J Mater Sci (2008) 43:5305–5312
DOI 10.1007/s10853-008-2763-2

Online shear viscosity and microstructure of PP/nano-$CaCO_3$ composites produced by different mixing types

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Received: 27 February 2008 / Accepted: 29 May 2008 / Published online: 24 June 2008

Abstract In this work, the online melt shear viscosity of polypropylene/nano-calcium carbonate composites was measured during the compounding to investigate the relationship between their rheological behavior and microstructure. Effects of dispersive mixing, distributive mixing, and chaotic mixing on online shear viscosity and microstructure of nanocomposites were analyzed. The results showed that the online shear viscosity of nanocomposites is lower than that of pure PP, when the nano-$CaCO_3$ content is lower than 5, 10, and 15 wt%, compounded by high dispersive mixing, dispersive/distributive mixing, and dispersive/distributive/chaotic mixing, respectively. This is greatly related with the dispersion of nanoparticles in PP matrix. It is deduced that there exists a critical percentage (Φ_{cr}) of the nano-$CaCO_3$ with size lower than 100 nm and a critical mean diameter (d_{cr}). The shear viscosity is lower than that of pure PP when the percentage is higher than the critical percentage and the mean diameter is lower than the critical diameter. In this work, the critical percentage is 80% and critical mean diameter is 60 nm.

Introduction

Nano-calcium carbonate (nano-$CaCO_3$) has been a commonly used filler for resins such as polyvinyl chloride (PVC) [1], polystyrene (PS) [2, 3], polypropylene (PP) [4, 5], and acrylonitrile-butadiene-styrene (ABS) [6] because of its ability to provide an increased stiffness, toughness, and dimensional stability. Moreover, the end-use properties of polymer nanocomposites are largely determined by the dispersion of nanofillers into the polymer matrix, which results from flow fields, processing conditions, properties of original polymers, and surface modification of nanofillers.

The improvement of mechanical properties, however, is always limited because nano-$CaCO_3$ with high surface energy is easy to agglomerate. So many efforts have been devoted to improve the dispersion of nanoparticles in polymer matrix. Zhang et al. [7] used polyoxyethylene nonyphenol (PN), a nonionic modifier, to improve the dispersion of nano-$CaCO_3$ in the PP matrix. It was found that by adding 1.5 wt% of PN to PP/$CaCO_3$ (85/15) nanocomposite, its tensile properties are not changed much but notched Izod impact energy is increased about three times. Wang et al. [8] employed an ultra-high-speed mixer to improve the dispersion of nano-$CaCO_3$ in PP. Results showed that the nano-$CaCO_3$ can be dispersed uniformly in the PP matrix even at a high content of nanoparticles (more than 15% by volume). Moreover, it is important to investigate the relationship between microstructure and mechanical properties of nanocomposites to improve the end-used properties. Chan et al. [9, 10] investigated the microstructure, mechanical properties, and deformation mechanisms of PP/nano-$CaCO_3$ composites. They proposed that much improved fracture toughness of PP/nano-$CaCO_3$ composites is largely determined by the extensive plastic deformation of PP matrix. Their work on the morphology and micro-deformation mechanism disclosed that there is a thin amorphous layer at the PP-nanoparticle interface, which is prone to plastic deformation.

Rheological analysis is considered as an effective tool to investigate the microstructure of nanocomposites. Huang et al. [11] investigated the relationship between the shear

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viscosity and microstructure of PP/nano-$CaCO_3$ composite. It was preliminarily deduced that there exists a critical percentage of the nano-$CaCO_3$ with size lower than 100 nm. The viscosity of the nanocomposites with the nano-$CaCO_3$ percentage higher than the critical one is lower than that of matrix. Jiang et al. [6] investigated the rheological behavior of ABS composites with nano-sized precipitated and micro-sized $CaCO_3$. It was found that the former exhibits the disappearance of Newtonian region, high storage modulus at low frequencies, and the appearance of yield phenomenon. However, contrary results were reported about the effect of nano-$CaCO_3$ on the rheological behavior of PVC matrix. The research by Wu et al. [12] showed that the addition of nano-$CaCO_3$ particles into PVC results in a remarkable increase in the melt viscosity. However, Xie et al. [13] reported that the apparent viscosity of PVC/$CaCO_3$ nanocomposites decreases with increasing nanoparticle loading and was lower than that of pristine PVC at high shear rate (>100 s^{-1}). Thus, it is very necessary to study the rheological behavior of polymeric nanocomposites.

