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The phenomenon of double yielding in polyamide 6/K resin blends

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Summary

The polyamide 6 (PA6)/K resin (K) blends of some kinds of compositions have been prepared by extrusion. During the process of tensile testing, we found that the PA6/K blend with 10% PA6 has the usual stress-strain behavior, and that the samples obtained with 30% and 50% PA6 show apparently double yielding behavior, while the PA6/PS blend does not show the double yielding phenomenon at all same mass ratio. Considering the microscopic morphology study and results of mechanical properties of the PA6/K blends, the first yield point which occurs at the lower tensile stress might be caused by the deformation of the K resin matrix, and the second one may be correlated to the permanent plastic deformation of the entanglement of PA6 chains and PB segments within chains of K resin.

Introduction

Conventionally, the yield point observed in a tensile test in polymers is accepted as being the point where the stress-strain curve shows a local maximum [1]. This point is related to the onset of necking, where the strain hardening of the necked material is not sufficient to counteract the reduction in the cross sectional area of the necked region [2]. The maximum may become less pronounced as the temperature is increased and/or the deformation rate is decreased, until it disappears.

However, since the recognition of the double yielding process in low-density polyethylene (PE) of different branch contents by Popli and Mandelkern [3], many studies have shown the existence of the double yielding phenomenon in several groups of semicrystalline polymers and their blends including different grades of polyethylenes [4-18].

Recently, Adhikari et al. [19] made an important discovery in that the double yielding exists in a nanostructured amorphous copolymer. This polymer involves a highly asymmetric styrene/butadiene star block copolymer of polystyrene (PS) and random PS-co-PB [poly (styrene-co-butadiene)] copolymer. They suggested it might be correlated with two different micromechanical processes taking place at the initial stage of deformation.

It is well known that there is a strong correlation between the character of the yield region and permanent deformation, understanding the yielding process is very important to the understanding of the complete deformation process. So far, the semicrystalline polymers are the most general materials that may be expected to observe the double yielding phenomenon under some appropriate conditions. Moreover, the microstructural origin of this phenomenon is highly controversial. Only a few studies have been reported on such a phenomenon in incompatible blend with structurally different polymer components [9]. While the complex phenomenon has not been reported in the blends containing block copolymer to the author's knowledge. In the present paper, we report the existence of two distinct yield points in a new type of PA6/K resin blend at some mass ratio. The tensile behaviors of these samples were examined to reveal the microstructural origin of the double yielding.

Experimental

Materials

Polyamide 6, trademark 5033B, was obtained from UBE Industries Ltd. (Japan). Polystyrene (PS), trademark PG33, was obtained from Qimei Co. (Taiwan). K-Resin® (KR03) was supplied by Phillips Co. (Korea). K-Resin® is the trademark for the Chevron Phillips Chemical Company LP family of clear styrene-butadiene copolymers. The polymer was synthesized by anionic polymerisation in cyclohexane with n-butyllithium as the initiator. This commercially available block copolymer consists of 25 wt. % butadiene and 75 wt. % styrene segments. This polymer has a star-shaped molecular architecture, with an average of about four arms (see Figure 1), with each arm consisting of a diblock copolymer of polybutadiene (PB) and polystyrene (PS) [20].

Specimen Preparation

Blends of various compositions have been prepared by extrusion. First, PA6 was dried at 90°C for 24 h. The polymers were blended using a twin-screw extruder made by Nanjing Xiangsu machine factory, China, with length to diameter ratio of 25. The temperature profile was in the range of 210–230°C. The materials were pelletized. After drying to remove the attached moisture during extrusion and palletizing, the pellets were injected into dumb-bell shaped on a HTB80 injection molding machine made by Haitian machine co., China. The temperature profile was 190, 200, 230 and 220°C from the feeding zone to the nozzle, and both the injection and holding pressures were 50.0MPa. For unmodified PA6, K resin and PS, the moulding temperature was 230°C, 190°C and 200°C, respectively.

Characterization

The tensile test was performed at room temperature according to ASTM D-638 using the injected dumb-bell shaped specimens on an Instron universal testing machine equipped with a 500 N load cell. The cross-head speed of the apparatus was adjusted at 50 mm/min. At least four samples were tested in each case.

Scanning Electron Microscopy pictures were taken to study the morphology of the blends. The specimens were frozen in liquid nitrogen for one hour then impact broken and etched with a suitable solvent: either formic acid to remove the PA6 phase or styrene to dissolve the K resin phase. Afterward, a gold–palladium layer was deposited on the samples for SEM observation. The SEM used was a JEOL JSM-6360 system.

