DYNAMICAL RHEOLOGICAL PROPERTY AND MICROSTRUCTURE DEVELOPMENT OF PP/NANO-CACO$_3$ COMPOSITE ALONG TWIN-SCREW EXTRUDER[∗]

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Abstract

Polypropylene (PP)/nano-calcium carbonate (CaCO$_3$) composite was compounded in a co-rotating twin-screw extruder. Samples were taken at four locations along the extruder. Dynamical rheological properties of samples were measured using a dynamical rheometer and their microstructure was observed by transmission electron microscopy (TEM). The results demonstrated that both storage modulus, loss modulus, and complex viscosity of samples and the size of nano-CaCO$_3$ particles decreased along the extruder. The relationship between dynamical rheological property and microstructure development was analyzed. The complex viscosity of the samples taken after turbine mixing elements decreased a slightly larger due to a large decrease of the mean diameter of nano-CaCO$_3$ particles from 140.3 nm to 70.2 nm.

Keywords: nanocomposite, rheological properties, microstructure development

Introduction

Polymer nanocomposites are used as engineering materials, owing to their improved mechanical and electrical properties, heat resistance, radiation resistance, and other properties as a result of the nanometric scale dispersion of the filler in the matrix [1]. Extruders are widely used to prepare polymer nanocomposites or blends. The morphology of polymer nanocomposites or blends is deeply related to the flow field during the 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 polypropylene (PP)/organic-montmorillonite (org-MMT) nanocomposite [2], PP/nano-calcium carbonate (CaCO$_3$) [3] composite or polymer blends [4,5] prepared by direct melt intercalation or melt blending.

In this work, PP/nano-CaCO$_3$ composite was compounded in a modular co-rotating, intermeshing twin-screw extruder. Dynamical rheological properties of the samples taken at different locations along the twin-screw extruder were measured using a dynamical rheometer. Microstructure development of the samples was observed by transmission electron microscopy (TEM) to investigate the dispersion of nano-CaCO$_3$ particles. The relationship between dynamical rheological property and microstructure development was analyzed.

Experimental

Materials

The polymer matrix was PP (J501, Sinopec Group Guangzhou Co.) with a melt index of 2.7 g/10min (at 230℃ and 2.16 kg). The nano-CaCO$_3$ was manufactured and pretreated by Inner Mongolia Mengxi High-Tech Materials Co. Ltd. Stearic acid was used as coupling agent.

Sample Preparation

The PP/nano-CaCO$_3$ composite was 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 distributive mixing. Five kneading block sections were used to impose high shear intensity. A reverse kneading block was 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 favored to the melting of the polymer. A left-hand screw element was set after the fourth kneading block section to extend the residence time of the material. Turbine mixing elements were added after the second and fourth kneading block sections to enhance the distributive mixing.

The nano-CaCO$_3$ was dried in a oven at 90℃ 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-CaCO$_3$. The PP and the nano-CaCO$_3$ particles with the weight ratio of 90/10 were dry-mixed thoroughly before feeding into the twin-screw extruder. The compounding was carried out at temperature profiles of 160-180-195-195-190-190-190-190-190 ℃ from the hopper to the strand die. The screw speed was set at 400 rpm and the feeding rate was set at 2 kg/h.

The sample at location SP4 (shown in Fig. 1) was taken at the exit of the extruder during compounding. The samples at locations SP1 to SP3 were taken on the screws after pulling them out.
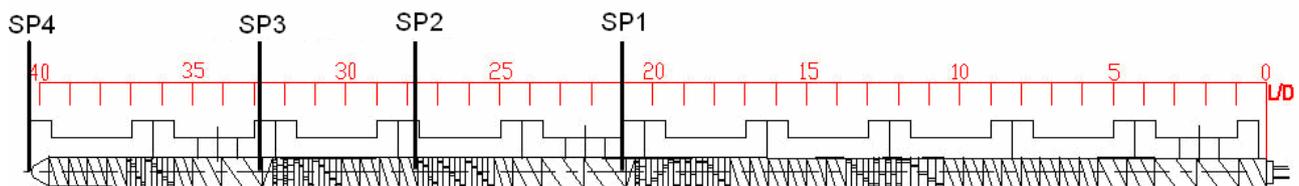

Figure 1. Screw configuration used and sampling locations (denoted as SP1 to SP4)

Rheological Measurement

The dynamic rheological properties were measured on the disks (with a size of ϕ25×1 mm) compression molded from above-prepared samples using Bohlin Gemini 200 Rheometer System in an oscillatory mode with a parallel plate geometry using 25 mm diameter plates at 190 ℃. The sweep range of frequency (ω) was from 0.01 to 50 rad/s using the strain level of 1% to ensure that the measurement was carried out in the linear viscoelastic region.

