Journal of Wuhan University of Technology-Mater. Sci. Ed. www.jwutms.net Aug. 2018

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Effects of Annealing Process on Crystallization and Low Temperature Resistance Properties of PP-R Composites

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Abstract: The effects of the annealing process on the mechanical properties and crystallization behaviors of polypropylene random copolymer (PP-R) composites were investigated using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). The experimental results indicated that the annealing process significantly influenced the comprehensive properties of PP-R composites. At temperatures below 23 ℃, the impact strength of the PP-R composites annealed at 120 ℃ for 6 h was relatively high at 74.73 kJ/m^2, which was 16.8% higher than that of the samples annealed at 80 ℃ for 6 h. At low temperatures (−30-0 ℃), the impact strength ranged from approximately 13.31 kJ/m^2 to 54.4 kJ/m^2. In addition, the annealing process conducted at 120 ℃ for 6 h improved the crystalline structure and low-temperature toughness of the PP-R composites and induced α-form to β-form crystal transformation. The work provides a possible method to reinforce and toughen the semi-crystalline polymer at low temperatures (-30-0 ℃) by annealing.

Key words: polypropylene; crystallization; annealing process; low temperature toughness

1 Introduction

Polypropylene random copolymer (PP-R) pipes are the third generation modified PP-R products that were originally developed in Europe in the early 20th century[1]. PP-R, one of the five most commonly used engineering plastics, is used as the matrix material in PP-R pipes. Furthermore, it possesses excellent performance characteristics, such as high strength, heat resistance, and compressive strength as well as low density. In recent years, PP-R has been widely used in various industries to manufacture pipes, automobile components, and furniture[2,3]. However, due to its high sensitivity to low temperatures and susceptibility to stress-induced cracks, the applications of PP-R in certain fields are limited. Therefore, methods of effectively reducing the sensitivity of PP-R to low temperatures are needed.

Various studies concerning methods of improving the low-temperature toughness of PP-R, such as copolymerization, blending, and annealing methods, have been conducted[4-6]. Ding J *et al*[7] used a synthetic process to improve the dispersion characteristics of the copolymerized monomers in PP-R materials. In addition, Zhu YL *et al*[8] added anti-impact polypropylene copolymer (IPC) and β nucleating agents to PP-R materials. The impact toughness of the resulting PP-R/IPC system was more than two times greater than that of pure PP-R. In addition, the ductile-brittle transition temperature of the PP-R/IPC system was 8 ℃ less than that of pure PP-R. In another study, Cheng ZG *et al*[9] annealed PP-R samples using supercritical carbon dioxide as a protecting atmosphere. This method increased the impact toughness of the PP-R from 29 to 56.8 kJ/m^2. Da SM *et al*[10] studied the effects of the annealing process on the properties of PP-R/β nucleating agents (β-NA)/elastomer (POE) composites. The results indicated that the annealing process rearranged the molecular structure of the crystal and elastomer phases, significantly improving the impact toughness and tensile strength of the PP-R/β-NA/POE. Furthermore, Hui LD *et al*[11] annealed a combination of EPDM and PP-R at 120 ℃, yielding a PP-R material with an impact toughness of 41.2 kJ/m^2 at −20 ℃. According to the results

of these studies, the toughness of PP-R can be significantly improved through the addition of modifiers and *β*-nucleating agents as well as the annealing process. However, these methods also reduce the overall strength and rigidity of PP-R materials[12-14]. Although numerous studies concerning the improvement of the impact toughness of PP-R at normal temperatures have been conducted, further research, especially on the low-temperature (−10-−30 ℃) toughness of PP-R, is needed[15-19].

In this study, PP-R composites were prepared by adding the elastomer TPR to PP-R materials. The crystallization properties and microstructures of the resulting material were used to analyze the effects of the annealing process on the low-temperature toughness of the PP-R composites in order to provide a theoretical basis for the research and development of PP-R pipes.

