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Nylon 6 nanocomposites prepared by a melt mixing masterbatch process

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Abstract

A melt mixing masterbatch process for preparing nylon 6 nanocomposites that provides good exfoliation and low melt viscosities has been investigated. It is known that high molecular weight (HMW) grades of nylon 6 lead to higher levels of exfoliation of organoclays than do low molecular weight (LMW) grades of nylon 6. However, LMW grades of nylon 6 have lower melt viscosities, which are favorable for certain commercial applications like injection molding. To resolve this, a two-step process to prepare nanocomposites based on nylon 6 is explored here. In the first step, a masterbatch of organoclay in HMW nylon 6 is prepared by melt processing to give exfoliation. In the second step, the masterbatch is diluted with LMW nylon 6 to the desired montmorillonite (MMT) content to reduce melt viscosity. Wide angle X-ray scattering, transmission electron microscopy, and stress–strain analysis were used to evaluate the effect of the clay content in the masterbatch on the morphology and physical properties of the final nanocomposite. The melt viscosity was characterized by Brabender Torque Rheometry. The physical properties of the nanocomposites prepared by the masterbatch approach lie between those of the corresponding composites prepared directly from HMW nylon 6 and LMW nylon 6. A clear trade-off was observed between the modulus and melt processability. Masterbatches that have lower MMT content offer a significant decrease in melt viscosity and a small reduction in modulus compared to nanocomposites prepared directly from HMW nylon 6. Higher MMT concentrations in the masterbatch lead to a less favorable trade-off.

Keywords: Nylon 6; Nanocomposites; Masterbatch

1. Introduction

Polymer layered silicate nanocomposites continue to generate much interest, principally due to the potential for exceptional improvements in physical and thermal properties at low filler levels. The property enhancements in these systems depend largely on the ability to exfoliate and disperse the nanometer-thick silicate platelets within the polymer matrix, which in turn is a function of the polymer–organoclay compatibility. Nylon 6 is one of the few polymers which readily forms well-exfoliated nanocomposites [1–4]. Recently, there have been published reports of the commercial applications in the automobile industry of such nanocomposites based on nylon 6 and polypropylene prepared by melt processing [5,6].

Extensive work concerning processing, modeling, morphology and thermal and mechanical properties of nylon 6 nanocomposites has been reported from this laboratory [7–13]. Our melt processing studies with nylon 6 have revealed that high molecular weight grades of nylon 6 (hereafter referred to as high molecular weight (HMW) nylon 6 or sometimes simply HMW) lead to higher levels of exfoliation of montmorillonite (MMT) based organoclays than do low molecular weight (LMW) grades of nylon 6 [9,10]. This is believed to be a result of the higher shear stresses generated by the HMW grade caused by its higher melt viscosity. On the other hand, LMW grades process much faster than the HMW grades in certain operations like injection molding. From a commercial standpoint, it is desirable to achieve similar exfoliation with LMW grades or ‘injection molding grades’ as seen in the HMW grades, since product throughput is essential for the economical manufacturing of injection-molded parts.

Hence, the objective of this study is to develop a viable means of achieving good exfoliation in nylon 6 with improved melt processability. This is done using a two step process: in the first, masterbatches of HMW nylon 6 with different clay contents are prepared by melt processing using a twin-screw extruder. Second, these masterbatches are then diluted with LMW nylon 6 under the same melt processing conditions mentioned above to produce

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nanocomposites with 2, 4 and 6.5% MMT. The premise underlying this strategy is to get good exfoliation in HMW nylon 6 and then reduce the viscosity by dilution with LMW nylon 6 while preserving the exfoliation obtained in HMW. From an economic standpoint, it is desirable to make the HMW masterbatches as concentrated in MMT as possible since it would lower the manufacturing and distribution costs. Also, a more concentrated masterbatch would result in a higher LMW/HMW ratio on dilution, which would lead to improved melt processability. The question is what is the upper limit of MMT concentration in the HMW nylon 6 masterbatch that can be formed for implementation of this strategy from a processing point of view? Can one get good exfoliation at high MMT contents in HMW nylon 6 and, if so, can it be preserved after dilution with LMW nylon 6? These questions are addressed in this study. The effects of the clay content of the masterbatches on the morphology and physical properties of the final nanocomposites are examined using wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and stress–strain analysis. In addition, these data are compared to that of equivalent nanocomposites prepared by direct melt processing from HMW and LMW nylon 6 (no masterbatches used). As will be seen, there is a tradeoff between the melt viscosity (characterized by Brabender Torque Rheometry) and the modulus of the final nanocomposite.

2. Experimental

2.1. Materials

A brief description of the materials used in this study is given in Table 1. Two commercial grades of nylon 6 from Honeywell, a high molecular weight grade, HMW ($M_n = 29,300$), and a low molecular weight grade, LMW ($M_n = 16,400$), were used.

The organically modified clay was generously donated by Southern Clay Products and was used as received. It was prepared by a cation exchange reaction between sodium montmorillonite (Na–MMT) and octadecyltrimethyl ammonium chloride (Arquad 18–50® quat), designated here as $M_3(C_{18})_1$. The quat, supplied by Akzo–Nobel, was made from the C_{18} fatty acid fraction distilled from palm oil. The choice of the organoclay used was based on a recent study of the effect of organoclay structure on clay exfoliation in nylon 6 nanocomposites made by melt processing [11] which revealed that greater exfoliation could be achieved using surfactants with (i) one long alkyl tail on the ammonium ion rather than two and (ii) methyl groups on the amine rather than 2-hydroxy-ethyl groups. In prior studies in this lab, trimethyl-hydrogenated tallow quaternary ammonium chloride, $M_3(HT)_1$, was used [11,15]; however, due to supply constraints, $M_3(C_{18})_1$ was used instead in this study. A comparison of the tensile modulus of nylon 6 nanocomposites prepared using these two organoclays shows nearly equivalent performance (see Fig. 1). The yield strength and ductility of samples prepared using these two organoclays were also found to be similar.