It is worth noting that mixing type and its intensity during the compounding of nanocomposites are important to the dispersion of the nanoparticles in polymer matrix. Huang et al. [14, 15] investigated the effects of extruder screw configuration and processing parameters on the microstructure of the PP/nano-$CaCO_3$ composite and PP/clay nanocomposites prepared by direct melt intercalation. Recently, a special mixing type named as chaotic mixing has been used to prepare polymer nanocomposites [16, 17]. For immiscible polyamide 6 (PA6)/PP blends, the adding of clay platelets helps to develop droplets of much smaller size and with the narrower size distribution due to their direct influence on the breakup of minor PP domain in chaotic mixing [17].

In this work, the rheological measurement was conducted online during the compounding to investigate the relationship between the rheological behavior and microstructure of PP/nano-$CaCO_3$ composite. Effects of flow fields (high dispersive mixing, dispersive/distributive mixing, and dispersive/distributive/chaotic mixing) on the online shear viscosity of nanocomposites were investigated. The microstructure of nanocomposites was observed by transmission electron microscopy (TEM). Finally, the relationship between the shear viscosity and microstructure of nanocomposites was analyzed.

Experimental

Materials and equipment

PP (J501, PetroChina Guangzhou Petrochemical Company) 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 nano-$CaCO_3$ was manufactured by Inner Mongolia Mengxi Co. Ltd. This nano-$CaCO_3$ was pretreated by the manufacturer and its mean size was 30 nm. Stearic acid was used as coupling agent. The content of the coupling agent was 1.5 wt% of the nano-$CaCO_3$.

