

ENHANCING CHAIN SEGMENTS MOBILITY TO IMPROVE THE FRACTURE TOUGHNESS OF POLYPROPYLENE*

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Abstract As a part of a serial work about the annealing inducing improvement of fracture toughness of polypropylene (PP) articles, in this work, a highly efficient mobilizer was introduced into PP and the injection-molded samples were annealed at different temperatures. The mobility of chain segments of PP was investigated by measuring the glass transition temperature. Differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD) were used to characterize the variation of crystalline structure of PP during the annealing process. The fracture behaviors including notched Izod impact fracture and universal tensile fracture were investigated to detect the mechanical properties in response to the variations of both chain segments mobility and crystalline structures. It was found that the mobilizer greatly improved the chain segments mobility. Further results showed that the mobilizer also induced apparent changes of the glass transition temperature and the degree of crystallinity of PP during the annealing process. Consequently, the annealed PP samples containing a few amount of mobilizer exhibited largely increased fracture toughness.

Keywords: Chain segments mobility; Fracture toughness; Mobilizer; Annealing.

INTRODUCTION

The toughening modification of polypropylene (PP) has been studied for a long time and different modification methods have been developed. The well-known modification methods are the introduction of elastomer, rigid particles and/or core-shell particles through the common melt compounding process. In these blends, the second component induces more severe crazing and/or shear-yielding of PP under the stress load, leading to more energy absorption. The other method is related to the so-called alloy in reactor, namely, during the polymerization process of PP, one or more comonomers are introduced, and the new material consists of PP, some elastomer part and homopolymer of comonomer. Impact polypropylene copolymer (IPC) is one of the representatives^[1–3] which exhibit much more excellent fracture toughness compared with the common isotactic PP. Furthermore, from a point of view of crystalline structure, formation of large amounts of β -phase PP has been proved to be another efficient way to improve the fracture toughness of PP^[4, 5]. In addition, it has been proved that mechanical pre-condition is also favorable to the improvement of the fracture toughness of PP^[6].

It is widely accepted that during the failure of PP samples, the occurring of shear yielding or plastic deformation of PP is more efficient for the consumption of energy compared with the occurring of multiple

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craze. The degree of shear yielding is related to the mobility of polymer chain segments. The higher the mobility of polymer chain segments, the easier the orientation of polymer chain segments along the stress direction is, and therefore, the more apparent the degree of shear yielding or plastic deformation of polymer is. This means that enhancing the mobility of polymer chain segments is favorable for the improvement of fracture toughness. Recently, it has been proved that after being annealed at a certain temperature, the mobility of chain segments of PP can be enhanced^[7–10]. The decrease of glass transition temperature (T_g) is a undoubted evidence for the enhancement of chain segments mobility. This is suggested to be the main reason for the largely improved fracture toughness of annealed PP materials.

Another way to enhance the mobility of polymer chain segments is the introduction of a mobilizer during the sample preparation process. With the presence of the mobilizer, the entanglement density of polymer matrix is decreased and the free-volume is increased. Specifically, mobilizer also acts as a lubricant to promote the motion of chain segments of polymer matrix. Consequently, plastic deformation of polymer matrix under the stress load is easily provoked and the material exhibits enhanced fracture toughness. Therefore, the mobilizer is also thought to be one of the toughening agents for brittle polymer such as poly(L-lactide)^[11]. In addition, the morphology and mechanical properties of semi-crystalline polymers can be adjusted through changing the melt temperature applied for the sample preparation because the melt temperature also influences the mobility of chain segments before crystallization^[12, 13].

In this work, we attempted to introduce a mobilizer into PP sample and investigate the effect of annealing on the fracture toughness of plasticized PP. It is expected that the presence of the mobilizer enhances the mobility of chain segments of PP during the annealing process, promoting the occurring of the second crystallization and the variation of molecular conformation in amorphous region, and finally facilitating the further improvement of fracture toughness of annealed PP samples. We believe that this work is favorable for the understanding of toughening mechanism of PP sample after being annealed.

EXPERIMENTAL

Materials

PP (T30S) with a melt flow rate (MFR) of 2.6 g/10min (230°C/2.16 kg) and a density of 0.91 g/cm³ was obtained from Lanzhou Petrochemical Co. Ltd., China. Mobilizer bis(2-ethylhexyl) adipate (DOA) was supplied by TCI Shanghai Huacheng Manufacture Co. Ltd., China.

