Structure and Properties of Polypropylene/High-Density Polyethylene Blends by Solid Equal Channel Angular Extrusion

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ABSTRACT: The solid equal channel angular extrusion (ECAE) process on polypropylene (PP)/high-density polyethylene (HDPE) blends was carried out. Scanning electron microscopy (SEM) was used to observe the sample structures. Results showed that ECAE process could make PP/HDPE blends to produce orientation structure. Impact performance of ECAE-PP/HDPE samples after ECAE process improved remarkably, especially for ECAE-PP/HDPE (90/10)-O whose impact strength reached 91.91 kJ/m^2, 18.1 times higher than that of pure PP and 11.2 times higher than that of PP/HDPE (90/10). The mechanism of enhancing between HDPE and PP was discussed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39759.

INTRODUCTION

Polypropylene (PP) and polyethylene (PE) are two major polymers in modern industry. PE has excellent properties in processing and low temperature impact resistance, while PP has good rigidity and heat resistance. In theory, blends of PE and PP in different proportions can obtain different required properties. However, due to a big discrepancy between PE and PP in melting temperature, PE and PP still have poor miscibility. Normally, blends with phase separation display poor physical and mechanical properties. In order to improve compatibility and performance of PP/PE blends, extensive researches have been reported.[1–6] Methods included the use of compatibilizer, chemical grafting, coupling, or physical modification etc.

Equal channel angular extrusion (ECAE) is a newly developed technique for processing solid polymer materials.[7–13] Cross-section of specimen remains constant during ECAE process, which is different from other polymer solid state processing method.[14] This processing method consists of extruding a specimen through a die with two channels of equal cross-section. A huge shearing force occurs at the crossing plane of two channels, leading to plastic deformation. Because the cross-section of solid processed specimen remains constant, the solid extrusion of the specimen can be processed repeatedly. We have reported the structure change of polypropylene/organic montmorillonite composites by ECAE processes.[15] Experimental results showed that both PP spherulites and OMMT particles were significantly deformed and orientated toward the shearing direction, and OMMT agglomeration particles were broken into needle-like primary particles, some even exfoliated into nanosilicate layers after twice ECAE processes due to the immense solid shear force. In this article, we reported the first use of ECAE processing on PP/HDPE blends based upon the previous work, and investigated the effect of ECAE process on structure and properties of PP/HDPE blends. Our research indicated that huge shearing force could not only orient PP/HDPE blends but also improve compatibility and performance.

EXPERIMENTAL

Materials
Polypropylene (PP) F401 was provided by Sinopec$^{\text{TM}}$ with melt flow index of 2.5 g/10 min. High-density polyethylene (HDPE) No.6098 was provide by QPEC$^{\text{TM}}$ with melt flow index of 10.0 g/10 min.

Specimen Preparation
PP and HDPE were blended in different proportions (90/10, 70/30/, 50/50) by open mill at 180°. The molten mixture was compressed into a 150 mm × 125 mm × 10 mm plate specimen mold and cooled down to the room temperature. PP/HDPE specimen plates were prepared and cut into specimen bars with cross-sections of 25 × 10 mm^2.
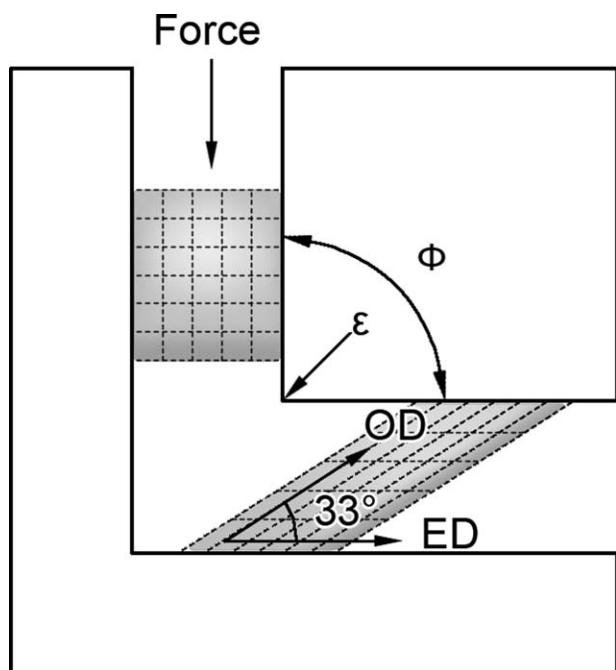
Figure 1. Schematic illustration of ECAE process.

