

Thermal Properties and Crystallization Behavior of Ultrafine Fully-Vulcanized Powdered Rubber Particle Toughened Polypropylene

Dachun Sun,¹ Qiang Yuan,^{2*} Wei Jiang²

¹Department of Education Technology, Baicheng Normal College, Baicheng 137000, Jilin Province, People's Republic of China

²State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, People's Republic of China

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ABSTRACT: Thermal properties and crystallization behavior of ultrafine fully-vulcanized powdered rubber (UFPR) toughened polypropylene (PP) were studied by Differential scanning calorimetry (DSC) and Wide angle X-ray diffraction (WAXD) measurements. It was found that the fraction of β -form in the PP crystal increased at first, then sharply decreased up to zero with increasing UFPR content. This trend did not rely on isothermal crystallization temperature. Moreover, DSC measurements implied that UFPR particles addition

affected both isothermal and nonisothermal crystallization behaviors, including the crystallization temperature and the half-time of crystallization. Furthermore, WAXD test results indicated that the addition of UFPR induced the orientation of the crystallites more or less. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1318–1323, 2008

Key words: toughened polypropylene; crystallization behavior; β crystal

INTRODUCTION

Polypropylene (PP) is a widely used thermoplastic due to its good process ability and low cost. However, PP is known to exhibit low notched impact resistance, limiting its use. Rubber, elastomer as well as rigid particle were successfully used to toughen PP in the past decades.^{1–11} Recently, Qiao and coworkers tried to use ultrafine fully-vulcanized powdered rubber (UFPR) to toughen the PP and find a synergistic toughening effect with the incorporation of styrene butadiene styrene (SBS) elastomer.^{4,5} On the other hand, PP exhibits three different crystallographic forms, i.e., monoclinic α -form, pseudo hexagonal β -form and orthorhombic γ -form,¹² respectively. The latter two occurrences depend on the crystallization conditions, usually as a minority component. Many studies have been devoted to the β -crystal of PP or particulate-filled-PP. Shi et al.^{14–16} and Varga et al.^{17–19} reported the method for preparation of the β -crystal

of PP by using specific β -nucleating agents or processing conditions. Yuan et al.¹³ found that the incorporation of glass bead can affect the amount of β -form in PP crystals. Tjong and Xu²⁰ studied the nonisothermal kinetic behavior of high purity β -PP and carbonate-filler β -PP blends by DSC. The results indicate that the crystallization temperature and crystallization rate coefficient of β -PP are considerably higher than those of pure α -PP homopolymer, furthermore the filler does not influence the mechanism of nucleation or growth of the PP crystal. It is generally known that the properties of a polymer were determined by the crystallization and its structure. Therefore, crystallization behavior of PP and its blend is an important topic in both polymer science and engineering.

In the present study, UFPR was used to blend with the PP. The purpose is to study the thermal properties and crystallization behavior of UFPR toughened PP.

Correspondence to: W. Jiang (wjiaang@ciac.jl.cn).

*Present address: Center for Structural and Functional Materials, University of Louisiana at Lafayette, P.O. Box 44130, Lafayette, Louisiana 70504-4130, USA.

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EXPERIMENTAL

Materials

A commercially available grade of polypropylene (PP), type 5004 produced by Liaoyang Petrochemical Fiber (People's Republic China) was used to study the effects of filler on the thermal properties and

crystallization behavior. The PP has a weight average molecular weight (M_w) of 3.72×10^5 ; number average molecular weight (M_n) of 6.90×10^4 ; molecular weight distribution (M_w/M_n) of 5.4; melt flow index of 3.3 g/10 min with a load 5 kg (ASTM D1238) and density of 0.9 g/cm^3 , respectively. The styrene butadiene UFPR manufactured by Beijing BHY Chemical Industry New Technology Company, China (NarpowTM VP-101) was used as the reinforcement filler and its average single particle size is $\sim 100 \text{ nm}$.