2 Experimental

2.1 Materials

PP-R (RP2400) with a 3.8wt% ethylene content and melt flow rate (MFR) of 0.25 g/10 min (2308C, 2.16 kg) was supplied by Korean Petrochemical Co. Polybutadiene modifiers (TPR2088A) with a melt flow rate (MFR) of 44 g/10 min (1908C/5 kg) were supplied by Jia Xinhao Plastic Co. Masterbatch(gray) and Liansu Technology Development (Guiyang) Co.

2.2 Sample preparation

Table 1 PP-R composite formulas

Sample	PP-R/wt%	2088A/wt%	Masterbatch/wt%
PP-R/TPR	90	10	2

Table 2 Annealing process

Duration/h	Temperature /℃			
	80	100	120	140
1	-	-	1 h	-
3	-	-	3 h	-
6	80 ℃	100 ℃	120 ℃, 6 h	140 ℃
9	-	-	9 h	-

The PP-R/modifier TPR/masterbatch was blended at temperatures of 190, 195, 200, 205, and 215 ℃ and a rotation speed of 200 r/min using a twin-screw extruder (PL860/290, Haitian Machinery Co., Ltd., Wuxi, China) according to the formulas presented in Table 1. The extrusion pellets were dried for 3 h at 90 ℃ and then stored for future use. The resulting PP-R composite materials were molded with an injection molding machine (PL860/290, Haitian Machinery Co., Ltd., Wuxi,

China). The molding process was conducted at temperatures ranging from 210 to 230 ℃ in 5 ℃ intervals under injection pressures of 55, 50, 45, and 40 MPa, respectively.

The standard samples were annealed under various conditions. After the annealing process, the samples were cooled to 23 ℃ for a minimum of 24 h before testing. The annealing process is displayed in Table 2.

2.3 Mechanical properties test

The standard tensile test was conducted using a universal tensile testing machine (CMT4204, MTS) at ambient temperature (23 ℃) in accordance with the ASTM D638-03. A tensile speed of 50 mm/min was used during the test. The average values of the five samples were obtained. The notched Izod impact strength of the specimens was measured using an Izod machine (ZBC1400-B, MTS) according to the ASTM D256-04. In the low-temperature impact tests, the specimens were first stored in a thermostat at ambient temperature (23 ℃) or low temperatures (−30, −20, −10, and 0 ℃) for 6 hours. Next, the samples were removed from the thermostat and immediately subjected to the impact test. The average values of the 5 samples in each group were then obtained.

2.4 Crystallization behaviors

The 6-7 mg samples of the PP-R composites were removed from the aluminum crucible after the annealing process. The melting curves of the PP-R composites were obtained through DSC (Q10, TA Co.) testing. During the tests, the temperature increased from 40 to 250 ℃ at a heating rate of 10 ℃/min. The crystallization curve of each PP-R composite at temperatures of up to 140 ℃ was tested at the same cooling rate. The crystallinity ($X_{C\text{-}DSC}$) of each PP-R composite was calculated according to the following equation[20]:

$$X_{C\text{-}DSC}(\%) = \frac{\Delta H_m}{\Delta H_m^0 (1-\varphi)} \times 100\% \qquad (1)$$

where, ΔH_m represents the melting enthalpies of the samples, ΔH_m^0 represents the thermal enthalpy when 100% crystallinity is achieved (177 J/g[21]), and φ represents the mass fraction of the modifiers in the PP-R composites.

2.5 Crystalline structure

The crystalline structures of the samples were characterized using Cu-K alpha target X-ray diffraction (XRD) (PW 3040/60, Holland PANalytical Company) with an X-ray wavelength of 0.154 nm, voltage of

40 kV, and current of 40 mA. The total crystallinity ($X_{C\text{-WAXD}}$) of the samples was calculated with the following equation[22]:

$$X_{C\text{-WAXD}}(\%) = \frac{\sum A_{cryst}}{\sum A_{cryst} + A_{amorp}} \times 100\% \qquad (2)$$

where, A_{cryst} represents the integral intensity of the crystalline structure and A_{amorp} represents the number of amorphous regions.

