Impact Fracture Behavior of Molecularly Orientated Polycarbonate Sheets

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ABSTRACT: The impact fracture behavior of molecularly orientated polycarbonate (PC) sheets was investigated. The molecular orientation was achieved via a newly developed equal channel angular extrusion (ECAE) process. Improvement in impact fracture propagation resistance was observed in the ECAE processed PC sheets. The improved impact resistance was found to be directly related to the changes in molecular orientation because of ECAE. The unique characteristics of the ECAE process for polymer extrusion are described. The potential benefits of ECAE in enhancing physical and mechanical properties of the extruded PC sheets are discussed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2060–2066, 2001

Key words: impact resistance; equal channel angular extrusion; molecular orientation; polycarbonate; anisotropy

INTRODUCTION

Impact fracture strength is one of the most important properties for engineering applications of polymers. However, because of the lack of fundamental knowledge on impact fracture behavior in polymers, there is no well-established fundamental structure-property relationship available for making impact-resistant polymers. As a result, trial-and-error has been the main methodology for actual material and product designs to improve impact strength of polymers. Most of the work published in this field has focused on molecularly isotropic systems.[1–8] There is little knowledge on how molecular orientation affects the impact fracture behavior in polymers. It is unclear whether or not molecular orientation can help resist impact fracture in polymers. Hence, it would be desirable to probe the impact fracture behavior in molecularly orientated polymers.

Polycarbonate (PC) is one of the most widely utilized engineering polymers. Knowledge on the physical and mechanical properties of PC and PC blends is well documented.[9–12] Nevertheless, the impact fracture behavior in molecularly orientated PC has not been thoroughly investigated.[1–8] Until now, most of the studies have been limited to the cold-rolled or injection molded systems.[13,14] The studies mentioned above indicate that impact strength is high only if the crack propagation direction is normal to the molecular orientation direction.[13–18] Because these results were generally based on the notched Izod or Charpy impact tests, they do not correlate well with the basic

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mechanical properties. Conflicting and confusing results are usually observed.[18] Another uncertainty with the above research is that cold rolling and injection molding cannot produce uniformly controlled molecular orientation across the thickness of the specimen. This contributes to the difficulties in precise analysis and proper interpretation of the findings.

The novel equal channel angular extrusion (ECAE) process has been shown to be capable of inducing molecular orientation in bulk polymers.[19–23] After ECAE, a uniform, through-thickness molecular orientation can be achieved in the extrudate.[24–26] The ECAE-induced molecular orientation has been shown to significantly improve the quasi-static fracture toughness of PC in both the flow and transverse directions.[19]

The focus for the present study was understanding the impact fracture behavior of ECAE-orientated PC sheets. The PC sheets were processed via two typical ECAE processing routes: route-A and route-C. In route-A, the sample is processed on the same billet orientation at each successive ECAE pass (Fig. 1). As a result, the orientation of the molecular chains is accumulated with each additional pass. This processing route will lead to a high level of molecular orientation in the extrudate. The drawback of the route-A ECAE process is the creation of weak planes parallel to the molecular orientation direction.[26] In route-C, the sample is rotated by 180° around its axis at each even-numbered pass. Polymer chains are oriented at each odd-numbered pass. Reversed molecular orientation will be created at each even-numbered pass. The primary benefit of route-C ECAE is that microscopic molecular orientation is accumulated inside the extrudate, whereas the macroscopic orientation is restored upon each even-numbered pass. As a result, the extrudate ductility can be maintained.

The purpose of this report was to understand how the ECAE-induced molecular anisotropy affects the impact fracture behavior of PC. The impact fracture behaviors of route-A one-pass (A-1) and route-C two-pass (C-2) ECAE-orientated PC sheets were studied using the instrumented falling weight dart impact test and the ballistic impact test. Because there are no precracks involved in the materials, the falling dart impact and ballistic impact tests can detect any possible off-axis weak planes in the sample.[27] It is hoped that the fundamental understanding of how the ECAE-induced molecular anisotropy influences the impact fracture behavior in PC can be gained. The

