

Effects of Process Conditions and Mixing Protocols on Structure of Extruded Polypropylene Nanocomposites

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ABSTRACT: Polymer melt-direct intercalation or exfoliation is a promising approach for the preparation of nanocomposites. The structure of nanoclay platelets in the nanocomposites depends not only on the properties of polymer matrix and nanoclay, but also on the operating conditions during processing. The objective of the present work is to investigate the effects of clay chemical modifiers, mixing protocols, and operating conditions upon the clay structure in nanocomposites prepared with a corotating twin-screw extruder. Two mixing methods were used for the nanocomposite preparation: two-step mixing and one-step mixing. Experimental results obtained from melt flow index and complex viscosity measurements suggest that nanoclay C15A is more exfoliated than C30B in a polypropylene ho-

mopolymer containing a maleic anhydride grafted PP (PB) as compatibilizer. The two-step mixing method results in better exfoliation for the nanofillers than the one-step mixing method. A numerical simulation has been carried out to evaluate the mean residence time and shear rate in different screw configurations under various process conditions. X-ray diffraction experiments indicate that the residence time is a dominant factor in producing satisfactory nanocomposites in extruders. However, high shear rate coupled with long residence time might result in poor exfoliation of clay.

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INTRODUCTION

Polymer-based clay nanocomposites are usually divided into three general types: conventional composites, in which the clay acts as a normal filler; intercalated nanocomposites, in which a small amount of polymer moves into the gallery spacing between the clay platelets; and exfoliated nanocomposites, in which the clay platelets are fully dispersed in a continuous polymer matrix. The last two structures are of main interest because a great improvement in mechanical properties and heat resistance is achieved, even at low clay concentrations.¹

The most commonly used clay is montmorillonite (MMT). With an ultimate platelet thickness of approximately 1 nm, MMT has a high surface area and a very large aspect ratio (equivalent diameter over thickness). However, MMT usually exists as “stacks,” built with nanometer-sized platelets. Stacking of the platelets leads to a Van der Waals gap or gallery between the platelets. The galleries (or interlayers) are normally occupied by cations that balance the charge deficiency, generated by isomorphous substitution

within the platelets. Generally, the inorganic MMT surface is modified by organic treatments to make the platelets more compatible with polymers. In current processing equipment, the nanoclays are in general partially exfoliated, i.e., the clay agglomerates break into small stacks of two to four layers, but not individual lamellae.²

The literature^{1–4} suggests that the exfoliation and dispersion of nanoclays in polypropylene depend on the organic modifier of the nanoclay, the initial interlayer spacing, the concentration of functional groups in the compatibilizer and its overall concentration in the composite, the viscosity (or molecular weight) of polypropylene, and the operational conditions (such as screw configurations of extruders, rpm, temperature, etc.). The above factors determine whether the exfoliation of clay in the polypropylene melt is possible. The optimization of operational conditions makes the systems, which make the clay able to be exfoliated, to process successfully.

Polymer melt-direct intercalation or exfoliation is a promising approach because of its high productivity, low cost, and compatibility with current polymer processing technology, such as extrusion and injection molding.¹ In the processing equipment, the agglomerates of nanoclays are broken down due to the external forces from the polymer melt and the diffusion of macromolecules into the gaps. It is known that the

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TABLE I
Properties of Polypropylene and Maleated Polypropylene^a

	Polypropylene	Maleated Polypropylene
Grade/supplier	PP6524NT/Basell	Polybond® 3200/Crompton
Melt flow rate (190°C/2.16 kg) (g/10 min)	4.0	110
Density at 23°C (g/ml)	0.9	0.91
Melting Temperature (°C)	162	157
Maleic anhydride level, (wt %)	N/A	1.0

^a Supplier's literature.

external force applied on the clay agglomerates from the polymer melt depends on shear rate, melt viscosity, surface area of clay, and surface tension at the interface (between melt and clay), whereas the diffusion of macromolecules relies among others on the melt temperature, chain structure, gap spacing, time, and type/concentration of surfactant modifiers at the clay surface.³⁻⁵ If the processing is carried out with a corotating twin screw extruder, the applied force on the clays and the diffusion of macromolecules would be affected by the operational conditions and screw configurations.

Recently, the effects of extrusion compounding conditions upon the properties of nanocomposites have attracted significant attention.⁶⁻¹³ The main conclusions of these studies are as follows: (1) Sufficient long residence time is necessary to intercalate or exfoliate the nanoclays in the polymer matrix. (2) Excessive shear intensity could cause poor exfoliation. (3) Even at equivalent residence times, exfoliation of the clay in composites prepared in single-screw extruders is generally poorer than that in twin-screw extruders. (4) The clay could be exfoliated even at low shear rate when the process temperatures are high, due to the fact that the diffusion of polymers into the interlayers is enhanced. Hence, the design of screw configuration and the selection of temperature and screw rotating speed in twin-screw extrusion is critical in the processing of nanocomposites.