Preparation of samples

The PP/UFPR blends with different rubber contents were mixed in a Thermo Haake Rheomix 600 apparatus equipped with two counter rotating roller rotors (Thermo Haake GmbH, Germany) at 190°C for 4 min. The roller speed used for blending was 50 rpm. The temperature, mixing time and roller speed remained unchanged for all the blends.

Impact measurement

Izod impact samples were molded into plaques by compression molding process at 190°C and cooled down to room temperature by air. Standard impact samples with dimensions of $63 \times 12.7 \times 4.0 \text{ mm}^3$ were cut from the plaques, and a v-notch with a tip radius of 0.25 mm was introduced into the specimen using a 45° V-shape knife. Then these notched impact samples were subjected to impact test in accordance with ASTM D256 using an XJU-2.75J Izod impact tester (made in Wuzhong, People's Republic of China) at room temperatures ($\sim 25^\circ\text{C}$).

Differential scanning calorimetry

The crystallization behavior of neat and UFPR-reinforced polypropylene was carried out using a Perkin-Elmer Diamond equipped with Intracooler 2P, Thermal Analysis System. The samples were first heated from 30 to 200°C and held at the high temperature for about 5 min to remove the previous thermomechanical history and then cooled at a cooling rate of $100^\circ\text{C}/\text{min}$ to the selected isothermal crystallization temperatures. The crystallization was carried out for adequate time to ensure complete crystallization of the sample at constant temperature. Subsequently, the melting curves were recorded at a heating rate of $10^\circ\text{C}/\text{min}$. Both heating and cooling scans were carried out in a nitrogen environment.

Dynamic mechanical analysis

The storage modulus, loss modulus and glass transition temperature of neat and UFPR-reinforced polypropylene were studied by a dynamic mechanic

analyzer 242 (NETZSH-Gerätebau GmbH, Germany). Dynamic mechanical analysis (DMA) was carried out on in a single cantilever mode from -100 to 100°C under nitrogen environment. The testing frequency was 1 Hz and heating rate was $3 \text{ K}/\text{min}$.

Wide angle X-ray diffraction

Izod impact samples were used directly for X-ray characterization. Wide angle X-ray diffraction (WAXD) was performed on a Rigaku D/MAX 2500V PC X-ray diffractometer (Japan) in reflection mode operating at 40 KV and 200 mA using Cu $K\alpha$ radiation as the X-ray source. Samples were scanned at $4^\circ/\text{min}$ in the 2θ range of $4\text{--}35^\circ$.

Field emission scanning electron microscopy

Scanning electron microscopy (SEM) measurements were performed on a XL 30 E-SEM (FEG, Micrion FEI PHILIPS). The blend specimen was cryofractured in liquid nitrogen. The sample was coated with a thin layer of gold prior to SEM observations.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the notched Izod impact strength with UFPR content for the PP/UFPR blends. It can be found that the addition of UFPR to PP continuously increases the impact strength (toughness) in the range of 0–26 wt %. A similar result was recently reported by Zhang and Qiao^{4,5} in their study on polypropylene-UFPR and polypropylene-UFPR/SBS blend systems. However, the crystallization behavior changes correspondingly. From the WAXD patterns of the PP/UFPR blends (Fig. 2), it is seen that the content of the β -PP in the samples depends on UFPR content. The content of

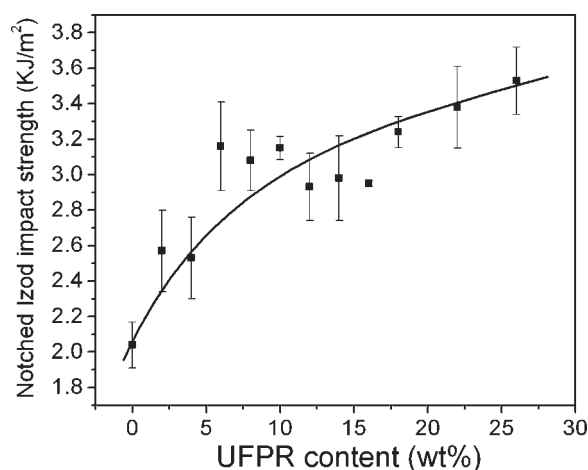


Figure 1 Variation of the Izod impact strength with UFPR content for PP/UFPR blends.