The dynamical–mechanical measurements were made using a thermal dynamical–mechanical analyzer DMTA (Perkin Elmer, model DMTA-V). The measurements were carried out in a bending mode, at the heating rate of 3°C/min from -120°C to 230°C at fixed frequencies of 1 Hz.

Results and Discussions

Tensile Deformation Behavior

Figure 1 presents the engineering stress-strain curve of pure PA6 and K resin specimen. The pure resin used in this work shows a typical stress-strain behavior. It may be easily noticed that the deformation of each sample is characterized by the

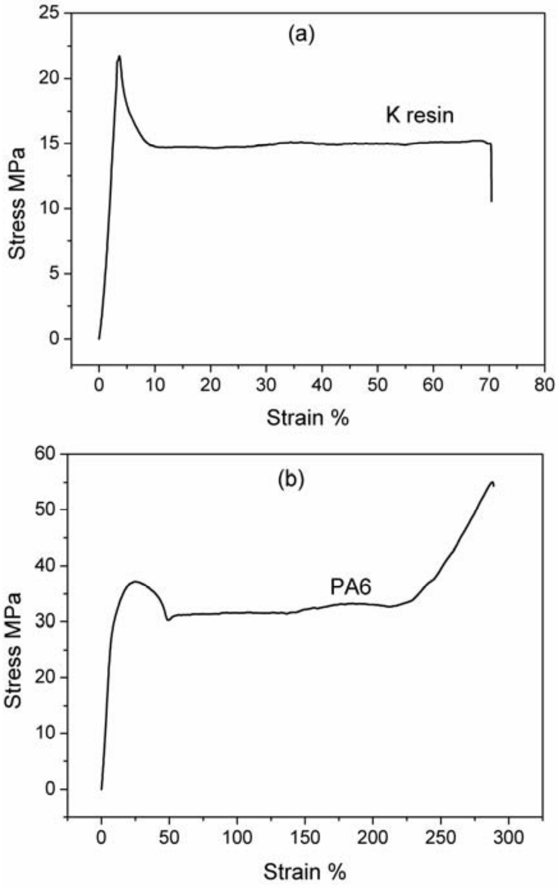

Figure 1 Stress-strain curve of injection molded pure resin specimen(a: K resin; b: PA6).

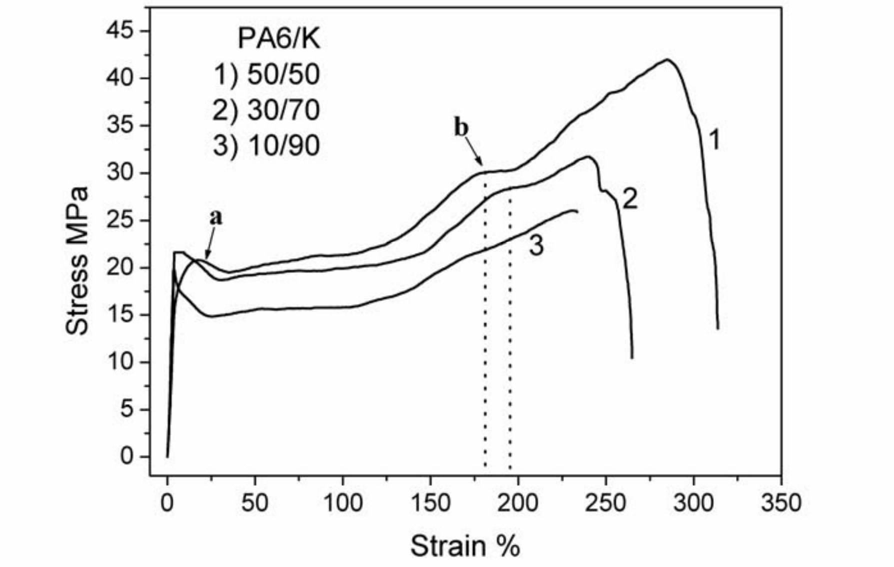

Figure 2 Stress-strain curve of PA6/K resin blends with different mass ratio(a: first yield point, b: second yield point).

presence of one yield point. The stress shows one maximum followed by a stress drop. Subsequently, the sample undergoes long cold drawing. Then, fracture and strain-hardening are shown for K resin and PA6 respectively.