Observation of Microstructure for Samples

Ultra-thin films with about 100 nm in thickness were cut from the samples in a nitrogen environment. Transmission electron microscopy (TEM, Jeol JEM-100CXⅡ), 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.

The equivalent diameter d of nano-CaCO$_3$ was calculated using the equation

$$d = \sqrt{\frac{4}{\pi} \cdot A_d} \qquad (1)$$

Then the numbers-averaged diameter (d_n) and the volume-averaged diameter (d_v) were calculated using the equations

$$d_n = \frac{\sum_i d_i}{n} \qquad (2)$$

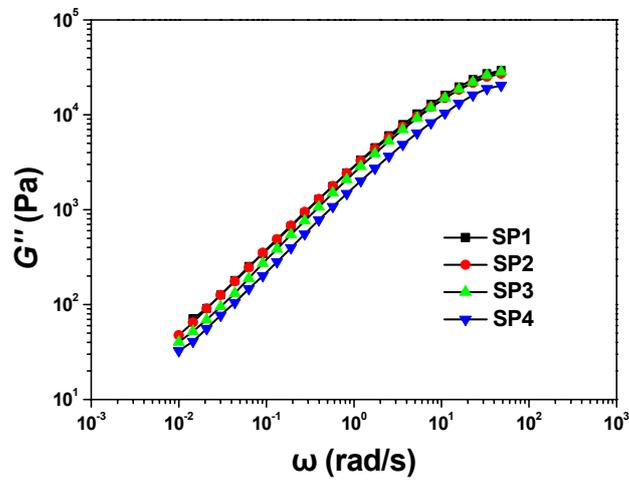$$d_v = \left(\frac{\sum_i d_i^3}{n} \right)^{1/3} \qquad (3)$$

Results and Discussion
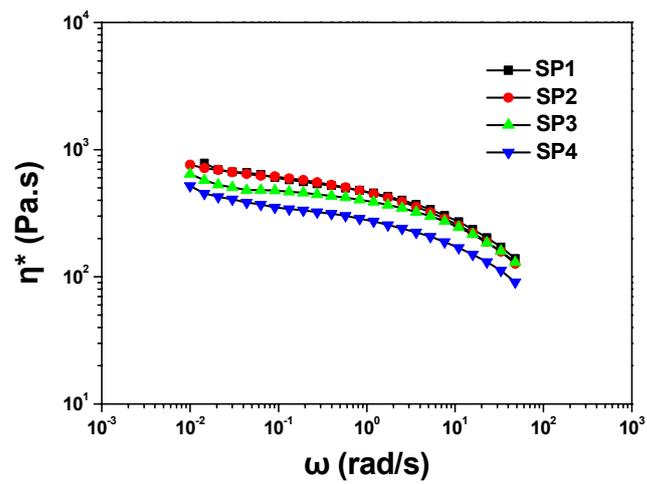
Dynamical Rheological Properties

Figure 2 presents the dynamical rheological properties of the samples taken at different locations along the twin-screw extruder. As can be seen, storage modulus (G') and loss modulus (G'') decrease little from locations SP1 to SP2 and slightly larger from SP3 to SP4. Similarly, the complex viscosity ($\eta *$) decreases from SP1 to SP4. The decrease of $\eta *$ from SP1 to SP2 is small. From SP3 to SP4, however, its decrease becomes larger.
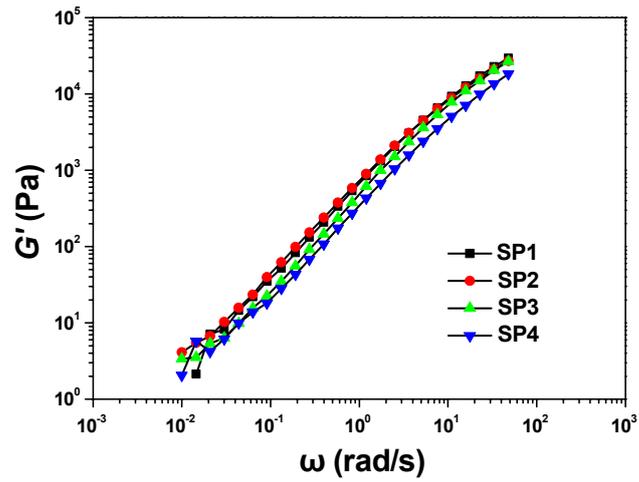
Figure 2. Dynamical rheological properties of samples taken from different locations along the twin-screw extruder: (a) Storage modulus, (b) Loss modulus, and (c) Complex viscosity