Sample Preparation

PP/DOA material containing only 5 wt% DOA was prepared by using a twin-screw extruder (SHJ-20, China) at a screw speed of 200 r/min and the temperatures of 150–165–180–190–190–185°C from hopper to die. After making droplets, the pellets were dried in an oven at 50°C for 10 h, and then were injection-molded, and the standard specimens were prepared using an injection-molding machine (PS40E5ASE, Japan) with the melt temperatures of 180–190–195–190°C from hopper to nozzle and mould temperature of 25°C. For comparison, pure PP injection-molded specimens were prepared through the same processing methods as the PP/DOA blend. Some specimens were annealed for 3 h in a fan-assisted oven at different temperatures (T_a = 120°C, 130°C, 140°C). After being annealed, the specimens were cooled in the ambient air and then conditioned at 23°C and 50% relative humidity for 48 h before testing. The sample notations for pure PP and plasticized PP samples were defined as PP- x and PP/DOA- x , respectively, where x indicated the annealing temperature.

Dynamic Mechanical Analysis (DMA)

The effect of DOA on the chain segments of PP during the annealing process was investigated by dynamic mechanical analysis (DMA) measurements, which were carried out by using a DMA Q800 analyzer (USA). The single cantilever mode was selected, and the measurement was carried out on a rectangular cross-sectional bar (length of 35 mm, width of 10 mm and thickness of 4 mm) from –60°C to 150°C at a heating rate of 3 K/min and a frequency of 1 Hz. Three samples were tested repeatedly for each composition, and the representative curve was reported.

Differential Scanning Calorimetry (DSC)

The crystallization and melting behaviors of the samples were investigated by differential scanning calorimetry (Netzsch STA 449C Jupiter, Germany) in nitrogen atmosphere. For the unannealed specimens, sample of about 8 mg was heated from 30°C to 200°C at a heating rate of 10 K/min, and maintained at 200°C for 5 min to eliminate any thermal history, then the sample was cooled down to 30°C at a cooling rate of 5 K/min. For the annealed specimens, the sample was heated directly from 30°C to 200°C at a heating rate of 10 K/min. The degree of crystallinity (X_c) of PP was calculated according to the following relationship:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 \times \phi} \times 100\% \quad (1)$$

where ΔH_m is the DSC measured value of fusion enthalpy of sample obtained during the heating process, ΔH_m^0 is the fusion enthalpy of the completely crystalline polymer, and ϕ is the weight fraction of PP in the sample. Here, the ΔH_m^0 of PP was selected as 177 J/g^[14].

Wide Angle X-ray Diffraction (WAXD)

The crystalline structures of PP were investigated by wide angle X-ray diffraction (WAXD, Panalytical X'pert PRO diffractometer with Ni-filtered Cu K α radiation at 40 kV and 40 mA). The angular range was from 5° to 35°.

Mechanical Measurements

Notched Izod impact strength was measured at room temperature (23°C) using an impact tester (XC-22Z, China) according to ASTM D 256-04. The universal tensile measurements were conducted on a universal testing machine (AGS-J, SHIMADZU, China) according to ISO 180/1A at the tensile speed of 50 mm/min. At least five specimens were tested repeatedly, and the average value was reported.

Scanning Electron Microscopy (SEM)

The impact-fractured surface morphologies of specimens were characterized by using a Fei Quanta 200 environmental scanning electron microscope (ESEM, USA) with an accelerating voltage of 20 kV. All the samples were sputter-coated with a gold layer prior to SEM characterizations.

RESULTS AND DISCUSSION

Variation of Chain Segments Mobility of PP

The chain segments mobility of PP was studied by investigating the relaxation behaviors of samples. The mechanical loss factor ($\tan\delta$) of pure PP and PP/DOA samples before and after being annealed at different temperatures are shown in Fig. 1, and the corresponding data related to the relaxation behaviors are shown in Table 1. As shown in Fig. 1, the $\tan\delta$ curves exhibit two maxima. The maximum at low temperatures (14–20°C or 1–4°C) is related to β -relaxation, accounted for the glass transition of the unrestricted amorphous PP, while the peak at the higher temperatures (60–120°C) is related to α_c -relaxation, accounted for the relaxation of restricted PP amorphous chain segments in the crystalline phase (defects), also known as rigid fraction^[15, 16]. Herein, T_g s were obtained by the maximum of the loss factor ($\tan\delta_{\max}$) or β -relaxation peak. For samples which were not annealed, the T_g of pure PP and PP/DOA are 19.5°C and 3.7°C, respectively. Interestingly, both pure PP and PP/DOA samples exhibit similar α_c -relaxation behaviors. The decrease of T_g in PP/DOA sample proves the plasticizing effect of DOA which leads to the enhancement of chain segments mobility. However, the different responses observed for β -relaxation and α_c -relaxation mean that the plasticizing effect of DOA is only efficient in the amorphous region rather than in the crystalline region of PP. After being annealed for a certain time, the T_g of both pure PP and PP/DOA samples decreases slightly. Increasing annealing temperature leads to the further decrease of T_g . The similar variation trends have been reported elsewhere^[8–10]. This further proves that annealing treatment facilitates the enhancement of chain segments mobility of PP. Furthermore, it should be noticed that pure PP and PP/DOA samples exhibit the different degrees of the reduction of T_g . For example,