Common analytical methods to determine exfoliation of nanoclays are TEM and XRD characterization. The objective of the current work is the understanding of the effects of processing conditions in melt extrusion on the exfoliation of nanoclays in a polymer matrix through rheology, rather than full structural analysis. In this study, two mixing methods were designed to compound polypropylene-based clay nanocomposites. A numerical simulation was carried out to visualize the conveying mechanisms of the polymer melt in the extruder. The effects of shear rate, residence time, and mixing protocols on the structures of nanocomposites produced in twin-screw extruders were investigated with rheology and X-ray diffraction analysis. Melt flow index (MFI) measurement was selected as a simple method to study the relationship between rheology and morphology of the melt-compounded composites. It is well known that the viscous behavior of a polymer composite at a given filler loading is sensitive to the aspect ratio of fillers, especially at low shear rates, such as those encountered in a plastometer, where the effects of flow orientation are minimized. At high shear rates, the distribution and orientation of fillers in the polymer may be changed significantly. Experimental data of complex viscosity measurements in a dynamic analyzer indicate that the MFI method is reliable.

TABLE II
Nanoclays and their Organic Modifiers^a

	Nanoclay C15A	Nanoclay C30B
Grade/supplier	Cloisite 15A/Southern Clay Products	Cloisite 30B/Southern Clay Products
Organic modifier	Dimethyl, dihydrogenated tallow, quaternary ammonium chloride, where HT is hydrogenated tallow (~ 65% C18; ~ 30% C16; ~ 5% C14); Anion: Chloride	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride, where HT is hydrogenated tallow (~ 65% C18; ~ 30% C16; ~ 5% C14); Anion: chloride
Structure of organic modifier	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{HT} \\ \\ \text{HT} \end{array}$	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{N}^+-\text{HT} \\ \\ \text{CH}_2\text{CH}_2\text{OH} \end{array}$
X ray d_{001} (Å)	31.5	18.5

^a Supplier's literature

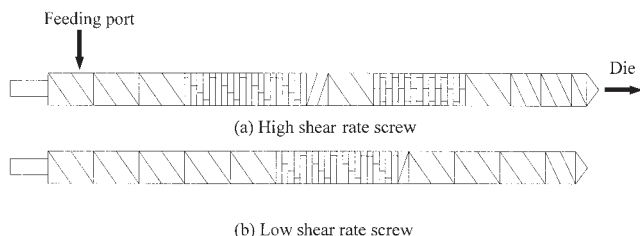


Figure 1 Screw configurations in the twin-screw extruder.

EXPERIMENTAL

Sample preparation

Polypropylene (PP6524NT, Basell, MFI = 4) was used as polymer matrix for the composites. Polybond® 3200 (PB), a maleic anhydride grafted PP from Crompton, was used as a potential compatibilizer. Its physical properties are listed in Table I. Two nanoclays, Cloisite® 15A and Cloisite® 30B, listed in Table II, both commercial products kindly provided by Southern Clay Products Co., were studied. These two clays are designated as C15A and C30B, respectively, in the discussion that follows.

The nanocomposites were prepared in the Twin Screw Mixing Evaluator Extruder (TSMEE, $D = 30$ mm, $L/D = 16.2$) at PPI,^{14,15} utilizing standard Werner and Pfleiderer ZSK-30 twin-screw extruder components. Two screw configurations designed for preparing the nanocomposites were denoted as high shear rate screw and low shear rate screw, and shown in Figure 1 and Table III. In the high shear screw, a forward kneading block followed by a reversed conveying screw element at a length of 20 mm is used to produce high shear; a neutral kneading block is designed to provide further mixing. In the low shear screw, the intensive mixing section is built with a forward kneading block, followed by a reversed conveying element at a length of 10 mm. Compared with the low shear screw, the high shear screw offers larger resistance to the conveying of the polymer melt along the screw, because it has not only a long reversed conveying element, but also a neutral kneading block. Thus, the fully filled length in the high shear screw would be longer than that in the low shear screw at identical operational conditions. Accordingly, the

mean residence time of the polymer in the high shear screw should be longer.

The nanocomposites were prepared by two different mixing methods, two-step mixing and one-step mixing. In the two-step mixing, the masterbatch of PB/clay (50/50) is first prepared with a high shear screw; then, the masterbatch is diluted with PP to reach a ratio of PP/PB/clay of 90/5/5 with either a high shear screw or a low shear screw. In the one-step mixing, direct mixing of PP/PB/clay (90/5/5) is carried out with a high shear screw or a low shear screw. In the present study, four mixing protocols were used, described with symbols 1- Step – High; 1- Step – Low; 2- Step - High/High; and 2- Step - High/Low, as shown in Table IV. Here, “High” and “Low” indicate that the mixing is carried out with a high shear screw or a low shear screw, respectively. As an example, 2-Step-High/Low indicates that the composite is made with a two-step mixing protocol, with the high shear screw for the masterbatch preparation (the first pass in the extruder) and the low shear screw for the dilution of the masterbatch (the second pass in the extruder).

The temperature of the barrel was set at 160/180/180°C, and the screw speed was set at 100 or 300 rpm. The feed rate in preparing the masterbatch was 3.6 kg/h, and 4.5 kg/h in diluting the materbatch and direct mixing (1-step mixing). The clay was dried in a vacuum oven at 80°C for 10 h before extrusion. The clay powders were dry blended with polymer pellets and then fed into the hopper of the extruder. Ten nanocomposite samples and three unfilled control samples were collected, as shown in Table IV.

