

Rheological Properties and Crystallization Behavior of Yttrium Oxide Filled Low Ethylene Content Polypropylene Copolymer

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SYNOPSIS

The rheological properties and crystallization characteristics of low ethylene content polypropylene (EPM) with and without Yttrium oxide (Y_2O_3) as a filler was investigated by cone-plate viscometer and differential scanning calorimetry. Yttrium oxide had a profound effect on the viscosities of the systems. To determine the nonisothermal crystallization rate of the materials, a new estimation method was used. From the results, we can conclude that Y_2O_3 acts as a nucleating agent, which increased the crystallization rate of the EPM.

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INTRODUCTION

Random and block propylene copolymer with low ethylene content are commercially important since they improve toughness of polypropylene (PP) without seriously detracting from the other desirable properties.¹⁻³ Because of the existence of ethylene sequences, the structural regularity of copolymer chain decreases and their crystallization behavior changed. Generally, the decrease of overall crystallization rate of copolymer may affect mechanical properties. Therefore, the addition of nucleating agents to these modified PPs to increase the crystallization rate is necessary.

Yttrium oxide used as a nucleating agent has been reported.^{4,5} Yttrium oxide has a profound effect on the resulted polymer materials. Unlike other nucleating agents, the addition of yttrium oxide produced an increase in flexural modulus and Izod impact strength, and other nucleating agents showed decrease in Izod impact strength.⁶ In the meantime, the addition of 1-5% yttrium oxide improved the thermostability of PP and low ethylene content polypropylene (EPM) significantly, the decompo-

sition temperature of PP and EPM increased about 30-40°C.⁶ The kinetics of crystallization in polypropylene filled with Y_2O_3 have been studied, mainly with regard to the isothermal process.^{4,5} However, practical processes such as extrusion and injection molding usually proceed under dynamic nonisothermal crystallization conditions. To reach the optimum conditions in an industrial process and to obtain products with better properties, it is necessary to estimate the rate of crystallization in the nonisothermal process.

In the present work, rheological measurements were carried out to confirm the effect of Y_2O_3 filler on the viscosities of the EPM. A method to estimate the nonisothermal crystallization rate proposed by Khanna⁷ and Zhang et al.⁸ was used to study the crystallization characteristics of EPM with and without Y_2O_3 .

EXPERIMENTAL

Materials

The EPM used in this work was obtained from Liaoning Panjin Gas Chemical Plant (China), its trade name is P340, and the melt flow index (MI) is 1.0 g/10 min. Yttrium oxide was supplied by the

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Table I The Composition of Y_2O_3 Filled EPM

Code	Y_2O_3 Content (%)
A	0.2
B	1.0
C	1.5
D	3.0
E	5.0

fifth laboratory in our institute; its particle diameter is in the range of 0.5–0.6 μm . The compositions of Y_2O_3 filled with EPM are listed in Table I. The mixtures were prepared by a Brabender single-screw extruder ($L/D = 20$) at 185–195°C.

Measurement of Melt Viscosities

The melt viscosity of the materials were measured with a cone-plate viscometer (Contraves Rheomat 120). The diameter of the cone-plate was 20 mm and cone angle was 0.5°. The experiments were carried out under a nitrogen atmosphere.

Measurement of Nonisothermal Crystallization Rate

Dynamic crystallization was performed in a Perkin-Elmer DSC-2C calorimeter with about 11.0-mg

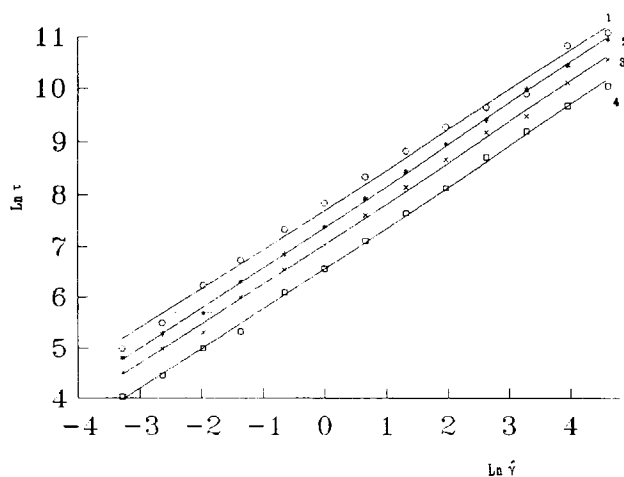


Figure 2 Shear stress versus shear rate for different compositions. (1) $Y_2O_3/EPM = 0/100$; (2) $Y_2O_3/EPM = 5/100$; (3) $Y_2O_3/EPM = 3/100$; (4) $Y_2O_3/EPM = 1/100$.