when the annealing temperature was increased to 140°C, the T_g of pure PP is decreased from 19.5°C to 14.6°C, about 25.1% reduction compared with unannealed sample. However, for PP/DOA sample, the T_g is decreased from 3.7°C to 1.5°C, about 59.5% reduction compared with unannealed one. This means that the presence of mobilizer facilitates the enhancement of chain segments mobility of PP during the annealing treatment.

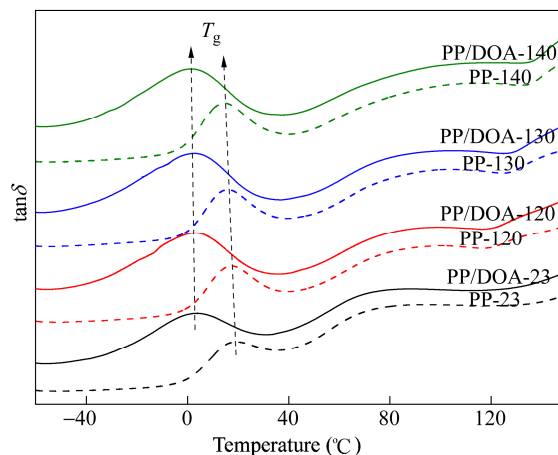


Fig. 1 Mechanical loss factor ($\tan\delta$) of PP and PP/DOA samples obtained before and after being annealed at different annealing temperatures as indicated in the graph

Table 1. β -relaxation parameters obtained from DMA measurements for unannealed and annealed PP and PP/DOA samples

Sample	T_g (°C)	$\tan\delta_{\max}$	I_R	Sample	T_g (°C)	$\tan\delta_{\max}$	I_R
PP-23	19.5	0.068	0.47	PP/DOA-23	3.7	0.074	1.05
PP-120	17.3	0.075	0.75	PP/DOA-120	2.9	0.082	1.79
PP-130	15.9	0.076	0.81	PP/DOA-130	2.7	0.085	2.03
PP-140	14.60	0.076	0.90	PP/DOA-140	1.5	0.082	1.99

The intensity of $\tan\delta_{\max}$ and the magnitude of β -relaxation (I_R) which is determined by the area under the relaxation peak were also detected and the results are shown in Table 1. It can be seen that annealing treatment promotes the increase of magnitude of β -relaxation. Generally, the magnitude of β -relaxation is representative of the total energy dissipated because of viscoelastic relaxation of PP. Finally, it can be seen that the α_c -relaxation in both pure PP and PP/DOA samples shifts to higher temperatures after being annealed. The higher the annealing temperature, the higher the temperature for the α_c -relaxation is. This indicates the perfection of crystalline structure of sample during the annealing is possibly induced by newly formed thin lamellae and/or the transition of mesophase to stable phase occurring near the surface of primarily formed lamellae, leading to the increase of rigid fraction^[17].

Crystalline Structure Changes during the Annealing Process

To better understand the effect of DOA on crystallization behavior of PP, the melting and crystallization behaviors of pure PP and PP/DOA samples without any thermal treatment were first investigated, and the results are shown in Fig. 2. For pure PP sample, the melting point (T_m) is 167.2°C. With the presence of DOA, the T_m of PP is decreased to 165.8°C. This means that DOA prevents the thickening of lamellae during the melt crystallization process. From Fig. 2(b) one can see that, although there is very small difference between the crystallization temperatures of pure PP and PP/DOA samples, DOA leads to the slightly decrease of the start crystallization temperature, indicating that DOA prevents the nucleation of PP. However, PP/DOA sample exhibits sharper exothermic peak compared with pure PP. This means that the growth rate of spherulites of PP in PP/DOA sample is larger than that of pure PP because of the enhanced chain segments mobility.