Sample characterization

Three testing methods, MFI, complex viscosity measurement, and X-ray diffraction, were used to evaluate the effects of screw configurations and screw rotating speed, mixing protocols, and types of organic modifiers upon the structure of nanocomposites. A modified PP testing method of MFI was used for the nanocomposites: the testing temperature was set at 180 instead of 230°C, and a weight of 2.16 kg was applied. For each specimen, two measurements were made, and the final results were the average of these two mea-

TABLE III
Screw Configurations

High shear screw configuration	$3 \times \text{SE}42/42 + 4 \times \text{KB}45^\circ/5/28 + 2 \times \text{SE}20/10(\text{R})^a + \text{SE}42/42 + 3 \times \text{KB}90^\circ/5/28 + \text{SE}42/42 + 2 \times \text{SE}28/28 + \text{SE}14/28$
Low shear screw configuration	$5 \times \text{SE}42/42 + 4 \times \text{KB}45^\circ/5/28^b + \text{SE}20/10(\text{R}) + 3 \times \text{SE}42/42 + \text{SE}28/28$

^a SE20/10(R) represents a reversed conveying screw element with a pitch of 20 mm and a length of 10 mm. R stands for reversed (i.e., left hand flight).

^b KB45°/5/28 represents a kneading block with a stagger angle of 45° and an axial length of 28 mm, built with five pieces of kneading discs.

TABLE IV
Sample Designation

Sample no. ^a	Mixing protocol	Component	rpm
+1	1- Step - Low	PP/PB/C15A (90/5/5)	100
+2	1- Step - High	PP/PB/C15A (90/5/5)	100
++3	2- Step - High/High	PP/PB/C15A (90/5/5)	100/100
++4	2- Step - High/Low	PP/PB/C15A (90/5/5)	100/100
+5	1- Step - High	PP/PB/C15A (90/5/5)	300
+6	2- Step - High/High	PP/PB/C15A (90/5/5)	300
++7	2- Step - High/Low	PP/PB/C15A (90/5/5)	300/300
+8	1- Step - Low	PP/PB/C30B (90/5/5)	100
+9	1- Step - High	PP/PB/C30B (90/5/5)	100
++10	2- Step - High/High	PP/PB/C30B (90/5/5)	100/300
Control +11	1- Step - Low	PP/PB (95/5)	100
Control +12	1- Step - High	PP/PB (95/5)	100
Control ++13	2- Step - High/High	PP/PB (95/5)	100/100

^a +, number of mixing steps.

surements. The blends of polypropylene and PB were used as controls. Complex viscosity was measured with a Rheometrics Mechanical Spectrometer RMS-800 in a parallel mode. X-ray diffraction was performed on a Philips APD 3720, with the range of scanned angles between 0 and 80°.

EXPERIMENTAL RESULTS AND DISCUSSION

Melt flow index of nanocomposites

The test results are listed in Table V. These data show that the differences in MFI of the controls (PP/PB, 95/5) prepared with various mixing protocols, such as two-step with a high shear screw, one-step with a high shear screw or with a low shear screw, are small. This implies that the mixing protocols do not have a significant effect on the viscosity of the blends. Such effects would be manifested by increased MFI as a result of degradative chain scission and MW reduction. Although GPC data are not available, such data would be expected to confirm the insignificant differences on MW resulting from the different mixing pro-

ocols. Compared with the controls, the PP/PB/clay (C15 A or C30B) composites have lower MFI, i.e., higher viscosity. This confirms the already accepted fact that the presence of clay in the blends increases the viscosity. The C15A composites have lower MFI than the C30B composites. This possibly indicates that C15A has larger aspect ratio in the composites, i.e., C15A has been exfoliated and dispersed more than C30B.

It was also found that the composites prepared by the two-step process with a high shear screw have lower MFI than those prepared by the one-step process with either a high shear screw or a low shear screw. This shows that sufficient high stress and sufficient long residence time are required for the exfoliation and dispersion of the clays in the polymer. However, the MFI for the composites prepared by the two-step with a high shear screw method is very close to those prepared by a two-step-high/low mixing protocol, in which the masterbatch is prepared with a high shear screw and the dilution is carried out in a low shear screw. This indicates that the shear intensity

TABLE V
Melt Flow Index of Nanocomposites at 180°C and 2.16 kg^a

	PP/PB, 2-Step-High/High [13] ^b	PP/PB, 1-Step-High [12] ^b	PP/PB, 1-Step-Low [11] ^b	
Control at 100 rpm				
MFI	1.58	1.47	1.50	
C30B composites at 100 rpm	PP/PB/C30B, 2-Step-High/High [10] ^b	PP/PB/C30B, 1-Step-High [9] ^b	PP/PB/C30B, 1-Step-Low [8] ^b	
MFI	1.11	1.29	1.27	
C15A composites at 100 rpm	PP/PB/C15A 2-Step-High/High [3] ^b	PP/PB/C15A 1-Step-High [2] ^b	PP/PB/C15A, 1-Step-Low [1] ^b	PP/PB/C15A, 2-STEP-High/Low [4] ^b
MFI	0.99	1.08	1.10	0.96
C15A composites at 300 rpm	PP/PB/C15A 2-Step-High/High [6] ^b	PP/PB/C15A, 1-Step-High [5] ^b		PP/PB/C15A, 2-STEP-High/Low [7] ^b
MFI	1.18	1.14		1.19

^a MFI of PP 6425 (Bassel) at 230°C and 2.16 kg is 1.23 g/10 min.