samples. The samples were first heated to 500 K for 10 min to remove the thermal history. The nonisothermal crystallization thermograms were obtained by cooling the sample at various cooling rates from 5 to 40 K/min.

Wide-Angle X-Ray Diffraction (WAXD) Measurements

Sheets of 2.0 mm thickness, obtained by compression molding at 190°C, were used in the X-ray ex-

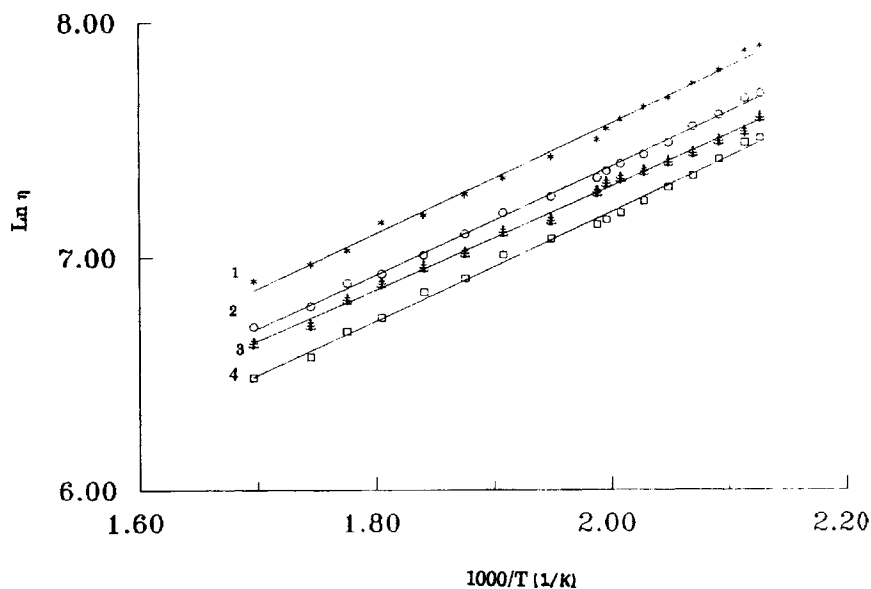


Figure 1 The dependence of viscosity of rare earth filled on temperature (fixed shear rate 1 S^{-1}). (1) $Y_2O_3/EPM = 0/100$; (2) $Y_2O_3/EPM = 5/100$; (3) $Y_2O_3/EPM = 3/100$; (4) $Y_2O_3/EPM = 1/100$.

Table II Newtonian Index (n) for Investigated Systems

Code	EPM	A	B	C	D	E
EPM content (%)	100	100	100	100	100	100
Y ₂ O ₃ content (%)	0	0.2	0.5	1	3	5
n	0.66	0.67	0.67	0.68	0.89	0.70

periments. WAXD profiles were carried out by a PW1700 diffractometer (CuK α , nickel-filtered radiation).

Methods to Estimate the Crystallization Rate

Supercooling ($\Delta T = T_m - T_c$) may be a measurement of a polymer's crystallinity, i.e., the smaller the ΔT , the higher the overall crystallization rate. Khanna⁷ introduced a new parameter for characterizing the crystallization rate, i.e., a "crystallization rate coefficient" (CRC), defined as $\Delta\beta/\Delta T_c$ (β is the cooling rate), which can be obtained from the slope of the line of cooling rate plotted against T_c . Zhang et al.⁸ proposed a new approach to determine the relative crystallization rate, and they obtained the half crystallization time as follows:

$$t_{1/2} = (T_{in} - T_{1/2})/\beta \quad (1)$$

where T_{in} is the initial crystallization temperature, $T_{1/2}$ is the temperature where the 50% area under the peak has been shown in this nonisothermal process. When the crystallization exothermic peak is

symmetric, the disparity between $T_{1/2}$ and T_c is negligible and $T_{1/2}$ can be replaced by T_c :

$$t_{1/2} = (T_{in} - T_c)/\beta \quad (2)$$

The reciprocal of $t_{1/2}$ is plotted against the cooling rate, and a straight line is obtained. The slope of this line (which may be defined as a crystallization rate parameter [CRP]) corresponds to the crystallization rate of polymer. The faster the crystallization rate of a polymer, the higher the slope. Thus, the slope can be considered as a parameter to represent the relative crystallization rate.

RESULTS AND DISCUSSION

Rheological Behaviors

As we very well know, increasing the temperature of a molten polymer decreases its viscosity, but the effect is vastly different for different polymers. There have been many theoretical and empirical equations proposed for characterizing the change in viscosity

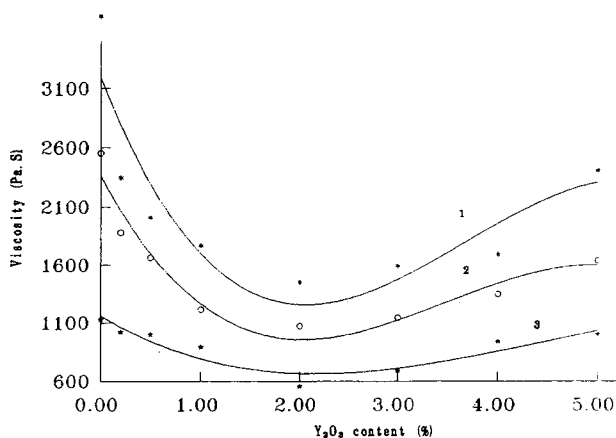


Figure 3 The relationship of viscosity and composition for Y₂O₃ filled EPM systems at different shear rates. (1) $r = 0.1 \text{ S}^{-1}$; (2) $r = 1.0 \text{ S}^{-1}$; (3) $r = 10 \text{ S}^{-1}$.

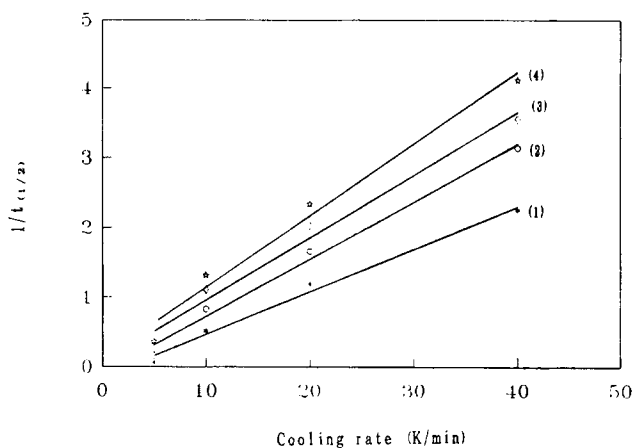


Figure 4 Plot of $1/t_{1/2}$ against the cooling rate of EPM with and without Y₂O₃. (1) Y₂O₃/EPM = 0/100; (2) Y₂O₃/EPM = 0.2/100; (3) Y₂O₃/EPM = 1.5/100; (4) Y₂O₃/EPM = 3.0/100.

Table III CRC and CRP Values of Various Samples

Code	EPM	A	C	D
CRC	2.023	2.029	2.732	2.976
CRP	0.0439	0.0781	0.0881	0.0949

with temperature, but perhaps the most useful formula is that proposed by Arrhenius, which says that

$$\eta = A \exp(E/RT) \quad (3)$$

where η is the viscosity, E the activation energy for viscous flow, and A is the constant. Figure 1 shows the variation in the viscosity at $1 S^{-1}$ shear rate for EPM with different Y_2O_3 contents plotted against the reciprocal of the absolute temperature. From the slope of the line of the Log of viscosities versus the reciprocal of the absolute temperature, we obtained the activation energy of filled EPM: 2.36, 2.33, 2.35, and 2.22 kJ/mol, for filler contents, respectively. It is seen that the activation energy for viscous flow with different Y_2O_3 contents changed only a little, the activation energy for viscous flow of EPM is not dependent on the content of Y_2O_3 .