Figure 2 shows the engineering stress-strain curves of PA6/K resin blends measured at a crosshead speed of 50 mm/min^{-1}. In all samples, tensile stress shows a well-defined yielding point at lower strain (<25%) followed by a stress drop. For the PA6/K 10/90 blend, the sample fractures in a ductile manner with strain-hardening behavior. On the other hand, it is notable that the PA6/K 30/70 and 50/50 blends show apparently double yielding behavior. At the beginning, similar to the PA6/K 10/90 sample, the common yielding occurs after some elastic deformation and the stress start to drop. After the sample undergo long cold drawing, the stress rises quite slowly while the strain continues to increase substantially. However, when the strain reaches about 180%, the stress starts to reach a second local maximum and has been maintained for a certain time implying a second yielding. Thereafter, the stress starts to rise again until the samples are fractured. Repetitious experiments were performed to assure the existence of the phenomenon of double yielding. Furthermore, a slight difference was found between the PA6/K 30/70 and 50/50 blends. The second yielding stress of the PA6/K 50/50 blend is slightly higher than that of the PA6/K 30/70 blend. The higher level of stress achieved by the PA6/K 50/50 sample might be attributed to the increasing content of PA6 in the blend.

Morphological Study

The morphologies of the PA6/K blends at three compositions, as obtained by SEM, are shown in Figure 3. It is found that these samples have different morphologies. The micrograph of the PA6/K 10/90 blend (Figure 3a) shows the presence of a PA6 minor phase, consisting of nearly spherical particles, dispersed in the K resin matrix.

For the PA6/K 30/70 blend, as shown in Figure 3b, the existence of dispersed phase consists of elliptic PA6 particles, the amount and diameter of particles increase relativing to the PA6/K 10/90 blend. Furthermore, PA6 minor phase disperses more unhomogeneous and unregulated, the fracture surfaces of matrix are very uneven. The PA6/K 50/50 blend is shown in Figure 3c. There is evidence of co-continuity, the K resin phase has been etched with styrene, leaving behind a three-dimensional porous network in and around the PA6 phase. Comparing with the PA6/K 10/90 blend, it is clear that there is a stronger interfacial interaction between the PA6 phase and K resin phase for the PA6/K 30/70 and 50/50 blends. This suggests that the PA6/K 30/70 and 50/50 blends maybe have much more different and complex plastic deformation than the PA6/K 10/90 blend.

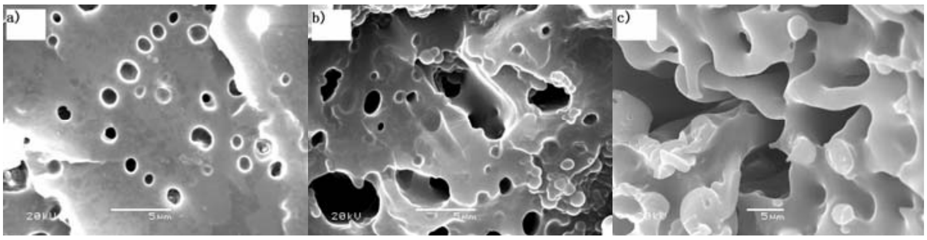

Figure 3 SEM micrographs of the PA6/K blends injection molded at various compositions: (a) 10/90, (b) 30/70, (c) 50/50.

Dynamic mechanical analysis

Course of changes in storage modulus E' as function of temperature with vibration frequency of 1Hz has been shown in Figure 4. Within the range of elastic deformation phase for PA6/K blends, it is easy to observe a little influence of temperature on E' modulus. The highest concentration of PA6 in the mixture, the more temperature

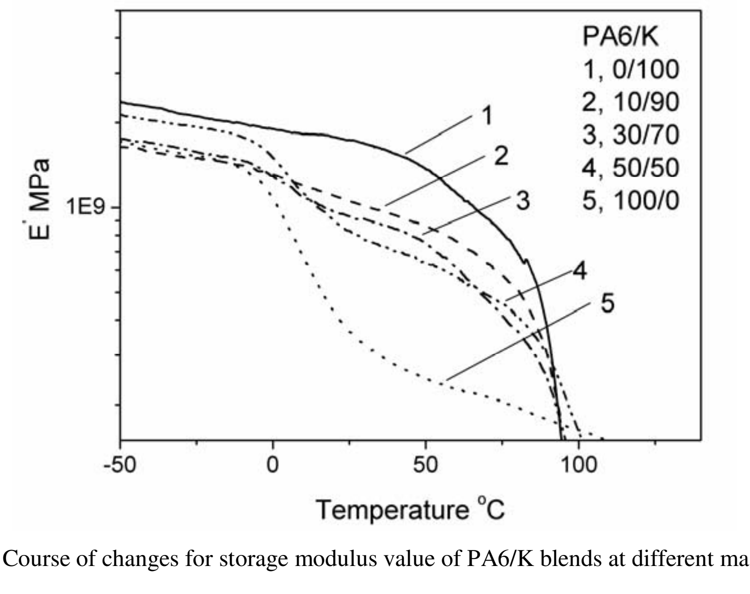

Figure 4 Course of changes for storage modulus value of PA6/K blends at different mass ratio.