^b Values in brackets are the sample numbers given in Table IV.

TABLE VI
Normalized Melt Flow Rate of Nanocomposites Prepared at 100 rpm (180°C and 2.16 kg)

C30B composites	PP/PB/C30B 2-Step-High/High [10]	PP/PB/C30B 1-Step-High [9]	PP/PB/C30B 1-Step-Low [8]
Normalized MFI	0.7	0.88	0.86
C15A composites	PP/PB/C15A 2-Step-High/High [3]	PP/PB/C15A 1-Step-High [2]	PP/PB/C15A 1-Step-Low [1]
Normalized MFI	0.63	0.73	0.74

in dilution may not have a significant effect on the mixing state. The possible reason is that the structures of clay platelets are mostly determined during the preparation of the masterbatch; thus, the change is small in the dilution process.

With increasing screw speed from 100 to 300 rpm, MFI rises. Since polypropylene may be degraded at a high shear rate, it is difficult to ascertain whether the clay has higher exfoliation, based only on the data from MFI. Thus, other experimental methods should be introduced, such as X-ray diffraction and TEM.

There are two factors determining the MFI of a composite, the viscoelastic properties of the polymer matrix and the distribution and structure of the fillers. To investigate the effect of the mixing protocol on the structure of the clays in the polymer, the dependence of the viscous properties (or MFI) of the polymer matrix on mixing history should be excluded. In this study, the normalized MFI is defined, assuming that the polymer matrix has the same MFI at identical processing history:

$$\text{Normalized MFI} = \frac{\text{MFI of composites}}{\text{MFI of corresponding control}}$$

Table VI summarizes the calculated results for the normalized MFI of nanocomposites prepared at 100 rpm. These data show that composites prepared by the two-step process in a high shear screw have a lower normalized MFI than those prepared by the one-step process with either a high shear or a low shear screw. At identical mixing protocols, the C15A composites have lower normalized MFI than the C30B composites. MFI of the samples prepared with the one-step process in a low shear screw is very close to that of samples made with the one-step process in a high shear screw.

It was expected that C30B would have better exfoliation and dispersion in polypropylene than C15A, because the organic modifier of C30B has two ethoxy groups (Table I), which should have stronger interactions with the PB. However, data in Tables V and VI show that C15A composites have higher viscosity than C30B composites (at low shear rate), which suggests that C15A was more exfoliated than C30B in polypropylene with PB as compatibilizer. This is consistent with the studies of Lee et al.¹⁶ In their work, compos-

ites PP/MA-g-PP/C30B were prepared at 210°C for 10 min by using a Brabender mixer at 50 rpm, and X-ray diffraction patterns showed that the interlayer spacing in the composites is smaller than the original spacing of the clay. As explained by the authors, the partial exfoliation of C30B in PP was due to its poor thermal stability and its initial smaller interlayer spacing. TGA data by the present authors indicate weight losses for C30B of about 3% and lower for C15A (less than 2%) at 200°C, at a scan rate of 10°C/min under nitrogen atmosphere. Higher melt process temperature, shear rate effects, and presence of oxygen may result in lower thermal stabilities during actual extrusion compounding, in agreement with the observations of Lee et al.¹⁶

Complex viscosity of nanocomposites

Figure 2 shows the results of the complex viscosity versus frequencies of nanocomposites, measured by RMS at 180°C and at a sweep strain of 10%. Figure 2 shows that the nanocomposites have higher viscosity than the unfilled blends. The complex viscosity of the blend PP/PB prepared with the two-step mixing in a high shear screw is slightly higher than that made with the one-step mixing in a low shear screw. The C15A composites prepared with the one-step mixing in a low shear screw has larger viscosity than the C30 composites made with the one-step mixing in a high shear screw. These trends are consistent with the data from MFI measurements, suggesting that it is reasonable to employ MFI to study the relationship between rheology and morphology of the nanocomposites.

X-ray diffraction analysis of nanocomposites

As discussed in the previous sections, C30B composites have lower viscosity than C15A composites, possibly due to the initial small interlayer spacing and the degradation of C30B during processing. This section focuses on the effect of mixing protocols on the structure of C15A nanocomposites as determined by X-ray diffraction. Figure 3 shows the X-ray intensity in C15A composites prepared with different mixing protocols. This plot indicates that C15A nanocomposites prepared by the two-step process with a high shear screw at 100 rpm have lower angle 2θ (about 1.8°) than those