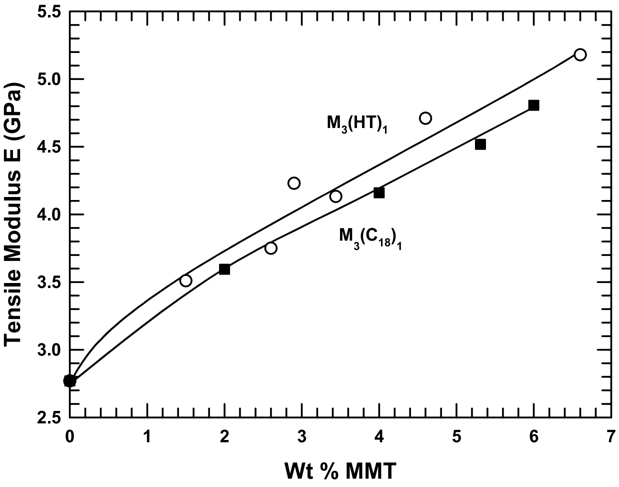


Fig. 1. Comparison of tensile modulus of nanocomposites prepared from high molecular weight (HMW) nylon 6 and trimethyl-hydrogenated tallow quaternary ammonium chloride ($M_3(HT)_1$) [11,15] versus octadecyltrimethyl ammonium chloride ($M_3(C_{18})_1$).

2.2. Melt processing

As mentioned above, a two-step process was used to prepare nanocomposites of the desired MMT content. In the first step, masterbatches containing 20, 14 and 8.25 wt% MMT (28.5, 19.9 and 11.7 wt% organoclay, respectively)

Table 1
Materials used in this study

Material (designation used here)	Supplier designation	Specifications	Supplier
Nylon 6 (LMW)	Capron 8202	$M_n = 16,400$,[a] MFI = 23	Honeywell
Nylon 6 (HMW)	Capron B135WP	$M_n = 29,300$,[a] MFI = 1.2	Honeywell
Organoclay ($M_3(C_{18})_1$)[b]	Octadecyltrimethyl ammonium chloride organoclay	Organic loading = 95 mequiv./100 g clay Organic content = 29.8%	Southern clay products

[a] M_n determined by intrinsic viscosity using *m*-cresol at 25 °C [9,14].

[b] The substituents on the quaternary ammonium counpound used to form the organoclay are identified in this short hand notation where M = methyl and (C_{18}) is the saturated octadecyl fatty acid fraction (96.6%) distilled from palm oil.

were prepared by melt blending the organoclay and HMW nylon 6 in a Haake co-rotating, intermeshing twin screw extruder (diameter = 30 mm, $L/D = 10$). The barrel temperature was set at 240 °C; whereas the screw speed and feed-rate were set at 280 rpm and 1200 g/h, respectively. The low melt strength of the extrudate caused problems in forming a strand which coupled with pelletizing difficulties arising form high hardness of the solidified strand prohibited use of higher organoclay contents in the masterbatch. Each of the masterbatches was then diluted with LMW nylon 6 using the same processing conditions to produce nanocomposites with 2, 4 and 6.5 wt% MMT. In addition to these, a HMW masterbatch containing 4 wt% MMT was also diluted down to 2 wt% MMT with LMW nylon 6. Prior to extrusion, all the polyamides (in steps 1 and 2) and masterbatches (in step 2) were dried in a vacuum oven at 80 °C for a minimum of 16 h. For comparison, nylon 6 nanocomposites with 2, 4 and 6.5 wt% MMT were prepared from the HMW only and LMW only materials using the same organoclay and processing conditions mentioned above. These were passed through the extruder twice so that they have the same thermal and shear history as nanocomposites made from masterbatches. The amount of MMT in each batch was confirmed by placing pre-dried nanocomposite pellets in a furnace at 900 °C for 45 min and weighing the remaining MMT ash. A correction for loss of structural water was made in the calculation [9]. A summary of the blends prepared is given in Table 2.

Table 2
Summary of nylon 6/$M_3(C_{18})_1$ organoclay nanocomposites prepared in this study

MMT content (wt%)	Matrix/starting material	Comments
20.0	HMW nylon 6	Masterbatch
14.0	HMW nylon 6	Masterbatch
8.25	HMW nylon 6	Masterbatch
6.5	HMW nylon 6	For comparison
4.0	HMW nylon 6	Masterbatch/For comparison
2.0	HMW nylon 6	For comparison
0.0	HMW nylon 6	For comparison
6.5	LMW nylon 6	For comparison
4.0	LMW nylon 6	For comparison
2.0	LMW nylon 6	For comparison
0.0	LMW nylon 6	For comparison
6.5	20% Masterbatch	Diluted with LMW nylon 6
4.0	20% Masterbatch	Diluted with LMW nylon 6
2.0	20% Masterbatch	Diluted with LMW nylon 6
6.5	14% Masterbatch	Diluted with LMW nylon 6
4.0	14% Masterbatch	Diluted with LMW nylon 6
2.0	14% Masterbatch	Diluted with LMW nylon 6
6.5	8.25% Masterbatch	Diluted with LMW nylon 6
4.0	8.25% Masterbatch	Diluted with LMW nylon 6
2.0	8.25% Masterbatch	Diluted with LMW nylon 6
2.0	4.0% Masterbatch	Diluted with LMW nylon 6

Tensile specimens (ASTM D638) were prepared by injection molding using an Arburg Allrounder 305-210-700 injection molding machine using a barrel temperature of 260 °C, mold temperature of 75 °C, injection pressure of 70 bar and a holding pressure of 35 bar. After molding, the samples were immediately sealed in a polyethylene bag and placed in a vacuum desiccator for a minimum of 24 h prior to tensile testing.