The crystallinity of the β-form crystals (X_β) was calculated using formula (3) as[21]:

$$X_\beta(\%) = K_\beta \times X_{C\text{-WAXD}} \qquad (3)$$

where, K_β represents the relative amount of β-form crystals. In addition, the value of K_β was calculated using formula (4) as[23]:

$$K_\beta = \frac{I_{\beta(300)}}{I_{\beta(300)} + I_{\alpha(110)} + I_{\alpha(040)} + I_{\alpha(130)}} \times 100\% \qquad (4)$$

where, $I_{\alpha(110)}$, $I_{\alpha(040)}$, and $I_{\alpha(130)}$ represent the integral intensities of the (110), (040), and (130) characteristic diffraction peaks of the α-form crystal at 2θ corresponding to 14.1°, 16.8°, and 18.68°, respectively. In addition, $I_{\beta(300)}$ represents the intensity of the (300) diffraction peak of the β-form crystal at $2\theta = 16.0°$.

2.6 Dynamic mechanical analysis (DMA)

The PP-R composite materials were subjected to DMA testing using a dynamic mechanical analyzer (Q800, TA Co.) with an oscillatory frequency of 1Hz and amplitude of 3 μm. Using a double-cantilever mode and nitrogen atmosphere, the DMA tests were conducted from −110 to 120 ℃ at a heating rate of 5 ℃/min.

2.7 Scanning electron microscopy (SEM)

The impact-fractured surfaces of the annealed PP-R composites, which fractured at 23 ℃ and −10 ℃, were analyzed using an SEM instrument (Quanta FEG250, FEI) with an acceleration voltage of 20 kV. All of the impact-fractured surfaces were sputter-coated before observation under SEM.

3　Results and discussion

3.1 Mechanical properties

On the basis of the research goal of this study, the effect of annealing process on the notch Izod impact strengths of PP-R composites material was investigated. As shown in Fig.1(a), as the annealing temperature increased from 80℃ to 120 ℃, the impact

toughness of the samples at −30-23 ℃ also increased. When the annealing temperature increased to 140 ℃, the impact strength of the PP-R composites decreased significantly. After the annealing process at 120 ℃, the impact strength at −30 ℃ to 23 ℃ among these samples was 74.73 kJ/m² (23 ℃), 54.4 kJ/m²(0 ℃), 37.56 kJ/m² (−10 ℃), 25 kJ/m² (−20 ℃), and 14.2 kJ/m²(−30 ℃), respectively. Moreover, the impact strength of the samples was one to two times better than that of the impact strength of the samples annealed at 80 ℃. Therefore, the PP-R composites annealed at 120 ℃ for 6 h exhibited the preferable low-temperature impact toughness compared with the samples under other conditions. For example, it's been reported previously that under different modifier and heat treatment conditions[4,6,11,21], the impact strength of the PP-R/TPR2095 composites ranged from approximately 5 kJ/m² to 53 kJ/m² at −30-23 ℃ [21] and 41.5 kJ/m² in the sample of PP-R/EPDM annealed at 120℃, at 23 ℃[11]. This may have been attributed to annealing, which improved the crystalline structure and may have induced large amounts of α-form to β-form crystal transformation. Therefore, this significantly increased the impact strength of the composites.

Fig.1(b) displays the impact strength of the PP-R composites after the annealing process at 120 ℃ for different time. As shown in the figure, the change of the impact strength of PP-R composites is not very significant with the increase of annealing time. The impact strength of PPR composites is the same as that of Fig.1(a) with annealing temperature of 120 ℃ when the annealing time is 6 h. Therefore, the annealing time of approximately 6 h should be used when the annealing temperature remains constant at 120 ℃. However, the impact strength of PP-R composites prepared in this paper was significantly higher than that of other PP-R Composites with the increase of annealing time. such as PP-R/TPR2095, PP-R/TPR2096[21]. This may be because the synergistic effect of annealing and TPR2088A increases the shear deformation of PP-R composites in the tensile fracture process, which increases the fracture resistance[11].