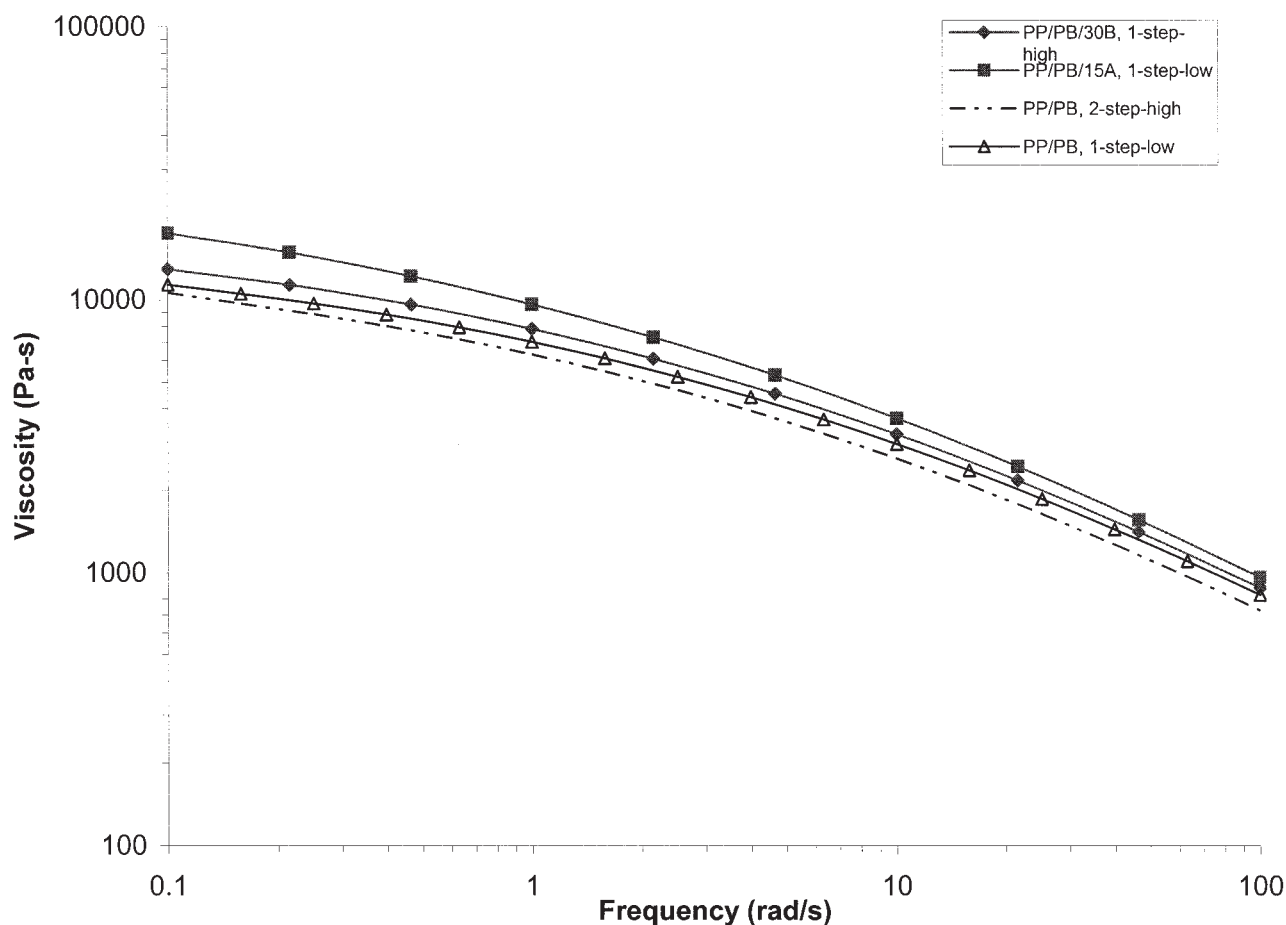


Figure 2 Complex viscosity versus frequencies of nanocomposites at 180°C.

prepared by the one-step process with a low shear screw at 100 rpm and by the two-step protocol with a high shear screw at 300 rpm. In the last two cases, angle 2θ is almost identical (about 2.5°). It is known that the interlayer spacing, d_{001} , can be calculated from peak positions using Bragg's law, $d_{001} = \lambda / (2\sin\theta)$, where λ is the X-ray wavelength (1.5418 \AA). Consequently, peak angle 2θ at 1.8° is corresponding to an interlayer spacing of 4.91 nm, whereas an angle 2θ at 2.5° represents a spacing of 3.53 nm. According to Table I, the initial interlayer space for clay C15A is 3.15 nm. This indicates that C15A composites prepared with the two-step process with a high shear screw at 100 rpm have been more exfoliated than others. Possible reasons are given in the next section.

The shift in the diffraction peak to lower 2θ value may not always offer evidence for exfoliation, but for ordered or disordered intercalation, which has been confirmed by various authors by TEM examination. Complete analysis by X-ray diffraction and TEM examination would have been highly beneficial, but tedious, considering the large number of formulations involved and the fact that it is beyond the scope of this article, as stated in the Introduction.

