

Research Article

Preparation and Crystallization Property of Ternary Composites of WBG/AA-RCC/PP

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A series of ternary composites of WBG/AA-RCC/PP were prepared and their crystallization behaviors were investigated by XRD and DSC. The results indicate that WBG and AA-RCC affect the crystallization of PP matrix with a mutual inhibition effect. This effect is enhanced with increasing content of WBG and induces the growth of β_2 crystal. AA-RCC promotes the heterogeneous nucleation of α crystal and offers a template for α crystal growth along a specific lattice plane and promotes the epitaxial crystallization of PP matrix, while the specific arranged α crystal could induce the formation of β crystal.

1. Introduction

Polypropylene (PP) is a kind of commercial polymers with good performance. However, some defects such as low notch impact strength and low-temperature brittleness restrict further application of PP. Because of this reason, some fillers or reinforcements have been introduced in order to develop PP composite with desired properties [1–10]. CaCO_3 is among the most frequently studied objects in modification research. As a typical rigid particle, CaCO_3 does indeed play an important role in performance improvement of PP. In particular, with the development of powder technology, the use of nanoscale CaCO_3 particles has received much attention for polymer-based nanocomposites. Compared to conventional microcomposites, the addition of CaCO_3 nanoparticles can ameliorate the mechanical, thermal, and wear properties of thermoplastics [6–10]. However, there is still dearth of some data about the influence of the CaCO_3 nanoparticles with different shapes (rhombohedral or spherical) on crystallization behavior of the nanocomposites.

At present, the PP modification products are emerging. Nevertheless, there are deficiencies in each product, which need to be improved. Studies have shown that β -nucleated PP has excellent impact resistance and creep resistance. However, the development and study of β nucleating agent

are far less than those of α nucleating agent. The research on new nucleating agent and compound modification system deserves attention.

2. Materials and Methods

2.1. Material. The isotactic polypropylene T30S with a melt flow index of 2.6 g/10 min was supplied by Lanzhou Petrochemical Company (China National Petroleum Corporation). The rhombohedra CaCO_3 was provided by Nano Materials Technology Co., Ltd., (Ruicheng, Shanxi, China), which will be denoted as “RCC” throughout the paper. The rare earth β nucleating agent (WBG) was provided by Guangdong Winner New Materials Technology Co., Ltd. (WINNER). The adipic acid was provided by Chengdu Kelong Chemical Co., Ltd. All other materials were of analytical grade and used without further purification. Water was distilled and deionized.

2.2. Surface Treatment of the CaCO_3 Particles. To improve the interfacial adhesion between the filler and the polymer matrix, CaCO_3 nanopowders were coated with 8 wt% adipic acid, which will be denoted as “AA-RCC” throughout the paper. The coating method was as follows. Firstly, 15 g of RCC was put into the single-neck flask and mixed with a 60 mL

TABLE 1: The compositions of composites (weight ration).

Samples	AA-RCC (g)	WBG (g)	PP (g)
1-1	0	0.2	100
1-2	2	0.2	98
1-3	4	0.2	96
1-4	6	0.2	94
2-1	4	0	96
2-2	4	0.1	96
2-3	4	0.2	96
2-4	4	0.3	96
2-5	4	0.4	96

solution mixture of water and ethanol with a volume ratio of 3 : 1. And then the system was maintained at 80°C with a magnetic stirrer for 2 h. Finally, the product was dried in an oven at 90°C for 24 h [10].

2.3. Preparation of the Composites. The composition of the composites used in the experiments is listed in Table 1. Before mixing, the pure PP and two fillers (AA-RCC and WBG) were dried at 100°C for 2 h. The mixtures were compounded in a single-screw extruder. The rate of the screw was 60 rpm. The temperature of the extruder from the hopper to the die was set at 195°C, 200°C, and 200°C, respectively.