Fig.2(a) displays the tensile strength of the PP-R composites after the annealing process at different annealing temperatures. As shown in the figure, the tensile strength of the PP-R composites increased as the annealing temperature increased. When an annealing temperature of 120 ℃ was used, the tensile strength of the samples was approximately 32.35 MPa, 2.21 MPa greater than that of the samples annealed at 80
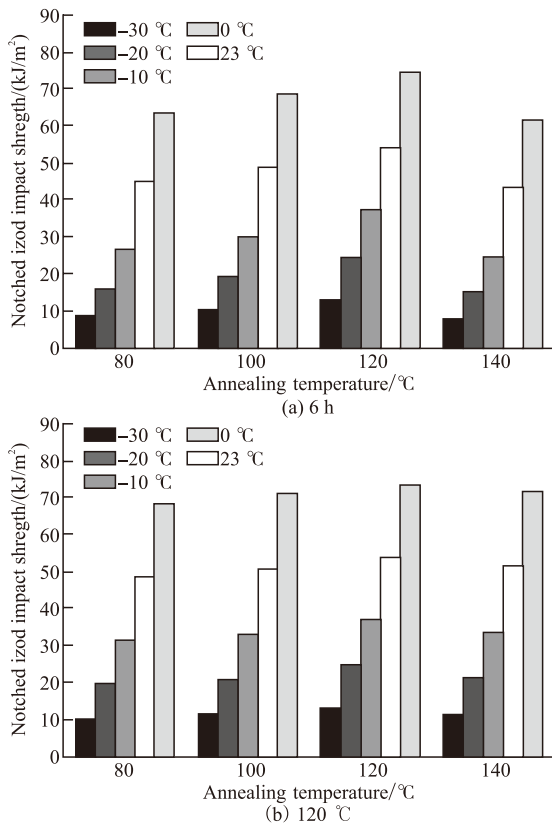
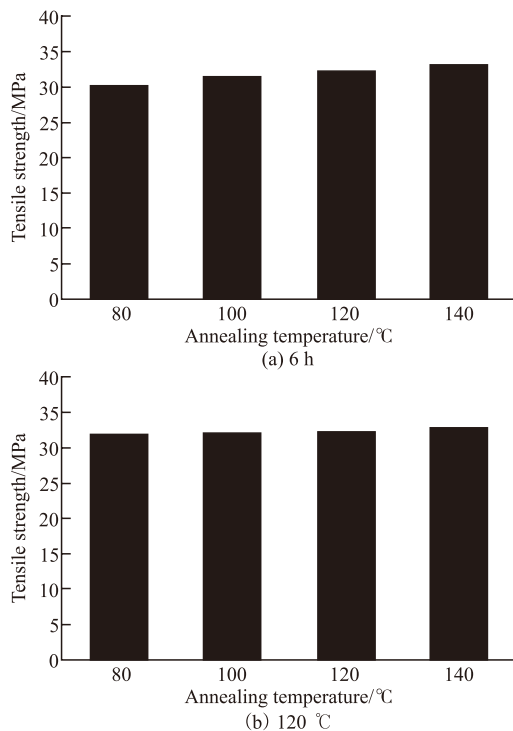Fig.1 Effects of the annealing process on the impact strength of the PP-R composites

Fig.2 Effects of the annealing process on the tensile strength of the PP-R composites

℃(30.14 MPa). When an annealing temperature of 140℃ was applied, the tensile strength of the samples was 33.21 MPa, 10.2% greater than that the samples that annealed at 80 ℃ (30.14 MPa). This may be due to

that annealing temperature changed the microstructure of the composite and reduced the residual stress in the matrix, thus improving the tensile strength of the composite. Fig.2(b) displays the impact strength of the PP-R composites after different annealing times at 120 ℃. As shown in the figure, as the annealing time increased from 1 to 9 h, the tensile strength of the PP-R composites increased from 31.83 to 32.56 MPa with an insignificant amount of variation.

