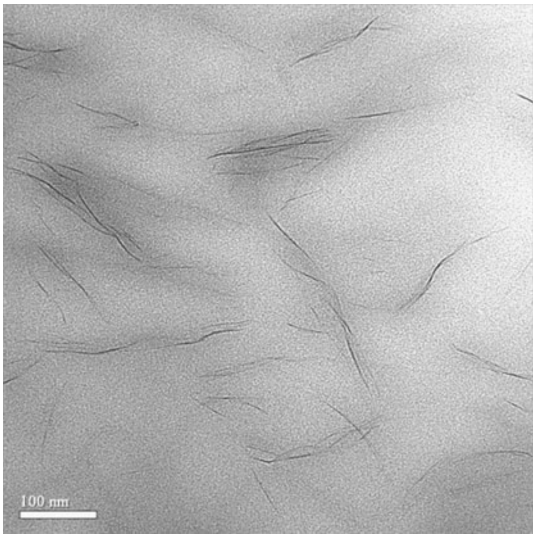


Fig. 6 TEM image of composite sample PA6-30B/250 showing individual layers, a few smaller stacks and overall improved dispersion

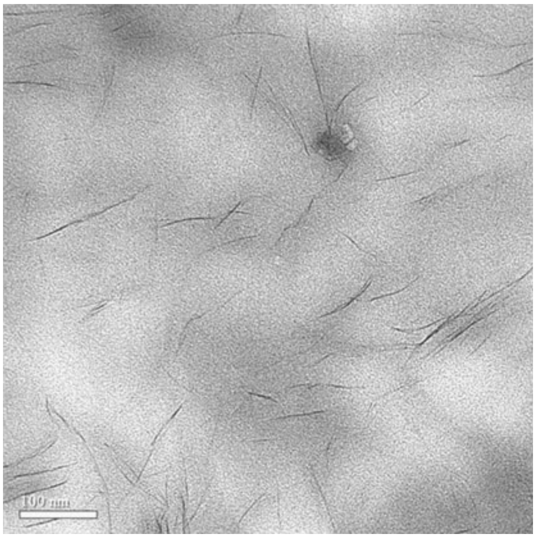


Fig. 7 TEM image of composite sample PA6-30B/230/250 showing mainly individual layers well dispersed in the polymer matrix

Russo et al. [12], who conducted TGA analysis of Cloisite 30B and reported that the first significant weight loss (corresponding to the loss of the alkylammonium ions) occurred at the temperature of 268 °C, which is significantly higher than the 250 °C used here.

General discussion

In this study, mechanical properties as well as TEM and XRD analyses have confirmed that processing temperature plays a key role in enhancing dispersion and preventing re-agglomeration when reprocessing in single-screw extruders, a shortcoming which has been reported by other researchers. Samples processed at 230 °C were found to contain partially exfoliated silicate layers which were not uniformly distributed. Raising the temperature to 250 °C was found to enhance dispersion but not lead to full exfoliation. Subjecting the samples to one reprocessing cycle at 250 °C was found to lead to full exfoliation as well as uniformly dispersed clay layers. In addition, limited polymer degradation seems to be taking place when processing at higher compounding temperatures and/or reprocessing. Figure 9 shows schematic diagrams summarizing the main findings of this study.

Researchers have attempted to propose mechanisms for delamination and dispersion in clay nanocomposites which could aid a better understanding of the effect of various processing parameters on the properties of the final composites. For example, Dennis et al. [9], who conducted an exhaustive study on how screw design affects structure, proposed that due to high shear, stacks of clay platelets are first decreased in height into tactoids. The residence time rather than high shear subsequently plays a role allowing the polymer chains to enter the clay galleries and push the platelets apart thus resulting in full delamination and dispersion. Fornes et al. [10], on the other hand, presented a somewhat similar but a 3-step mechanism in which the micron-sized clay particles are first sheared into tactoids, which are then sheared into smaller tactoids, followed by polymer diffusion into the clay galleries. In their mechanism, shear intensity results in total platelet exfoliation. Both, the aforementioned mechanisms focused on exfoliation but overlooked the effect of processing conditions on dispersion of the clay platelets in the matrix. Our investigation aims to correlate the observed exfoliation and dispersion of the clay platelets to the melt viscosity.

Figure 9 illustrates the structure of the microcomposite where silicate layers are stacked. It is thought that when processing at low temperature, the high-melt viscosity of the polymer during processing provides effective shear mixing by transferring the shear forces from the polymer to the clay; however, this hinders the mobility of silicate layers during processing. The stacked layers are thought to have been separated into smaller tactoids and further smaller ones, while being confined within the regions around the original clay stacks due to the high viscosity of the polymer matrix. This yields the structure depicted in Fig. 9a and the TEM image in Fig. 5 with areas of partially exfoliated clay and other areas of the neat polymer. When processing the composite at the higher temperature of 250 °C, the viscosity of the polymer blend is less and thus shear mixing is not as effective in exfoliating the silicate layers. However, due to the lower viscosity, the mobility of the clay particles within the matrix improves resulting in better dispersion (Fig. 9b and the TEM image in Fig. 6). This leads to partial exfoliation and better dispersion.