2.4. Characterization. Wide-angle X-ray diffraction (WXR) analyses were performed on an XRD-6000 diffractometer (Shimadzu, Japan) with an X-ray generator of 3 kW, graphite monochromatic, and Cu K α radiation (wavelength = 1.5406 Å) and were operated at 40 kV and 20 mA. The samples were scanned at room temperature from 10° to 50° at a scanning rate of 2°/min. The content of the β -crystal in the crystalline part was calculated according to the standard procedures as follows [1]:

$$K_{\beta 1} = \frac{H_{\beta}(300)}{H_{\beta}(300) + H_{\alpha}(110) + H_{\alpha}(040) + H_{\alpha}(130)}, \quad (1)$$

$$K_{\beta 2} = \frac{H_{\beta}(301)}{H_{\beta}(301) + H_{\beta}(300)},$$

where $H_X(hkl)$ denotes the intensity of respective (hkl) peak belonging to phase X.

The crystallization behavior of PP composites was studied by DSC Q2000 (TA Instruments, USA). For nonisothermal crystallization, the samples were first treated isothermally at 200°C for 3 min to erase previous thermal history and quenched to 20°C, then heated up to 200°C at 10°C/min, held at 200°C for 1 min, and cooled to 20°C at the constant cooling rates 10°C/min. The endothermic and exothermal traces were recorded for the later data analysis. All measurements were

TABLE 2: The content of the β -crystal with different measurement methods.

Samples	$K_{\beta 1}$	$K_{\beta 2}$	$X_{\beta 1}$	$X_{\beta 2}$	X_{α}
1-1	0.87	0.26	/	0.38	0.06
1-2	0.63	0.36	0.11	0.02	0.22
1-3	0.55	0.63	0.54	0.12	0.06
1-4	0.72	0.58	0.58	0.12	0.06
2-1	/	/	/	/	0.56
2-2	0.70	0.57	0.55	0.13	0.06
2-3	0.55	0.63	0.54	0.11	0.06
2-4	0.52	0.85	0.73	0.05	0.06
2-5	0.49	0.84	0.68	0.03	0.06

carried out at the nitrogen atmosphere environment. The crystalline (S_{β}) of the composites is calculated with

$$X_{\alpha} = \frac{\Delta H_f^{\alpha}}{\Delta H_f^1},$$

$$X_{\beta} = \frac{\Delta H_f^{\beta}}{\Delta H_f^2}. \quad (2)$$

Here ΔH_f^{α} and ΔH_f^{β} are the fusion heat of α and β crystal from DSC thermograms, respectively. ΔH_f^1 is the perfect α crystal fusion heat of the hypothetically 100% crystalline PP (177 J/g), and ΔH_f^2 is the perfect β crystal fusion heat of the hypothetically 100% crystalline PP (168.5 J/g) [11].

Polarized optical microscopy (POM) studies were carried out with an ECLIPSE LV100POL microscope (Nikon, Japan) in conjunction with a HSC621 V hot stage (Instec, USA). The specimens were heated to 230°C on a hot stage and held at this temperature for 3 min to eliminate the thermal history and then quenched to the fixed crystallization temperature (130°C). The photographs were provided by a digital camera.

3. Results and Discussion

3.1. Wide-Angle X-Ray Diffraction Analysis. Figures 1 and 2 show the XRD patterns of composites and the K_{β} values calculated according to (1) are listed in Table 2. It is clear that the main diffraction peaks are at $2\theta = 14.1^\circ$, 16.9° , and 18.6° , which are attributed to the reflections of (110), (040), and (130) lattice planes, respectively. The peaks at $2\theta = 16.1^\circ$ and 21.3° are assigned to (300) lattice plane of β_1 crystal and (301) lattice plane of β_2 crystal, respectively. According to the XRD curve 1-1, the strongest diffraction peak is at $2\theta = 16.1^\circ$ and assigned to (300) lattice plane of β_1 crystal. The XRD results show that the content of β -crystal is 0.87 when the WBG addition content is 0.2 phr, which is in accord with previous report [12]. As seen at 2-1 line for 4 phr AA-RCC/PP, the strongest diffraction peak is at $2\theta = 16.9^\circ$ and assigned to (040) lattice plane of α crystal. It can be concluded that, with addition of WBG or AA-RCC, composites crystallize along a specific lattice plane and orientation. Therefore, WBG acts as a kind of β -crystal nucleating agent, while AA-RCC acts as a kind of α -crystal nucleating agent.