2.3. Mechanical testing

Tensile tests were conducted at room temperature according to ASTM D696 using an Instron model 1137 machine equipped with digital data acquisition capabilities. Modulus and yield strength were measured using an extensiometer at a crosshead speed of 0.51 cm/min. Elongation at break was measured at crosshead speeds of 0.51 and 5.1 cm/min. Typically, data from six specimens were averaged to determine mechanical properties with standard deviations of the order of 4–5% for modulus, 2% for yield strength and 5–25% for elongation at break.

2.4. Wide angle X-ray diffration (WAXD)

WAXD was conducted using a Sintag XDS 2000 diffractometer in the reflection mode with an incident X-ray wavelength of 1.542 Å at a scan rate of 1.0 °/min. X-ray analysis was performed at room temperature on Izod bars except for the organoclay itself which was in powder form. The Izod specimens were oriented such that the incident beam reflected off the major face.

2.5. Transmission electron microscopy (TEM)

Samples for TEM analysis were taken from the core portion of an Izod bar perpendicular to the flow direction. Ultra-thin sections approximately 50 nm in thickness were cut with a diamond knife at a temperature of −40 °C using a Reichert-Jung Ultracut E microtome. Sections were collected on 300 mesh grids and subsequently dried with filter paper. These were then examined using a JEOL 2010F TEM equipped with a Field Emission Gun at an accelerating voltage of 120 kV.

2.6. Brabender rheology

For rheological characterization, various nanocomposites were tested in a Brabender Plasticorder with a 60 ml mixing head and standard rotors. A constant mass of 58 g for each sample was mixed at 240 °C at 70 rpm for 15 min. The melt viscosity characterized by the Brabender torque plateaued after 7–9 min of operation. The torque values at 10 min are reported here for each sample.

3. Mechanical properties

Fig. 2 shows the tensile modulus of nylon 6 nanocomposites made by the masterbatch process. For clarity, the moduli are plotted as a function of both the MMT content of the final nanocomposites, Fig. 2(a), and the MMT content of the masterbatches, Fig. 2(b). The corresponding values for nanocomposites prepared directly from HMW and LMW nylon 6 are also plotted for comparison. As expected [9,10], stiffness of nylon 6 improves substantially with the addition of organoclay and although there is not much difference between the moduli of virgin HMW and LMW nylon 6, the moduli of nanocomposites based on HMW nylon 6 are 10–15% higher than that of nanocomposites based on LMW nylon 6. Stiffness values of all samples prepared using the masterbatch approach fall between that of the equivalent HMW and LMW nanocomposite samples. It is interesting to note that the moduli of samples prepared from 4 and 8.25 wt% masterbatches are much closer to those of the corresponding samples prepared from HMW nylon 6 only. Also, there is not much difference between the moduli of equivalent samples made from the 14 and 20 wt% masterbatches. Table 3 summarizes the moduli and other mechanical properties of the virgin materials, nanocomposites prepared by direct melt processing (no masterbatches used), and nanocomposites prepared from masterbatches.

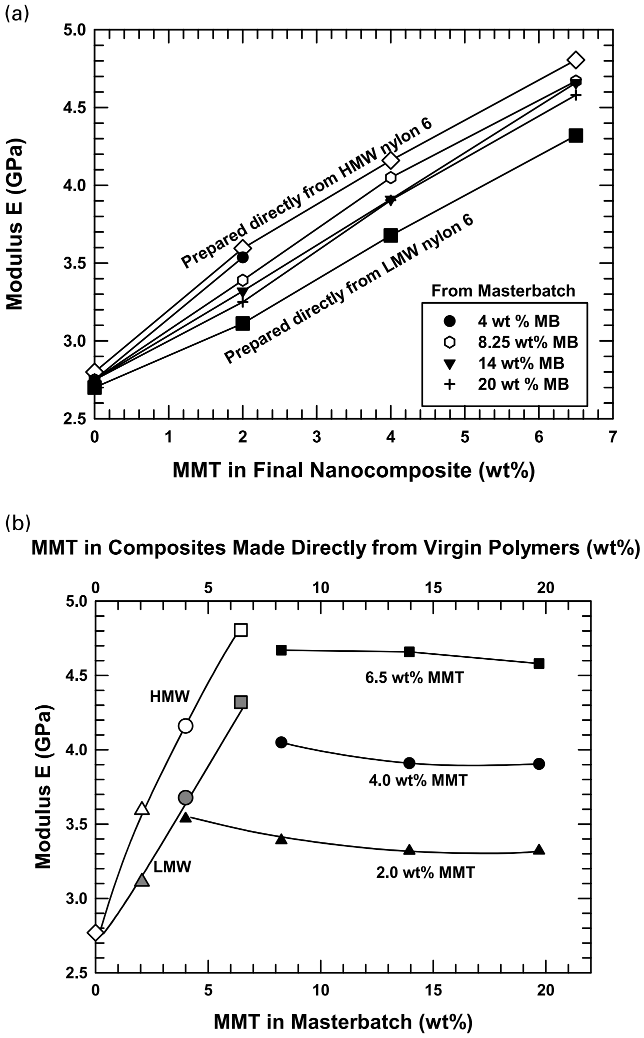


Fig. 2. (a) Effect of montmorillonite content on the tensile modulus of nanocomposites prepared from four masterbatches containing different MMT concentrations (b) Tensile modulus of nanocomposites containing 2.0 wt% MMT (triangles), 4.0 wt% MMT (circles) and 6.5 wt% MMT (squares) are plotted as a function of the MMT content of the masterbatch they were made from (bottom axis). Data for nanocomposites made directly from HMW nylon 6 only (unfilled symbols) and LMW nylon 6 only (gray symbols) are plotted versus the top axis for comparison.

