

Microstructure and on-line shear viscosity of PP/nano-CaCO₃ composites prepared by twin-screw extruder

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Polymer-based nanocomposites have been extensively studied in research and application because the addition of the nanoparticles provides an increased stiffness, toughness, and dimensional stability. The aggregation of the nanoparticles, however, owing to their high surface energy, strongly decreases the properties of the nanocomposites, which enormously limits their engineering applications. Nano-calcium carbonate (CaCO₃) is one of the most commonly used nanoparticles for thermoplastics, such as polypropylene (PP) and poly(vinyl chloride) (PVC). Many efforts have been devoted to decrease the aggregation of the nano-CaCO₃ particles. The surface modification of the nano-CaCO₃ is believed to be one of the effective ways, which can increase the polymer–nanoparticle interactions [1–4].

The morphology and properties of the polymer nanocomposites or polymer blends are deeply related to the flow field during their processing. The research by Huang et al. showed that the type of the mixing and the intensity of the shear in the extruder screw exhibit a distinct influence on the microstructure of the PP/organic-montmorillonite (org-MMT) nanocomposite [5] or polymer blends [6, 7] prepared by direct melt intercalation or melt blending. In the preparation of the polymer/nano-CaCO₃ composites by a twin-screw extruder, screw configuration and speed play an important role in the dispersion of nano-CaCO₃. Jiang

et al. [8] prepared acrylonitrile-butadiene-styrene (ABS)/nano-CaCO₃ composite in a Haake conical twin screw extruder at a screw speed of 50 rpm. Morphology observation of nanocomposites showed that a large aggregation (~16.7 μm) for the nanocomposite with the CaCO₃ content of 20 wt% was observed. Zhang et al. [9] prepared PP/nano-CaCO₃ composites using a co-rotating twin screw extruder. Although the screw speed was set at 300 rpm, the dispersion of nano-CaCO₃ (treated by fatty acid) in PP was poor, especially at high CaCO₃ content (15 wt%).

Recently, rheological analysis is considered as an effective tool for investigating the microstructure of polymer nanocomposites [10–13]. However, there exist contrary results about the effect of nanoparticles on the rheological behavior for polymer. For example, for the polymer/nano-CaCO₃ composites, the research by Wu et al. [14] showed that the addition of nano-CaCO₃ particles into PVC resulted in a remarkable increase in the melt viscosity. However, Xie et al. [15] reported that the apparent viscosity of PVC/CaCO₃ nanocomposites decreased with increasing nanoparticle loading and was lower than that of pristine PVC at high shear rate (>100 s⁻¹). In the previous studies, the melt shear viscosity of nanocomposites was measured using a rheometer offline.

In this work, the PP/nano-CaCO₃ composites were prepared using a twin-screw extruder. The melt shear viscosity of nanocomposites was measured using an on-line rheometer. The major focus was on the relationship between the microstructure and the on-line melt shear viscosity of the nanocomposites.

PP (J501, Sinopec Group Guangzhou Co.) with a melt index of 2.7 g/10 min at 230 °C and 2.16 kg was used as a polymer matrix in this study. The

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nano-CaCO₃ was manufactured by Inner Mongolia Mengxi High-Tech Materials Co. Ltd. This nano-CaCO₃ was pretreated by the manufacturer. Stearic acid was used as coupling agent. The PP/nano-CaCO₃ composites were prepared using a modular co-rotating, intermeshing twin-screw extruder with a screw diameter of 35 mm and a length-diameter-ratio of 40:1. The screw elements were selected and arranged to provide high shear intensity and help decrease the aggregation of the nano-CaCO₃. In more detail, five kneading block sections alternate with the common conveying elements along the screw. A reverse kneading block is set in the second kneading block section to increase the filled degree in the screw elements. The addition of two neutral kneading elements extends the residence time of materials and further increases the shear intensity.

The nano-CaCO₃ was first dried in an oven at 90 °C for 4 h and then mixed with the coupling agent for about 10 min to facilitate the dispersion of the nanoparticles in the PP matrix. The content of the coupling agent was 1.5 wt% of the nano-CaCO₃. The PP and the nano-CaCO₃ particles were dry-mixed thoroughly before feeding into the twin-screw extruder. The compounding was carried out at temperature profiles of 160-180-195-195-190-190-190-190 °C from the hopper to the strand die. The screw speed was set at 400 rpm unless otherwise noted. The Haake ProFlow on-line rheometer, which was designed for measuring the melt viscosity and flow index, was side-mounted at the end of the twin-screw extruder and the melt shear viscosity of nanocomposites was measured online during the compounding. The ProFlow system continuously diverted a small flow of material from the end of the twin-screw extruder and pushed that material through a capillary by means of a melt pump. The pressure before the melt pump was controlled by an automatic bypass valve to avoid the disturbance of the process during the measurement. The extruded nanocomposites (strands) were collected and then used for the microstructure observation.