SIMULATION RESULTS AND DISCUSSION

To visualize the flow of the polymer melt in the screw elements, a 3-D numerical simulation with isothermal Newtonian conditions has been carried out. The screw channel is assumed to be fully filled. In the process for the masterbatch dilution or the direct mixing, the polymer melt has a viscosity of 500 Pa-s and a density of 0.77 g/cm^3 , and the flow rate is 4.5 kg/h. In the preparation of masterbatch, the viscosity and the density of the melt are 150 Pa-s and 1.03 g/cm^3 , respectively, and the flow rate is 3.6 kg/h. The numerical simulation used the commercial computational fluid dynamics software FLUENT 6.0.

Based on the numerical simulation results, the pressure gradient along the axial length in different screw elements at a flow rate of 4.5 kg/h is calculated and shown in Figure 4. Here, KB45 and KB90 represent the kneading blocks with stagger angles of 45° and 90° ; SE20R and SE42 stand for conveying elements with pitches of 20 mm (reversed) and 42 mm, respectively, as shown in Table III. Figure 4 shows that SE42 has a higher capability in building pressure along the axial length than KB45, while the pressure drops faster in

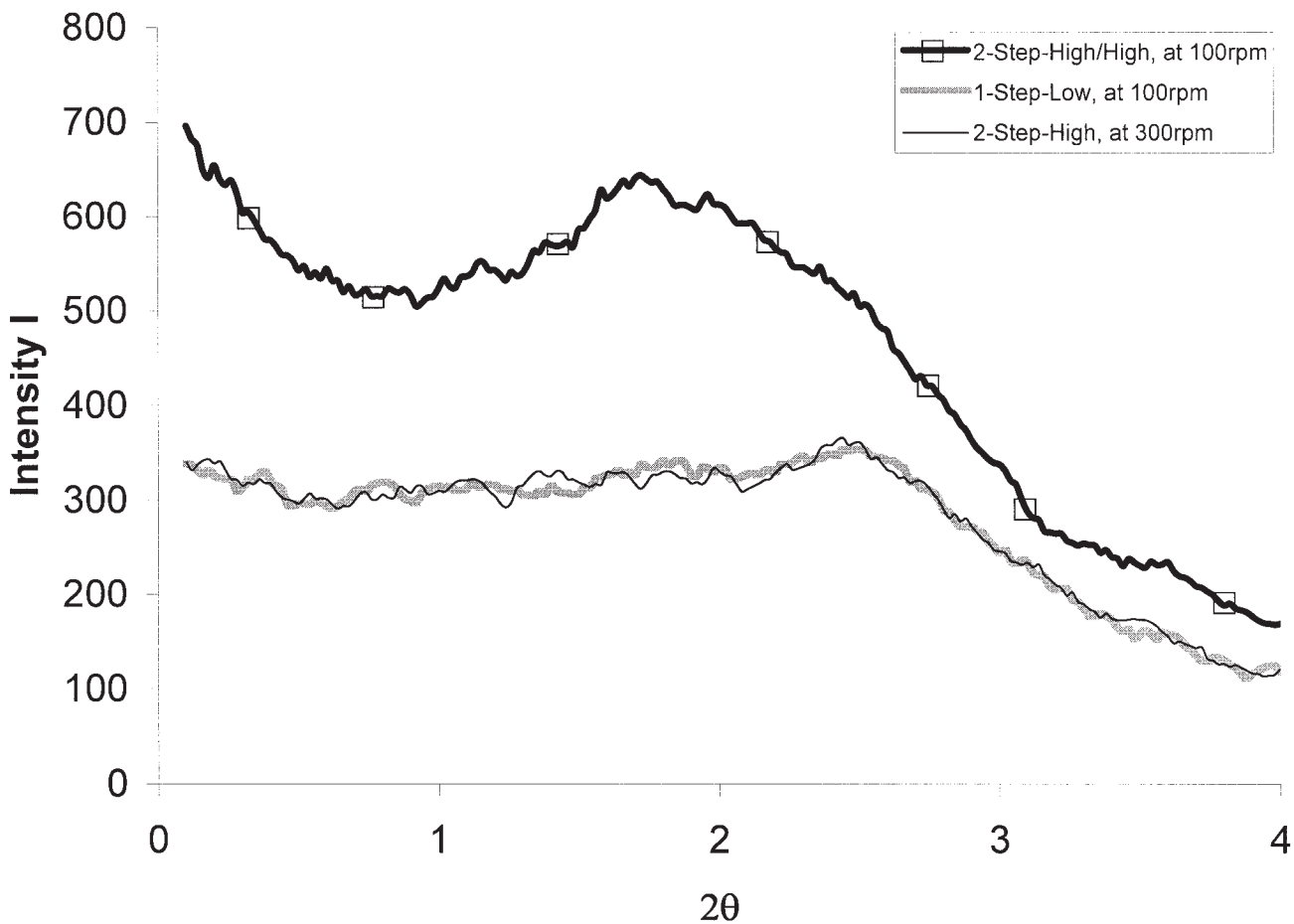


Figure 3 X-ray diffraction of PP/PB/C15A nanocomposites.