Figs.1 and 2 indicate that the annealing temperature plays an important role in the strengthening and toughening of PP-R composites. In contrast, the effects of the annealing time are not significant. The optimum comprehensive mechanical properties were obtained when the PP-R composites were subjected to annealing at 120 ℃ for 6 h. Accordingly, the effects of the annealing temperature on the crystallization of the PP-R composites are further discussed in the following passages.

3.2 Crystallization behaviors

Table 3   Crystallization and melting values of the PP-R composites annealed at different temperatures

Annealing condition	$T_c/℃$	$T_f/℃$	$T_m/℃$	$\Delta H_m/(J·g^{-1})$	$X_{C\text{-DSC}}$
80 ℃, 6 h	102.07	4.09	139.89	57.72	32.6%
100 ℃, 6 h	103.11	3.93	140.55	53.63	30.3%
120 ℃, 6 h	103.57	4.24	141.23	54.40	30.7%
140 ℃, 6 h	102.64	4.03	149.26	50.20	28.4%

(Note: T_c, crystallization temperature; T_f, half peak width; T_m, melting temperature; ΔH_m, melting enthalpy; $X_{C\text{-DSC}}$, crystallinity)

Figs.3(a) and 3(b) display the crystallization and melting behaviors of the PP-R composites at different annealing temperatures, respectively. According to Fig.3(a) and Table 3, as the annealing temperature increased from 80 to 120 ℃, the value of T_c increased from 102.07 to 103.57 ℃. However, the value of T_c decreased as the annealing temperature increased to 140 ℃. On the one hand, this was likely because of the increase in the amount of heterogeneous nucleation in the TPR elastomer, which promoted the crystallization at high temperatures. On the other hand, it was likely owing to the significant increase in the crystalline plate thickness[23]. As shown in Fig.3(b) and Table 3, the PP-R materials exhibited a single melting peak, indicating that the increase in the annealing temperature decreased the formation ability of *β*-form crystals in the PP-R composites. In addition, the melting peak width of the PP-R materials significantly decreased after the annealing process at 140 ℃, indicating that the

crystalline plate thickness distribution of the samples decreased. This caused the initially tiny crystalline plate to grow thicker, completing the crystalline structure[24,25]. The X_{C-DSC} of the PP-R composites decreased from 32.6% to 30.7% as the annealing temperature increased from 80 to 140 ℃. This was due to the accelerated thermal degradation of the molecular chains, which weakened the intermolecular forces, inhibited the crystallization process, and decreased the X_{C-DSC} of the PP-R composites, hence greatly boosting the impact strength.[26]
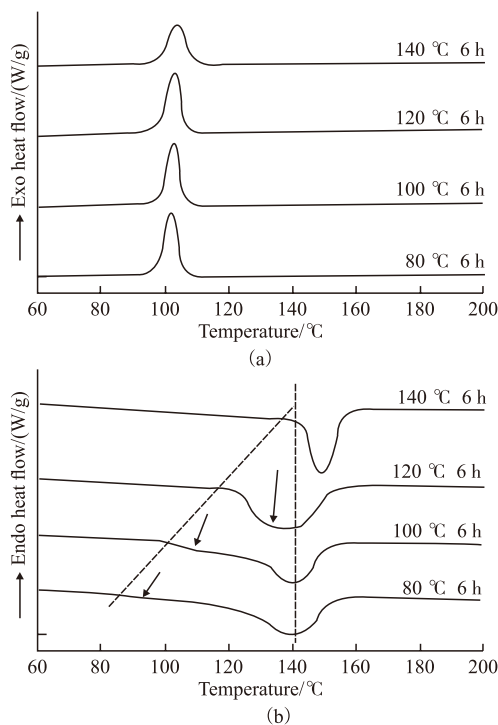