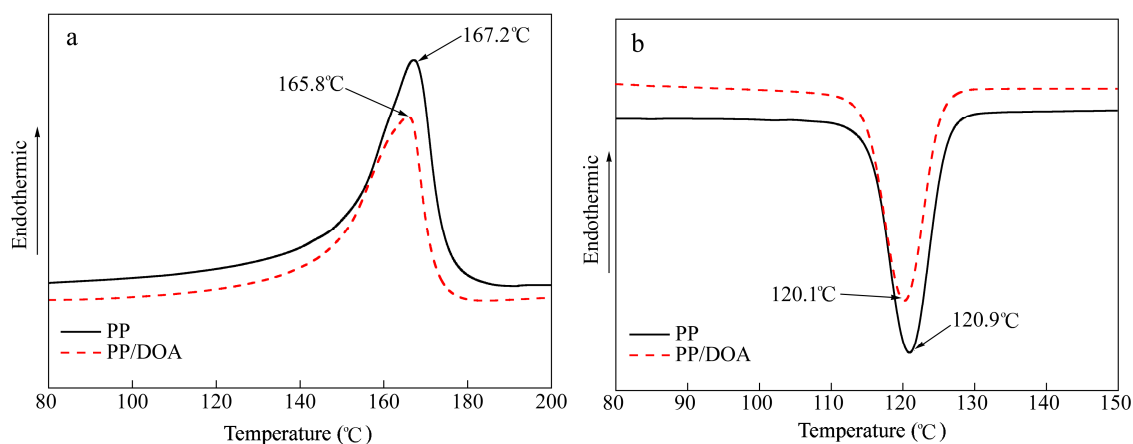


Fig. 2 DSC heating curves (a) and cooling curves (b) showing the melting and crystallization behaviors of PP and PP/DOA samples, respectively