Fig. 8 FTIR of original Cloisite 30B versus Cloisite 30B heated at 250 °C for 2 h

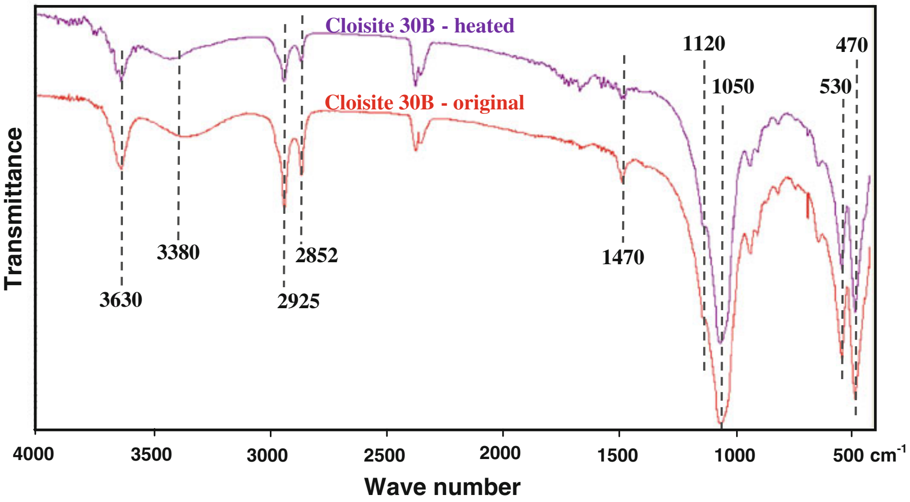
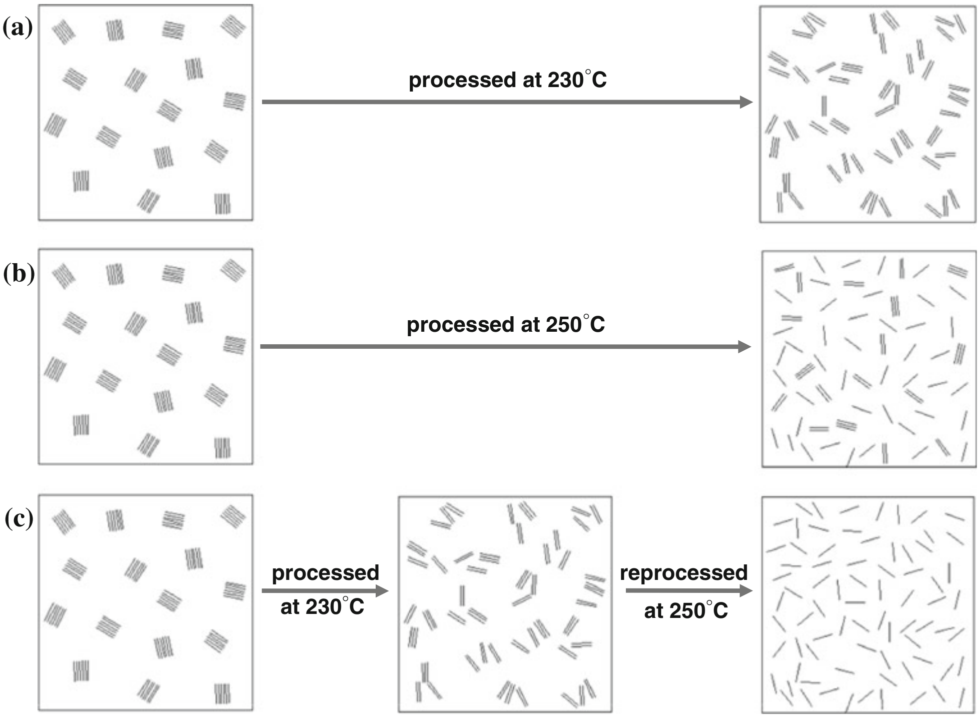


Fig. 9 Effect of processing conditions on clay exfoliation/dispersion: Nylon 6–Cloisite 30B processed at **a** 230 °C; **b** 250 °C; **c** 230 °C then reprocessed at 250 °C



Composite samples originally processed at 230 °C then reprocessed at the higher temperature of 250 °C, being subjected to longer residence time, exhibit the two effects of enhanced exfoliation and dispersion (Fig. 9c and the TEM image in Fig. 7).

The limited neat polymer degradation due to processing at the higher temperature and/or reprocessing is noteworthy. This is clearly displayed in the neat polymer behavior in Figs. 2–4. It is believed that melt compounding using a single-screw extruder, with the associated lower shear intensity, limits polymer degradation, contrary to what has been observed in studies using twin-screw extruders [8, 12].

Conclusions

Although researchers were only successful in obtaining partially delaminated clays when melt compounding nylon 6–Cloisite 30B in single-screw extruders, in this investigation, we have shown that a fully exfoliated structure could be obtained using controlled reprocessing. Both mechanical properties as well as TEM and XRD analyses have confirmed that processing temperature plays a key role in enhancing dispersion and preventing re-agglomeration when reprocessing in single-screw extruders, a shortcoming which has been reported by other researchers. We have shown that the high-melt viscosity associated with the lower processing temperatures resulted in higher shear stresses during melt blending and thus initiated exfoliation but hindered homogeneous dispersion. It was only upon using a higher processing temperature that improved exfoliation as well as uniform dispersion is achieved. Upon reprocessing the same samples at a higher temperature, both uniform dispersion and full exfoliation, facilitated by the longer residence time, were possible. In addition, the observed polymer degradation with increasing temperature and/or reprocessing was found to be limited. It is believed that this is due to the low shear intensity in the single-screw extruder used.

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