Solid Equal Channel Angular Extrusion (ECAE)

ECAE process was schematically shown in Figure 1. An internal angle of 90° between two channels with cross-section dimensions of 25 × 10 mm² was adopted. When a specimen passes through the ECAE die, the plastic shear strain assigned to the specimen can be given by the following theoretical expression[16]:

$$\varepsilon = \frac{2}{\sqrt{3}} \cot\left(\frac{\varphi}{2}\right) \tag{1}$$

In our case, $\varphi = 90°$, eq. (1) gives a plastic shear strain $\varepsilon = 1.15$.

Solid extrusion was conducted at room temperature (about 25°C) with constant ram speed of 2 mm/min. Because ECAE processing speed was very slow, PP/HDPE specimen had little temperature change when processing through ECAE channel. When the ram speed was 2 mm/min, temperature and external force change of PP/HDPE specimen are shown in Figure 2. ECAE process would make specimen to produce orientation due to shearing force, in our case the angle of orientation direction(OD) and extrusion direction(ED) was 33° (Figure 1).

Characterizations

Surface morphology of PP/HDPE blend was observed with a JSM-5910 scanning electron microscope (SEM). Before observation, samples were treated with etching agent[17,18] (a solution of KMnO$_4$, 1.3 wt %; H$_2$SO$_4$, 65.8 wt %; H$_3$PO$_4$, 32.9 wt %) for 24 h, then washed out the etching agent thoroughly with H$_2$O$_2$ and H$_2$O, dried at room temperature and sputter-coated with gold. Impact fracture surface of PP/HDPE blends was directly observed by SEM.

Notch impact strength tests were carried out by UJ-4 Izod impact equipment (China). Notch impact strength values were obtained by the following formula (2):
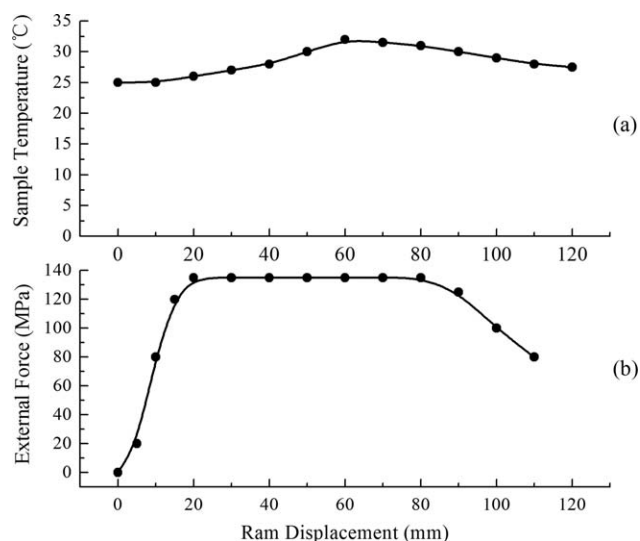

Figure 2. (a) Temperature change and (b) external force change of PP/HDPE specimen in ECAE process.

$$\sigma = \frac{A}{bd} \tag{2}$$

A: loss of energy of specimen (J), b: width of specimen (m), d: thickness on the cross-sectional area of specimen (m). In our case, the impact strength is the average of five samples.

Notch impact test specimens after ECAE process respectively were cut along extrusion direction (ED, signed ECAE–PP/HDPE-E), and along orientation direction (OD, signed ECAE–PP/HDPE-O, at 33° angle to extrusion direction), as shown in Figure 3.

RESULTS AND DISCUSSION

Effect of ECAE Process on the Morphology of PP/HDPE Blends

Specimens were etched with mixed acid and observed by SEM in order to examine influence of ECAE process on the morphology of PP/HDPE blends. Figure 4(b), (d), and (f) showed HDPE became aligned and oriented in PP after ECAE process compared with structures before extrusion [Figure 4(a,c,e)]. Phase contact area between PP and HDPE increased and contacted closer, especially in ECAE-PP/HDPE (90/10) specimen. The orientation of HDPE can be clearly observed in Figure 4(g).