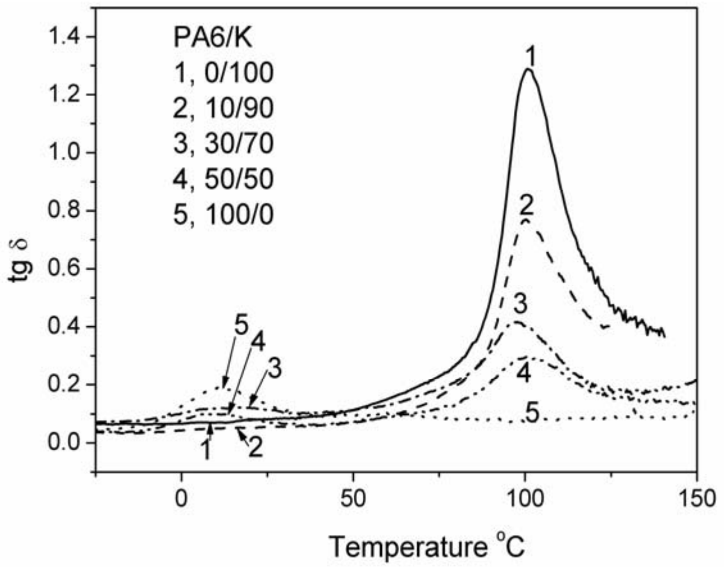

Figure 5 Course of changes for mechanical loss coefficient of PA6/K blends at different mass ratio.

influences $E^{'}$. Glass transition is very visible for K resin and PA6, while for PA6/K blends the scope of glass transition is less clear, especially with 10% concentration of PA6. Within the range of high-elastic deformation the strongest influence of temperature on $E^{'}$ modulus is visible for PA6. It is caused by more intensive activity of PA6 macromolecules.

Temperature dependency of mechanical loss angle tangent is presented in Figure 5. The blends display two distinct transitions: one at 10.6°C, which corresponds to the glass transition of the PA6 phase and the other at around 100.6°C, related to the transition of the hard rigid PS phase of the component parts of K resin. The distinct transiting region corresponding to the glass–rubber transition of the flexible elastomeric PB phase is not obtained as expected. Because of a little content of PA6, the PA6 transiting peak is hardly visible for the PA6/K blend with 10% concentration of PA6. But with the increasing of the PA6, the corresponding temperature where glass transition of the PA6 phase moves to the high temperature direction and the peak width become broad. It indicates that there is a certain interaction existing between the PA6 and K resin molecular chain, and the movement of the segment of PA6 is restricted much more for the PA6/K 30/70 and 50/50 blends.

Proposed Mechanism

The phenomenon of ‘‘double yielding’’ has mostly been discussed in connection with semi-crystalline polymers (such as polyethylene). Several proposals have been suggested to account for the existence of double yielding. According to a widely accepted viewpoint, the yielding in semi-crystalline polymers is governed by two thermally activated rate processes that depend on the temperature and strain rate [14, 19]. The first yield point was attributed to the slip of the crystal blocks past each other in the mosaic crystalline structure. The process involved was called as heterogeneous slip and marks the onset of plastic deformation, which is assumed to be totally (or at least in part) slowly recoverable. The second yield point was attributed to the homogeneous shear of the crystal blocks (also called homogeneous slip) which marks the onset of effectively irrecoverable plastic deformation, which is manifested as a sharp necking in the tensile specimen [9, 19]. From the macroscopic point of view, the first yield point is intrinsic because of a strain softening process and the second one is geometric arising from a necking of the materials [6]. Adhikari et al. studied the double yield phenomenon for a highly asymmetric styrene/butadiene star block copolymer and suggested that the double yielding behavior in this nanostructured copolymer was observed because of the amorphous nature of the nanostructures [19]. They claimed that the first yield point that occurs at the lower tensile strain might be caused by the deformation of the styrene chains present in or mixed into the PS-co-PB random copolymer. The second yield point may be correlated to the permanent plastic flow (micronecking and yielding) of the pure polystyrene domains. However, the both model developed for describing the yielding processes mentioned above are hardly directly applied to our incompatible amorphous/semicrystalline blend because of its multi-phase morphology depending on many parameters, such as the different composition as observed above.

