Double-Yielding Behavior in Injection-Molded Polycarbonate/High-Density Polyethylene/ Ethylene–Vinyl Acetate Copolymer Blends

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ABSTRACT: A uniaxial tensile test was performed for polycarbonate (PC)/high-density polyethylene (HDPE)/ ethylene–vinyl acetate copolymer (EVA) blends with a fixed EVA content but various PC contents. The double-yielding phenomenon and its composition dependence, as observed in the PC/HDPE blend, were again detected. EVA did not serve as a successful compatibilizer of PC and HDPE in the PC/HDPE/EVA blend. The incorporation of EVA resulted in a larger size and a more irregular shape of the PC fibers, as indicated in the scanning electron microscope observations; this, consequently, produced a higher serious stress concentration in the blend. This more complicated and instable morphology produced different double-yielding behaviors in the PC/HDPE/EVA blends compared with the binary one. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 287–294, 2008

Key words: blends; fibers; necking; polycarbonates; yielding

INTRODUCTION

Double-yielding behavior, featured by two stress maxima on the engineering or true stress–strain curve, has been observed in uniaxial tensile tests of polyethylene (PE) and the like[1–13] and, lately, in structurally different and immiscible polycarbonate (PC)/high-density polyethylene (HDPE) blends in our studies.[14–16] The mechanisms of the double yielding in these two categories of polymer materials are quite different due to their great structural differences. The double-yielding behavior of PE has long been investigated, and its mechanism is well established. The widely accepted mechanism proposed by Seguela and coworkers[17–20] is that the yielding behavior of PE is controlled by the shear and sliding of crystal blocks on the basis of the concept of the mosaic block structure[21] of crystalline lamellae. However, because the neat HDPE in our studies showed only one yielding point under the same processing and tensile conditions, the previously mentioned mechanism was not valid any more for the double-yielding behavior of the PC/HDPE blend. Additionally, the PC/HDPE blend with spherical PC particles presented typical single-yield-ing behavior like neat HDPE, whereas the blends with a certain content of PC fibers induced during mold filling in the subskin layer exhibited double-yielding behavior.[14] Therefore, we expected that the double yielding in the PC/HDPE blend was related to the PC fibers. It was the yielding of PC fibers that induced the second yielding, which was, to a great extent, supported by the observation that the PC fibers yielded and even broke at the second yielding point.[16] We discuss this further in the Discussion part of this article.

Because of the immiscibility between PC and HDPE, the compatibilization between PC and HDPE makes sense in the investigation of the morphological structure and properties and their relationship.[22,23] Ethylene–vinyl acetate copolymer (EVA) may serve as a compatibilizer of the PC/HDPE blend by reason of its possibilities of good compatibility with PE and ester exchange reaction with PC.[24] It is divinable that if the incorporation of EVA can change the morphology and structure of the PC/HDPE blend to some extent, it will, accordingly, give rise to differences in double-yielding behavior. This will, on the other hand, prove the validity of the suggested mechanism of double yielding in this kind of blend. In this study, we attempted to use EVA as a compatibilizer of the PC/HDPE blend and study the tensile deformation of the PC/HDPE/EVA blends, focusing on the presence of double-yielding behavior. The results were compared with a previous investigation on PC/HDPE blends.[16]

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The resins used in this study were HDPE, PC, and EVA. Their properties and characteristics have been summarized elsewhere.[14,25] Before use, PC and EVA were vacuum-dried to prevent their hydrolytic degradation for at least 6 h at 120°C for PC and at least 10 h at 50°C for EVA. PC, HDPE, and EVA were simultaneously added to a two-screw extruder and blended. The screw speed was 120 rpm, and the highest processing temperature was 270°C. The blends were injection-molded into the desired samples after drying. The detailed description of the sample preparation was summarized elsewhere.[14] There were five compositions of PC/HDPE/EVA blends in this study. We kept an invariable weight ratio of EVA to the amount of PC and HDPE at 1 : 10, and the weight ratios of PC to HDPE were 5/95, 7.5/92.5, 10/90, 15/85, 20/80, and 22.5/77.5. For the sake of brevity, the molded bars here are mentioned according to the weight ratio of PC and EVA; for example, the molded PC/HDPE/EVA blend bar with a weight ratio of 15/85/10 is denoted as PE15-10, and the molded PC/HDPE blend bar with a weight ratio of 15/85 is denoted as PE15. Note that when the weight ratio of PC and HDPE was the same for the PC/HDPE blend and its counterpart, the actual PC weight percentage in the PC/HDPE/EVA blend was slightly lower than that in the PC/HDPE blend. For example, PE15 had a PC content of 15 wt %, whereas PE15-10 had a PC content of 13.6 wt %.