The Logs of the shear stress of the polymers are plotted as a function of Log shear rate at $240^\circ C$ in Figure 2. In this plots, they give approximately straight lines. The curves for the EPM and Y_2O_3 filled EPM may be expressed by the equation proposed by Ostwald and Dewaele:

$$\tau = K\dot{\gamma}^n \quad (4)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, and K and n are constants. The exponent n in the equation can be used as a measure of deviation from Newtonian flow. We can obtain the n value by the slope of Log $\dot{\gamma}$ versus Log τ . The calculated n value of various Y_2O_3 contents are listed in Table II. It is seen that the n value in all cases was below 1 and increased with the increase of Y_2O_3 content. Using the n value as a guide, we see that Y_2O_3 filled EPM are more Newtonian-like than plain EPM.

The composition dependence of viscosities for Y_2O_3 filled EPM is reported in Figure 3. It shows viscosity as a function of composition for several shear rates. The viscosities of Y_2O_3 filled EPMS were all lower than that of EPM within the scope of the investigated compositions. In the beginning, the viscosities decreased with augmentation of Y_2O_3

concentrations, and then a minimum viscosity at the critical Y_2O_3 content was observed. After this critical content was exceeded, the viscosity increased with increasing filler concentration. The composition dependence of viscosities for yttrium oxide filled EPM reported here is different from usual inorganic fillers. Usual inorganic fillers, such as $CaCO_3$, carbon black, etc.,^{9,10} often showed increase in viscosity with increase of the filler content in the polymer.

Crystallization Characteristics

The line of the reciprocal of $t_{1/2}$ against cooling rate is shown in Figure 4. According to the method proposed by Zhang et al.,⁸ CRP is obtained from the line of the reciprocal of $t_{1/2}$ plotted against the cooling rate. The results obtained from differential scanning calorimetry are summarized in Table III. From the results of CRP, we find that the CRP values of EPM with Y_2O_3 are higher than the value of EPM without Y_2O_3 . In PP homopolymer, the Y_2O_3 used in our experiment was shown to be a highly efficient nucleating agent,^{4,5} and it increases the crystallization rate. The higher CRP values in EPM with higher Y_2O_3 contents confirm the expected trend.

According to the treatment proposed by Khanna,⁷ the cooling rate is plotted against T_c , as shown in Figure 5, and the slope of the line is the cooling rate coefficient CRC (Table III). From the results, we find that the CRC value of EPM with Y_2O_3 is higher than the CRC value of EPM without Y_2O_3 . As in-

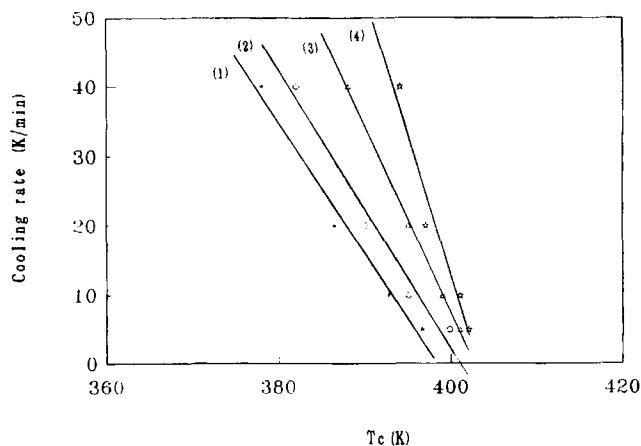


Figure 5 Plot of the cooling rate against T_c of EPM with and without Y_2O_3 . (1) $Y_2O_3/EPM = 0/100$; (2) $Y_2O_3/EPM = 0.2/100$; (3) $Y_2O_3/EPM = 1.5/100$; (4) $Y_2O_3/EPM = 3.0/100$.