Fig. 3 shows the yield strength as a function of the MMT content of masterbatches for nanocomposites with 2 and 4 wt% MMT loading. Yield strength data for nanocomposites containing 6.5 wt% MMT are not available since all samples (except for the HMW based composites) failed before reaching the yield point. As before, yield strength data for nanocomposites based on virgin HMW and LMW nylon 6 are plotted for comparison. Once again, the yield strengths of the nanocomposites prepared using the masterbatch process are between those of equivalent nanocomposites prepared by direct melt processing of pure HMW or LMW nylon 6.

The relationship between the MMT content of the masterbatch and elongation at break for the different nanocomposites is shown in Fig. 4 for two rates of extension. As observed in prior studies [9,10], the virgin polyamides are very ductile at a test rate of 0.51 cm/min, but increasing the clay content sacrifices ductility. The drop in ductility with increasing organoclay content is much steeper for the LMW based composites than with HMW nylon 6 based composites (Table 3). It is interesting to note, that composites with 2 wt% MMT prepared by the masterbatch process, maintain

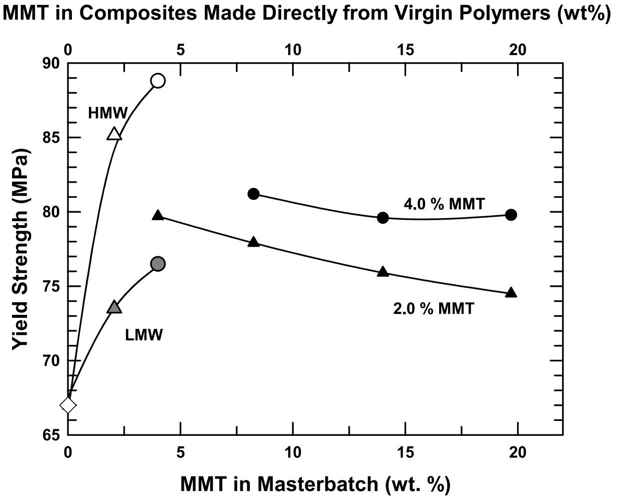


Fig. 3. Yield strength of nanocomposites containing 2.0 wt% MMT (triangles), and 4.0 wt% MMT (circles) are plotted as a function of the MMT content of the masterbatch they were made from (bottom axis). Data for nanocomposites made directly from HMW nylon 6 only (unfilled symbols) and LMW nylon 6 only (gray symbols) are plotted versus the top axis for comparison.

Table 3
Select mechanical properties of nylon 6/$M_3(C_{18})_1$ organoclay nanocomposites

MMT in final nanocomposite (wt%)[a]	Mechanical property	HMW	LMW	MMT in masterbatch (wt%)[a]			
				20%	14%	8.25%	4%
0.0%	Tensile modulus (GPa)	2.77	2.78				
	Yield strength (MPa)	67.0	67.3				
	Elongation at break at 0.51 cm/min (%)	273	205				
	Elongation at break at 5.1 cm/min (%)	136	24.6				
2.0%	Tensile modulus (GPa)	3.60	3.11	3.32	3.32	3.39	3.54
	Yield strength (MPa)	85.2	73.5	74.5	75.9	79.7	79.7
	Elongation at break at 0.51 cm/min (%)	201	84.0	127	141	146	169
	Elongation at break at 5.1 cm/min (%)	85.3	13.6	26.1	27.6	30.7	44.7
4.0%	Tensile modulus (GPa)	4.16	3.68	3.91	3.91	4.05	
	Yield strength (MPa)	88.8	76.5	79.8	79.6	81.2	
	Elongation at break at 0.51 cm/min (%)	67.0	16.1	11.5	11.7	26.1	
	Elongation at break at 5.1 cm/min (%)	39.8	9.57	8.71	7.46	10.5	
6.5%	Tensile modulus (GPa)	4.81	4.32	4.58	4.66	4.67	
	Yield strength (MPa)	93.1	74.7[b]	79.3[b]	77.9[b]	81.4[b]	
	Elongation at break at 0.51 cm/min (%)	3.19	2.81	2.94	2.82	2.96	
	Elongation at break at 5.1 cm/min (%)	3.60	3.10	2.94	3.32	2.89	

[a] Masterbatches were prepared from HMW nylon 6 and were diluted down to the desired MMT content with LMW nylon 6.

[b] Tensile strength at break, i.e. samples failed before reaching the yield point.

reasonable levels of ductility. Elongation at break values of samples prepared from the 20 wt% masterbatch are 50% higher than corresponding samples prepared directly from LMW nylon 6 while those prepared from the 4 wt% masterbatch are more than twice that for samples prepared directly from LMW nylon 6. The degree of improvement for nanocomposites containing 4 wt% MMT prepared by masterbatch dilution is not as pronounced as those with 2 wt% MMT. At higher MMT concentrations of 6.5 wt%, the ductility is seriously compromised across the board and there is not much difference in the elongation at break values between samples based on the different grades of nylon 6 or those made from masterbatches. On increasing the testing speed to 5.1 cm/min (Fig. 4(b)), similar trends are seen, but the absolute levels of elongation at break values are significantly lower.

4. Characterization

Fig. 5 compares the WAXD patterns for the $M_3(C_{18})_1$ organoclay and the $M_3(C_{18})_1$/HMW masterbatches with different MMT contents. The organoclay pattern reveals an intense peak at around $2\theta = 4.9°$, corresponding to a basal spacing of 18.1 Å. The X-ray pattern for the masterbatch with 4.0 wt% MMT does not show a characteristic basal reflection; this is indicative of a homogeneous exfoliated structure. On the other hand, patterns for the 20 and 14% masterbatches reveal a low broad peak that suggests these systems have a mixed morphology consisting of regions of intercalated clay tactoids and regions of exfoliated clay platelets. The WAXD pattern of the masterbatch with 8.25 wt% MMT does not show a distinct peak; however, there is a slight hint of curvature, which could be interpreted as an extremely broad peak indicating that the system is almost exfoliated. This agrees well with the mechanical property results that show nanocomposites formed from masterbatches containing 4 and 8.25 wt% MMT have stiffness similar to the corresponding nanocomposites based on HMW nylon 6 while the nanocomposites based on masterbatches containing 14 and 20 wt% MMT have lower modulus values.