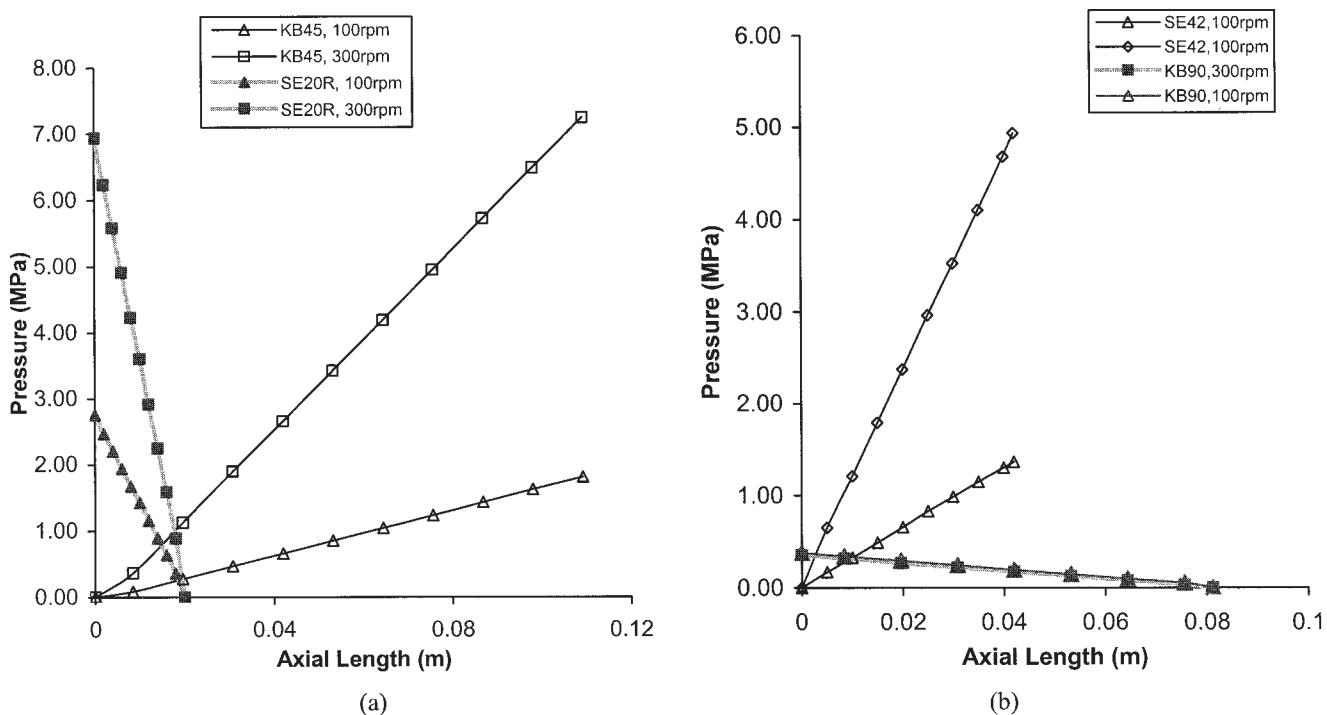


Figure 4 Pressure gradients along axial length at a flow rate of 4.5 kg/h in different screw elements (a) KB45 and SE20R and (b) SE42 and KB90.