Fig.3 Effects of the annealing process on the (a) crystallization behaviors and (b) melting behaviors of the PP-R composites
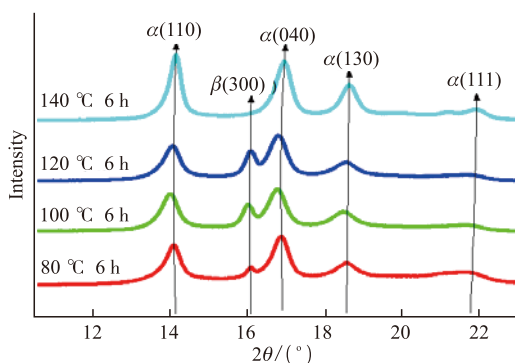

Fig.4 XRD diffraction curves of the PP-R composites at different annealing temperatures

XRD analysis was used to further study the influence of the annealing temperature on the crystallization behaviors of the PP-R composites. The results of this analysis are shown in Fig.4.

The crystalline structure of PP-R composites annealed at different temperatures was also investigated by WAXD as shown in Fig.4. As the annealing temperature increased from 80 ℃ to 120 ℃, the PP-R composites exhibited obvious diffraction peaks when 2θ was equal to 14.1°, 16.8°, 18.6°, and 21.7°, corresponding to the $\alpha(110)$, $\alpha(040)$, $\alpha(130)$, and $\alpha(111)$ crystal plane diffraction peaks, respectively. However, a $\beta(300)$ crystal diffraction peak was also observed at 2θ=16.1°, indicating that the annealing process induced α-form to β-form crystal transformation in the PP-R composites. However, the $\beta(300)$ crystal diffraction peak was not observed when the temperature increased to 140 ℃. The X_{C-XRD} of the PP-R composites gradually decreased as the annealing temperature decreased, as shown in Table 4. These results were consistent with the DSC analysis. In addition, the samples annealed at 120 ℃ yielded the maximum value of K_β (13.9%). This increase in the β crystal content further improved the energy distribution and low-temperature toughness of the PP-R materials[27]. These results also indicated that high annealing temperatures can hinder the improvements in the crystalline structures of materials.

Table 4　XRD test values of the PP-R composites at different annealing temperatures

Annealing condition	XC-XRD/%	X_α /%	X_β/%	K_β/%
80 ℃, 6 h	83.1	81.9	1.2	1.5
100 ℃, 6 h	57.8	50.8	7.0	12.2
120 ℃, 6 h	55.6	47.9	7.7	13.9
140 ℃, 6 h	58	58	0	0

(Note: $X_{C-XRD,}$ XRD test crystallinity; X_α, α crystal crystallinity; X_β, β crystal crystallinity; K_β, the relative content of β crystal)

3.3 Dynamic mechanical properties analysis

In order to further study the effects of the annealing process on the toughness of PP-R composites at low temperatures, a dynamic mechanical analysis (DMA) was conducted. The results are shown in Fig.5 and Table 5.

Fig.5 displays the loss factor (tanδ) curve of the PP-R composites at different annealing temperatures. The tanδ curve of the PP-R composites exhibited three relaxation peaks as the annealing temperature increased from 80 ℃ to 140 ℃. The first peak, which corresponded to the relaxation of α_c at 80 ℃, was associated with the limitation of the rigid, amorphous molecular chains in the PP-R composites. The second peak at 7 ℃, defined as the β relaxation peak, was primarily related to the transition of the molecular glass chains in the PP-R composites, which influenced the

Table 5 Relaxation parameters of the PP-R composites at different annealing temperatures

Annealing condition	T_g /℃	tan δ_{max}	T_e /℃	I_β	I_α	I
80 ℃, 6 h	7.62	0.146	−90.39	7.66	0.94	8.6
100 ℃, 6 h	7.38	0.156	−80.41	7.69	1.17	8.86
120 ℃, 6 h	4.57	0.170	−72.71	7.95	1.10	9.05
140 ℃, 6 h	6.27	0.149	−79.76	7.74	0.95	8.69

