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Material properties

Study on the fracture behavior of annealed immiscible polypropylene/poly(ethylene oxide) blend

Hai-Yan Wu, Jing-Wei Chen, Xue-Chong Du, Jing-Hui Yang, Ting Huang, Nan Zhang, Yong Wang*

Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Erhuan Road, North I, No. 111, Chengdu 610031, China

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ABSTRACT

Immiscible polypropylene/poly(ethylene oxide) (PP/PEO) blend was injection molded and the specimens were annealed at different temperatures (90-150 °C). Dynamic mechanical analysis (DMA) was used to investigate the relaxation behavior of the PP matrix before and after being annealed. The fracture behavior of the annealed specimens was comparatively investigated by notched Izod impact and single-edge single-notched three-point bending measurements. The fractured surface morphologies obtained from different measurements were characterized by using scanning electron microscopy (SEM). The results showed that annealing not only improved the mobility of chain segments but also improved the damping behavior of PP matrix. Greatly increased impact strength was observed for the annealed PP/PEO specimens. The formation of a saw-shaped plastic deformation zone at the edge of the annealed specimen was suggested to be the main reason for the increased impact strength. The results also showed that annealing caused a change from plain strain induced fracture to plain stress induced fracture. Further results obtained from three-point bending measurements showed that annealing was favorable for the enhancement of the maximum load (F_{max}), the critical stress intensity factor (K_c) and the critical strain energy release rate (G_c) of the immiscible PP/PEO blend.

1. Introduction

Annealing treatment, which is carried out at temperatures below the melting point (T_m) of semicrystalline polymers, is thought to be one of the efficient ways to improve the mechanical properties of articles by promoting the reorganization of microstructure. During the annealing process, secondary crystallization of semicrystalline polymer is provoked, leading to the thickening of raw lamellae which are obtained during melt processing, i.e. extrusion, injection and compression et al., and the formation of new thin lamellae in the amorphous region. The latter usually exhibit a low-temperature melting peak with a maximum slightly above the annealing temperature on the differential scanning calorimetry (DSC) curve [1–3].

Generally, the fracture resistance of semicrystalline polymer articles deteriorates with increase of the degree of crystallinity (X_c). Due to the occurrence of secondary crystallization during the annealing process, annealed semicrystalline polymer articles usually show enhancement of X_c and improvement of crystalline structure compared to the unannealed articles, which seems unfavorable for fracture resistance. However, it is widely reported that annealing promotes the improvement of fracture resistance of semicrystalline polymers. For example, the fracture resistance of polyethylene (PE) can be greatly enhanced by annealing, and the toughening mechanism is attributed to the occurrence of micro-voids (or cavities) as the material yields under load [4,5]. More substantial researches are focused on another semicrystalline polymer, i.e.

* Corresponding author. Tel.: +86 28 87602714; fax: +86 28 87600454.
E-mail address: yongwang1976@163.com (Y. Wang).

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polypropylene (PP). It is well known that PP is a polymorphic material with a rather complicated crystalline morphology, such as smectic mesophase (intermediate state between ordered and amorphous phase, and is usually present in quenched specimens), monoclinic α-phase (a thermodynamically stable phase and predominating under normal processing conditions), the trigonal β-phase (a thermodynamically metastable phase and sporadically observed in commercial grades of PP products at higher undercooling) and the orthorhombic γ-phase (a thermodynamically metastable phase and only obtained when crystallization of PP occurs at elevated pressure). With the aid of annealing at relatively high temperature, besides the transition from the metastable phases to the thermodynamically stable α-phase, the microstructure rearrangements including lamellae thickening and relaxation of oriented structure in the annealed injection molded articles are usually detected [6–11]. As a consequence of microstructure rearrangements, annealed PP articles usually exhibit different mechanical responses compared with unannealed samples [12–19]. The most exciting aspect of mechanical properties change is the improvement of impact strength which has been widely reported in literature [20–26]. This is very significant for the potential application of PP articles since PP is very sensitive to notches and normally shows poor impact strength. More detailed research shows that annealing inducing the improvement of impact strength is mainly related to the variation of chain segment mobility in the amorphous region [20–27]. After being annealed at a certain condition, the intensity of β-relaxation of PP is enhanced to a certain extent, which is suggested to be the main reason for the improvement of impact strength [28].