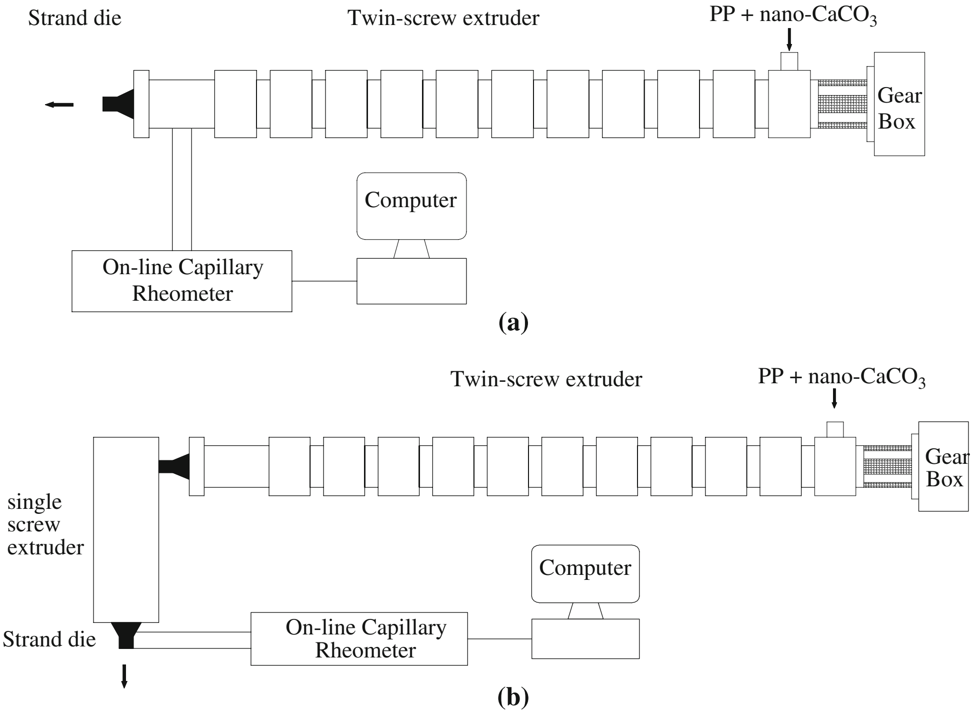


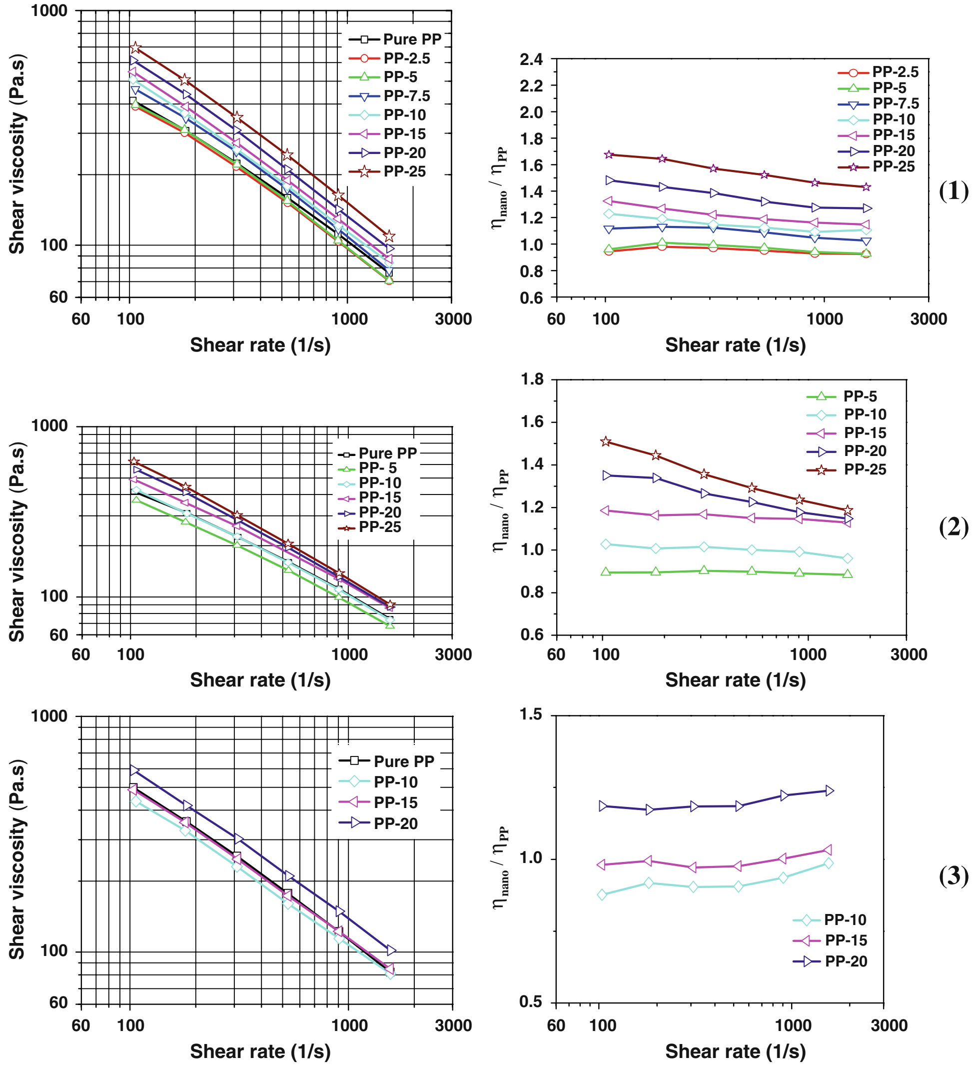
Fig. 1 Schematic of online shear viscosity measurement and compounding setup with screws (**a**) A or B, and (**b**) B + HP

A modular co-rotating intermeshing twin-screw extruder with a screw diameter of 35 mm and a length-diameter-ratio of 40:1 was used to prepare the PP/nano-$CaCO_3$ composites. Two types of screw configurations were selected, denoted by screws A and B, respectively. Screw A consists of conveying elements and five kneading block sections, providing high dispersive mixing or shearing intensity. In more detail, a reverse kneading block is set in the second kneading block section to increase the filled degree of the screw elements. The addition of two neutral kneading elements in the first and second kneading block sections favors to the melting of the polymer. A left-handed screw element is set at the forth kneading block section to extend the residence time of polymer melt. In order to enhance the distributive mixing during the compounding, turbine mixing elements, with 11 teeth around the circumference, are added after the second and forth kneading block sections in screw B. Moreover, chaotic mixing is induced by adding a single screw extruder with a convective screw (denoted as HP) at the end of the twin-screw extruder with screw B.

Compounding of nanocomposites

The nano-$CaCO_3$ was 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 PP and nano-$CaCO_3$ particles were dry-mixed thoroughly before feeding into the twin-screw extruder. The weight ratio of nano-$CaCO_3$ particles changed from 5 to 20 wt%. The composition of nanocomposites in this work was denoted by PP-X, where X denoted as the content of nano-$CaCO_3$.

Temperature profile of 160–180–195–195–190–190–190–190–190 °C was set from the hopper to the end of the twin-screw extruder and its screw speed was set at



(a) (b)

Fig. 2 (**a**) shear viscosity versus shear rate and (**b**) shear viscosity ratio of PP/nano-$CaCO_3$ composites prepared by screws (1) A, (2) B, and (3) B + HP

400 rpm. The temperature of single screw extruder was set at 190 °C and its screw speed was set at 30 rpm.