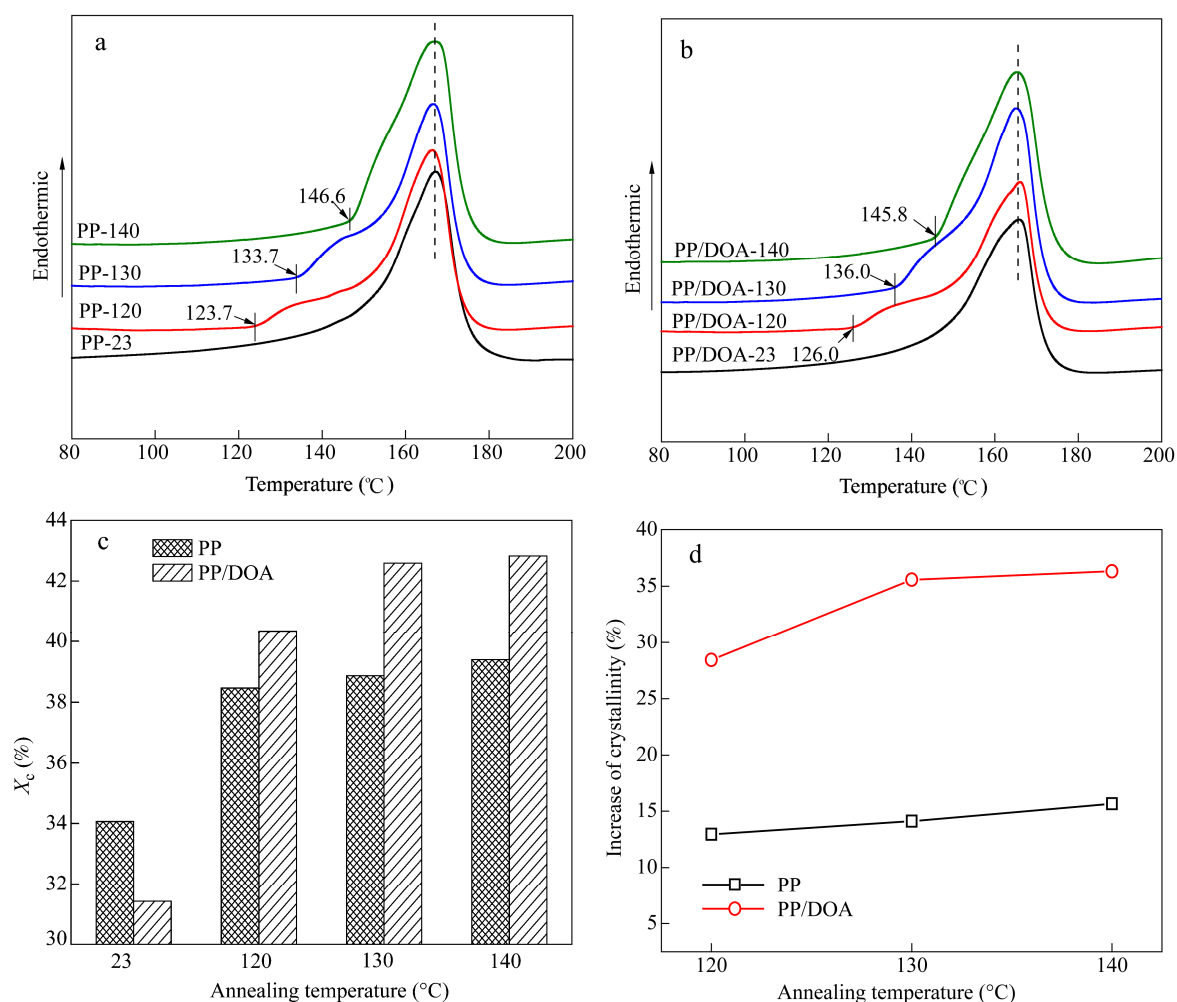


Fig. 3 DSC heating curves of (a) PP and (b) PP/DOA samples after being annealed at different temperatures; (c) The comparison of the X_c values of different samples; (d) The increase of X_c of different samples with annealing temperature

Figure 3 exhibits the DSC heating curves of annealed samples and the corresponding thermal properties. After being annealed, both PP and PP/DOA samples exhibit a shoulder on the left side of the endothermic peak, indicating the fusion of thin lamellae formed during the annealing process. Furthermore, it should be noticed that there is a small difference between the melting behaviors of pure PP and PP/DOA samples, namely, the start fusion temperature (T_{onset} , as shown by arrows) of PP/DOA samples is slightly higher than that of pure PP. For example, when the samples were annealed at 120°C, pure PP exhibits the T_{onset} of about 123.7°C, lower than the 126.0°C of PP/DOA. This means that mobilizer DOA facilitates the formation of new lamellae with relatively larger thickness during the annealing process most likely due to the enhanced mobility of chain segments. However, at annealing temperature of 140°C, both PP and PP/DOA exhibit the similar values of T_{onset} . Because the annealing temperature is very close to the T_m of PP, the two samples have similar mobility of chain segments, and in this case, the effect of mobilizer is weakened. The variation of X_c of pure PP and PP/DOA samples during the annealing process was calculated, and the results are shown in Fig. 3(c). For unannealed sample, PP/DOA sample exhibits lower X_c compared with pure PP. As expected, annealing induces the increase of X_c in both PP and PP/DOA samples due to the occurring of the second crystallization. Specifically, with the presence of DOA which leads to the largely enhanced chain segments mobility, annealed PP/DOA samples exhibit higher X_c compared with PP samples at all annealing temperatures. The increase of crystallinity shown in Fig. 3(d) also shows that PP/DOA sample exhibits much more apparent change of X_c .

The crystalline structures of pure PP and PP/DOA samples were further investigated by using WAXD, and the results are shown in Fig. 4. It can be seen that all samples exhibit the typical characteristic diffraction peaks of α -form PP. Although the presence of DOA and annealing treatment can not change the crystalline structure of PP, it can be seen that DOA still induces small change of the WAXD profiles. For pure PP, the intensity of diffraction of (040) crystal plane is stronger than that of (110) crystal plane, indicating the selectively growth of crystal during the crystallization process. Annealing does not change the selectively growth trend in pure PP. However, for PP/DOA sample, (110) and (040) crystal planes exhibit the similar intensity of diffraction. This indicates that the enhanced mobility of chain segments of PP is favorable for the homogeneous growth of crystal.