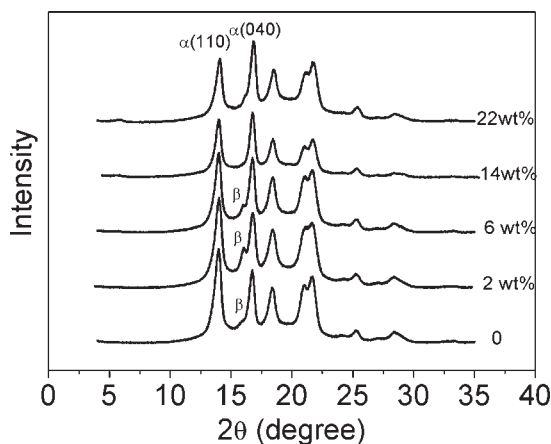


Figure 2 WAXD spectra for the PP and PP/UFPR blends.

β -crystals increases with increasing UFPR particles up to 6 wt %, thereafter it decreases rapidly with increasing UFPR particles content. This result has been further confirmed by DSC analysis (Fig. 3). On the other hand, it can be found that although the overall nature of the diffraction patterns for α -crystal remains unchanged, the intensity of the 110 and 040 reflections are different for different UFPR contents. The result suggests that the crystalline phase remains the same in all cases, but the crystallites are likely to be orientated somewhat in the presence of UFPR.²¹ The crystal orientation degree ($I(040)/I(110)$) for the PP increases from 0.76 to 1.27 when the particles content increases from 0 to 22 wt %. This may result from the presence of UFPR particles. They can affect the PP chains motion during crystallization because the viscosity of the UFPR particles and the PP are quite different.

The melting curves after isothermal crystallization at various temperatures for the PP and PP/UFPR blends are shown in Figure 3. It can be seen from these melting curves that at a given isothermal crystallization temperature, it is noticed that there are two melting peaks in the melting curves, belonging to β -PP (about 153°C) and α -PP (about 166°C),

respectively for the blends with lower UFPR content (≤ 6 wt %). However, the melting enthalpy of β -crystal dropped markedly with further increasing UFPR particles content. This result is in accordance with the previous result by WAXD. It is generally known that the formation and the content of β -crystal rely on the type and content of fillers.²² At low content of UFPR particles (≤ 6 wt %), the particles act as an effective β -crystal nucleating agent and the amount of β -PP increase with increasing the filler content. However, for higher filler content, coalescence occurs easily and may lead to the suppression of β -crystal formation. In this case, the amount of β -PP decreases with increasing the filler content.

Table I shows the effect of UFPR particles on the crystallization behaviors of the PP from DSC measurements. The degree of crystallinity (X_c) is calculated from the heat evolved during crystallization (ΔH_c) by eq. (1),

$$X_c (\%) = \frac{\Delta H_c}{(1 - \phi)\Delta H_m} \times 100 \quad (1)$$

where $\Delta H_m = 209$ J/g is the enthalpy of fusion for a fully crystalline polypropylene and ϕ is the weight percentage of the UFPR particles in the blends. The data in Table I indicates that the addition of UFPR has little effect on the crystallinity of the PP. The crystallization temperatures listed in Table I show that with lower UFPR content (≤ 6 wt %), the PP/UFPR samples possess lower crystallization temperatures (T_p) than pure PP, but with increasing the UFPR content further (≥ 6 wt %), the PP/UFPR samples exhibit relatively higher crystallization temperatures than pure PP. These results are different from that reported, in which all the rubber toughened samples have higher crystallization temperature than pure PP.⁵ The difference results from the different PP samples used. The PP used in the present study possesses β -form crystalline, whereas the PP used in Ref. ⁵ does not. The data for the half-time of crystallization ($t_{0.5}$), which is the value of the time