Microstructure Development

The photomicrographs of the samples at different locations are showed in Fig. 3. It is observed that the size of the nano-CaCO$_3$ particles decreases along the extruder.

The particle diameters of samples taken at different locations are shown in Fig. 4 and the size comparison is shown in Table 1. As can be seen, the nano-CaCO$_3$ size of the samples decreases from SP1 to SP4. The size of the largest nano-CaCO$_3$ particles in these TEM photomicrographs decreases from 9.5 μm (SP1) to 6.7 μm (SP2), 1.0 μm (SP3), and 300 nm (SP4). The number-averaged diameter d_n decreases correspondingly from 148.2 nm to 140.3 nm, 70.2 nm, and 54.5 nm. In addition, the percentages of nano-CaCO$_3$ with size lower than 100 nm increases from 16.9% (SP1) to 37.7% (SP2), 75% (SP3), and 79% (SP4).

Microstructure development of samples can be used to analyze the change of their dynamical rheological properties. With the melt flow from locations SP1 to SP4, the size of the nano-CaCO$_3$ particles gradually becomes small. The hindering of the nano-particles to the polymer melt flow becomes weaker and the melt is easier to flow. So the complex viscosity of samples decreases along the twin-screw extruder. In addition, the results of the dynamic rheological properties show that the decreases of G', G'', and η^* from SP1 to SP2 are small. From SP2 to SP3 and SP3 to SP4, however, the decreases become larger. It may be explained by the change of the number-averaged diameter d_n of samples taken from SP1 to SP4. The d_n decreases little from SP1 to SP2. However, d_n decreases from 140.3 nm (SP2) to 70.2 nm (SP3), which results in a slightly larger decrease of η^* from SP2 to SP3. Between the locations SP2 and SP3, turbine mixing elements were added. So it may be concluded that the addition of turbine mixing elements is one of the factors due to the decrease of complex viscosity of PP/nano-CaCO$_3$ composite. Similarly, G', G'', and η^* of the sample in SP4 decrease greatly, owing to the decrease of d_n to 54.5 nm.

Table 1. Comparison of nano-CaCO$_3$ size of the samples taken at different locations