TABLE 3: Nonisothermal crystallization kinetics parameters of WBG/AA-RCC/PP.

	T_c^β (°C)	ΔH_c^β (J/g)	T_c^α (°C)	ΔH_c^α (J/g)	$T_m^{\beta 1}$ (°C)	$\Delta H_m^{\beta 1}$ (J/g)	$T_m^{\beta 2}$ (°C)	$\Delta H_m^{\beta 2}$ (J/g)	T_m^α (°C)	ΔH_m^α (J/g)
1-1	/	/	126.81	73.92	/	/	152.38	64.22	167.23	10.06
1-2	120.36	98.17	/	/	128.76	18.34	146.65	4.23	160.77	38.68
1-3	118.58	89.30	126.74	30.70	131.13	90.87	149.52	19.58	162.49	9.96
1-4	118.41	90.78	126.84	28.11	131.07	97.02	149.56	19.74	162.70	10.00
2-1	/	/	123.89	100.40	/	/	/	/	161.78	99.93
2-2	118.52	86.09	126.61	31.68	130.85	93.00	149.14	21.93	162.41	11.15
2-3	118.58	89.30	126.74	30.70	131.13	90.87	149.52	19.58	162.49	9.96
2-4	118.48	127.50	126.94	5.95	130.84	122.80	148.58	8.74	161.85	9.90
2-5	118.54	121.1	/	/	130.92	114.20	147.47	5.95	160.39	11.25

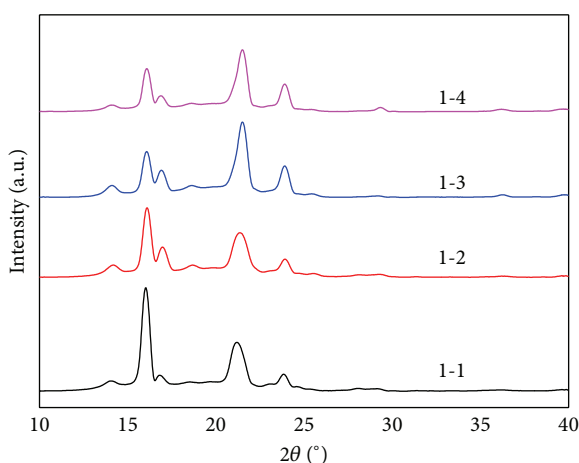


FIGURE 1: WAXD spectra of PP with the different AA-RCC content.

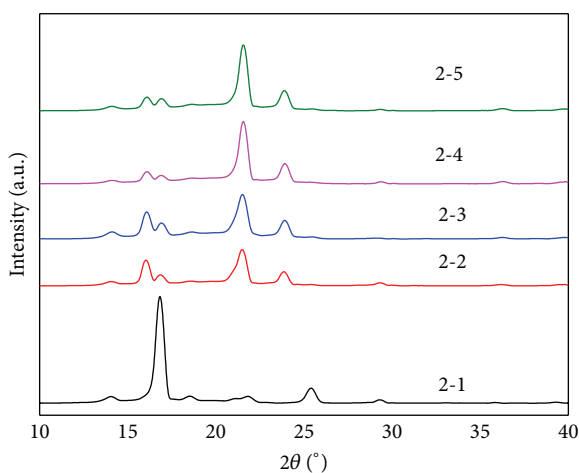


FIGURE 2: WAXD spectra of PP with the different WBG content.

It can be seen from Figure 1 that when the WBG content is 0.2 phr, the peak intensity at $2\theta = 16.1^\circ$ decreases sharply with increasing AA-RCC, while the peak intensity at $2\theta = 16.1^\circ$ increases. As reported in Table 2, quantitative analysis shows that the β_1 crystal content falls to lowest value of 0.55, and the

β_2 crystal content increases from 0.26% to 0.63. In Figure 2, when the AA-RCC content remains constant (4 phr), the peak intensity at $2\theta = 16.1^\circ$ firstly increases and afterwards decreases with increasing WBG, and the β_1 crystal content decreases from 0.70 to 0.49. However, the peak intensity at $2\theta = 16.9^\circ$ decreases sharply but peak at $2\theta = 21.3^\circ$ increases, indicating the emergence and increase of β_2 crystal content. There is no doubt that WBG and AA-RCC act with mutual inhibition effect in the crystallization of PP matrix and the effect increases with increasing content of WBG. Moreover, the mutual inhibition effect induces the growth of β_2 crystal.