The tensile test was performed at room temperature according to ASTM D 638 with dog-bone specimens. The crosshead speed was 50 mm/min. At least five samples were tested, and the representative stress–strain curve is presented. Morphological observation was carried out with a Jeol JSM-5900LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). The specimens were immersed in liquid nitrogen for about 30 min and then impact fractured to produce surfaces for morphological observation.

RESULTS

Stress–strain curves of the PC/HDPE/EVA blends

Figure 1 shows the engineering stress–strain curves of the PC/HDPE/EVA blends. It is clearly shown that the second yielding process took place only when the PC content was in a moderate range, and higher or lower PC contents made the blends exhibit only single yielding behavior. In other words, double yielding in the PC/HDPE/EVA blend was composition-dependent; this resembled the behavior in the PC/HDPE blend.[16] Nevertheless, the range of PC content in which double yielding occurred was
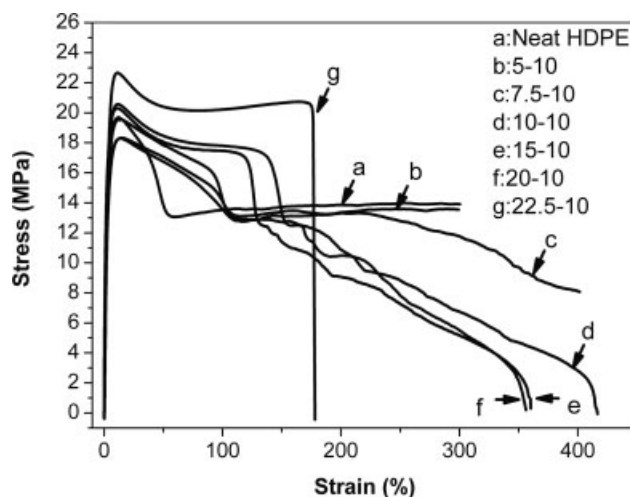

Figure 1 Representative engineering stress–strain curves of all of the PC/HDPE/EVA blends covered in this study at a crosshead speed of 50 mm/min.