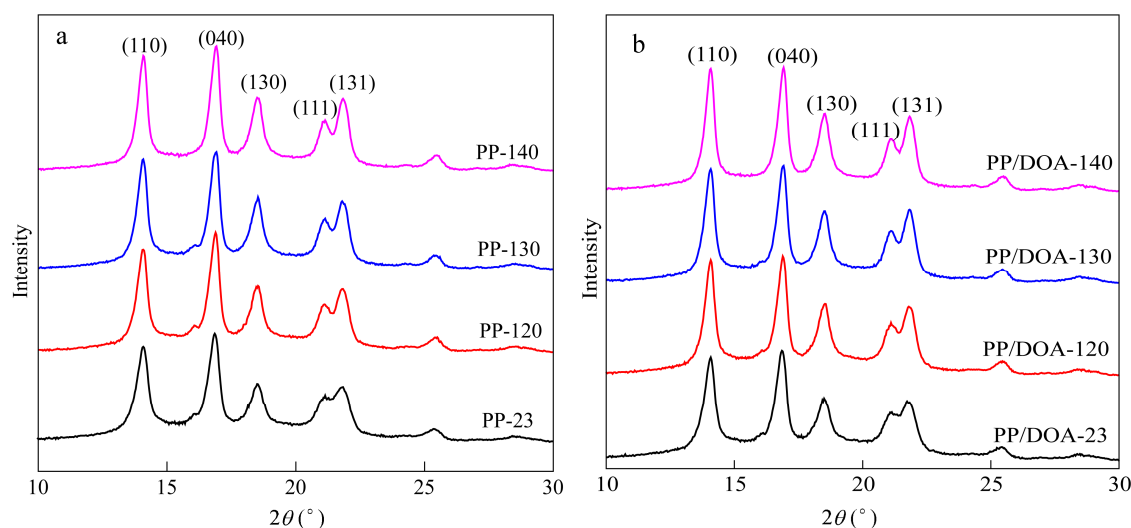


Fig. 4 WAXD profiles of (a) PP and (b) PP/DOA before and after being annealed at different temperatures

Fracture Behavior of Plasticized PP

Figure 5 shows the variation of notched Izod impact strength of pure PP and PP/DOA samples. Due to the plasticizing effect of DOA which induces the enhancement of chain segments mobility of PP, PP/DOA-23 sample exhibits larger impact strength compared with PP-23 sample. After being annealed, both PP and PP/DOA samples show the increase of impact strength. However, the degrees of the improvement of fracture resistance

are different. For example, at annealing temperature of 120°C, PP-120 sample shows the impact strength of 8.2 kJ/m², about 64% higher than that of PP-23 sample. Further increasing the annealing temperature just leads to a slight increase of impact strength. However, for PP/DOA samples, the impact strength increases gradually with the increase of annealing temperature. At annealing temperature of 140°C, the impact strength is increased up to 17.3 kJ/m², nearly 131% higher than that of PP/DOA-23 sample, and even 246% higher than that of PP-23 sample. This means that through the combination of adding mobilizer and application of annealing treatment, the fracture resistance of PP can be greatly enhanced.

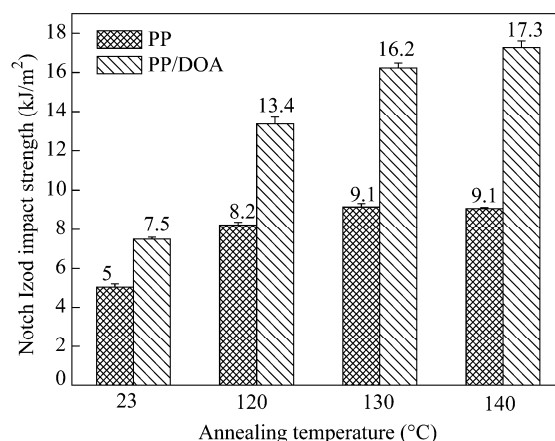


Fig. 5 Comparison of the notched Izod impact strength of PP and PP/DOA samples obtained at different annealing temperatures

To better understand the change of the fracture behavior of annealed samples, the impact-fractured surface morphologies of representative PP and PP/DOA samples annealed at 140°C were also characterized by using SEM, and the results are shown in Fig. 6. From Fig. 6 one can see that at small magnification, there are at least two differences between the impact-fractured surface morphology of PP-140 and PP/DOA-140 samples. The first one is that the impact-fractured surface of PP/DOA-140 sample is much rougher than that of PP-140 sample, indicating more energy absorption during the fracture process. The second one is that PP-140 sample exhibits a small zone with a parabolic ridge or a thin curved band (as shown by dash curve), relating to the change in the stress state. Such morphology disappears completely in the fractured-surface of PP/DOA-140 sample. As is well known, near the notch tip a plane strain state prevails while near the opposite edge of the sample, a plane stress state dominates. Obviously, the presence of DOA changes the stress state of the sample. Furthermore, one can see that whether for PP-140 or for PP/DOA-140 sample, there is a stepped surface morphology at the edge of the samples. With the presence of DOA, the area of the stepped surface is apparently enlarged. Normally, the center of the specimen experiences the plane strain fracture, while the edge experiences the plane stress fracture associated with the local plastic deformation of specimen. This also means that DOA changes the stress state of the sample during the fracture process. In addition, the fracture of sample under the load condition includes at least two stages: crack initiation and crack propagation processes. Therefore, the surface morphology was carefully investigated at higher magnifications, and the results are also shown in Fig. 6. It can be seen that, whether in crack initiation zone (a1) or in the crack propagation zone (a2), PP-140 sample exhibits relative smooth surface features, which means that the fracture occurs at relatively high speed due to the high sensitivity of PP to the prefabricated notch. For PP/DOA-140 sample, one can observe the presence of plastic deformation zone on the impact-fractured surface (b1 and b2). Furthermore, some tiny voids can also be observed, indicating the cavitation of sample during the fracture process^[18, 19]. Obviously, both the plastic deformation and the cavitation of PP are favorable for the energy absorption, leading to higher impact strength as previously shown in Fig. 5. In this work, although the content of DOA is 5 wt%, it can not form a dispersed phase in the PP. In other words, DOA can not exhibit the role of stress concentrator to promote the plastic

