INFLUENCE OF SCREW PROFILE AND EXTRUSION CONDITIONS ON THE STRUCTURE OF POLYPROPYLENE/ORGANOCLAY NANOCOMPOSITES

W. Lertwimolnun*, B. Vergnes

CEMEF, Ecole des Mines de Paris, UMR CNRS 7635, BP 207, 06904 Sophia Antipolis Cedex, France, wbln@kmitnb.ac.th, bruno.vergnes@ensmp.fr

Abstract - Direct melt mixing in a twin screw extruder is a simple and classical technique for preparing nanocomposites by dispersing nanoclay in a thermoplastic matrix. We are interested here in the preparation of organoclay/polypropylene nanocomposites, using maleated polypropylene as compatibilizer. The objective of the work is to characterize the influence of screw profile and processing conditions on the microstructure of the nanocomposite (intercalation and exfoliation). Different screw profiles, more or less severe in terms of mixing elements, have been investigated. For each profile, different processing conditions (feed rate, screw speed) have been tested. Samples were collected and analyzed (X-ray diffraction, transmission electron microscopy and rheometry) both at die exit and all along the screw profiles. Numerical simulation has been used to quantify the thermomechanical treatment experienced by the material inside the extruder. The results show that the severity of the profile does not lead necessarily to the best microstructure.

Introduction

Melt intercalation is one of the most promising techniques for preparing polymer/organoclay nanocomposites. On the basis of this method, the organoclay is dispersed within the polymer in the melting state. If different techniques may be used for mixing process, co-rotating twin screw extrusion remains the most popular, principally in reason of its great flexibility: screw profile can be easily modified and adapted to the application, feed rate and screw speed could be independently varied, materials could be fed or removed at different positions along the screws, etc. All of these aspects have an important influence on the state of intercalation and exfoliation of organoclay. Generally speaking, it is well admitted in the literature that an increase in screw speed leads to a better dispersion. This has been observed on different systems, including polyamide- and polypropylene-based nanocomposites [1-7]. It can be explained by the fact that a higher shear rate allows to break the agglomerates in smaller aggregates. Moreover, Homminga et al. [8] have shown that intercalation and exfoliation are largely accelerated in presence of flow. However, it should be noted that a negative effect of the screw speed on exfoliation was also observed in the specific case of a PBT/organoclay system [9].

The influence of other parameters, including feed rate and temperature, have also been reported in the literature. Increasing feed rate induces mainly a strong reduction in residence time and specific energy. Lertwimolnun et Vergnes [3] and Nassar et al. [10] have found no effect of feed rate on the state of intercalation. However, the state of exfoliation was significantly improved when feed rate decreased. The improvement of exfoliation was probably related to the corresponding increase in the residence time as feed rate decreased [3, 11-13]. The results reported in the literatures for the effect of regulation temperature are relatively controversial. Cho and Paul [1] did not observe a clear impact of the temperature. Kwak et al. [14] reported a better dispersion at high temperature (230°C instead of 170°C). On the contrary, Modesti et al. [5,6] obtained better results at low temperature (170°C instead of 200°C). In fact, it seems that the temperature cannot be considered independently of the other parameters, screw speed and feed rate [13]. As temperature increases, viscosity decreases, and thus the stress necessary to break the clay aggregates decreases. At the same time, diffusion is improved, that can help to intercalate and exfoliate the platelets. In addition, a too high temperature could cause a degradation of the organoclay intercalants, leading to a collapse of the interlayer galleries and a decreased intercalation [15].

Beside the processing conditions, the screw profile may have an important effect on the state of dispersion of organoclay. The final morphology of the nanocomposite is not only a question of shear stress or residence time, but a complex result of all the thermal and mechanical history supported by the material along the screw profile. In comparison to the effect of processing conditions, only a few numbers of studies were focused on the influence of screw profile, especially on the evolution of the nanocomposite structure along the screws [3, 16-18]. In the present study, we have used stop dead experiments to investigate the evolution of morphology all along the screws. The objective was to characterize the influence of screw profile and processing conditions on the microstructure of the nanocomposite (intercalation and exfoliation) and eventually to identify the key parameters for the formation of nanocomposites.

*Present address: King Mongkut’s Institute of Technology North Bangkok, THAILAND

The Polymer Processing Society 23rd Annual Meeting
Experimental

Materials

All polymers used in this study were provided by Atofina (presently Arkema and Total Petrochemicals). The homopolymer polypropylene (PP) of extrusion grade (PPH 5060) had a melt index (MFI) of 6 g/10 min and a melting temperature of 164°C. A maleic anhydride grafted polypropylene (PP-g-MA) was used as a compatibilizer (OREVAC© CA100). It contained 1 wt.% of maleic anhydride and had a MFI of 10 g/10 min and a melting temperature of 161°C. The organoclay used was Cloisite®20A, purchased from Southern Clay Products (Gonzales, TX). It is a Na⁺-montmorillonite, chemically modified with dimethyl dehydrogenated tallow quaternary ammonium chloride.

