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Temperature dependence of tensile behavior in poly(butylene terephthalate) with different crystallinity

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ABSTRACT

The tensile behavior of PBT with different crystallinity was investigated at various temperatures. It turned out that the origin of stress whitening is different for PBT crystallized at 100 °C and 180 °C. The deformation of PBT crystallized at 100 °C involves crazing/tearing and fibrillation at different temperatures. The complicated fracture morphologies including brittle fracture, fibrillation and ductile ploughing are linked to the temperature-dependent deformation mode of PBT crystallized at 180 °C. The yield behavior could be described based on the Ree-Eyring model for PBT crystallized at 100 °C and 180 °C. The effect of temperature on Young's modulus, fracture strain and yield stress was analyzed and the fracture morphology was discussed in detail.

1. Introduction

It is known that structure and tensile temperatures have a significant effect on the tensile properties of crystalline polymers. The tensile behavior of crystalline polymers can be divided into distinctive regions in stress-strain curves encompassing elastic deformation, yielding, strain softening, strain hardening and fracture [1]. Polymers are usually described as viscoelastic materials which exhibit features of elastic solids at low temperatures or high strain rate; while at high temperatures or low strain rate, polymers can behave like viscous liquids [2]. The yield behavior of polymers is sensitive to temperature and strain rate. The strain rate and temperature dependence of the yield stress can be described by Eyring's equation for thermally activated processes [3,4]. The Eyring approach assumes that the yield process is velocity controlled and that the yield stress of polymers is consistent with this property [5–13].

In general, polymeric materials have a tendency to exhibit a whiter appearance in external force fields during deformation, which is termed as 'stress whitening'. Numerous systems have shown the characteristic of stress whitening due to the formation of voids or cavities [14–18] with micrometer or nanometer sizes. It has been reported that the occurrence of crazing also contributes to the stress whitening. It was proved by Bucknall and Smith that crazes were the causes of stress whitening in deformed high-impact polystyrenes under stress [19]. However, other dominant micromechanisms including kinking, microcracking and ductile ploughing were proposed for stress whitening. The whitening was shown to be related to kink band formation in the drawing of linear polyethylene [20]. In particulate-filled epoxy resins, matrix cracking in compression contributes to the stress whitening at higher strains [21]. Thus, much effort has been devoted to explore the origin of stress whitening.

Many studies on the fracture behavior of different polymeric materials have been reported [22–24]. Brittle and ductile failure can be distinguished from the energy dissipated in fracture and the nature of the fracture surface. A number of glassy polymers are susceptible to brittle fracture at low temperature [25,26]. To avoid catastrophic failure, the toughening of polymers is a crucial aspect of improving the strength and ductility at various temperatures and deformation rates. The deformation behavior of ductile polymers is usually characterized by deformation bands, crazing/tearing and fibrillation. For example, a combination of brittle failure and crazing/tearing is responsible for fracture morphology in homopolymer polypropylene [27].

In present work, we explore the temperature dependence of tensile behavior in poly(butylene terephthalate) (PBT) with different crystallinity. PBT is a crystalline thermoplastic polyester with a high crystallization rate, good dimensional stability and excellent chemical resistance [28]. Stress whitening was observed during tensile deformation in the glassy state of PBT. The effect of temperature of the tensile deformation on stress whitening and mechanical behavior of PBT with different crystallinity under tensile loading is discussed.

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2. Experimental section

2.1. Materials and preparation

PBT is a commercial product purchased from Du Pont. It is an injection molding grade with density 1.30 g/cm^3, MFI 34 (250 °C, g/min). The glass transition temperature and melt temperature are 54 °C and 225 °C, respectively. The PBT was dried at 120 °C for 12 h in a vacuum oven. The samples wrapped in aluminum foil were melt-pressed at 250 °C for 5 min between two sheets of iron under a pressure of 20 MPa. On removal from the press, the samples were quickly quenched into an oil bath at 100 °C (PBT-100) and 180 °C (PBT-180) for crystallization. Dumbbell-shaped tensile bars with dimensions of 26.0 mm (length) × 2.0 mm (neck width) × 2 mm (neck length) were cut for tensile measurements.

2.2. Tensile tests

Uniaxial tensile tests were carried out at various temperatures from 30 °C to 180 °C with a constant deformation rate of 20 μm/s (corresponding to the strain rate of $10^{-2}\,s^{-1}$) on a Linkam TST-350 tensile hot stage (Linkam Scientific Instruments, Ltd., U. K.). At least five tensile bars were used under each testing condition. Average values of mechanical parameters were obtained from stress-strain curves.

2.3. X-ray diffraction analysis

The WAXD measurements were performed at room temperature using a Rigaku D/max 2500 V instrument with a Cu-Kα source (λ = 1.54 Å, 40 kV and 200 mA). The measured angle 2θ ranged from 10 to 35° with a scan speed of 2°/min.