The tensile properties of PA6/K blends obtained from the tensile testing are listed in Table 1. Generally, the tensile strength of the PA6/K blends increase with the increase of the content of PA6 in the range used in this study, while the PA6/K 30/70 and 50/50 blends actually exceed the pure PA6 in the ultimate elongation. It is remarkable that the first yield Stress of the three blends with different mass ratio is extraordinarily close to that of neat K resin and that the value of the second yield Stress for the PA6/K 30/70 and 50/50 blends is slightly lower than the yielding point of pure PA6. It seems that the first yield point of the PA6/K blend takes place as a result of the K resin matrix.

Table 1. Tensile Stress, Yield Stress and ultimate elongation of the PA6/K blends at different mass ratio:

PA6/K mass ratio	Tensile Stress (MPa)	1st Yield Stress (MPa)	2st Yield Stress (MPa)	Ultimate elongation (%)
0/100	21.7	21.7	-	70.4
10/90	26.1	19.8	-	233.1
30/70	31.1	21.6	28.4	264.4
50/50	41.2	20.7	30.1	313.6
100/0	54.8	36.9	-	289.2

In order to further reveal the phenomenon of double yielding of PA6/K blends, the tensile behaviors of PA6/PS blends with different compositions were investigated under the same conditions. As can be seen in Figure 6, the PA6/PS blend with any mass ratio doesn't presence the double yielding, and they all exhibit a brittle behavior. In contrast to the conventional polystyrene, the K resin under investigation has a highly asymmetric star architecture, the star molecule consists of arms with a diblock copolymer of PB and PS, and the volume content of polystyrene is approximately 75%. It seems that the second yielding point of PA6/K blends may be related to the PB segments of K resin, but not the PS segments. Considering the microscopic morphology and results of mechanical properties of the PA6/K blends, we propose the following possible mechanism responsible for the existence of two distinct yield processes.

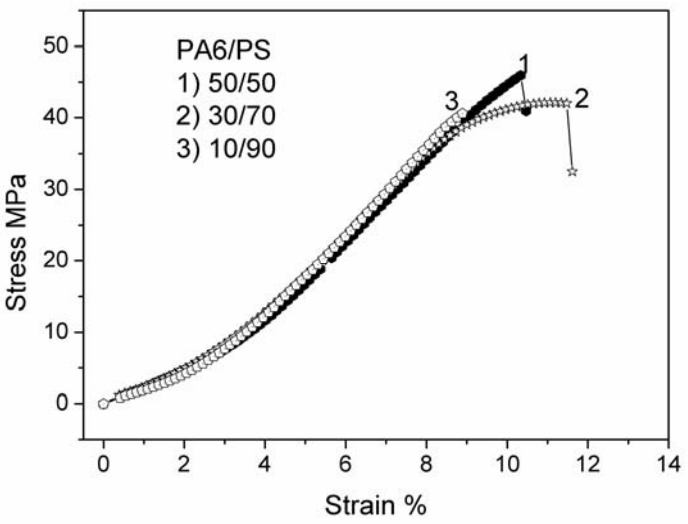

Figure 6. tensile curve of PA6/PS blends with different composition by weight.

In general, the external stress first reaches the maximum yielding stress of K resin during tensile deformation, since the maximum yielding stress of PA6 is much lower than that of K resin. Hence, the first yield point occurs at the lower tensile stress might be caused by the deformation of the K resin matrix, as can be confirmed by the comparability between the yielding value of the blends and the pure K resin. At the same time, the matrix contracts in the transverse direction, thus a higher interfacial contact maybe take place between PA6 and K resin after the first yielding. With further stretching, the entanglement of PA6 chains and styrene-butadiene copolymer chains (especially PB segments within chains of K resin) begins to exert, the tensile stress rises quite slowly, and the deformation behavior becomes to present the property of the PA6. The PA6 molecule chains were possibly mixed of PB rubbery chains at the interfacial region. The second yield point may be correlated to the permanent plastic deformation of the entanglement of PA6 chains and PB segments. Because the content of PA6 is very little, the double yielding phenomenon was indistinct for the PA6/K 10/90 blend. The difference between the K resin and PS on molecular architecture might be attributed to no double yielding point existence of the PA6/PS blends.

Conclusions

An unusual double yielding phenomenon was observed in injection molded specimens of PA6/K resin blend containing 30% and 50% PA6, while the PA6/K 10/90 blend has usual stress-strain behavior. The results show that this phenomenon is in correlation with the composition of the blends. Under the same conditions, the tensile behaviors of PA6/PS blend with different compositions were investigated, no double yielding phenomenon was observed in any mass ratio. Considering the results of SEM, DMTA and the mechanical properties testing, a possible double yielding mechanism was proposed for the PA6/K blends.

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