Preparation of polypropylene-organoclay nanocomposites

The series of PP/PP-g-MA/Cloisite®20A nanocomposites were prepared in an industrial self-wiping co-rotating twin screw extruder Clextral BC45 (Clextral, Firminy, France), with following characteristics: centerline distance 45 mm, screw diameter 50 mm, barrel length 1.2 m, L/D = 24. Three different screw profiles, shown in Figure 1, were built in order to increase mixing and residence time, by including more and more kneading blocks and left-handed elements along the screws. Profile 1 included a left-handed element for the melting and three blocks of kneading discs with positive (+30°), neutral (90°) and negative (-45°) staggering angles. In profile 2, melting was assured by a block of negative staggered kneading discs, and mixing by three blocks of kneading discs and a left-handed screw element. Finally, profile 3 included a left-handed element for the melting and four intensive mixing zones with kneading discs and a second left-handed element.

Figure 1. Screw profiles used for the preparation of PP/PP-g-MA/Cloisite®20A nanocomposites.

The organoclay (Cloisite®20A) and the compatibilizer (PP-g-MA) were dried at 80°C for 12 h in a vacuum oven prior to compounding. PP, PP-g-MA pellets and dried organoclay were tumble mixed and introduced simultaneously in the hopper. The formulation used was fixed for all the experiments and equal to 80/15/5 (PP/PP-g-MA/Cloisite®20A), expressed in mass fraction.

Compounding was carried out at fixed barrel temperatures (80°C for the barrel 1, 180°C for the others). Feed rate and screw speed were varied independently from 5 to 30 kg.h⁻¹ and 100 to 300 rpm, respectively. For each condition and each screw profile, samples were collected at the die exit (after having reached steady-state extrusion conditions) and immediately quenched in water. Afterwards, screw rotation and feeding were suddenly stopped and the barrel was quickly cooled to a temperature of 100°C by internal water circulation. After a few minutes (~ 5 to 10 min), the barrel was removed, allowing access to the screws. Morphological changes along the screws can then be characterized by collecting samples at different locations, as indicated in Fig 1. These locations are represented by the points A to G.
Structure and morphological characterization

The state of intercalation was quantified by wide angle X-ray diffraction (WAXD). WAXD data were collected on a Philips X’Pert PRO with Cu Kα radiation of wavelength 1.54 Å. The accelerating voltage was 40 kV. Diffraction spectra were obtained over a 2θ range of 2°–10° and the interlayer spacing \( d \) was calculated using the Bragg’s equation:

\[ \lambda = 2d \sin \theta, \]

where \( \lambda \) is the wavelength. The samples were prepared as discs of diameter 50 mm and thickness 1 mm by compression molding at 180°C. Each measurement was repeated four times, on two different surfaces. The state of exfoliation was characterized by transmission electron microscopy (TEM) and rheological measurements in small amplitude oscillatory shear (SAOS) [2]. TEM observations were performed on a Philips CM12 with an accelerating voltage of 120 kV. TEM samples, around 90 nm thick, were cut from the material as taken out from the screws and at die exit. Sections were made using a cryo-microtome equipped with a diamond knife at a temperature of - 80°C. SAOS measurements were performed in the linear viscoelastic domain, using a parallel plate rheometer (RMS 800, Rheometrics), with samples of diameter 25 mm and thickness1 mm. As for WAXD, samples were prepared by compression molding at 180°C. Frequency sweep tests were carried out between 0.01 and 100 rad.s\(^{-1}\) at 180°C under nitrogen to prevent from degradation.

Flow modeling

Flow along the twin screw extruder was simulated using the Ludovic© software [19] developed a few years ago. It is a global 1D model of the twin screw extrusion process, which allows one to calculate, from hopper to die exit, the values of the main flow parameters (such as pressure, filling ratio, shear rate, temperature…) for non-Newtonian, non-isothermal and even reactive systems. Experimental validations [20, 21] and intensive use of Ludovic© software in many applications have shown its ability to depict adequately the flow conditions inside a twin screw extruder [22-25].

Results and Discussion

Effect of screw profile on the final morphology

We first investigate the effect of screw profile on the state of intercalation, using WAXD measurements, for the samples collected at the die exit. Fig. 2 shows WAXD spectra of samples prepared with different feed rates at same screw speed (\( N = 200 \) rpm), for the different screw profiles. In all cases, the peak characteristic of the \{001\} basal reflection of organoclay is clearly observed. Compared to the native Cloisite®20A, the peak is shifted toward lower angles, indicating the formation of an intercalated structure after extrusion process. The interlayer spacing, \( d_{001} \), calculated using the Bragg’s equation, is shown in Fig. 3, as function of feed rate and for the different screw profiles.