deformation of PP. On the other hand, as shown by Fig. 3(c), PP/DOA-140 exhibits higher X_c compared with PP-140, which is believed to be unfavorable for the improvement of fracture toughness. Therefore, the severe plastic deformation of PP observed in PP/DOA-140 is mainly ascribed to the largely enhanced mobility of chain segments achieved by the homogeneous distribution of DOA molecular in the amorphous region of PP. This also indicates that in determining the fracture toughness of PP, the positive role of chain segments mobility in amorphous region is more apparent than the negative role of the enhancement of crystallinity in crystalline region.

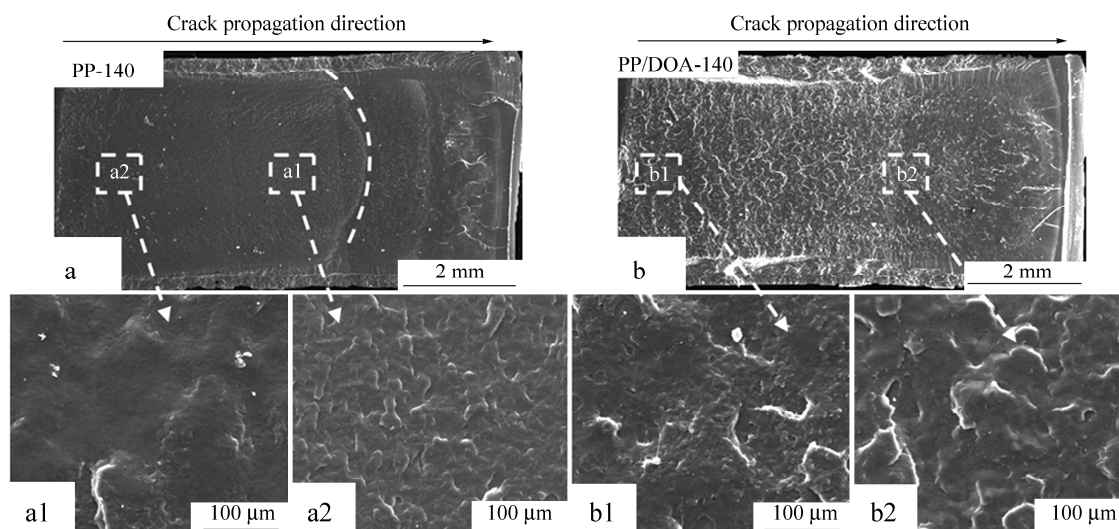


Fig. 6 SEM images show the impact-fractured surface morphologies of representative PP-140 (a, a1, and a2) and PP/DOA-140 (b, b1, and b2) samples

Figure 7 shows the engineering stress-strain curves of annealed PP/DOA samples obtained during the universal tensile measurements and the corresponding parameters of tensile properties. Due to the largely enhanced mobility of chain segments of PP, PP/DOA-23 sample exhibits excellent ductility and the elongation at break (%) is 414.7%, much higher than 147.5% of the PP-23 sample (not shown here). After being annealed, one can notice that the stress-drop phenomenon where the engineering stress dramatically decreases with the engineering strain during the tensile process becomes inconspicuous. Generally, the nucleation and propagation of some microcracks mainly contributes to the stress-drop phenomenon during the tensile process. Herein, the variation of the stress-strain curves indicates that with the increasing of annealing temperature, the defect of the sample is reduced and the stress transfer becomes easier during the universal tensile process. In other words, the structure discrepancy can be removed through annealing^[20]. As shown in Fig. 7(b), although annealing greatly induces the decrease of elongation at break (%), both tensile strength and tensile modulus tend to increase most likely due to the increased X_c . The different variation trends of impact strength and ductility in response to annealing treatment may be attributed to the different mechanical measurement methods.