(Note: T_e, α relaxation temperature; I_β, integral area of the β relaxation peak ; I_α, integral area of the α relaxation peak)

mobility of the molecular chains. This peak, defined as the glass transition temperature (T_g), is the temperature at which the β relaxation peak of a material occurs[27]. The third mechanical loss peak (tanδ_0), which occurred at low temperatures of −100-−70 ℃(T_e), was associated with the α relaxation area of the PP-R composites. This peak could be used to explain the mobility of the elastomer molecule chains. Moreover, the maximum value of T_e(−72.71 ℃) was obtained at an annealing temperature of 120 ℃. The values of tanδ_0 were ranked as tan$\delta_{120℃}$＞tan$\delta_{100\ ℃}$＞tan$\delta_{140\ ℃}$＞tan$\delta_{80\ ℃}$, indicating that viscoelastic relaxation in the PP-R composites annealed at 120 ℃ increased the amount of energy dissipation, improving the impact toughness of the material[28]. In addition, according to the results shown in Fig.5 and Table 5, the value of T_g increased as the annealing temperature increased. More specifically, the value of T_g was 4.57 and 7.62 ℃ when annealing temperatures of 120 and 80 ℃were used.
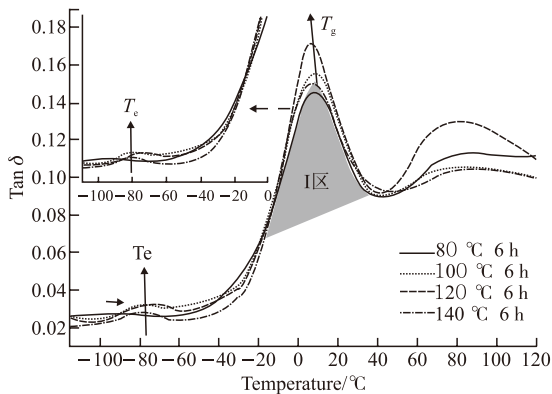

Fig.5 Loss factor (tanδ) curves of the PP-R composites under different annealing temperatures

These results indicated that the annealing process can improve the low temperature mobility of amorphous area molecular chains and plays a vital role in the low-temperature toughness of PP-R composites.

In a previous study, Grein C *et al*[29] investigated the relationship between the integral area of relaxation peaks and the impact strength of materials. According to the results, the impact strength of a material increases as the integral area of its relaxation peaks increases. Therefore, in this study, Origin software was used to

obtain the integral area of the relaxation peaks via Gaussian fitting. The results are shown in Table 5. As shown in this table, the integral area of the relaxation peaks increased as the annealing temperature increased. In addition, the maximum impact strength was obtained when the annealing process was conducted at 120 ℃. Therefore, the optimum impact properties were obtained when the PP-R composites were annealed at 120 ℃. These results were consistent with the low-temperature properties of the PP-R composites shown in Fig.1.

3.4 Microstructure morphological

Fig.6 displays the microstructures of the annealed PP-R composites at 23 ℃. As shown in the figure,
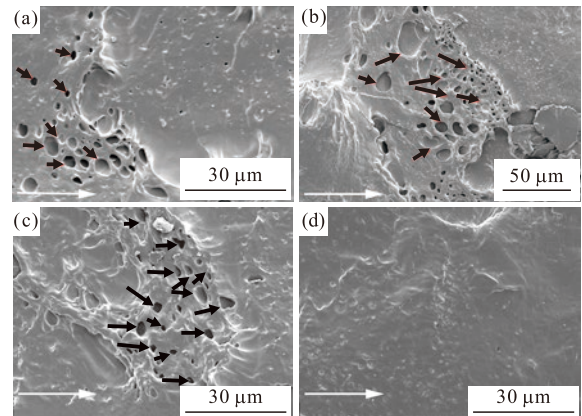