Fig. 6 compares WAXD scans of nanocomposites with three different MMT levels that were formed from HMW and LMW nylon 6 only with those formed by dilution of a masterbatch containing 20% MMT. Composites formed from the masterbatch containing 20 wt% MMT were selected for this comparison because they require the greatest dilution with LMW nylon 6 and, thus, offer the greatest ease of processing. X-ray patterns of the organoclay and the parent masterbatch are also shown in each figure for comparison. As expected [9], the WAXD scans of the HMW nylon 6 composites are devoid of any characteristic peaks, which is consistent with the well-exfoliated character of these systems; whereas the nanocomposites prepared from LMW nylon 6 show a distinct broad peak indicative of the presence of intercalated clay tactoids. The X-ray patterns of the masterbatch-based nanocomposites have a characteristic peak similar to that of the parent masterbatch. However, the intensity of this peak is lower than both that of the nanocomposite based on LMW nylon 6 and the parent masterbatch suggesting a greater degree of exfoliation than

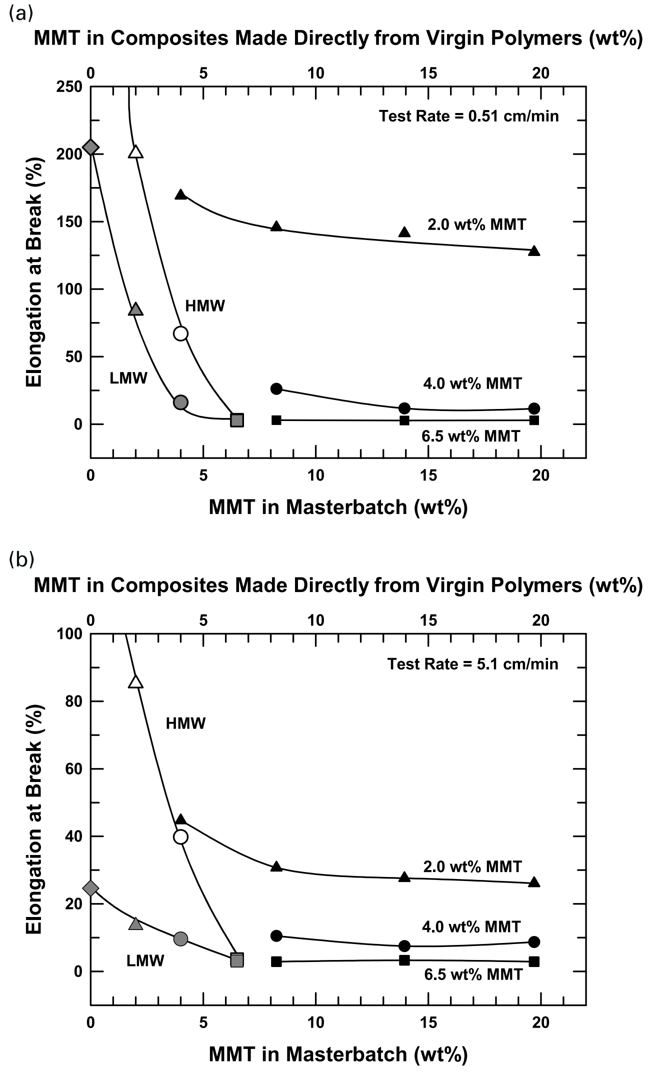


Fig. 4. Elongation at break of nanocomposites containing 2.0 wt% MMT (triangles), 4.0 wt% MMT (circles) and 6.5 wt% MMT (squares) are plotted as a function of the MMT content of the masterbatch they were made from (bottom axis), measured at crosshead speeds of (a) 0.51 cm/min and (b) 5.1 cm/min. Data for nanocomposites made directly from HMW nylon 6 only (unfilled symbols) and LMW nylon 6 only (gray symbols) are plotted versus the top axis for comparison.

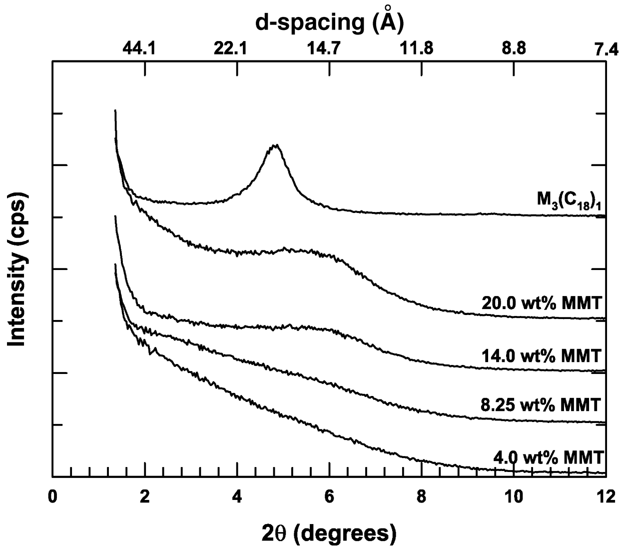


Fig. 5. WAXD patterns for $M_3(C_{18})_1$ organoclay and $M_3(C_{18})_1$ organoclay nanocomposite masterbatches based on HMW nylon 6 containing 20, 14, 8.25, and 6.5 wt% montmorillonite. The curves are shifted vertically for clarity.