3.2. Nonisothermal Crystallization and Melting Behavior Characterization. Figure 3 presents the crystallization ((a) and (c)) and melting ((b) and (d)) DSC curves of WBG/AA-RCC/PP. The corresponding data is listed in Table 3. It is known that the crystallization peak temperature (T_{cp}) is $118\sim 119^\circ\text{C}$ [9, 13]. When 0.2 phr WBG or 4 phr AA-RCC is added to PP, either of the DSC curves has a single peak and T_{cp} is 126.81°C and 123.89°C , respectively. When the content of WBG remains at 0.2 phr level, with increasing AA-RCC, two peaks emerge in the curve of composites. The peak at low temperature is for β crystal and the other at higher temperature for α crystal. When the content of AA-RCC remains at 4 phr level, with increasing WBG, one of the two peaks gradually disappears resulting in a single peak at 118.54°C . This indicates that WBG and AA-RCC affect the nucleating of PP and promote its crystallization. With the increasing content of WBG, a highly effective nucleating agent of β crystal, the number of crystal nucleus, and crystallization rate increase, resulting in the increase of peak area of β crystal [12].

Figures 3(b) and 3(d) show the melting curves of composites and relevant data are listed in Tables 2 and 3. According to DSC curve 2-1, when AA-RCC was added to PP, the melting curve has a single peak and T_m is 161.78°C . However, with only WBG being added to PP, the DSC curve 1-1 has two peaks and the crystallization peak temperatures are 152.38°C and 167.23°C , respectively. When both WBG and AA-RCC were added to PP, the curves of ternary composites have three peaks and their peak temperatures are 130°C , 149°C , and 162°C , respectively. It is also noted that the three peaks move to lower temperature and their peak areas increase with