Rheological measurement

The online rheometer, Haake ProFlow, was side-mounted at the exit of extruder to measure the melt shear viscosity of nanocomposites online during the compounding. The ProFlow system continuously diverted a small flow of melt from the exit of extruder and pushed that melt 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. In this work, the online shear viscosity of nanocomposites was measured during the compounding, as depicted in Fig. 1.

Microstructure observation

Ultra-thin films with about 100 nm in thickness were cut from the samples in a nitrogen environment. TEM (Jeol JEM-100CX II), operated at an accelerating voltage of 100 kV, was used to observe the microstructure of samples. The size distribution of nanoparticles was quantitatively determined by analyzing the TEM photomicrographs using image software Scion (Beta 4.02, Scion Corp). At least three TEM photomicrographs were analyzed for each sample.

Results and discussion

Rheological properties

The online shear viscosity versus shear rate curves and viscosity ratio curves are displayed in Fig. 2a and b, respectively. In Fig. 2, η_{PP} is the viscosity of PP matrix and η_{nano} is the viscosity of nanocomposite. As shown in Fig. 2a, with the increase of the nano-$CaCO_3$ content, the melt shear viscosity decreases first and increases then. Figure 2b shows that the viscosity ratio increases with the increasing of the nanoparticle content.

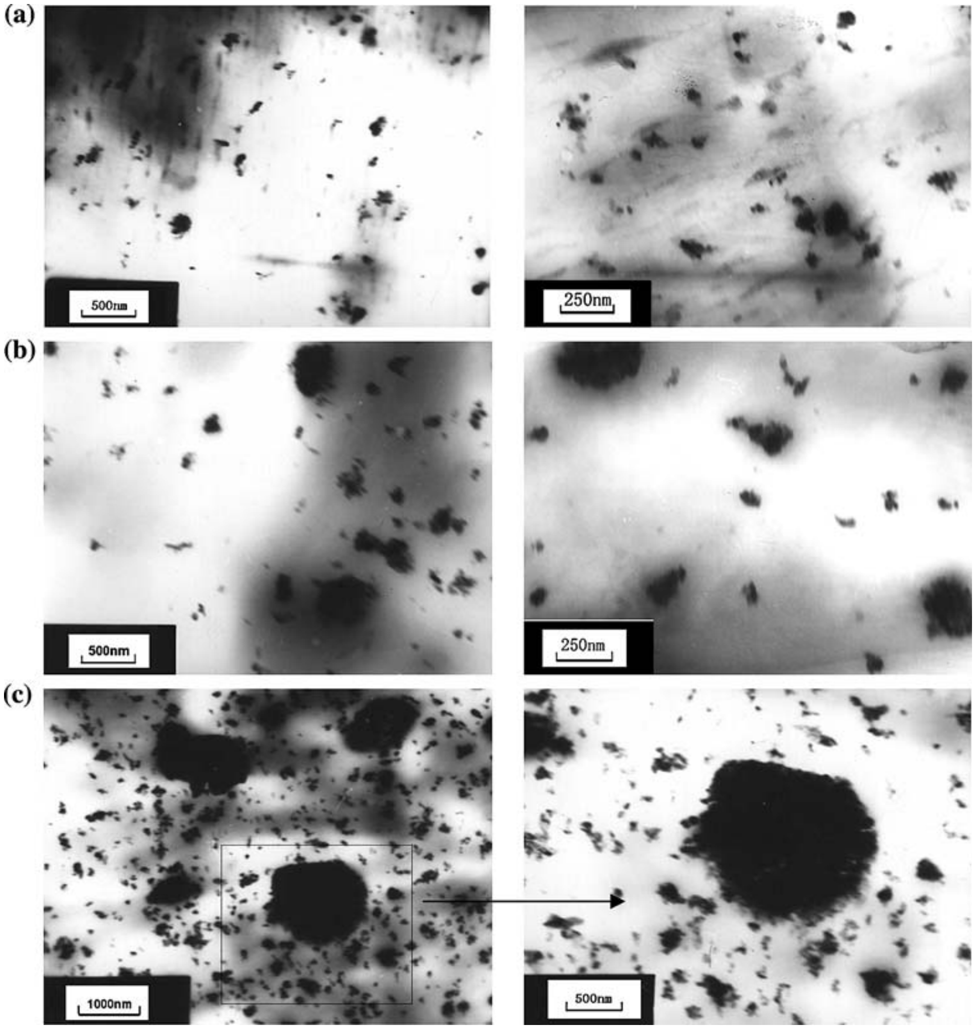


Fig. 3 TEM photomicrographs of nanocomposites with nano-$CaCO_3$ content of (**a**) 5 wt%, (**b**) 10 wt%, and (**c**) 20 wt% prepared by screw A