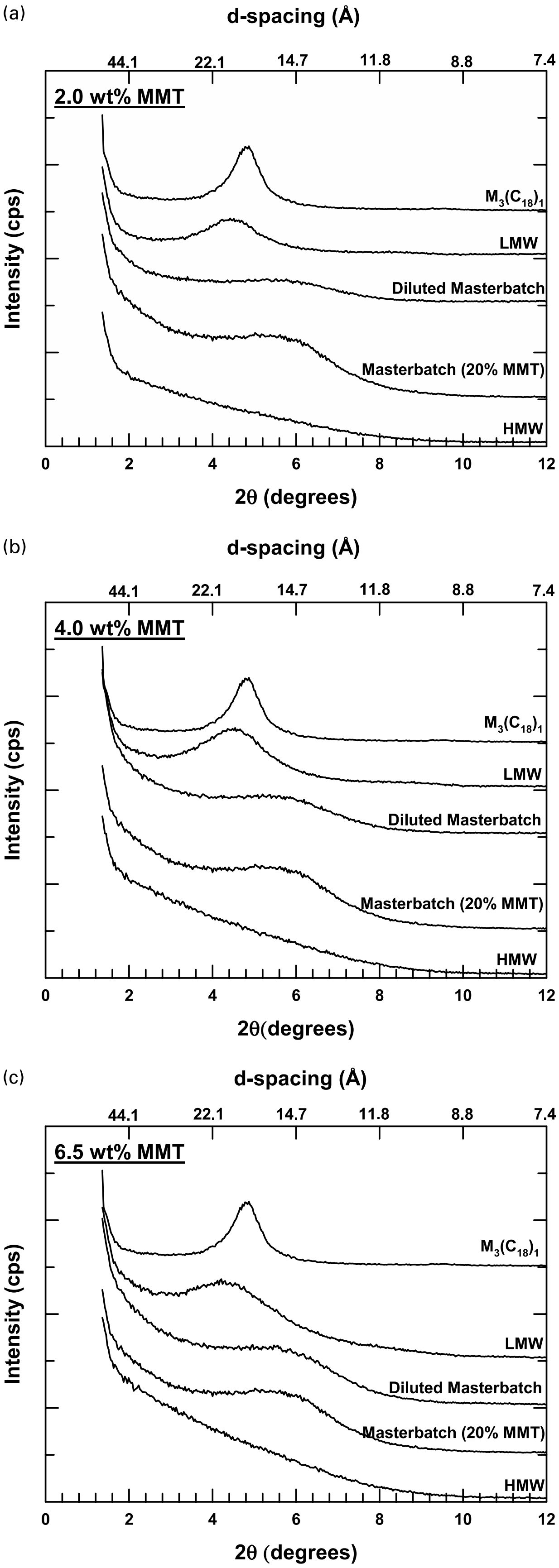
observed in the latter two. These results support the mechanical property results which show the masterbatch-based composites have better properties than comparable LMW nylon 6 based composites.

Careful observation of the WAXD patterns reveals shifts in the peak position for the nanocomposites and masterbatches relative to that of the pristine organoclay. These shifts apparently reflect the net result of two counteracting phenomena occurring concurrently during melt processing, viz. intercalation of the clay galleries by the matrix polymer and degradation of the organic component of the organoclay. TGA studies have shown that the organic component of organoclays begins to breakdown at temperatures as low as 180 °C. The thermal degradation of alkyl ammonium MMT organoclays has been discussed in detail by Xie et al. [16,17] and VanderHart et al. [18,19]. More degradation may occur in the masterbatch owing to viscous heat dissipation from the combined effects of higher filler levels and higher melt viscosity of the virgin HMW nylon 6. This would explain the shift of the peak to the right corresponding to a reduction of the interlayer spacing by 2–5 Å compared to the pure organoclay. In the case of LMW-based nanocomposites with low filler concentration, the amount of degradation is believed to be considerably less and the intercalation of polymer into the clay galleries prevails since the peak shifts to the left corresponding to an increase in the *d*-spacing of the organoclay stacks by 1–3 Å.

The TEM micrographs of nanocomposites formed from the $M_3(C_{18})_1$ organoclay and nylon 6 shown in Fig. 7 provide a more direct visualization of the degree of exfoliation of these materials. The micrograph of the HMW nylon 6 nanocomposite, Fig. 7(a), reveals a well-exfoliated structure; whereas the LMW nylon 6 nanocomposite, Fig. 7(c), reveals partial exfoliation with areas containing exfoliated platelets plus some tactoids. The TEM image of the masterbatch-based nanocomposites, Fig. 7(b) also showed a mixed morphology; however, the unexfoliated clay stacks were fewer in number and smaller in size than those found in LMW nanocomposite micrographs. These results are in good agreement with the WAXD and mechanical property data.

5. Processability

Fig. 8 compares the Brabender torques of virgin HMW and LMW nylon 6, their blends, and nanocomposites based on them. The torque for HMW nylon 6 is about three times