somewhat different in these two blends, that is, from about 6.8 wt % (PE7.5-10) to 18.2 wt % (PE20-10) in the PC/HDPE/EVA blends and from 10 wt % (PE10) to 22.5 wt % (PE22.5) in the PC/HDPE blends.[16] Apparently, the incorporation of EVA shifted the PC content region of the double yielding to a lower one. Presumably, this tensile behavior should have been due to the changes in the morphology and structure of the blends as a result of the incorporation of EVA. In addition, the strain at the first yielding point in the blend did not vary with PC content and was nearly identical to that of neat HDPE (ca. 12%), although the strain at the second yielding point increased with PC content, from about 92% in PE7.5-10 to 134% in PE20-10. As for the mechanical properties, the yielding strength increased with PC content from 18.3 MPa in PE5-10 to 22.6 MPa in PE22.5-10; this indicated that the PC phase, especially the injection-induced PC fiber, was an effective reinforcement to the HDPE matrix. The reinforcement became effective through high-interface compressive stress between the HDPE matrix and the PC phase.[14–16,26,27] During cooling after mold filling, HDPE shrank more than the dispersed PC phase due to its crystallization contraction,[28–30] which resulted in a high compressive stress between the PC fibers and the matrix. The transverse contraction of the sample during extension also contributed to the compressive stress at the interfaces. Simultaneously, a relative motion (at early stretching due to the incompatible nature between the PC fibers and the matrix) or relative motion trend (during subsequent stretching due to higher compressive stress) existed.[14] In this case, the PC fibers were imposed on the tension stress (σ) during stretching; that is, the PC fibers shared the applied stress partially and,
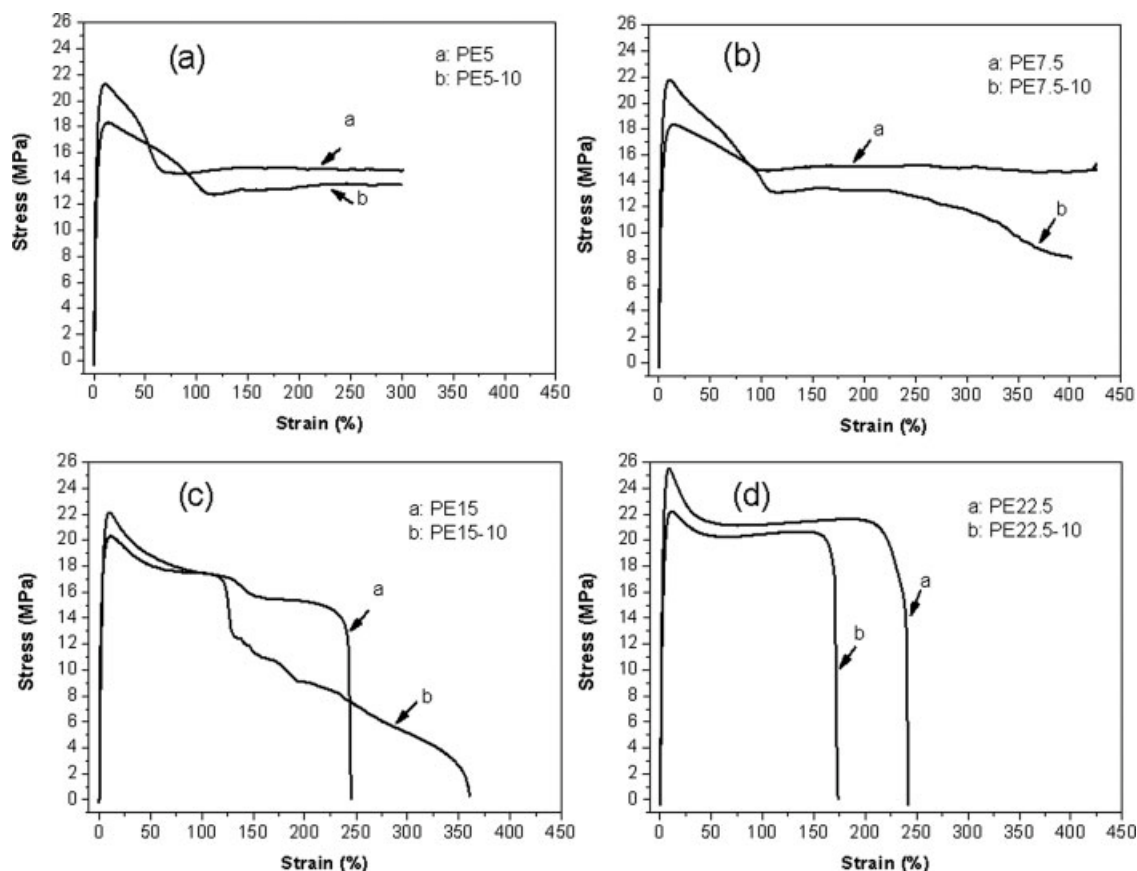
Figure 2 Comparison of the engineering stress–strain curves between the PC/HDPE/EVA and PC/HDPE blends with the same weight ratios of PC to HDPE: (a) PE5 and PE5-10, (b) PE7.5 and PE7.5-10, (c) PE15 and PE15-10, and (d) PE22.5 and PE22.5-10.