2.4. Differential scanning calorimetry

The DSC melting curves of the PBT samples were obtained, employing differential scanning calorimeter (TA-Q20). The samples were heated from 30 °C to 250 °C at a rate of 10 °C/min in a nitrogen atmosphere.

2.5. Optical imaging-stress whitening

To observe the stress whitening of deformed samples, a digital camera was used in white and black mode. The images were recorded every four seconds during deformation.

2.6. Scanning electron microscopy

The deformed samples associated with the stress whitening region were observed using field emission scanning electron microscope (SEM). The morphology of the fractured surface of samples was observed by SEM after sputter coating with gold powder.

3. Results and discussion

3.1. Tensile behavior

The typical engineering stress–strain curves of PBT crystallized at 100 °C (a) and 180 °C (b) at various temperatures are shown in Fig. 1. The results show a similar aspect: a notable yield point can be seen after the initial elastic region; subsequently, a plateau region is observed in the tensile curves just after the strain softening and then a marked strain hardening behavior at high temperatures. It is worth noting that at the same stretching temperature, the length of the plateau in the engineering stress-strain curves of PBT crystallized at 180 °C is greater than that crystallized at 100 °C.

Fig. 2 shows that the Young's modulus and fracture strain of PBT-100 and PBT-180 at various temperatures. Three distinct regions associated with the different mechanical response are identified for both PBT-100 and PBT-180. In the temperature range (30–40 °C) below the glass transition temperature of PBT (54 °C), high Young's modulus values and low fracture strains can be observed. A rapid decrease in the Young's modulus and a prompt increase in the fracture strain can be seen near the glass transition region (50–80 °C). A slow, approximately linear decrease in the young's modulus and relatively high fracture strain are observed in the rubbery state of amorphous PBT (above 80 °C). The Young's modulus (elastic modulus) is an important mechanical parameter of materials because it is related to the ability of a material to resist elastic deformation when loaded. Young's modulus is indicative of the rigidity of the material. In the glassy state, segmental motions are largely restricted and the polymer has high rigidity, leading to a relatively high Young's modulus and low fracture strain; in the glass transition region, the frozen-in chain segments in the amorphous region begin to move, resulting in a rapid decrease in Young's modulus and a significantly increase in fracture strain. In the rubbery state, polymer chains show greater stress relaxation at high temperatures, leading to a relatively low modulus and enhanced ductility. Compared with PBT-100, PBT-180 displays a significantly larger Young's modulus and a small fracture strain at a given temperature. We believe that these differences arise from the different crystallization conditions.

3.2. WAXD profiles and DSC curves

The effect of heat treatment on the crystalline structure and thermal property of PBT was investigated by WAXD and DSC technique. As shown in Fig. 3(a), five prominent diffraction peaks: $(0\bar{1}1)$ at 2θ = 16.0°, (010) at 2θ = 17.3°, $(\bar{1}02)$ at 2θ = 20.5°, (100) at 2θ = 23.1°, (111) at 2θ = 25.0° are observed in PBT in the α-crystalline form [29]. The WAXD peak intensities increase and the widths of the peaks decreases with increasing temperature, indicating the enhancement of crystallinity and the formation of larger crystals. Fig. 3(b) depicts DSC melting curves of PBT samples crystallized at 100 °C and 180 °C. The heating curve of PBT-100 displays a small exothermic peak (T_{re}) at around 206.5 °C prior to the endothermic peak (T_{m2}); the heating curve of PBT-180 has two endothermic peaks, T_{m1} and T_{m2}. The T_{m1} peak is considered to be due to the melting of lamellae crystallized from the melt and the T_{m2} peak is ascribed to the re-melting of the crystal recrystallized during heating [30]. The crystallinity was estimated according to the ratio of the measured heat of fusion to the heat of fusion (140 J/g) of 100% crystalline PBT [31]. The values of crystallinity are 30.2% and 44.9% for PBT-100 and PBT-180, respectively. The result shows that an increase in crystallinity enhances the Young's modulus independent of tensile temperatures and the strain-to-fracture of PBT samples with higher crystallinity is less than for lower crystallinity samples. The rigidity of polymers increases with the increase of crystallinity, resulting in a relatively larger Young's modulus. Increasing rigidity reduces the mobility of molecular chains leading to low fracture strains. For example, PBT-180 shows a significant decrease in fracture strain compared with PBT-100 at 80 °C due to the reduced molecular mobility.

3.3. Modeling the yield stress

As mentioned in the Introduction, polymers show different viscoelastic behavior at different temperatures. The yield behavior can be described as velocity controlled, and the yield stress of polymers which is sensitive to strain rate and temperature can be described by Eyring's equation:

$$\frac{\sigma y}{T} = \frac{k}{V}\sinh^{-1}\left(\frac{\dot{\delta}}{\dot{\delta}_o \exp(-\frac{\Delta H}{kT})}\right) \quad (1)$$

where σ_y is the yield stress, T the absolute temperature, k the