Annealing inducing the microstructure and physical properties change of PP blends or PP composites also attracts attention of researchers since these materials have more potential applications. Lin et al. [29,30] investigated the effect of annealing on impact toughness of PP/calcium carbonate ($CaCO_3$) and found that the annealed nanocomposites had much higher impact toughness than its unannealed counterparts. Their results also suggested that the plastic deformation zone that formed in the crack initiation stage was responsible for the high impact toughness of the annealed nanocomposites. Ceccia et al. [31] investigated the intercalation and exfoliation of layered silicates in PP induced by annealing and found that annealing facilitated the diffusion of PP chain segments into galleries of clay, but they did not report the variation of mechanical properties of the nanocomposites before and after being annealed.

In our previous work, the joint action of annealing and β-phase nucleating agent in influencing the impact toughness of PP materials, such as PP/$CaCO_3$ [32], PP/organic montmorillonite (OMMT) [33], PP/Ethylene-Octene Copolymer (POE) [34] and PP/poly(ethylene oxide) (PEO) [35], was also investigated in detail. All the materials showed largely improved impact toughness at annealing temperatures ranging from 90-140 °C. Besides the enhanced chain segments mobility and the increased intensity of β-relaxation of the annealed PP matrix, which were suggested to be the main reasons for the improvement of impact toughness, it was observed that the annealed samples exhibited different impact-fractured surface morphologies compared with their unannealed samples. Namely, a stepped surface or serrated surface at the edge of the annealed sample was widely observed. Such special surface morphology is seldom observed for common injection molded PP samples. Therefore, we believe that there is a relation between the impact toughness and the stepped or serrated surface morphology of annealed samples. To further understand the fracture behavior of annealed PP samples, in this work, our attention is focused on the different mechanical responses of the annealed immiscible PP/PEO blend under different stress conditions, including notched Izod impact test and single-edge single-notched three-point bending test. It is expected that the comparative study on the different fracture behavior of annealed PP/PEO blend will help the understanding of the toughening mechanism of annealed PP materials.

2. Experimental part

2.1. Materials

PP (F401) with a melt flow rate (MFR) of 2.5 g/10 min (230 °C/2.16 kg) and a density of 0.91 g/cm^3 was obtained from Lanzhou Petrochemical Co, Ltd., Lanzhou, China. PEO with a molecular weight of 2.86×10^5 was purchased from Shanghai Liansheng Chemical Co, Ltd., China. Antioxidant was added in order to prevent the degradation of PP during processing and annealing.

2.2. Sample preparation

Before the melt blending of materials, both PP and PEO were dried in an oven at 40 °C for 4 h. PP/PEO blend with 10 wt% PEO was melt-compounded using a twin-screw extruder (SHJ-20, China) at a screw speed of 200 rpm and temperatures of 150-200 °C from hopper to die. After being granulated, the pellets were dried in an oven at 40 °C for 6 h, and then injection molded. The standard specimens for notched Izod impact and single-edge single-notched three-point bending measurements were prepared using an injection molding machine (K-TEC40, Germany) with melt temperatures of 190-215 °C from hopper to nozzle and a mould temperature of 25 °C. The width and the thickness of the injection molded specimen are 10 mm and 4.2 mm, respectively. Some specimens were annealed for 12 h in a fan assisted oven at different temperatures (T_a = 90-150 °C). After being annealed, the specimens were cooled in ambient air and then conditioned at 23 °C and 50% relative humidity for 48 h before testing. Correspondingly, the specimen without additional annealing treatment was also conditioned at 23 °C.

2.3. Mechanical measurement

Dynamic mechanical analysis (DMA) measurement was carried out on a DMA Q800 analyzer (USA) using the three-point bending mode. A rectangular bar with length of 50 mm, width of 10 mm and thickness of 4.2 mm was used.