For screw A, as can be seen from Fig. 2(1), the viscosity of nanocomposites is lower than that of pure PP and the viscosity ratio is lower than unity when nano-$CaCO_3$ content is 2.5 and 5 wt%. This means that the addition of 5 wt% or less nano-$CaCO_3$ does not reduce the processability of polymer melt during the compounding. When the nano-$CaCO_3$ content is higher than 5 wt%, the viscosity ratio is higher than unity. This may be explained by the characterization of nano-$CaCO_3$. With the increase of the nanoparticle content, the nanoparticles are easy to aggregate and exhibit rigid property. So the flow of the polymer melt may be hindered by these rigid particles and then the viscosity of PP/nano-$CaCO_3$ composites is increased.

The online shear viscosity and the viscosity ratio curves of nanocomposites prepared by screw B are illustrated in Fig. 2(2). As can be directly observed, with the increase of nano-$CaCO_3$, the viscosity ratio is increased. When the loading of nano-$CaCO_3$ is lower than 10 wt%, the viscosity of nanocomposite is lower than that of PP matrix and the viscosity ratio of nanocomposite is lower than unity.

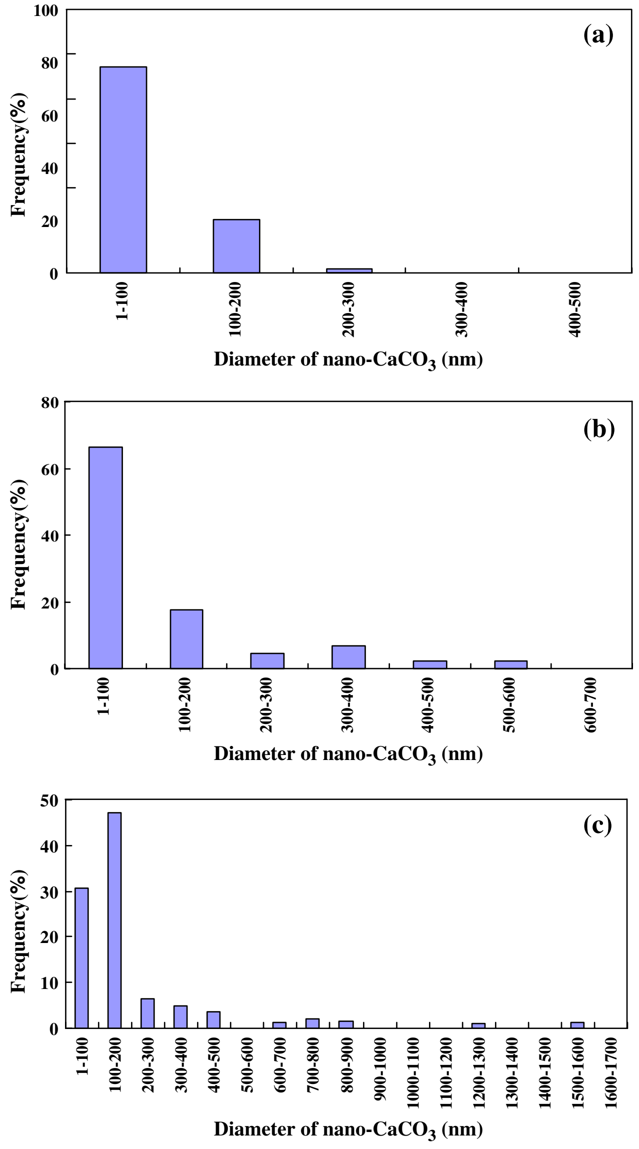


Fig. 4 Diameter distribution of nano-$CaCO_3$ with the content of (**a**) 5 wt%, (**b**) 10 wt%, and (**c**) 20 wt% in nanocomposites prepared by screw A

Figure 2(3) presents the online shear viscosity and viscosity ratio of the nanocomposites compounded by screw B + HP. When the loading of nano-$CaCO_3$ is lower than 15 wt%, the viscosity of nanocomposite is lower than that of PP matrix and the viscosity ratio of nanocomposite is lower than unity. That is, the viscosity of nanocomposites prepared by screw B + HP is still lower than that of pure PP when nano-$CaCO_3$ content increases to 15 wt%. When the content is increased from 15 to 20 wt%, the viscosity increases and becomes higher than that of PP matrix. It is implied that the processability of the nanocomposites is improved by adding a single screw extruder with a convective screw, compared with the results for screws A and B.