thus, reinforced the matrix. The total strain presented the opposite trend with PC content. Neat HDPE, PE5-10, and PE7.5-10 did not show the ultimate rupture due to the limit of the distance between two crossheads, whereas PE22.5-10 showed a brittle failure manner with a total strain of about 177%. These results were attributed to more flaws and more serious stress concentration in the blends with higher PC contents because increasing the PC content tended to generate larger and possibly more irregular PC particles that served as stress concentration points.[16]

Unstable deformation of the PC/HDPE/EVA blend

Figure 2 shows the engineering stress–strain curves of the PC/HDPE/EVA and PC/HDPE blends (only the representative curves are displayed here). For these PC/HDPE/EVA blends showing double-yielding behavior, the stress gradually decreased with strain after the second yielding until complete failure of the sample was reached, whereas for the PC/HDPE blends, there was a flat region. Macroscopically, after the second yielding point, the PC/

HDPE/EVA samples delaminated from the exterior to the interior when stretched, as shown in Figure 3. The stress decreased after the rupture of each layer,
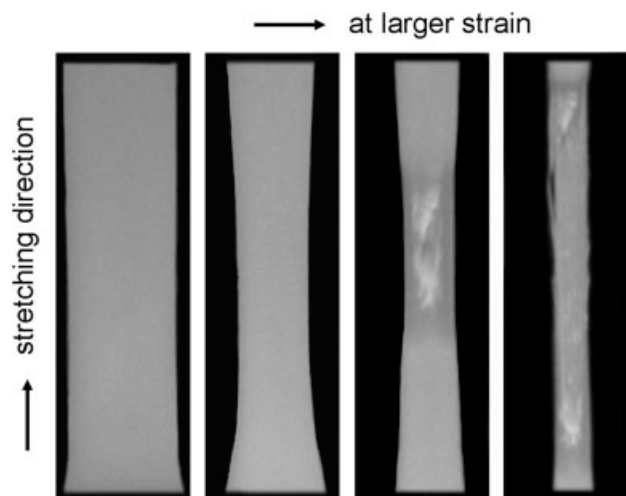

Figure 3 Digital photos of the partial macroscopic deformation process of PE20-10.
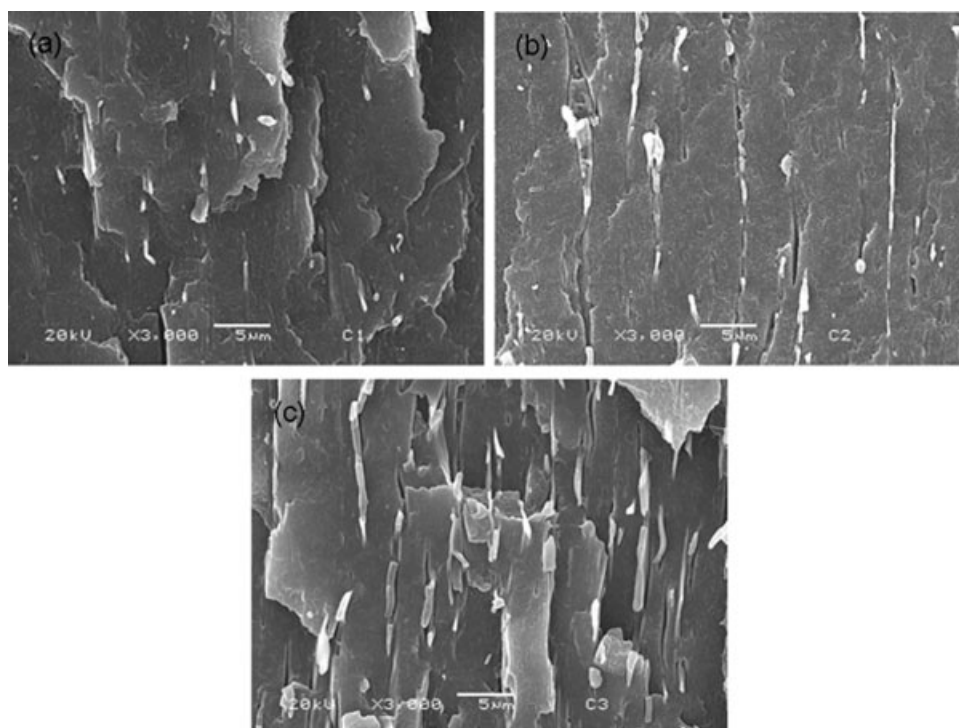
Figure 4 SEM micrographs of the subskin layers of (a) PE7.5-10, (b) PE15-10, and (c) PE22.5-10.