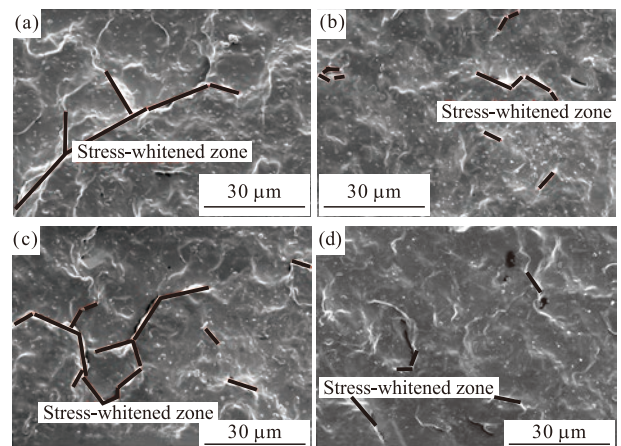Fig.6 Impact-fractured surfaces of the annealed PP-R composites at 23 ℃

Fig.7 Impact-fractured surfaces of the annealed PP-R composites at −10 ℃

Table 6 Stress whitening zone of the annealed PP-R composites

Annealing condition	80 ℃, 6 h	100 ℃, 6 h	120 ℃, 6 h	140 ℃, 6 h
Stress-whitened length/μm	100.346	63.828	146.953	53.491

the white arrows represent the direction of crack propagation. The materials were rugged and rough after the annealing process, with stress-induced areas of whitening, yielding characteristics, and features typical of ductile fracture. Moreover, the impacted portion of the PP-R composites exhibited a large number of micro-holes representative of quasi-cleavage fractures. These micro-holes, indicated by the arrows in Figs.6(a-c), dissipated the impact energy generated by the impaction of the PP-R composites, significantly improving the impact strength.

Fig.7 displays the microstructure features of the annealed PP-R composites at −10 ℃. The white arrows in the figure represent the direction of crack propagation. As the annealing temperature increased from 80 to 120 ℃, the PP-R composites exhibited significant stress-induced areas of whitening, as shown by the line in Figs.7(a-c), and rough fractured surfaces at low temperatures. In a previous study, Chen GL *et al*[30] found that the length of stress whitening areas and impact toughness of polymers are directly correlated. Therefore, long stress whitening areas are associated with high impact toughness. The stress whitening areas of the annealed PP-R composites studied herein were analyzed using Image-Pro Plus software, as shown in Table 6. As shown in this table, the stress whitening areas of the PP-R composites were approximately 100.346 μm and 146.953 μm in length when the annealing process was conducted at 80 ℃ and 120 ℃, respectively. However, the length of the stress whitening area was significantly smaller at 53.491 μm when the annealing process was conducted at 140 ℃, indicating that the optimum impact toughness at −10 ℃ was obtained when the annealing process was conducted at 120 ℃. These results were consistent with the data presented in Fig.1.

As shown in Figs.6 and 7, the PP-R composites annealed at 120 ℃ for 6h exhibited the optimum impact toughness at normal and low temperatures. In addition, through the study of this paper, it is proved that the appropriate annealing process could induce brittle-to-ductile fracture transformation and improve the low-temperature toughness of PP-R materials.

4 Conclusions

According to the results of this study, the low-temperature toughness and crystallization behaviors of PP-R composite materials are strongly dependent on the annealing process. In this study, the comprehensive performance of the PP-R composites improved as the annealing temperature increased. In contrast, the annealing time did not significantly affect the performance of the PP-R composites. The PP-R composites annealed at 120 ℃ for 6 h exhibited the optimum comprehensive mechanical properties. At temperatures below 23 ℃, the impact strength of the samples annealed at 120 ℃ for 6 hours increased to 74.73 kJ/m², 16.8% higher than that of the samples annealed at 80 ℃ for 6h. In addition, at low temperatures of −30-10 ℃, the impact strength of the PP-R composites ranged from 6.85 kJ/m² to 37.56 kJ/m², which is attributed to the microstructure changes of PP-R composites during the annealing process. On the one hand, the annealing process improved the crystalline structure, refined the grains, reduced the crystallinity, and increased the low-temperature toughness of the PP-R composites. On the other hand, annealing at moderate temperatures induced α-form to β-form crystal transformation. For shortness' sake, our work proves a feasible way to ameliorate the low temperature(−30 ℃-0 ℃) toughness of PP-R composites by improving the integrity of the crystal structure and the relative content of β-phase.

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