Microstructure

The TEM observation was conducted to investigate the dispersion of nano-$CaCO_3$ particles in the PP matrix. The TEM photomicrographs of nanocomposites compounded by screws A, B, and B + HP are presented in Figs. 3, 5, 7

Table 1 The nano-$CaCO_3$ size in nanocomposites prepared by screw A

Nanoparticle content (wt%)	5	10	20
Mean nano-$CaCO_3$ size (nm)	59	88	225
Percentage of nano-$CaCO_3$ with size lower than 100 nm (%)	78.1	66.5	30.7
The largest nano-$CaCO_3$ size (nm)	220	600	1,600

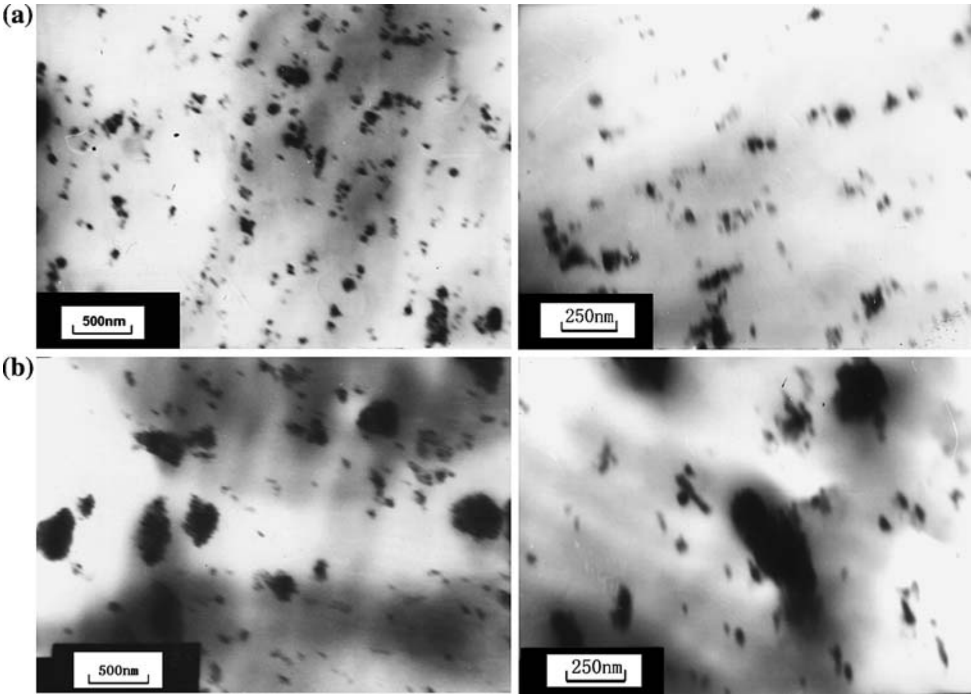
Table 2 The nano-$CaCO_3$ size in nanocomposites prepared by screw B

Nanoparticle content (wt%)	10	20
Mean nano-$CaCO_3$ size (nm)	54	156
Percentage of nano-$CaCO_3$ with size lower than 100 nm (%)	79	50
The largest nano-$CaCO_3$ size (nm)	300	400

Table 3 The nano-$CaCO_3$ size in nanocomposites prepared by screw B + HP

Nanoparticle content (wt%)	15
Mean nano-$CaCO_3$ size (nm)	61
Percentage of nano-$CaCO_3$ with size lower than 100 nm (%)	81.6
The largest nano-$CaCO_3$ size (nm)	439

Fig. 5 TEM photomicrographs of nanocomposites with nano-$CaCO_3$ content of (**a**) 10 wt% and (**b**) 20 wt% prepared by screw B



and the size distribution of nano-$CaCO_3$ is shown in Figs. 4, 6, 8, respectively. The dispersion of nanoparticles in PP matrix is analyzed both qualitatively, in terms of these typical TEM photomicrographs, and quantitatively, in terms of nano-$CaCO_3$ mean diameter. The comparisons of nanoparticle size are listed in Tables 1–3.