Ultra-thin films with about 100 nm in thickness were cut from the nanocomposites in a nitrogen environment. The ultra-thin films were then examined by transmission electron microscopy (TEM, Jeol JEM-100CX II) operated at an accelerating voltage of 100 kV to observe the dispersion state of nano-CaCO₃ particles. The size distribution of nanoparticles was quantitatively determined by analyzing the TEM photomicrographs using Scion image software (Beta 4.02, Scion Corp.). At least three TEM photomicrographs were analyzed for each nano-CaCO₃ content.

Figure 1 shows the TEM photomicrographs of the nanocomposites containing 5, 10, and 20 wt% nano-

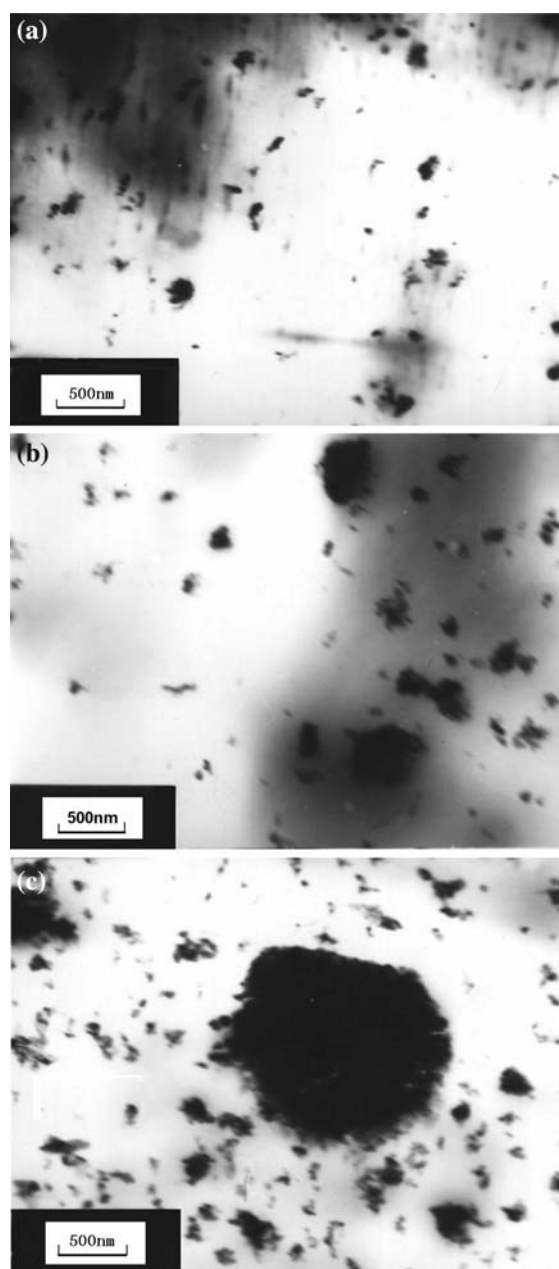


Fig. 1 TEM photomicrographs of the nanocomposites with the nano-CaCO₃ content of (a) 5 wt%, (b) 10 wt% and (c) 20 wt%

CaCO₃, respectively. As can be seen, most nanoparticles were dispersed well in the PP matrix. It is demonstrated that the screw design used in this work is good for the dispersion of the nanoparticles. With the increase of nano-CaCO₃ content, the particle size becomes larger and some large aggregates occur at the CaCO₃ loading of 20 wt%.

The quantitative analysis on the TEM photomicrographs showed that the sizes of most nanoparticles are less than 100 nm and the smallest one is lower than 5 nm. With the increase of nanoparticles, the size of the particles becomes larger. The comparison of

nano-CaCO₃ size distribution in composites with three nano-CaCO₃ contents is listed in Table 1. As can be seen that the percentage of the nano-CaCO₃ particles with the size of lower than 100 nm decreases and the largest particle size increases gradually with increasing the nano-CaCO₃ content. When the content is increased from 5 wt% to 10 wt%, the percentage of the nano-CaCO₃ particles lower than 100 nm is changed from 78.1% to 66.5% and decreased by 11.6%. With the content increasing from 10 wt% to 20 wt%, however, the percentage is decreased by 35.8% and changed to 30.7%. In addition, for the nanocomposite containing 20 wt% nanoparticles, some large aggregate with size of 1.6 μm is observed.

Figure 2 shows the on-line melt shear viscosity as a function of shear rate for the nanocomposites containing 0, 2.5, 5, 7.5, 10, 15, 20 and 25 wt% nano-CaCO₃. With the increase of the nano-CaCO₃ content, the melt shear viscosity decreases first and increases then. The viscosity ratio of the nanocomposites to the pure PP is shown in Fig. 3, which exhibits the effect of nano-CaCO₃ content on the on-line shear viscosity of the nanocomposites. It is clearly shown that the viscosity ratio increases with the nano-CaCO₃ content and is lower than one when the nano-CaCO₃ content is less than 5 wt%. Figure 4 shows the effect of screw speed on the on-line melt shear viscosity of nanocomposite with nano-CaCO₃ content of 5 wt%. It is obvious that the shear viscosity decreases with increasing

Table 1 Comparison of nano-CaCO₃ size distribution in nanocomposites with three particle contents