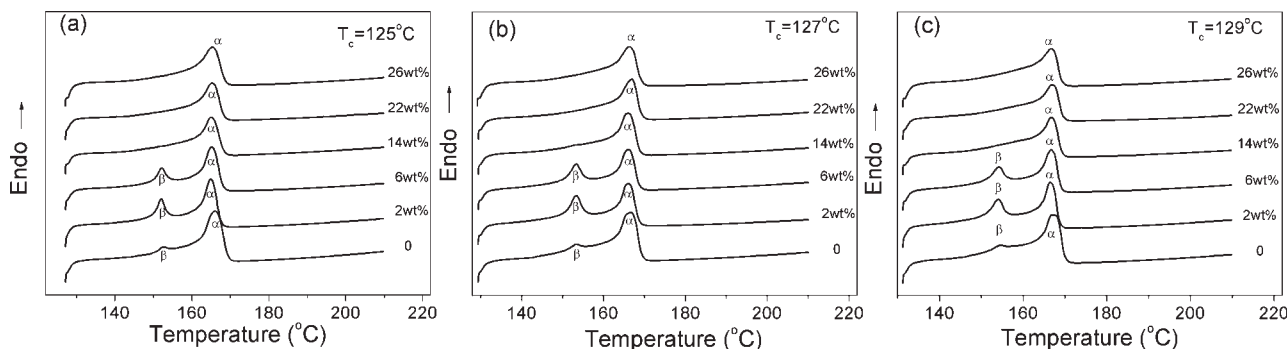


Figure 3 Melting curves after isothermal crystallization at various temperatures for the PP and PP/UFPR blends. (a) 125°C; (b) 127°C; (c) 129°C.

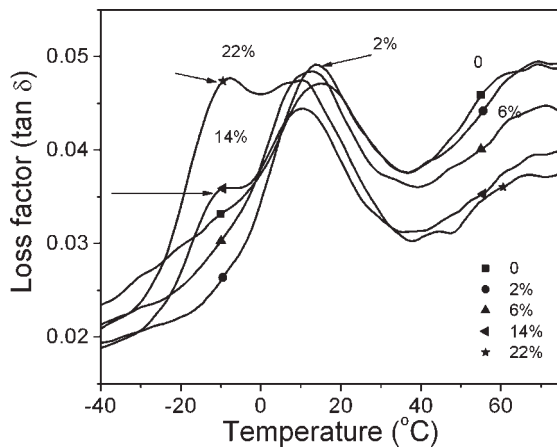


Figure 5 Loss factor ($\tan \delta$) spectra for the PP and PP/UFPR blends.

temperature with increasing UFPR content. Figure 6 gives the relationship between the T_g and filler content for the PP/UFPR blends. It is found that the T_g of PP decreases from 15 to 10°C with increasing the UFPR content from 0 to 22 wt %. In addition, the lower temperature peak at about -7.8°C , which corresponds to the glass transition of UFPR particles, appears obviously in the $\tan \delta$ curves for the blends with 14 and 22 wt % UFPR particles. It is found that the two peaks tend to shift close to each other with increasing UFPR content, indicating that the UFPR possesses good compatibility with PP.