Figure 3 presents the TEM photomicrographs of the nanocomposites prepared by screw A, and the size distributions of nano-$CaCO_3$ are shown in Fig. 4. It is shown that high shear intensity is good for the dispersion of the nanoparticles. However, with the increase of nano-$CaCO_3$ content, the nanoparticle size becomes larger and some large aggregates occur at the $CaCO_3$ loading of 20 wt%. As can be seen from Table 1, the diameter of most nanoparticles is less than 100 nm and the smallest one is lower than 5 nm when the nanoparticle content is 5 wt%. When the nanoparticle content is 5, 10, and 20 wt%, the mean diameter of nano-$CaCO_3$ is 59, 88, and 225 nm and the percentage of the nano-$CaCO_3$ particles with size lower than 100 nm (Φ) is decreased from 78.1, 66.5, to 30.7%, respectively. The largest size is increased from 220 to 1600 nm when the content is increased from 5 to 20 wt%. This is mainly attributed to the aggregation of nanoparticles, especially with high-content nanoparticles in PP matrix.

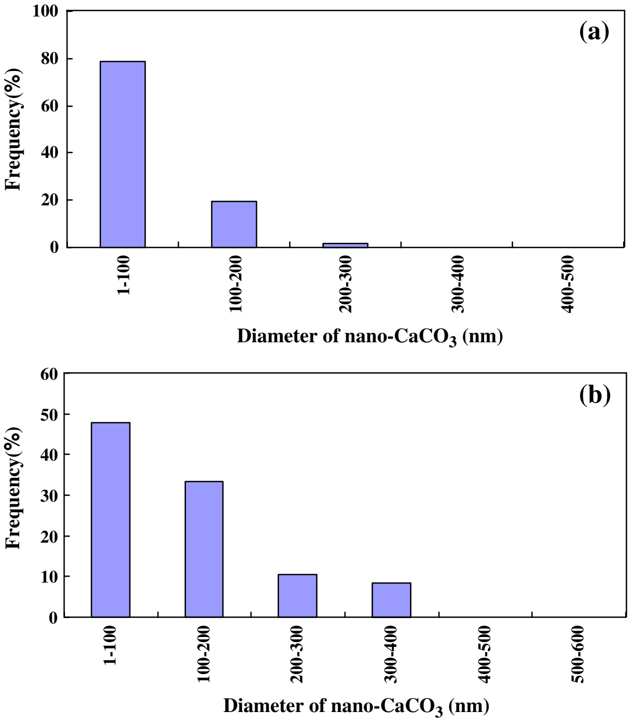


Fig. 6 Diameter distribution of nano-$CaCO_3$ with the content of (**a**) 10 wt% and (**b**) 20 wt% in nanocomposites prepared by screw B

Figure 5 presents the TEM photomicrographs of the nanocomposites prepared by screw B, and the size distributions of nano-$CaCO_3$ are shown in Fig. 6. Screw B can provide stronger distributive mixing than screw A owing to the adding of turbine mixing elements. As can be seen from Fig. 5, the nanoparticles exhibit a greater extent of dispersion. As shown in Table 2, the mean diameter is 54 and 156 nm and Φ is 79 and 50% when the content of nanoparticles is 10 and 20 wt%, respectively. The large aggregates are not found. This indicates that the addition of

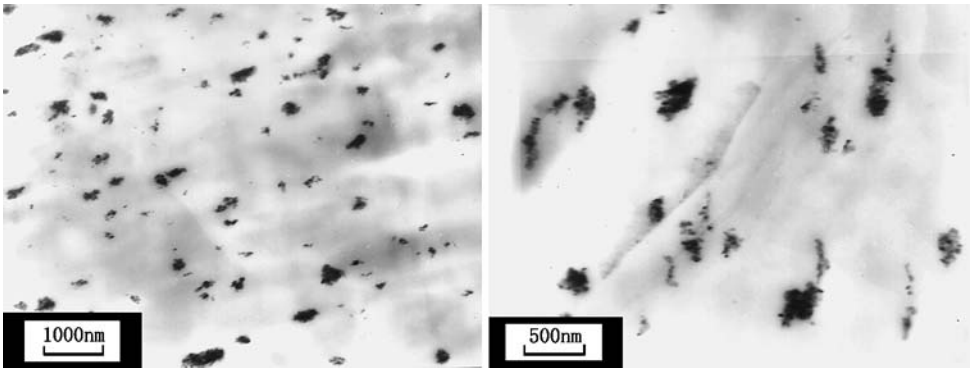


Fig. 7 TEM photomicrographs of nanocomposite with nano-$CaCO_3$ content of 15 wt% prepared by screw B + HP

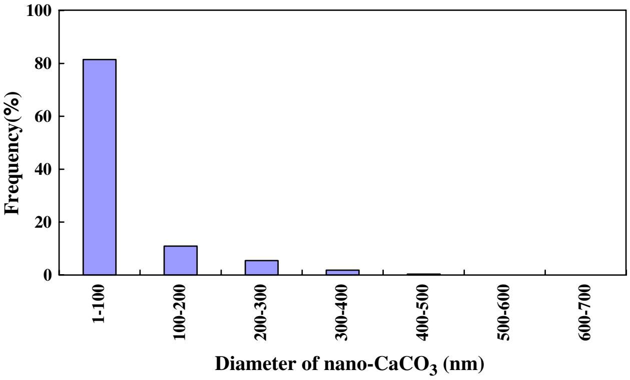


Fig. 8 Diameter distribution of nano-$CaCO_3$ with the content of 15 wt% in nanocomposites prepared by screw B + HP

turbine mixing elements, which enhances the distributive mixing, favors to the size reduction of the nanoparticles.