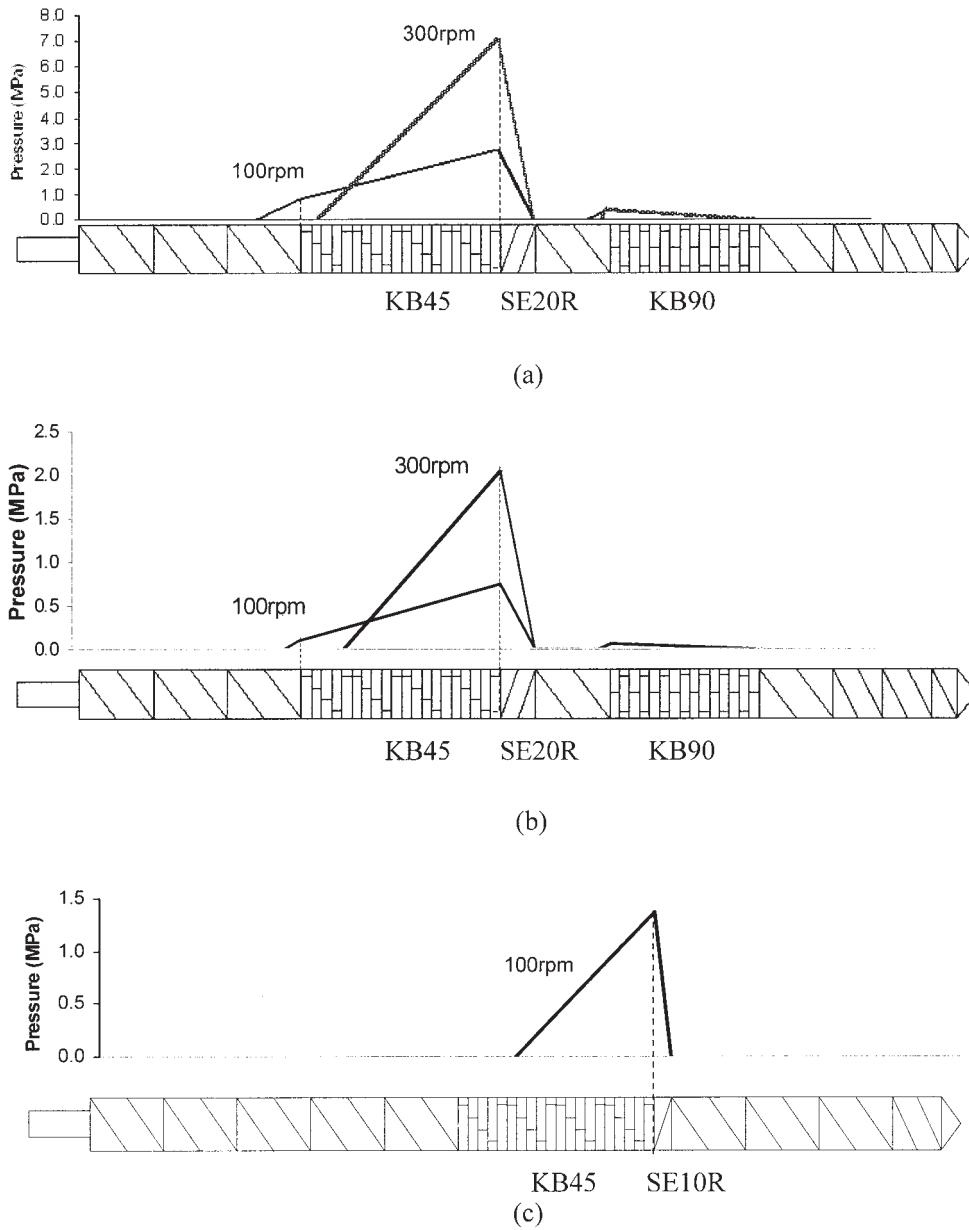


Figure 5 Pressure profile along axial length in (a) high shear screw in masterbatch dilution, (b) high shear screw in masterbatch preparation, and (c) low shear screw in direct mixing or masterbatch dilution.

the SE20R than KB90. According to the relationship between pressure and axial length given in Figure 4, the pressure profile along the axial length could be calculated, as illustrated in Figure 5. In Figure 5, the pressure near the screw tip is not displayed.

Figure 5(a) shows that in the high shear screw, the maximum pressure located at the inlet of SE20R, is raised significantly with increasing screw speed. The pressure profile in KB90 does not change greatly at different screw speeds. The fully filled length along the screw is reduced when the screw speed is raised from 100 to 300 rpm, but not to a large extent. Hence, in processing with the high shear screw, the mean residence time of the polymer melt is slightly longer at

100 than at 300 rpm. Table VII shows the residence time in the fully filled length of these two screw configurations.

Figures 5(a and b) show that, in the masterbatch preparation, the maximum pressure is much lower,

TABLE VII
Calculated Mean Residence Time at 4.5 kg/h Extruder Output

Screw	High shear screw		Low shear screw	
	100	300	100	300
Rotational speed (rpm)	100	300	100	300
Residence time (s)	68.9	58.9	24.6	18.0

and the fully filled length along the screw length is slightly shorter than that in the masterbatch dilution. This is because, in the former, the system has lower viscosity and lower flow rate. Figure 5(c) indicates that the fully filled length and the maximum pressure are much lower in the low shear screw than in the high shear screw [Fig. 5(a)]. That is, the mean residence time in the former is much shorter than in the latter (Table VII). Another important parameter for mixing is the shear rate, which rises with increasing screw speed. For example, simulation shows that the average shear rate in KB45 at 100 rpm is about 59.6 s^{-1} , but is about 181.2 s^{-1} at 300 rpm.

Thus, it is easily understood that the composites made with the one-step process in a low shear screw have less exfoliated platelets than those prepared by the two-step processing in a high shear screw (Fig. 3), because the former has both shorter residence time and lower shear rate. As shown in Figure 3, the nanocomposite prepared with the two-step process with a high shear screw at 300 rpm has a similar interlayer spacing as that made with the one-step process with a low shear screw at 100 rpm, although the latter has much shorter residence time. This is possibly due to the fact that high shear rates coupled with long residence time in the two-step mixing protocol with a high shear screw at 300 rpm may break the platelets stacks or make the partially intercalated structures collapse.

CONCLUSION

In this study, the effects of screw configurations and mixing protocols on the nanoclay structure in polypropylene were investigated. Experimental results of MFI show that C15A composites have higher viscosity (lower MFI) than C30B composites. This indicates that C30B was less exfoliated, which agrees with some recent publications.¹⁶ The mixing protocols have some effects on the MFI of the composites. Generally, in a two-step mixing method, nanocomposites have lower MFI. That is, the composites prepared by the two-step mixing method may have better exfoliation than those produced by the one-step mixing

method, in which polypropylene, PB, and clay are mixed directly in an extruder. The complex viscosity measurement from the dynamic analyzer indicates that the MFI method is reliable. A numerical simulation has been carried out to calculate the mean residence time and shear rate in different screw configurations under various operational conditions. The X-ray diffraction testing results indicate that the mixing time (or residence time) of the polymer within the extruder is a critical factor in the preparation of nanocomposites, but high shear rates combined with long residence times may break the exfoliated structures and stacks of the nanoclays.

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