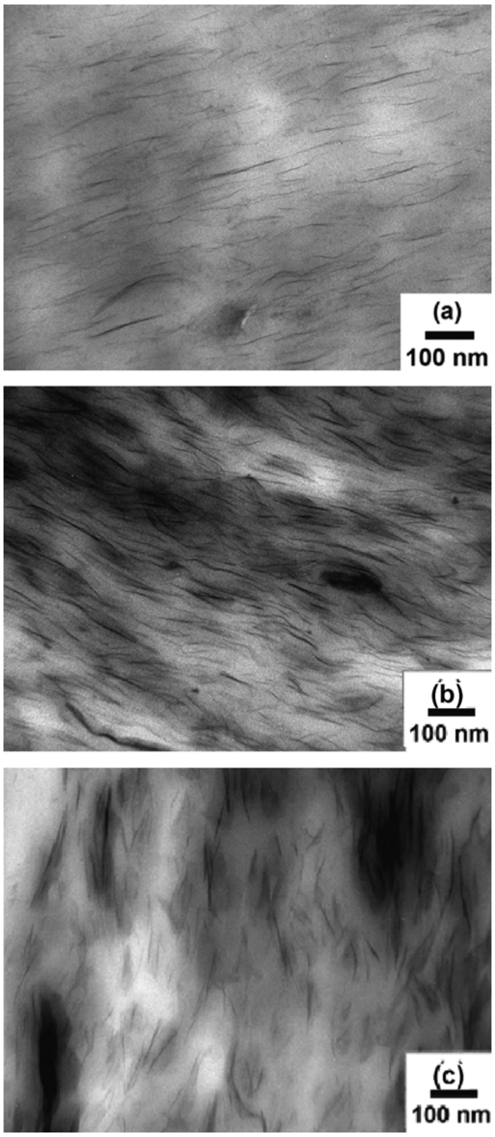


Fig. 7. TEM micrographs of nanocomposites containing ~2.0 wt% montmorillonite based on (a) HMW nylon 6 (b) HMW masterbatch containing ~20 wt% montmorillonite diluted down with LMW (c) LMW nylon 6.

higher than that for LMW nylon 6, with the HMW–LMW nylon 6 blends in between. The addition of $M_3(C_{18})_1$ organoclay does not result in large changes in the torque values. The relative gains in processability are presented in Table 4. Contrary to expectation, addition of small amounts of organoclay (2 wt% MMT) results in a slight reduction in the torque relative to the nylon 6 mixture for most compositions. At higher MMT loadings (6.5%), the torque for

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Fig. 6. WAXD patterns for $M_3(C_{18})_1$ organoclay nanocomposites containing (a) ~2 wt% (b) ~4 wt% and (c) ~6.5 wt% montmorillonite based on HMW nylon 6, LMW nylon 6 and a diluted masterbatch. WAXD patterns of the $M_3(C_{18})_1$ organoclay and the parent masterbatch (~20 wt% MMT) are plotted for comparison. The curves are shifted vertically for clarity.

Table 4
Relative melt viscosity

Nanocomposite	HMW:LMW ratio	Brabender torque[a] (N.m)	Relative melt viscosity
2.0 wt% MMT			
From HMW	100:0	9.2	1.00
From masterbatch containing 4.00% MMT	48.5:51.5	5.5	0.60
From masterbatch containing 8.25% MMT	23.5:76.5	4.0	0.43
From masterbatch containing 20% MMT	6.6:93.4	3.5	0.38
From LMW	0:100	3.1	0.34
6.5 wt% MMT			
From HMW	100:0	9.7	1.00
From masterbatch containing 8.25% MMT	72.7:27.3	7.2	0.74
From masterbatch containing 20% MMT	25.6:74.4	4.7	0.48
From LMW	0:100	4.9	0.51

[a] Torque was measured at 240 °C temperature after 10 min of operation.

LMW nylon 6 increases by ~40% over that of virgin LMW nylon 6; however, a small decrease is observed for HMW nylon 6. These trends in the Brabender torque values reflect two opposing phenomena. The addition of MMT tends to increase the matrix melt viscosity and, thus, the torque; however, degradation of the organic component of the organoclay leads to matrix molecular weight degradation, which lowers the Brabender torque as recently described by Fornes et al. [20]. That study concluded that for a given organoclay, the level of polymer molecular weight reduction was greatest for nanocomposites based on high molecular weight nylon 6 materials owing to the greater

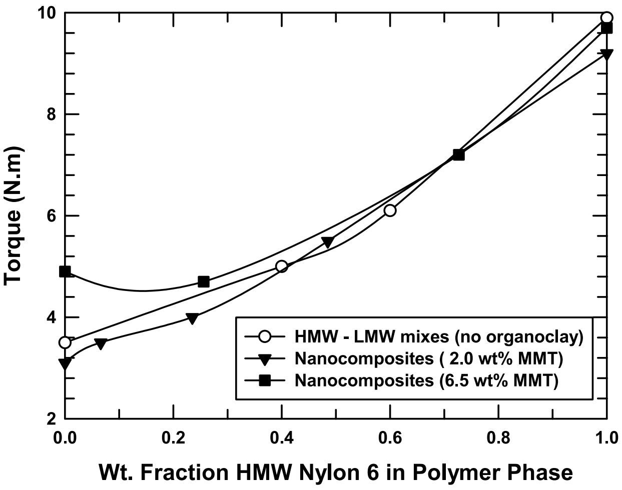

Fig. 8. Brabender torque at 10 min (steady state), for nylon 6–montmorillonite nanocomposites containing ~2.0 and 6.5 wt% montmorillonite, prepared by diluting HMW masterbatches with LMW nylon 6. The torque values for HMW–LMW nylon 6 mixes (no organoclay added) are plotted for comparison.