which resulted in a gradual stress drop in the stress–strain curve. The unstable deformation implied that EVA did not produce a good compatible effect on PC and HDPE and led to the earlier rupture of PE22.5-10 [see Fig. 2(d)]. In addition, the lower tension strength of the PC/HDPE/EVA blend was due to the lower strength and modulus of EVA compared to those of HDPE.

Morphology of the EVA/HDPE and PC/HDPE/EVA blends

Figure 4 displays scanning electron microscopy (SEM) micrographs of the subskin layers of PE7.5-10, PE15-10, and PE22.5-10. Note that the fracture surfaces were parallel to the direction of mold flow. There existed a large amount of irregular or broken PC fibers in the fracture surfaces. This was attributed to unstable flow with strong shear during mold filling due to the complicated phase morphology of the PC/HDPE/EVA blend because it was impossible that the operation of the fabricating fracture surface for SEM observation allowed so many PC fibers to be broken. In addition, the clearly observed interfaces in Figure 4 indicated that the incorporation of EVA seemed not to be very effective on improving the compatibility between the HDPE matrix and the PC phase. Figure 5 presents the SEM micrographs of the core and subskin layers of PE7.5 and PE7.5-10,

from which one can observe that both the diameters of the PC particles in the core layers and the PC fibers in the subskin layers were larger in PE7.5-10. The statistic sizes are listed in Table I.

DISCUSSION

Mechanism of double yielding in the PC/HDPE/EVA blends

We considered that the first yielding of the PC/HDPE/EVA blend was contributed by the yielding of HDPE matrix.[14–16] This was supported at least by two pieces of evidence. One was that the first yielding of all of the PC/HDPE/EVA samples with various PC contents began almost at the same strain as that of neat HDPE (ca. 12%), as shown in Figure 1. The other consisted of the fact that the first yielding stress of the PC/HDPE/EVA samples (<25 MPa) was fairly comparable with that of neat HDPE (ca. 20 MPa) but much lower than that of neat PC (ca. 80 MPa).