Table IV The Comparison of Yttrium Oxide With Other Nucleating Agents

Nucleating Agents	Yttrium Oxide	Talc	Sodium Benzoate
Particle diameter (μm)	0.60	0.58	0.60
EPM content (wt %)	100	100	100
Filler content (wt %)	1	1	1
CRC	2.732	2.055	2.432
CRP	0.0881	0.0545	0.0678

indicated by Khanna, the higher the value of CRC, the higher the crystallization rate. For our investigation, copolymers with Y_2O_3 were consistent with the higher crystallization rate. Thus, using CRC to characterize the crystallization behavior of polymers in our case is reasonable.

To make a comparison with other nucleating agents, we used talc and sodium benzoate as references. As reported in the literature,^{11,12} talc and sodium benzoate are effective nucleating agents of PP homopolymer and EPM copolymer. The calculated CRC and CRP were listed in Table IV. From the results, we found yttrium oxide is a more effective nucleating agent for EPM crystallization than talc and sodium benzoate.

WAXD patterns for EPM and filled EPM are shown in Figure 6, where the intensities in arbitrary unites are plotted against the diffraction angle. The diffractograms show that the addition of filler into EPM leads to some changes in the crystal structure of EPM. The intensity of the peak at $2\beta = 16.1$, which corresponds to the (300) diffraction peak of β -form (hexagonal phase), decreases markedly with

the increase of the filler contents. The relative amount of the β -form is usually described in terms of the K value, which is defined as

$$K = \frac{H(300)}{H(300) + H(100) + H(040) + H(130)}$$

where $H(110)$, $H(040)$, and $H(130)$ are the heights of three strong equatorial α -form peaks (110), (040) and (130), and $H(300)$ is the height of the strong single β -form peak (300). Using this equation, we obtained the K values of pure EPM and filled EPM with different filler contents as follows: 28.3%, 23.4%, 12.1%, 1.79%, for filler contents, respectively.

It may be concluded that, by addition of rare earth into EPM copolymer, the proportion of the monoclinic (α -form) and hexagonal (β -form) phases is modified in the EPM. The proportion of these two forms usually depends on the molding conditions and the nucleation process. From our experiments, the molding conditions were the same for all specimens. Therefore, it can be suggested that the filler shows some effect on the nucleation of α - and β -EPM phases.

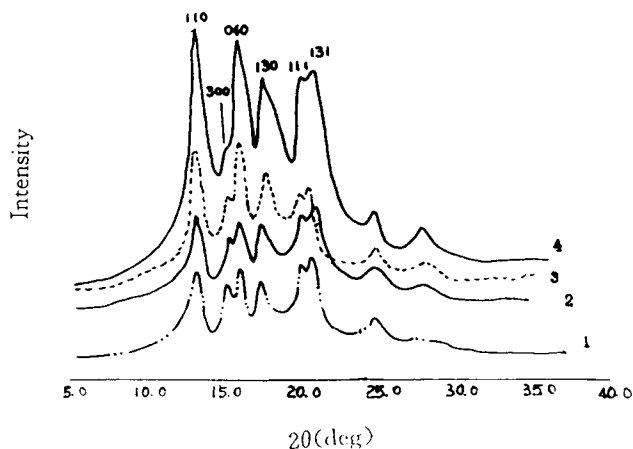


Figure 6 WAXD patterns for EPM and Y_2O_3 filled EPM. (1) $\text{Y}_2\text{O}_3/\text{EPM} = 0/100$; (2) $\text{Y}_2\text{O}_3/\text{EPM} = 0.2/100$; (3) $\text{Y}_2\text{O}_3/\text{EPM} = 1.5/100$; (4) $\text{Y}_2\text{O}_3/\text{EPM} = 3.0/100$.

CONCLUSIONS

The viscosity measurements show that the melt flow behavior of Y_2O_3 filled EPM is different from that of plain EPM. The addition of Y_2O_3 has some effect on the viscosity of the system. Crystallization characteristics indicate the filler acts as a nucleating agent, increasing crystallization rate of the investigated polymer, and changing β crystal form content.

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