The dynamic mechanical properties of PP/DOA samples before and after being annealed were further investigated by DMA, and the results are shown in Fig. 8. One can see that annealing induces the improvement of the storage modulus below T_g . This obviously can be attributed to the improvement of crystalline structure of PP during the annealing process. As expected, the higher the annealing temperature, the more perfect the crystalline structure is, and consequently, the higher the storage modulus is.

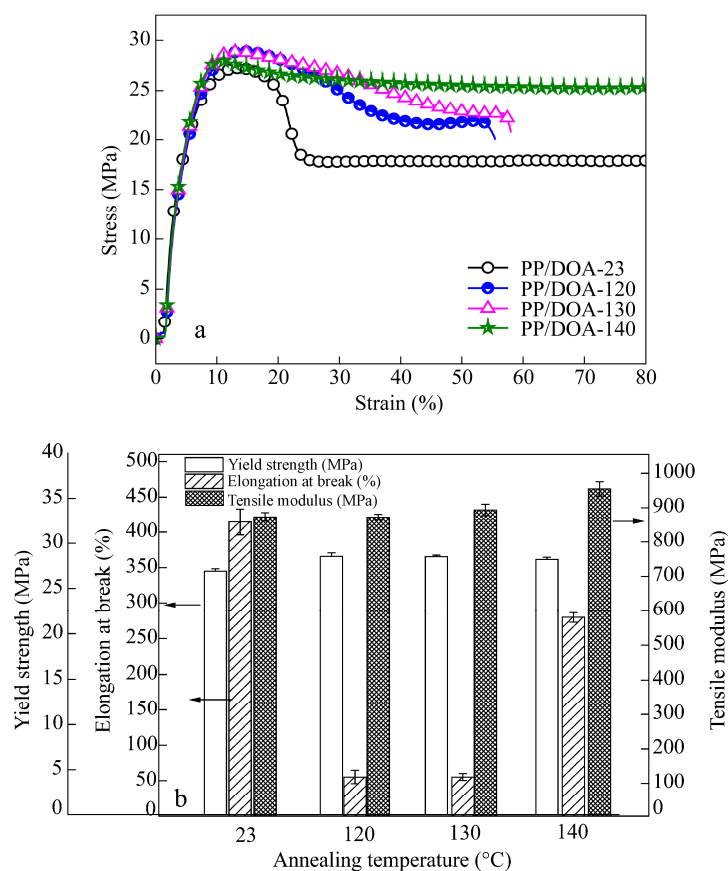


Fig. 7 (a) The typical engineering stress-strain curves for PP/DOA samples before and after being annealed at different temperatures; (b) The variation of tensile properties versus annealing temperatures

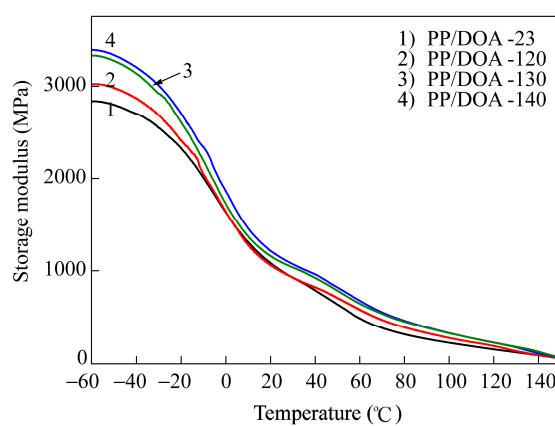


Fig. 8 Storage modulus of PP/DOA samples before and after being annealed at different temperatures

CONCLUSIONS

In summary, mobilizer was introduced into PP and the plasticized PP samples were further annealed at different temperatures. The results show that mobilizer greatly improves the chain segments mobility in amorphous region, leading to the dramatic decrease of T_g . During the annealing process, the enhanced chain segments mobility of PP is favorable for the occurring of the second crystallization. Specifically, compared with annealed

pure PP samples, plasticized PP samples exhibits much more apparent change in both T_g and X_c . The mechanical property measurements show that annealed PP samples containing a few amount of mobilizer have better fracture resistance compared with annealed pure PP samples, further proving the role of chain segments mobility in toughening PP materials. Anyhow, this work is favorable for the understanding of the toughening mechanism of PP during the annealing process.

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