The second yielding point of the PC/HDPE/EVA blend, according to the experimental observations, indicated the onset of sharp necking of the samples, which generally led to an engineering stress drop, as observed in the double-yielding behavior of PE. In other words, the second yielding of the PC/HDPE/EVA blend was geometric. Furthermore, according to a previous investigation,[16] the mold-filling-
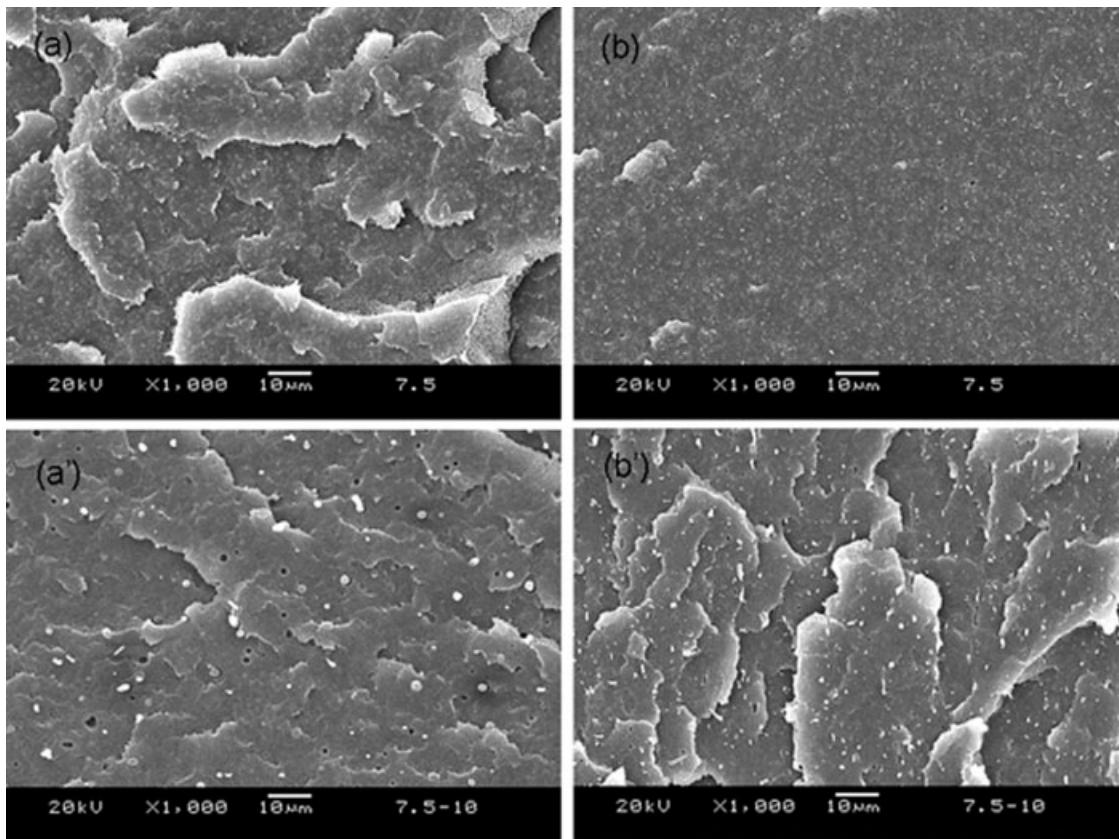
Figure 5 SEM micrographs of the PE7.5 and PE7.5-10 blends: (a) core and (b) subskin layers of PE7.5 and (a′) core and (b′) subskin layers of PE7.5-10.

induced PC fibers will yield at the strain nearby the second yielding point. We, therefore, concluded that the second yielding in the PC/HDPE/EVA blend was actually an engineering stress-drop process contributed by the sharp necking of the sample, which must have been tightly related to the PC fiber yielding. Then, how sample necking and PC fiber yielding interact was an important issue in the interpretation of double yielding in the PC/HDPE/EVA blend. It was the yielding of the PC fibers that induced the onset of macroscopic sample necking, which formed the second yielding process.

Then, what is the reason that PC fibers made the yielding of HDPE matrix and sample necking separate with a strain span of 100%; that is, how did they delay the necking of the PC/HDPE/EVA blend considerably compared with that of neat HDPE?

According to the results of a series of studies by Strobl and coworkers,[31–33] the activation of a special lamellar deformation during tensile deformation, including a heterogeneous slip process that results in necking, will happen at an invariable strain for a semicrystalline polymer, such as HDPE, despite the crystallinity, temperature, strain rate, and crystalline thickness. In this connection, the heterogeneous slip

of crystal blocks in the HDPE matrix would have occurred when the PC/HDPE/EVA blend bar was stretched to the strain near which neat HDPE began to neck. This was because the characteristics of most crystalline and amorphous regions in the HDPE matrix would not change too much, when one considers that only the regions close to the PC fibers would be affected. However, the sharp necking of the sample could not form at this strain for the blend. The potential reason was that the existence of numerous PC fibers with high strengths and large aspect ratios (L/D's) suppressed the sharp narrowing of the sample. Obviously, this suppression effect did not disap-

TABLE I
Statistical Average Diameters of the PC Particles in the Core Layers and the PC Fibers in the Subskin Layers in PE7.5 and PE7.5-10