![Figure 2. WAXD spectra of nanocomposites prepared with different feed rates at fixed screw speed (N = 200 rpm) using different screw profiles.](image)

At high feed rates (15 and 30 kg.h\(^{-1}\)), all results present a similar interlayer distance, around 3.2 nm. This independence of intercalation with the screw profile was also reported by Andersen [26]. However, at low feed rate (5 kg.h\(^{-1}\)), it means at longer residence time and higher specific energy (mean residence times for profiles 1, 2, and 3 are respectively 197 s, 250 s, and 320 s, at feed rate of 5 kg.h\(^{-1}\)), we observe a shorter interlayer distance for profiles 2 and 3, indicating a partial collapse of the crystallites. This effect could be related to the temperature. As profiles 2 and 3 are
more restrictive, they induce a higher melt temperature by viscous dissipation. Combined to higher residence times, this can lead to the degradation of the organic intercalant or to the expulsion of the intercalated polymer chains, resulting in a shorter interlayer distance.

Figure 3. Interlayer distance as function of feed rate at constant screw speed ($N = 200$ rpm) for the different screw profiles.

The state of exfoliation at the die exit has been characterized by rheological measurements (SAOS). The complex viscosity $|\eta^*|$ of all nanocomposites is presented in Fig. 4. An increase of $|\eta^*|$ at low frequency is observed for all samples. Such increase is generally attributed to an improvement in the level of exfoliation [27-31]. In order to characterize the state of exfoliation quantitatively, we have recently proposed [2, 3] to use a Carreau-Yasuda model with yield stress, originally introduced by Berzin et al. [32]:

$$\eta^*(\omega) = \frac{\sigma_0}{\omega} + \eta_0 \left[1 + (\lambda \omega)^n\right]^{-1}$$  \hspace{1cm} (1)

where $\sigma_0$ is the melt yield stress, $\eta_0$ is the zero shear viscosity, $\lambda$ is the time constant, $\alpha$ is the Yasuda parameter and $n$ is the dimensionless power law index. These five parameters were adjusted for obtaining the best fit with the experimental data. The superposition between the experimental data and the fit curves are also shown in Fig. 4. The level of exfoliation has been related to the parameter $\sigma_0$, which controls the increase of complex viscosity a low frequency at constant organoclay loading.

Figure 4. Complex viscosity of PP/PP-g-MA/Cloisite®20A nanocomposites prepared with different feed rates at same screw speed ($N = 200$ rpm) for the different screw profiles (symbols are experimental values, full lines are theoretical fits using Eq. (1)).

Fig. 5 shows the evolution of the melt yield stress $\sigma_0$ as function of $N/Q$ ratio (screw speed to feed rate) for the different screw profiles. For each profile, we observe a linear increase of exfoliation with $N/Q$. But the curves are distinct, indicating the influence of screw profile on the nanocomposite microstructures and, surprisingly, exfoliation is better for the profile having less mixing elements. In the literature, comparisons are often made on only two profiles, a "low shear" one and a "high shear" one. In these conditions, no clear effect of profile on dispersion was noted by Zhu.
and Xanthos [33], whereas a better result was observed on the “high shear” profile by Mehrabzadeh and Kamal [34] and Borse and Kamal [35]. In some cases, an improvement of the dispersion was noticed when the material was extruded a second time [1, 33], what can be roughly considered as equivalent to chose a more restrictive screw profile.

Figure 5. Evolution of the melt yield stress as function of \( N/Q \) ratio for the different screw profiles

Morphology evolution along the screws

To characterize the evolution of the nanocomposites along the screws, a possibility is to stop the extruder in steady state conditions, to rapidly cool the barrel and then to remove it to have access to the screws (dead stop experiment). Fig. 6 shows an example for the profile 3, with the samples collected at different locations for structural analyses.

Figure 6. Example of dead stop experiment for screw profile 3 (\( N = 200 \text{ rpm}, Q = 15.2 \text{ kg.h}^{-1} \)).

Let us first consider the evolution of the state of intercalation, that has been characterized using WAXD. Fig. 7 shows the interlayer distance along the screws at different feed rates (\( N = 200 \text{ rpm} \)) for the different screw profiles. For the profile 1 (Fig. 7a), compared to the original Cloisite\(^{\circledast}\)20A (\( d_{001} = 2.51 \text{ nm} \)), we observe an intercalated structure (\( d_{001} \approx 3.2 \text{ nm} \)) whatever the location of the sample along the screws. Similar results were observed for other conditions of feed rate and screw speed [36]. The increase in interlayer spacing is observed very early in the flow, just after the melting section of the profile. It indicates that, in these strong flow conditions, intercalation is a very fast process, taking place in less than 20 s. This was already shown by Homminga et al. [8] on a Couette system, but a much lower shear rate and thus much longer times. Here, we show that the intercalation of polymer chains into the organoclay galleries can be achieved in a few tenths of seconds.