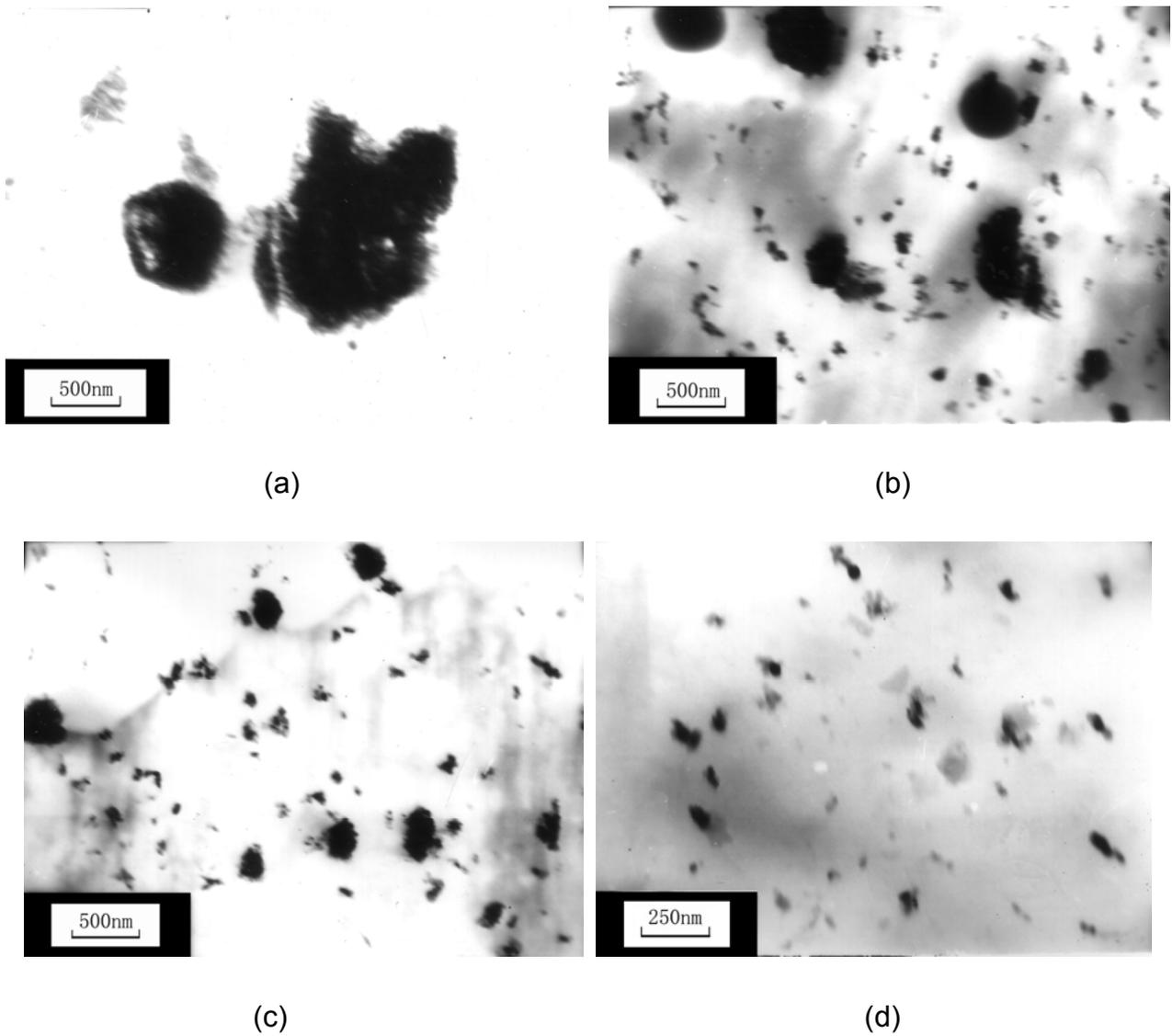| Sampling Locations	SP1	SP2	SP3	SP4
Percentage of nano-CaCO$_3$ with size lower than 100 nm	16.9	37.7	75.0	79.0
The largest size (nm)	9531	6770	1020	300

(a)

(b)

(c)

(d)

Figure 3. TEM photomicrographs of samples taken at a) SP1, b) SP2, c) SP3, d) SP4
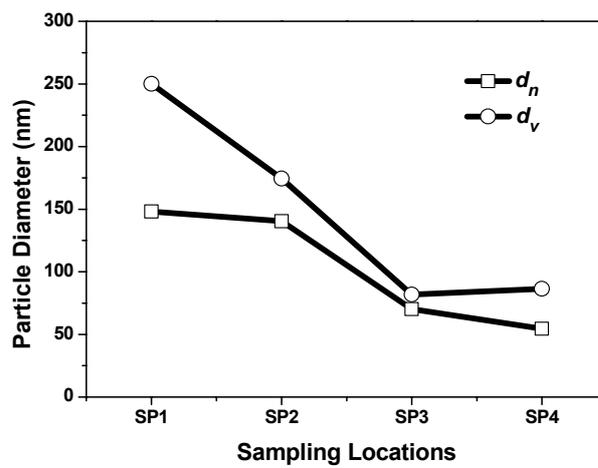

Figure 4. Nano-particle diameter of samples at different locations along the twin-screw extruder

Conclusion

Polypropylene (PP)/nano-calcium carbonate (CaCO$_3$) composite was compounded and samples at different locations along the twin-screw extruders were taken. Rheological results show that the storage modulus, loss modulus, and complex viscosity of the samples decrease from the initial sampling position to the exit of the extruder. The TEM photomicrographs show that the size of nano-CaCO$_3$ decreases and the percentage of nano-CaCO$_3$ with size lower than 100 nm increases from 16.9% (SP1) to 37.7% (SP2), 75% (SP3) and 79% (SP4). The number-averaged diameter decreases from 140.3 nm (SP2) to 70.2 nm (SP3), which results in a slightly larger decrease of complex viscosity from SP2 to SP3.

References

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