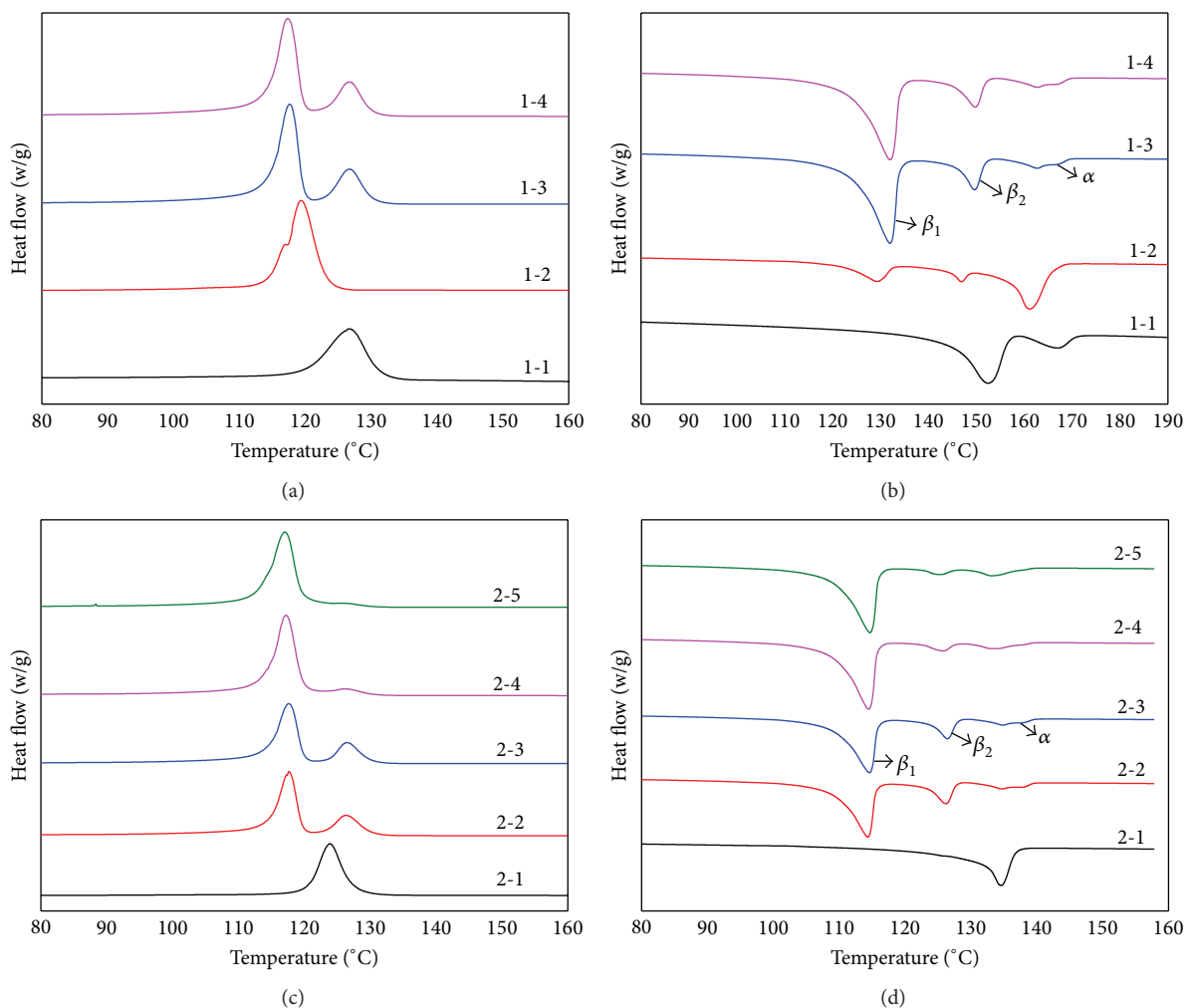


FIGURE 3: DSC crystallization ((a) and (c)) and melting ((b) and (d)) curves of WBG/AA-RCC/PP.

increasing content of WBG and AA-RCC. It is known that the melting peak of α crystal appears at a temperature range from 160 °C to 170 °C, while it appears at a lower temperature for β crystal [13]. There are two kinds of β crystal melting peaks for WBG/AA-RCC/PP composites according to Figures 3(b) and 3(d). The peak at lower temperature was attributed to β_1 crystal and the other peak at higher temperature to the recrystallization melting peak of β_1 and β_2 crystal [14]. From Figures 3(b) and 3(d), it is clear that the crystallization peak temperatures of β_1 and β_2 crystal vary remarkably. The peak area of β_1 crystal decreases gradually with increasing content of WBG and AA-RCC. It could be concluded that the two peaks suggest two kinds of crystals which might be assigned to (301) lattice plane of β_1 crystal and (300) lattice plane of β_2 crystal. These results are in accord with XRD analysis.

3.3. Crystal Morphology of WBG/AA-RCC/PP by POM. Figure 4 shows the POM micrographs of 0.2 phr/WBG/4 phr AA-RCC/PP at 130 °C. Just as shown in Figure 4(b), line shape crystal nucleus emerges at the beginning of crystallization. The line shape crystal nucleus becomes thicker gradually by

growing towards outside symmetrically over time, resulting with a tightly arranged network structure with uniform density. Because α crystal occurs before β crystal, AA-RCC promotes the heterogeneous nucleation of α crystal and RCC offers a template for α crystal growth along a specific lattice plane and promotes the epitaxial crystallization of PP matrix as shown in XRD analysis, while the specific arranged α crystal could induce the formation of β column crystal. When spherocrystal grows faster than column crystal, α crystal gradually transforms into β crystal [15]. Therefore, it finally comes out to be β crystal with a tightly arranged network structure.