Effect of ECAE Process on the Impact Property of PP/HDPE Blends

The blends after ECAE process show anisotropy. In order to explore the impact property of anisotropic blends, notched impact specimens were prepared as shown in Figure 3.
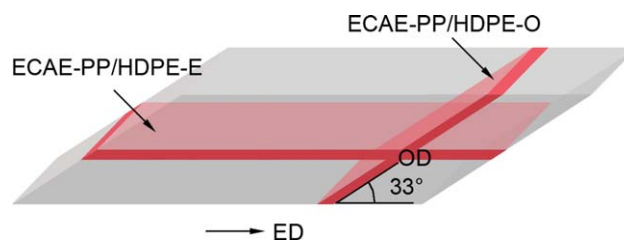

Figure 3. Schematic of impact test specimen cut after ECAE process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
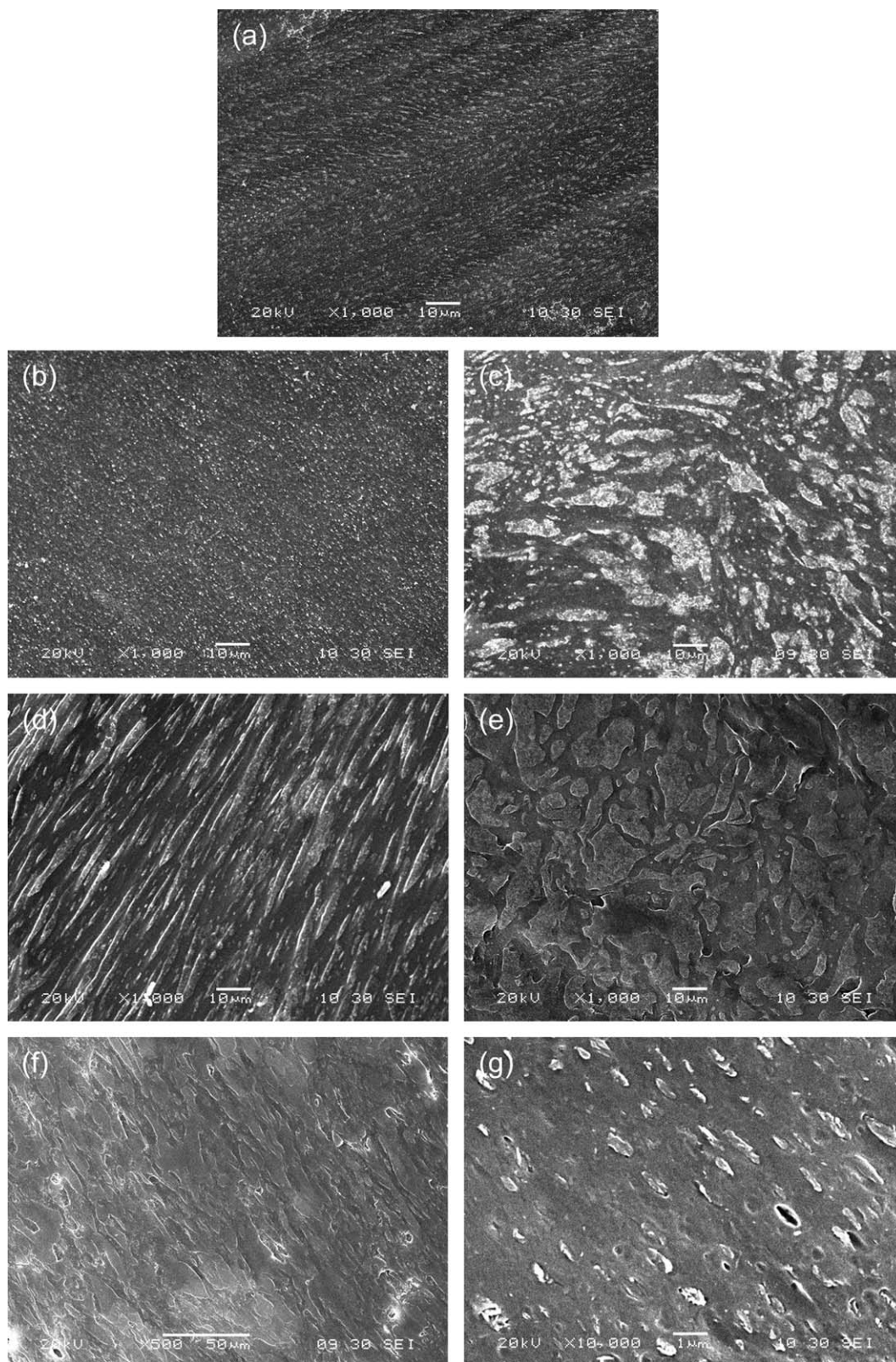
Figure 4. SEM images of PP/HDPE and ECAE-PP/HDPE specimen (a) PP/HDPE(90/10), (b) ECAE-PP/HDPE(90/10), (c) PP/HDPE(70/30), (d) ECAE-PP/HDPE(70/30), (e) PP/HDPE(50/50), (f) ECAE-PP/HDPE(50/50), and (g) ECAE-PP/HDPE(90/10).