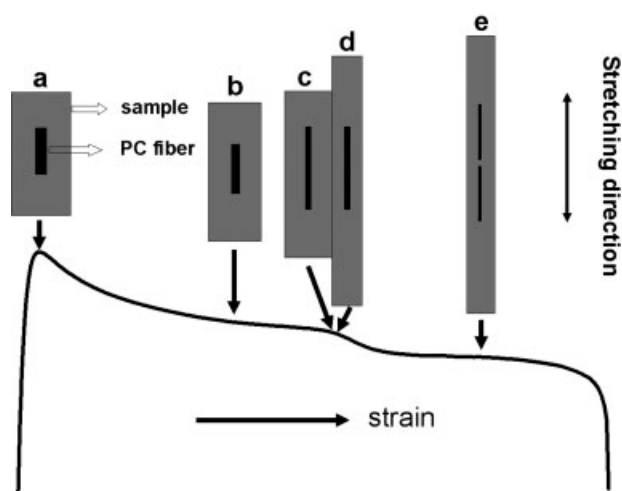| Sample	Average diameter of the PC particles in the core layer (μm)	Average diameter of the PC fibers in the subskin layer (μm)
PE7.5	0.6	0.25
PE7.5-10	1.8	0.5

Figure 6 Schematic representation of the microscopic deformation of the PC fibers with straining in the injection-molded PC/PE or PC/HDPE/EVA blend: (a) at the first yielding point, (b) between the two yielding points, (c) at the point at which the PC fibers yielded, (d) at the point at which the sample necking began (at the second yielding point), and (e) after the second yielding point.

pear until the strain reaches the value at which the PC fibers yielded. The force making the PC fibers yield came from σ at the interface between PC and HDPE, as mentioned previously. The marked necking formed immediately after the yielding of the PC fibers. Therefore, we observed a large strain span between the two yielding points in the PC/HDPE/EVA blend. The interfacial slip during tensile deformation went against the stress transfer and yielding of the PC fiber, with the consideration that the static friction stress was greater that the dynamic friction stress. This was another factor that made the second yielding lag very much behind the first yielding.

How the deformation of PC fibers was correlated to the double-yielding behavior is schematically represented in Figure 6. When stretched to the strain at which neat HDPE began to yield, the blend showed the first yielding. Up to this point, the PC fibers received low σ and had little or no deformation because a slight interfacial slip may have taken place at the interfaces between the PC fiber and matrix due to the nature of compatibility. Between the two yielding points, the PC fibers were imposed on higher σ and deformed to some extent because of the higher compressive stress and the relative motion trend at the interfaces. The stress increased with strain but was still not enough for the yielding of the PC fibers. When the strain was at the second yielding, the PC fibers could not endure the stress any more and yielded. This resulted in the disappearance of the suppression of the PC fibers to sharp necking, which quickly formed subsequently.

With further stretching, the PC fibers underwent a larger deformation and a final failure.

The EVA phase (discussed later) may have also deformed and yielded before the second yielding of the blend. However, this should not have contributed a perceptible influence on the stress–strain behavior because of the low content and low strength of EVA itself.

The PC/HDPE/EVA and PC/HDPE blends had a similar PC microfibrillar morphology, deformation characteristic up to the second yielding point, and similar composition dependence characteristics of double yielding. We, therefore, suggest that the PC/HDPE blend should obey the identical mechanism of double-yielding behavior existing in the PC/HDPE/EVA blend. We proposed in a previous work that the second yielding was attributed to the yielding of the PC phase.[16] However, this proposition should be corrected in view of the fact that sample necking was not taken into account. In fact, according to the definition of yielding in our case, the second yielding was a process of engineering stress drop and was mainly contributed by the sharp sample necking. The yielding of the PC fibers was actually an inducement of the formation of this lagged necking, which was responsible for the second yielding. The modified mechanism explains the observed double-yielding behavior in both the PC/HDPE/EVA and PC/HDPE blends.

