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Data Interpretation

Effect of crystallinity level on the double yielding behavior of polyamide 6

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Abstract

A complex double yielding behavior is observed in the engineering stress–strain curves of injection molded specimens of polyamide 6 (PA6) under tensile loading, and a simple method is put forward to judge the apparentness of the double yielding process. By thermal treatment, the effect of the crystallinity level on the double yielding behavior is studied in some detail. The results show that the second yield stress becomes larger than the first after the thermal treatment, which is contrary to the case without thermal treatment. With the annealing time decreasing and the annealing temperature increasing, the percentage crystallinity becomes higher, and the second yield point is much more apparent with a decrease of crystallinity of the specimens. A possible crystallinity window may exist in double yielding behavior of PA6 material. These results indirectly show that the second yield point is not only associated with the deformation of the crystalline region.

Keywords: Polyamide 6; Crystallinity; Double yielding; Stress-Strain behaviour

1. Introduction

It has long been known that the deformation behavior and yielding properties are very important characteristics of semi-crystalline polymers. Conventionally, the yielding behavior of thermoplastics under tensile loading is often characterized by only one yield maximum [1]. Since the recognition of the double yielding process in branched and heated pressed polyethylene specimens by Popli and Mandelkern in 1987 [2], many related investigations have concentrated in understanding this complex phenomenon and some researchers have deemed that the double yielding behavior is a general phenomenon to be expected in semi-crystalline polymers but not in amorphous ones [3–7]. Recently, Adhikari et al. [8] have made an important discovery and detected the existence of double yielding in nanostructured amorphous polymer. Subsequently, Li et al. [9] have also reported the morphology-dependent double yielding behavior in injection molded polycarbonate/polyethylene blend, which is a typically incompatible blending system. Some possible deformation models and mechanisms have been postulated to

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explain the origin of this special phenomenon [10–12]. For example, Séguéla et al. [11,12] have pointed out that the two yield points are due to the slip of the crystal blocks past each other in the mosaic crystalline structure (heterogenous slip) and the homogeneous shear of the crystal blocks (homogeneous slip).

While attempting to understand the double yielding behavior of polyethylenes and other polymer systems, several factors, including the structure changes, deformation temperature, strain rate, crystallinity degree, lamellae thickness, perfection of crystallites, composition distribution, branching degree and branching content, etc., must be evaluated [2–7,10–12]. A series of investigations concerning the influence of crystallinity level on double yielding in crystalline polymers has been carried out in the recent years. Lucas et al. [5] have studied a set of linear polyethylene with different crystallinity levels and observed that samples with crystallinity contents higher than 50% show only one yield point, samples with crystallinity levels in the range 20–50% show two yield points and samples with crystallinity levels less than 20% only display a very broad yield process, similar to a rubber-like deformation. Séguéla and Darras [13] have made a comprehensive study on the double yield of polyethylenes and drawn the conclusion that the double yielding behavior is a common feature to polyethylene and ethylene copolymers, regardless of the crystallinity level. Furthermore, the experimental results from Muramatsu and Lando [4] have proved that the first yield point of poly(tetramethylene terephthalate) and its copolymers becomes less apparent with an increase of crystallinity level of the specimens, and the second yield point becomes much more apparent with the increase of crystallinity level.

In our previous papers [14,15], the special double yielding phenomenon of injection molded polyamide 6 (PA6) and glass bead-filled PA6 composites under tensile loading has been studied by means of various measurements such as differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In this study, to further elucidate the relation between the crystallinity level and the double yielding behavior, PA6 injection specimens with a wide range of crystallinity level were prepared and a simple method to judge the first and second yielding grade was considered.

2. Experimental procedure

2.1. Material

The Polyamide 6 (PA6) resin used in this study was a commercial product of Xinhui Meida-DSM Nylon Slice Company Ltd, supplied in pellets, with the trade mark M52800, as described previously [14,15]. The melting temperature of PA6 measured by DSC was 225 °C. The resin was dried for 12 h under vacuum at 100 °C before processing to avoid its hydrolytic degradation.

2.2. Sample preparation

After drying in vacuum at 100 °C over 12 h to remove the moisture, PA6 were injection molded into dog-bone tensile samples and impact samples on an injection-molding machine made by Nissan, Japan, with a temperature profile of 230, 240, 250, and 245 °C from the feeding zone to the nozzle, an injection velocity of 14% (the maximal injection velocity is 45 g/s), and an injection pressure and holding pressure of 30% (the maximal injection pressure is about 187 MPa), respectively. The mold temperature was 40 °C. The molded samples were then annealed at 100 °C and 190 °C for different time and annealed for 2 h at 130, 160, 190, and 205 °C, respectively.

2.3. Tensile deformation

The tensile test was performed at room temperature according to ISO 527-1-1993 on an Instron Series IX universal test machine by using the dog-bone specimens. The distance between the grips was 110 mm as recommended in the standard. The crosshead speeds of the apparatus were 5, 10, 20, 50, 100, and 200 mm/min respectively, with the strain being determined on a 50 mm length zone in the middle part of the specimens by an extensometer. At least five specimens were used for each measurement and the average results were reported here. The nominal stress and nominal strain are defined as the ratio of the draw force to the initial cross-section of the sample and the ratio of the extensometer displacement to the initial gauge length of the sample, respectively. On the other hand, the nominal strain rate is the ratio of the crosshead speed to the initial gauge length of the sample. Thus the strain rates were 1.67×10^{-3}, 0.33×10^{-2}, 0.67×10^{-2},