For the profile 2 (Fig. 7b), at high and intermediate feed rates (15 and 30 kg.h\(^{-1}\)), the situation is similar to the case of profile 1: intercalation appears at the end of the melting zone and remains identical along the screws (\( d_{001} = 3.0 \text{ -} \))
3.2 nm). But, at low feed rate (5 kg.h⁻¹), we observe a decrease of the interlayer distance in the second block of kneading discs. As previously explained, a combination of local high temperature and long residence time (in this case, we can estimate it, using Ludovic© software, to 220°C and 110 s [36]) can induce either a degradation of the organic intercalant or an expulsion of the already intercalated polymer chains. This is confirmed with profile 3 (Fig. 7c) where a decrease in interlayer spacing is also observed at low feed rate.

The evolution of the state of exfoliation is characterized, as previously, by using the values of the melt yield stress. Fig. 8a shows the results obtained with profile 1 at different feed rates. As already observed, the general level of exfoliation tends to increase when feed rate decreases. But the evolution along the screws depends strongly on the value of the feed rate. For low or intermediate values, the exfoliation is already obtained, like intercalation, after the melting zone, and it remains more or less constant along the screws. At low feed rate, however, exfoliation increases gradually through the different mixing sections and the maximum is obtained at the die exit.

Results concerning profiles 2 and 3 are shown in Figs. 8b and 8c. In all conditions, a partially exfoliated structure is already observed after the melting zone. Further evolution of this structure is controlled by the feed rate: for profile 2 (Fig. 8b) at low feed rate (5.5 kg/h), exfoliation increases progressively. At intermediate value (14.8 kg/h), it remains unchanged. At high feed rate (30.7 kg/h), exfoliation surprisingly decreases between melting section and die exit. These results are confirmed on profile 3 (Fig. 8c).

These different results show that, in the conditions we tested, both intercalation and exfoliation are fast mechanisms that take place in a few tenths of seconds during the melting phase. Afterwards, depending on profile and processing conditions, this microstructure can be improved or not. But the role of individual parameters (temperature, shear rate, residence time) or specific screw elements (left-handed elements, kneading discs) remains difficult to explain and would necessitate complementary experiments. The complexity of the problem may explain the results sometimes contradictory found in the literature.

**Theoretical interpretation**

In order to try to find adequate parameter allowing to link the level of exfoliation to processing conditions, we have used numerical modeling of the twin screw extrusion process. Based on the linear relationships between melt yields stress \(\sigma_0\) and \(N/Q\) ratio (Fig. 5), we may imagine that global deformation or specific energy could be possible candidates able to control the exfoliation process [3]. Indeed, these parameters are linear functions of \(N/Q\) ratio. Fig. 9
shows the plot of melt yield stress as a function of computed deformation (Fig. 9a) and specific energy (Fig. 9b), for the three screw profiles, the different processing conditions and the various sample locations. It is clear that, for a fixed screw profile, a mastercurve independent of processing conditions and sample locations can be obtained, choosing either deformation or specific energy as parameter. However, these curves are different for the different profiles, indicating that other influences have to be taken into account, and that the key parameters are not only deformation or specific energy. We may imagine that temperature, through possible degradation of both matrix and organoclay, could be one of these additional parameters.

Figure 9. Evolution of the melt yield stress $\sigma_0$ as function of computed deformation (a) and specific energy (b) for the different screw profiles.

Conclusion

In this study, the effect of screw profile for various processing conditions was investigated. The results show that the intercalation process appears as a rapid mechanism, generally observed as soon as the matrix is melted. The level of intercalation is quite independent of the processing conditions and, except in the case of severe conditions (high speed, high temperature, long residence time), remains identical all along the process. On the contrary, exfoliation may be partially controlled by processing conditions. For a fixed screw geometry, the level of exfoliation is proportional to the ratio $N/Q$, (screw speed/feed rate) and seems controlled by the total deformation (shear rate $\times$ residence time) or by the specific energy experienced by the material. However, this is not exactly true if we want to compare different screw profiles: in this case, the most severe profile is not the more efficient, indicating that other parameters have to be taken into account in the exfoliation mechanism.

Acknowledgements

Polymers used in this study (PP, PP-g-MA) were kindly provided by Atofina (now, Arkema and Total Petrochemicals), which is gratefully acknowledged.

References

2. W. Lertwilomnun; B. Vergnes, Polymer, 2005, 46, 3462.
5. M. Modesti; A. Lorenzetti; D. Bon; S. Besco Polymer, 2005, 46, 10237.
27. R. Wagener; T.J.G. Reisinger *Polymer*, 2003, 44, 7513.