Table I. Impact Strength of PP/HDPE Composites Before and After ECAE Process

	Impact strength (kJ/m^2)		Impact strength (kJ/m^2)
PP	4.8 ± 0.1	ECAE-PP-E	13.2 ± 1
		ECAE-PP-O	48.8 ± 1
PP/HDPE(90/10)	7.5 ± 0.2	ECAE-PP/HDPE(90/10)-E	17.8 ± 1
		ECAE-PP/HDPE(90/10)-O	91.9 ± 4
PP/HDPE(70/30)	6.4 ± 0.2	ECAE-PP/HDPE(70/30)-E	9.0 ± 1
		ECAE-PP/HDPE(70/30)-O	31.5 ± 3
PP/HDPE(50/50)	4.8 ± 0.2	ECAE-PP/HDPE(50/50)-E	6.3 ± 1
		ECAE-PP/HDPE(50/50)-O	26.8 ± 2

Impact test results were shown in Table I. When adding HDPE to PP, impact strength of PP/HDPE blends increased first, compared with pure PP, and declined later along with increasing amount of HDPE. PP/HDPE blend with 10% HDPE showed the best impact strength performance, which indicated HDPE was a toughening agent for PP in certain dosage range. This is because the addition of HDPE refined PP spherulites, which contributed to improve the impact strength of PP/HDPE.[19–21] Nonetheless, excess HDPE can cause phase separation with PP, resulting in decrease of impact strength of PP/HDPE. After ECAE process, impact strength of ECAE-PP/HDPE improved remarkably. Dispersion and orientation of HDPE in PP lead to high impact performance. According to polymer toughening theory,[22] dispersed phase in blends can terminate the crack growth in brittle matrix. The best size of dispersed phase is around 0.5 μm. Results from Figure 4(a,b) indicated the sizes of dispersed phase of HDPE in PP/HDPE (90/10) and ECAE-PP/HDPE (90/10) were around 0.5 μm. Meanwhile HDPE phase was oriented in ECAE-PP/HDPE (90/10) [Figure 4(g)] after ECAE process, whose shape changed from particle to long strip, largely increased the contact area between HDPE and PP. The increased bonding strength between HDPE and PP led to the improvement of HDPE and PP compatibility. Therefore, the impact performance of PP/HDPE (90/10) and ECAE-PP/HDPE(90/10) increased.

SEM photographs of impact fracture surfaces of PP/HDPE and ECAE-PP/HDPE-E with different addition amount of HDPE were shown in Figure 5. Impact fracture surfaces of PP/HDPE(90/10) [Figure 5(a)] showed HDPE uniformity dispersed in PP matrix in form of particles with a size of about 0.5 μm and no obvious cavities in dispersed phase, indicating a certain degree of bonding strength between HDPE and PP. On the other hand, impact fracture surface of PP/HDPE (90/10) was uneven but smooth, revealing that it was a quasi-ductile fracture surface. Therefore, the impact strength of PP/HDPE (90/10) blend improved slightly than pure PP. After ECAE process, impact fracture surface of ECAE-PP/HDPE (90/10)-E [Figure 5(b)] showed textures of fracture surface were delicate. HDPE dispersed phase formed fibrous structure which firmly anchored in PP matrix and became reinforced phase, no cavitation between PP and HDPE. These characteristic illustrated the impact fracture was a kind of ductile fracture. A lot of impact

energy could be consumed by the blends during impact process, showing a good impact resistance.