Effect of the PC content on the strain at the second yielding point

As shown in the stress–strain curves in Figure 1, the strain at the second yielding point increased with PC content. This was a combined result of two factors. First, the higher PC content apparently meant more PC fibers; accordingly, the suppression to sharp sample necking by the PC fibers was stronger after the heterogeneous slip of crystal blocks, which resulted in the necking of neat HDPE. Second, the higher PC content meant a larger diameter of PC fibers, and quite possibly, L/D was smaller.[16] The tension stress imposed on the PC fiber (σ_f) during stretching could be estimated with eq. (1)[16]:

$$\sigma_f = 4\mu\sigma L/D \qquad (1)$$

where μ represents the friction factor at the interfaces between the PC fibers and HDPE and σ is the interfacial compressive stress. From eq. (1), one can easily understand that for PC fibers with smaller L/D, larger strain was required to make enough compressive stress and σ for the yielding of PC fibers, as well as the sharp necking of the sample or the second yielding.

Composition dependence of double yielding for the PC/HDPE and PC/HDPE/EVA blends

Compared with the PC/HDPE blend, the PC content region in which double yielding existed in the PC/HDPE/EVA blend shifted to a lower one. At a low PC content, PE7.5 showed a single yielding point, whereas PE7.5-10 showed double yielding points. At a high PC content, however, PE22.5 and PE22.5-10 showed double- and single-yielding behaviors, respectively. Clearly, the morphological change of the PC fibers resulting from the incorporation of EVA was the key factor in the difference of composition dependence characteristics of double yielding because the second yielding process was directly related to the PC fibers. As shown in Table I, the average diameters of the PC fibers of PE7.5 and PE7.5-10 in the subskin layers were 0.25 and 0.50 μm, respectively. The larger diameter of PC fibers in the PC/HDPE/EVA blend was attributable to the effect of the addition of EVA on the viscosity of the matrix of the blend. The torque values of HDPE and HDPE/EVA (90/10 w/w) were 0.053 and 0.041 Nm at 270°C (our processing temperature), respectively. That is, the PC/HDPE/EVA blend had a larger viscosity ratio (the ratio of the viscosity of the dispersed phase to that of the matrix) than the PC/HDPE blend. This went against the formation of good fiber-like morphology of the PC domain in the PC/HDPE/EVA blend due to the lower shear stress imposed on melting PC particles during mold filling. So, the PC/HDPE/EVA blend should have had a larger diameter and smaller L/D of PC fibers compared with the PC/HDPE blend. In this case, the yielding of PC fibers in PE7.5-10 became more difficult in terms of eq. (1), and the suppression of the sample necking by the PC fibers was accordingly more effective. This led to the separation of matrix's yielding and sample necking, which formed two discernable engineering stress-drop processes (double yielding). For PE7.5, in despite of more PC fibers, the much smaller diameter and larger L/D allowed the PC fibers to receive higher stress and yield more easily in early deformation, maybe just after the yielding of the HDPE matrix. Thus, the suppression of sample necking by the PC fibers in PE7.5 was very weak, and PE7.5 showed single-yielding behavior. At a very high PC contents, the HDPE matrix had a lower volume fraction and a more serious stress concentration due to its incompatible nature, compared with the blend with a low PC content,[16] and thus was apt to destruct after necking. PE22.5-10 had a lower actual HDPE matrix content of 70 wt % (77.5 wt % in PE22.5), more flaws, and a more serious stress concentration because of its more complicated phase morphology compared with that of PE22.5. This intensified the destructibility of the HDPE matrix, and the sample broke up immediately after necking. Relatively, PE22.5 had a higher HDPE content and a more regular phase morphology. After necking, the sample could still be elongated to some extent, which showed the cognizable second yielding point, although the strain was very short.

CONCLUSIONS

We compared the double-yielding behavior of the PC/HDPE/EVA blend with the PC/HDPE blend. The common mechanism of double-yielding behavior in this kind of incompatible blend was further illustrated. The yielding of dispersed PC fibers resulted in the formation of sample necking, which was responsible for the second yielding. The addition of EVA into the PC/HDPE blend changed the double-yielding behavior of the blend through changes in the morphology and structure.

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