Nanoparticle content (wt%)	5	10	20
Percentage of nano-CaCO ₃ with size lower than 100 nm (%)	78.1	66.5	30.7
The largest size (nm)	220	600	1600

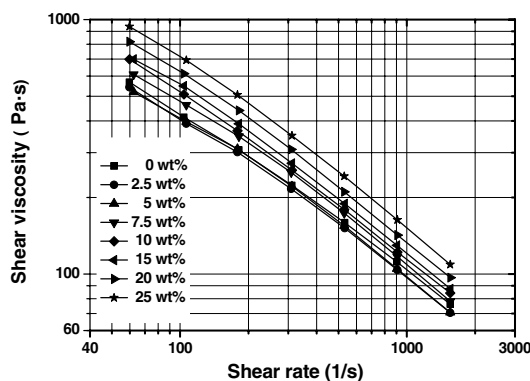


Fig. 2 Effect of the nano-CaCO₃ content on the shear viscosity of nanocomposites

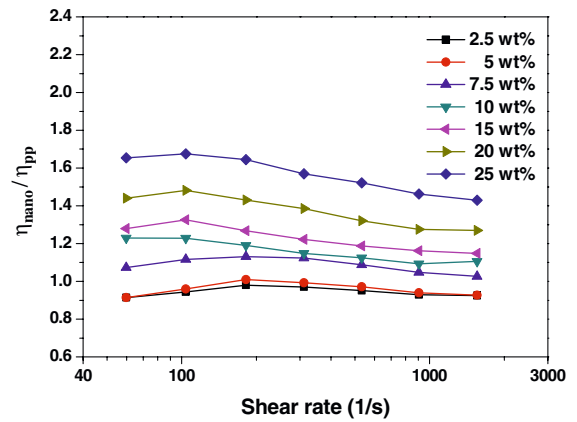


Fig. 3 Viscosity ratio of nanocomposites to pure PP

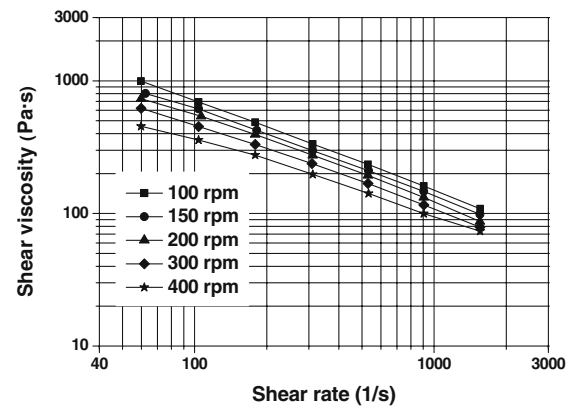


Fig. 4 Effect of screw speed on the shear viscosity of the nanocomposite with 5 wt% CaCO₃

the screw speed. As can be seen from Figs. 2 and 4, all these nanocomposites exhibit non-Newtonian characteristics in the range of applied shear rates.

From Fig. 2 it is clear that the viscosity of nanocomposites is lower than that of pure PP when nano-CaCO₃ content is less than 5 wt%. Some previous studies also showed the decrease of the viscosity of nanocomposites and analyzed its cause. For example, the research carried out by Xie et al. [15] showed that the viscosity of PVC/CaCO₃ nanocomposites is lower than that of pure PVC. They proposed that spherical nano-CaCO₃ particles serve as ‘ball bearing’, reducing the interlayer interaction of PVC melts and thereby decreasing the viscosity for the nanocomposites. However, few investigations have reported the effect of the microstructure for the PP/nano-CaCO₃ composite on their rheological properties. It is worth noting that the rheological behavior of polymer nanocomposites is strongly determined by their microstructures, so the reduction of the shear viscosity for PP/nano-CaCO₃ composites was investigated from the

microstructure point of view in this work. As shown in Table 1, for the nanocomposite with the nano-CaCO₃ content of 5 wt%, nearly 80% nanoparticles have the size lower than 100 nm. It may be preliminary deduced that there exists a critical percentage of the nano-CaCO₃ with the size lower than 100 nm. When the percentage of the nano-CaCO₃ particles lower than 100 nm is higher than the critical one, the addition of the nano-CaCO₃ can decrease the viscosity of polymer matrix. On the contrary, more nanoparticles with the size larger than 100 nm hinder the polymer melt flow and thereby increase the viscosity of nanocomposites. In this work, the critical percentage of the nano-CaCO₃ particles lower than 100 nm is about 80%.

In summary, PP/nano-CaCO₃ composites were prepared in an industrial-scale co-rotating twin-screw extruder in this work and a high shear intensity screw configuration was used. The TEM photomicrographs show that high shear intensity screw configuration favors to the dispersion of the nano-CaCO₃. In addition, the on-line melt shear viscosity of the nanocomposites with the nano-CaCO₃ content less than 5 wt% is lower than that of pure PP and then increases with the nano-CaCO₃ content. It is preliminary deduced that there exists a critical percentage of the nano-CaCO₃ with the size lower than 100 nm. The viscosity of the nanocomposites with the percentage higher than the critical one is lower than that of polymer matrix. The critical percentage is about 80% in this work.

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