Impact fracture surface of PP/HDPE(70/30) [Figure 5(c)] showed the size of dispersed phase was about 10.0 μm. Oversize dispersed phase led to stress concentration and interface damage, causing a loss of impact strength of blends. Although ECAE process led to PE orientation and improved the interface bonding strength between PP and HDPE, cavitation produced by oriented HDPE sticks in impact process could be observed [Figure 5(d)], which is the main reason for unobvious impact resistance improvement.

For PP/HDPE (50/50) [Figure 5(e)], HDPE and PP formed co-continuous phase. Slice fracture characteristics were observed because of incompatible component striped off smoothly, leading to further performance deterioration. Even after ECAE process, specimen ECAE-PP/HDPE (50/50)-E [Figure 5(f)] formed oriented structure, but phase separation still greatly reduced the impact resistance. Despite these, ECAE-PP/HDPE (50/50)-E showed better impact resistance than that of pure PP, indicating ECAE played an important role in enhancing material property.

ECAE-PP/HDPE-O specimen formed different notch impacted fractures in the impact test (Figure 6). After ECAE process, impact strength of ECAE-PP/HDPE-O improved remarkably, especially the impact strength of ECAE-PP/HDPE (90/10)-O, which reached 91.91 kJ/m^2, 18.1 times higher than that of pure PP and 11.2 times higher than that of PP/HDPE (90/10) (Table I). Such a high impact resistance was mainly derived from the oriented arrangement of molecules in ECAE-PP/HDPE-O specimen. In the notch of ECAE-PP/HDPE-O specimen, molecular orientation was perpendicular to the direction of the notch. When impact force acted on the notch and went forward along the notch direction, the oriented molecules resisted the impact force and made the direction of impact force deflect, causing the stress scatter. Z-shaped fracture pattern could be observed from Figure 6, proving the stress was deflected and dispersed by the oriented molecules. When a small amount of HDPE and PP were blended, the dispersed phase of uniformly distributed small HDPE could play an effect of toughening PP. Because while the dispersed phases cause stress concentration and produce the micro-cracks (crazing), they also prevent micro-cracks from further development in the matrix. The stress whitening phenomenon is a macro expression of a large number of micro-
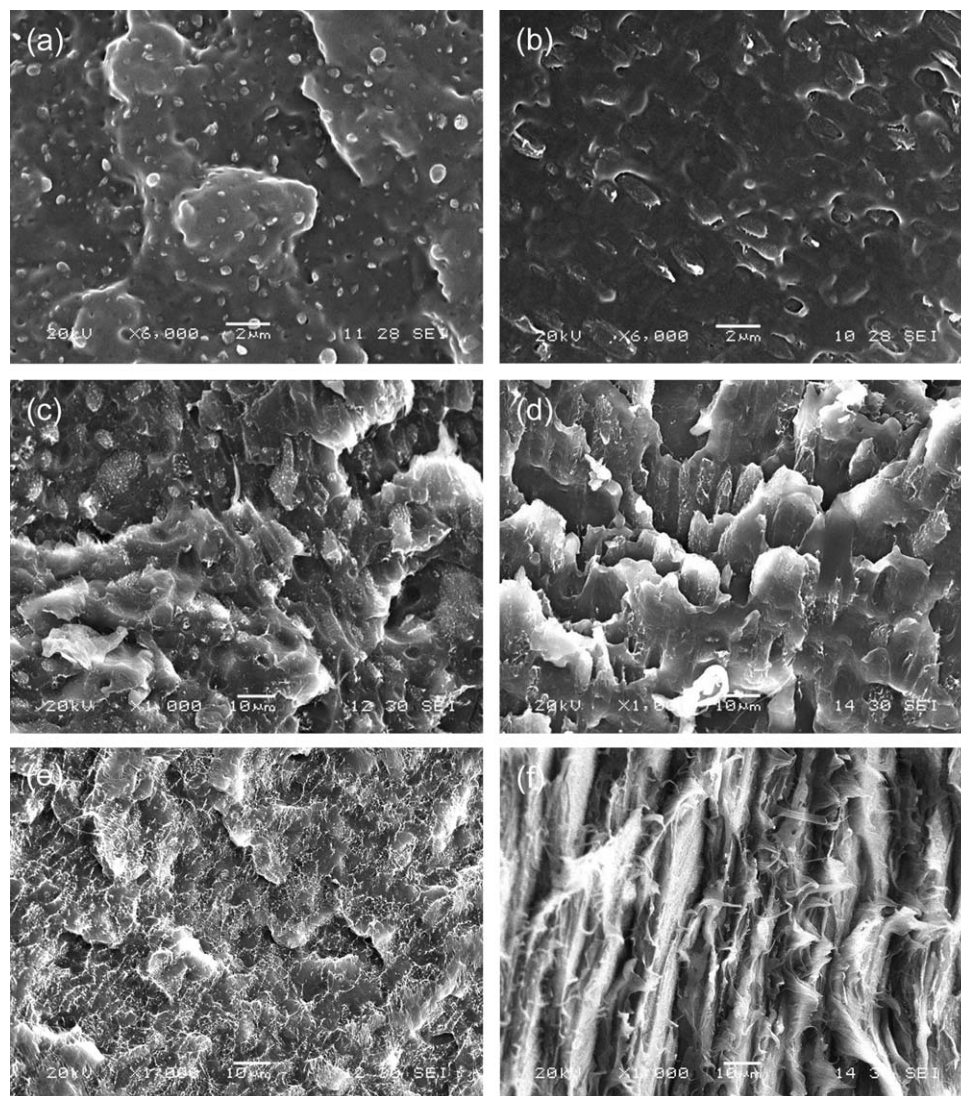
Figure 5. SEM of impact fracture surface of PP/HDPE and ECAE-PP/HDPE-E specimen (a) PP/HDPE (90/10), (b) ECAE-PP/HDPE (90/10)-E, (c) PP/HDPE (70/30), (d) ECAE-PP/HDPE (70/30)-E, (e) PP/HDPE (50/50), and (f) ECAE-PP/HDPE (50/50)-E.