Finally, Figure 7 gives a low and a high magnification SEM fractographs for the PP/UFPR (92/8 by weight) blend sample, respectively. It can be found that the UFPR particles were well dispersed and embedded in the PP matrix, further indicating that the UFPR possesses good compatibility with the PP. However, some big UFPR particles (more than 20 μm) were observed. These big particles reduce the

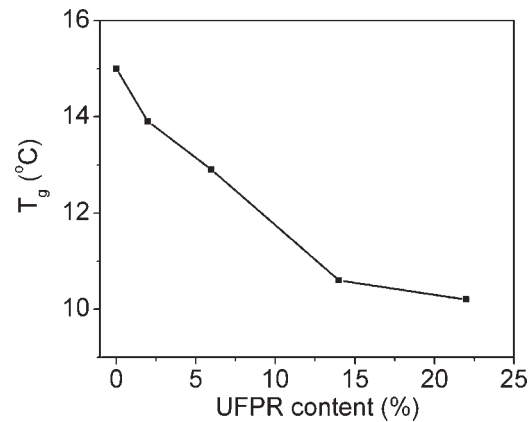


Figure 6 Glass transition temperature (T_g) for the PP as a function of UFPR content.

toughening efficiency of the UFPR. This is a main reason that the toughness of the PP increases slowly with the addition of the UFPR. Nevertheless, the increase of the toughness of the blend is mainly from the contribution of the UFPR, rather than the β -PP because the content of β crystal increases with increasing the UFPR particles up to 6 wt %, thereafter it decreases rapidly with increasing the UFPR particle content. However, the toughness of the blend increases continuously with the increase of the UFPR content.

CONCLUSIONS

The UFPR was used to blend with the polypropylene (PP). Thermal properties and crystallization behavior of the resulting blends were studied by Differential scanning calorimetry (DSC) and WAXD measurements. The results showed that the fraction

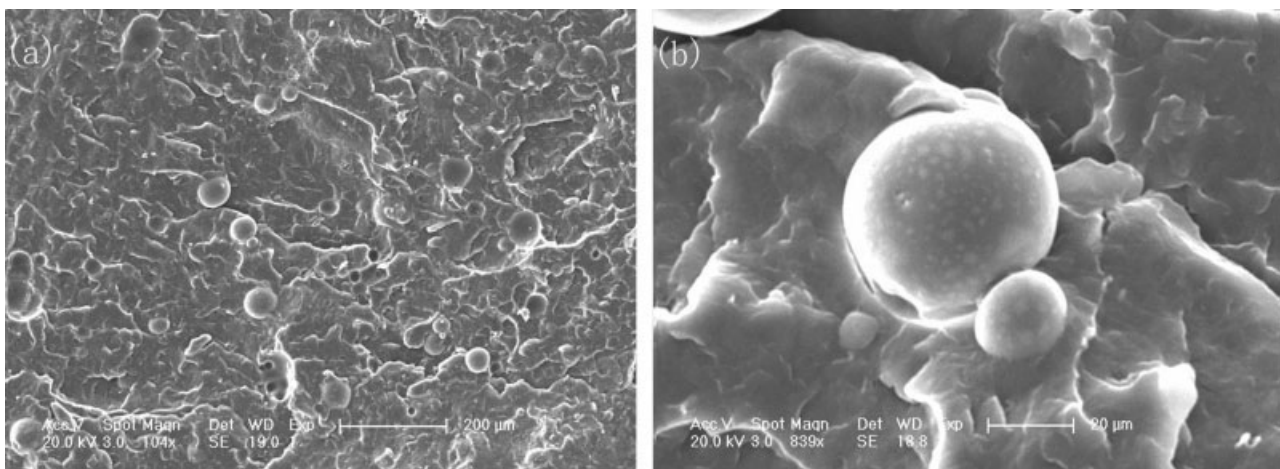


Figure 7 SEM fractographs for the PP/UFPR (92/8 by weight) blend sample. (a) low magnification; (b) high magnification.

of β -form in the PP crystals increased at first, then decreased markedly with increasing the UFPR particles content. This trend did not rely on isothermal crystallization temperature. Moreover, the results of DSC analysis implied that the addition of UFPR rubber particle affected the PP crystallization behaviors obviously, including the crystallization temperature and the half-time of crystallization. Furthermore, WAXD test results indicated that the addition of UFPR could induce the orientation of the crystallites more or less.

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