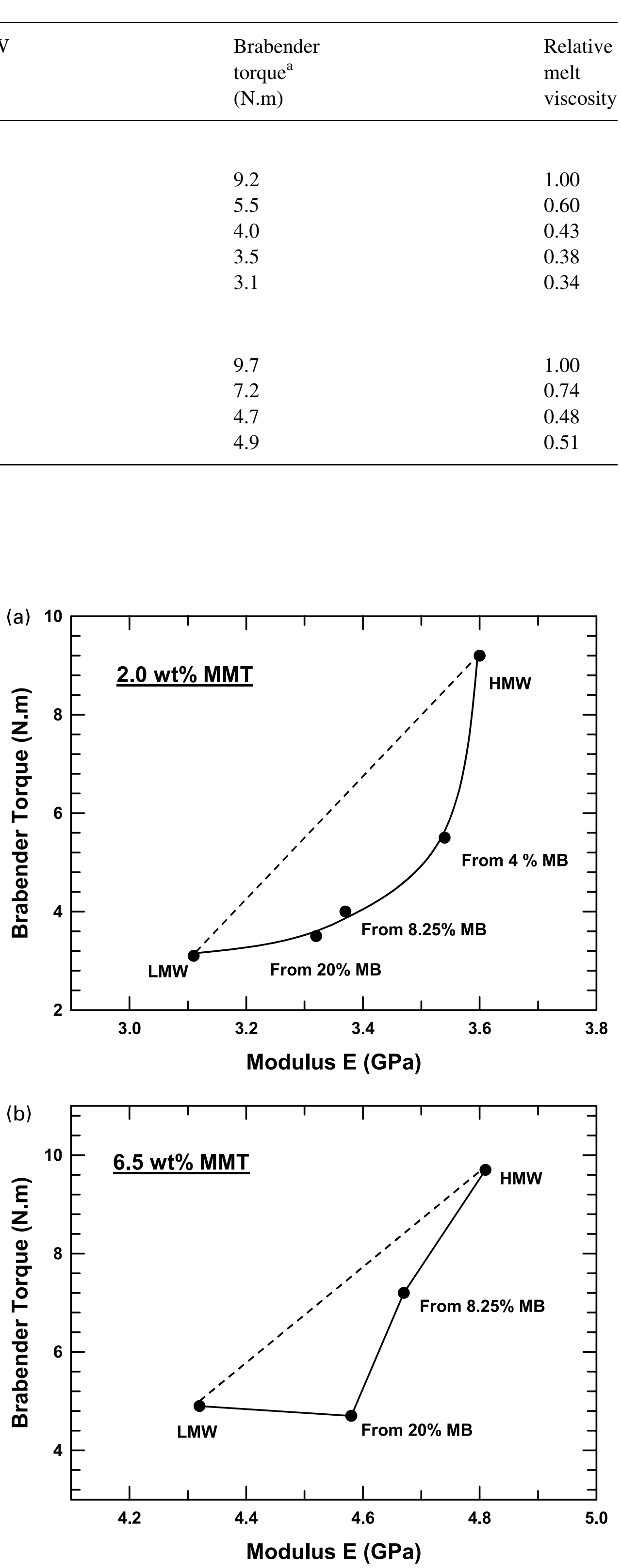

Fig. 9. The trade-off between tensile modulus and Brabender torque, a measure of melt viscosity or processability, of nylon 6-montmorillonite nanocomposites containing (a) 2.0 wt% MMT (b) 6.5 wt% MMT, prepared using a masterbatch approach.

exposure of the surfactant to the nylon 6 caused by increased levels of organoclay exfoliation. Similar matrix degradation has been reported for nanocomposites based on poly(ethylene terepthalate) (PET) [21] and polycarbonate [22] prepared by melt processing. At 2% MMT loading, the viscosity effects of matrix degradation apparently exceed the intrinsic increase caused by addition of MMT, thus, shifting the curve lower. At higher loadings (6.5%), the viscosity enhancement gained by the addition of MMT, evidently exceeds the reduction resulting from polymer degradation in LMW nylon 6. On the other hand, at the same high loadings in HMW nylon 6, the two effects seem to offset each other resulting in little change in the torque values.

Fig. 9 shows the tradeoff between processability as quantified by the Brabender torque and tensile modulus of the nanocomposites based on nylon 6 for two MMT loading levels. As shown in Fig. 9(a), the relationship between the melt viscosity and the tensile modulus of nanocomposites is not linear. By using a masterbatch that has a lower MMT content (< 8.25 wt%), a significant reduction in melt viscosity (Brabender torque) is achieved over HMW based nanocomposites for a relatively smaller penalty in modulus. A further increase in the MMT content of the masterbatch results in a marginal reduction in the melt viscosity but causes the modulus to drop precipitously. Nanocomposites with a higher MMT concentration (6.5 wt%) display similar trends as shown in Fig. 9(b).

6. Conclusion

A two-step masterbatch process for preparing nylon 6 nanocomposites that provides good exfoliation and low melt viscosities (for shorter cycle times in injection molding) has been investigated. In the first step, masterbatches of HMW nylon 6 with different clay contents were prepared by melt processing to get good exfoliation. In the second step, the masterbatch was diluted with LMW nylon 6 to the desired MMT content to reduce the melt viscosity. It was difficult to produce masterbatches containing more than 20 wt% MMT (or 28.5 wt% organoclay) owing to problems of stranding the extrudate arising from its lower melt strength and of pelletizing the solidified strand because of its hardness.

Masterbatches containing 4 and 8.25 wt% MMT were quite well exfoliated, and nanocomposites prepared by diluting them with LMW nylon 6 exhibited properties close to those seen with composites based on HMW nylon 6 alone. On the other hand, masterbatches containing 14 and 20 wt% MMT, were not so well exfoliated; however, mechanical property, TEM and WAXD analysis of nanocomposites prepared by diluting these masterbatches revealed better exfoliation than corresponding nanocomposites prepared directly from LMW nylon 6.

A distinct trade-off between the tensile modulus of these nanocomposites and the reduction of melt viscosity was observed. Nanocomposites prepared from HMW masterbatches that have a lower MMT concentration (< 8.25 wt%), offer a significant decrease in melt viscosity over those prepared directly from HMW nylon 6, for a small reduction in modulus. On increasing the MMT content of the masterbatch further, the tradeoff becomes less favorable. However, if it is absolutely necessary to have throughput rates similar to LMW nylon 6, the use of nanocomposites prepared from a more concentrated masterbatch (> 8.25 wt%) could offer up to a 10% improvement in modulus over nanocomposites prepared from LMW nylon 6 only.

While two extrusion steps were used in this work, the concept illustrated could be implemented in a single extrusion through the use of larger twin-screw extruders that have downstream feed ports. In this case, the organoclay and HMW nylon 6 would be fed to the hopper while LMW nylon 6 could be injected in a downstream feed port.

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