cracks. A short Z-shaped crack and stress whitening zone near the crack were observed in ECAE-PP/HDPE (90/10)-O [Figure 6(a)]. It was a large number of micro-cracks formed in the stress whitening zone which could absorb massive impact energy that resulting in great improvement in impact resistance of ECAE-PP/HDPE (90/10)-O.

ECAE-PP/HDPE (50/50)-O formed larger Z-shaped crack than that of ECAE-PP/HDPE (70/30)-O due to the higher HDPE content. Bigger dispersed phase led to larger Z-shaped crack. This macroscopic phase separation blends could not effectively form micro-cracks in PP matrix, therefore presented lower impact strength.
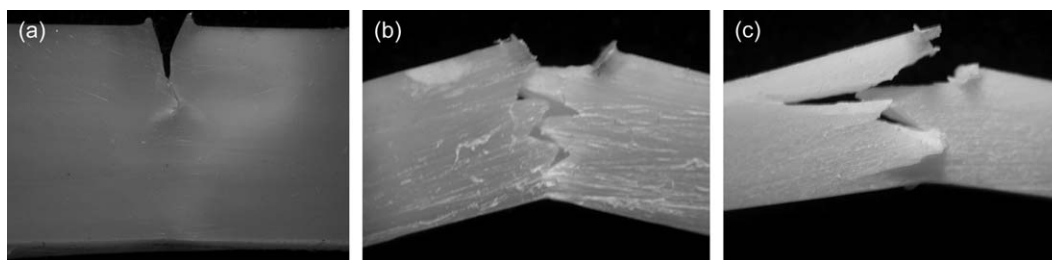

Figure 6. Photographs of notched impact fracture of ECAE-PP/HDPE-O specimen (a) ECAE-PP/HDPE(90/10)-O, (b) ECAE-PP/HDPE(70/30)-O, and (c) ECAE-PP/HDPE(50/50)-O.

CONCLUSION

Solid state ECAE process can make PP/HDPE blends to produce orientation structures by huge shearing force. Impact performance of ECAE-PP/HDPE specimens after ECAE process improved remarkably, especially for ECAE-PP/HDPE (90/10)-O specimen whose impact strength reached 91.91 kJ/m^2, 18.1 times higher than that of pure PP and 11.2 times higher than that of PP/HDPE (90/10). Such a high impact resistance was mainly derived from the oriented arrangement of molecules in ECAE-PP/HDPE (90/10)-O specimen, which could deflect the direction of impact force. Small HDPE uniformly distributed to form dispersed phase, which terminated the crack growth in brittle matrix, causing the stress scatter, producing the microcracks (crazing) and absorbing massive impact energy.

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