4. Conclusions

In this paper, the ternary composite materials of WBG/AA-RCC/PP were prepared and their crystallization behaviors were investigated by XRD and DSC. WBG and AA-RCC promote the formation of β crystal and β_2 crystal increases but β_1 crystal decreases, suggesting that there is a competition between α and β crystal growth which is in favor of the formation of β crystal.

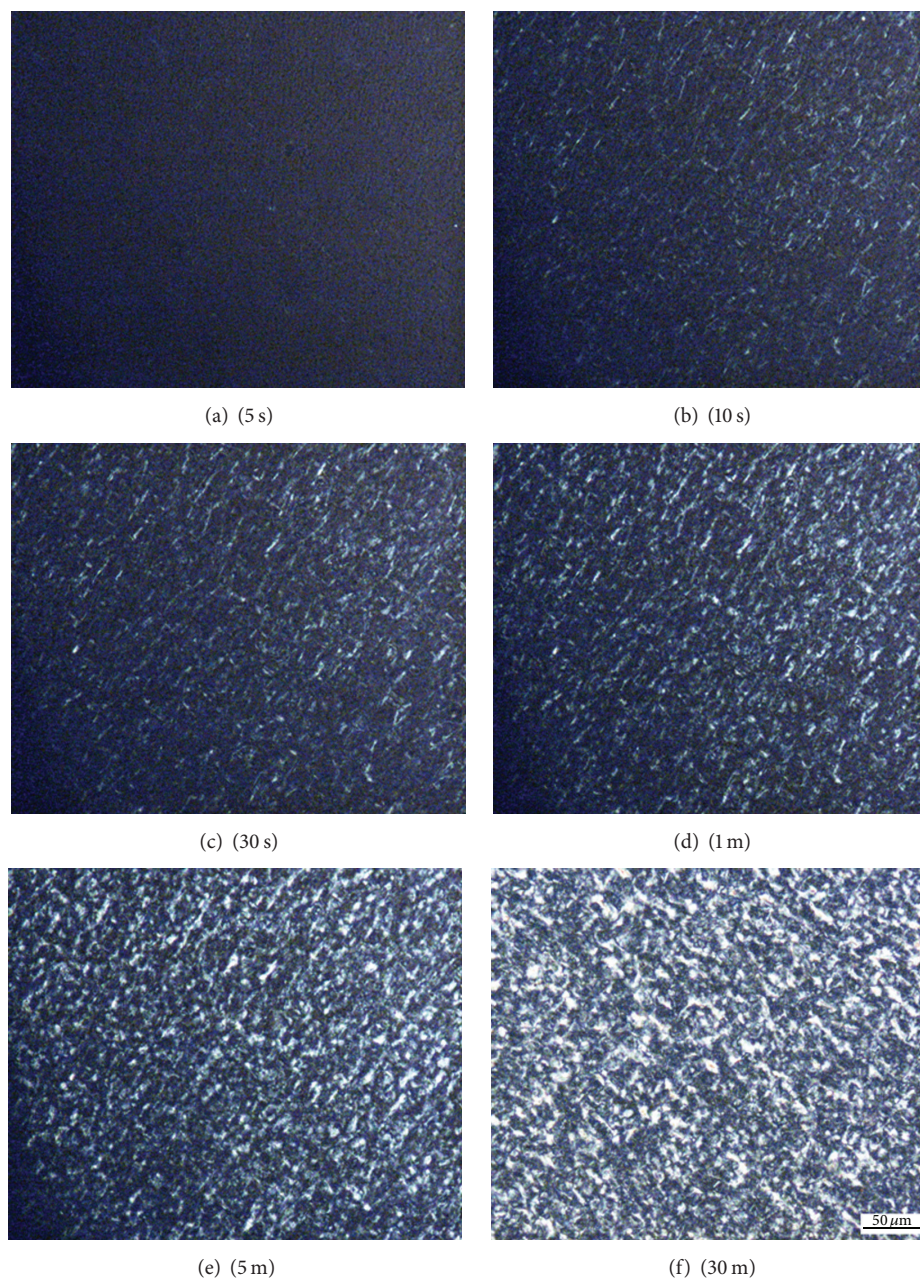


FIGURE 4: POM micrographs of WBG/AA-RCC/PP.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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