Figure 7 presents the TEM photomicrographs of the nanocomposites prepared by screw B + HP, and the size distribution of nano-$CaCO_3$ are shown in Fig. 8. As shown in Table 3, the mean diameter of nano-$CaCO_3$ is 61 nm and Φ is 81.6%. The dispersion of nano-$CaCO_3$ in PP matrix is better than that prepared by screws A and B. This is attributed to chaotic mixing provided by HP screw. Mixing across the convective screw is a fully stretching and folding and exhibits characterization of chaotic mixing. The chaotic mixing characterization in HP screw was investigated by Huang [18]. It is demonstrated in this study that the chaotic mixing favors to the dispersion of nano-$CaCO_3$ in PP matrix.

So based on our experimental results, it is found that the shear viscosity of PP/nano-$CaCO_3$ composites is lower than that of pure PP when the nano-$CaCO_3$ content is lower than 5, 10, and 15 wt%, compounded by screws A, B, and B + HP, respectively. Microstructure results show that for the nanocomposites compounded by screw A, when the nano-$CaCO_3$ content is 5 wt%, there is 78.1% nanoparticles with the size lower than 100 nm and the mean diameter of nanoparticles is 59 nm. Compounded by screw B, nearly 80% nanoparticles have the size lower than 100 nm and the mean diameter is 54 nm, when the nano-$CaCO_3$ content is 10 wt%. Compounded by screw B + HP, when the nano-$CaCO_3$ content is 15 wt%, 81.6% nanoparticles have the size lower than 100 nm and the mean diameter is 61 nm. So it may be deduced that the decrease of shear viscosity of PP/nano-$CaCO_3$ composites is deeply related with dispersion of nano-$CaCO_3$ in PP matrix.

This can be explained based on the rheological behavior and microstructure observation of nanocomposite. The percentage of the nano-$CaCO_3$ particles with size lower than 100 nm (Φ) and mean diameter (d) of $CaCO_3$ particles were used to characterize the dispersion of nanoparticles in PP matrix. If there exist more nanoparticles with the size lower than 100 nm (higher Φ) in PP matrix, these nanoparticles may be served as lubricates, decreasing the viscosity of PP/nano-$CaCO_3$ composites. When Φ decreases in the nanocomposite, the particles aggregate and serves as rigid particles. These rigid nanoparticles may hinder the flow of the melt and then the viscosity increases. It may be preliminarily deduced that there exists a critical percentage (Φ_{cr}) of the nano-$CaCO_3$ with size lower than 100 nm and a critical mean diameter (d_{cr}). In this work, the Φ_{cr} is about 80% and d_{cr} is about 60 nm. When the percentage of the nano-$CaCO_3$ with size lower than 100 nm is higher than the critical percentage and the mean size of nano-$CaCO_3$ is lower than the critical diameter, the addition of the nano-$CaCO_3$ can decrease the viscosity of PP matrix.

Conclusion

Effects of dispersive mixing, distributive mixing, and chaotic mixing on the online shear viscosity and microstructure of PP/nano-$CaCO_3$ composite were analyzed. It is shown that chaotic mixing favors to enhance the processability of nanocomposite. The relationship between the shear viscosity and dispersion state of nano-$CaCO_3$ in PP matrix is built. Rheological behavior shows that there exists a maximum nano-$CaCO_3$ content, below which the online shear viscosity of nanocomposite is lower than that of pure PP and the viscosity ratio is lower than unity. This can be explained by the dispersion state of nanoparticles in PP matrix. There exists a critical percentage of the nano-$CaCO_3$ with size lower than 100 nm and a critical mean diameter. The shear viscosity is lower than that of pure PP when the percentage is higher than the critical percentage and the mean diameter is lower than that of critical diameter. In this work, the critical percentage is 80% and critical mean diameter is 60 nm.

Acknowledgements Financial support provided by the National Natural Science Foundation of China (10672061) and Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, P.R.C., is gratefully acknowledged.

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