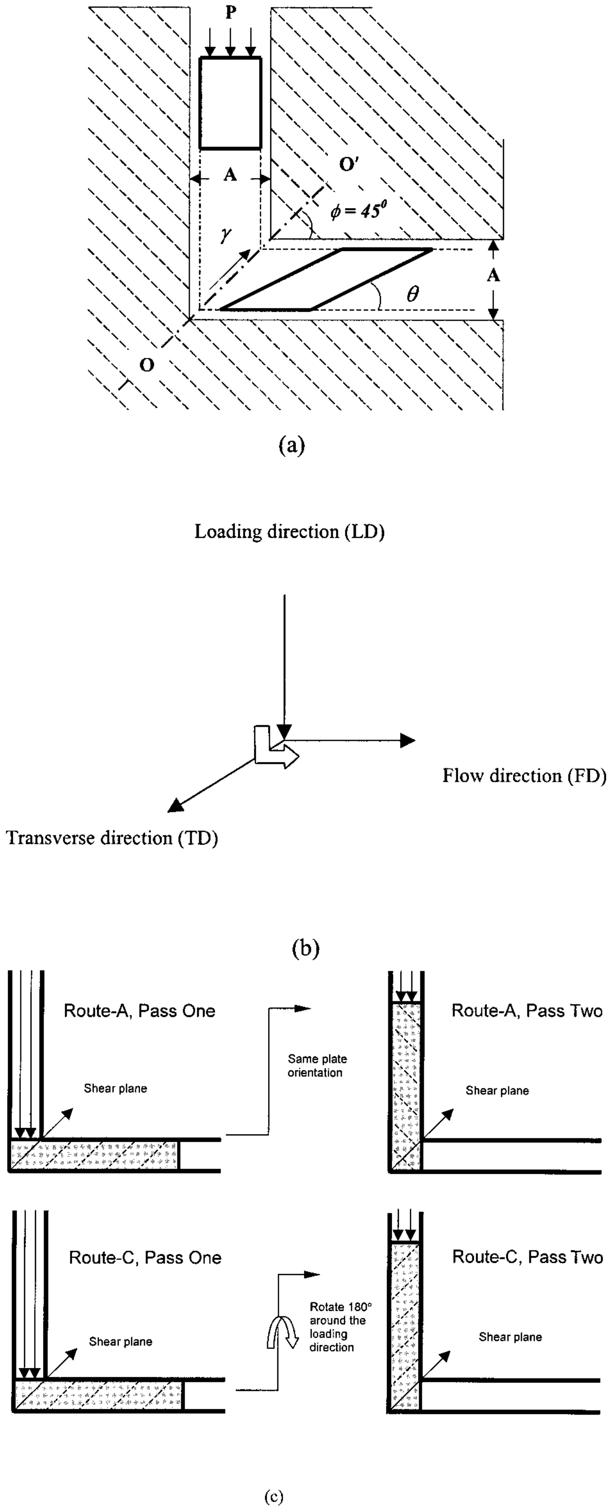


Figure 1 (a) The ECAE schematic. Line OO′ is the shear plane for the deformation. (b) The definition of the directions chosen in the report. (c) Schematic diagrams showing route-A and route-C processes.

potential significance of the ECAE process for improving physical and mechanical properties of polymers is also addressed.

EXPERIMENTAL

Materials and Sample Preparation

Extruded bisphenol-A PC sheets (LEXAN® 103), with a density of 1.20 g/cm^3 and a thickness of 9.6 mm, were obtained from GE Plastics (Schenectady, NY). The as-received PC sheets were machined into dimensions of 152.4 × 152.4 × 9.5 mm (6″ × 6″ × 3/8″) to fit into the predesigned ECAE die fixture (Fig. 1). Grid lines, 1 × 1 mm in size, were milled on the two side surfaces of the PC plate to experimentally quantify the shear strain caused by the extrusion. The PC plates were annealed at 150°C for 15 h and slowly cooled in an oven to ambient temperature to minimize any preexisting thermal history as well as residual stresses before extrusion. A reference PC was prepared by annealing the as-received PC sheet through the same thermal history as those processed by ECAE. The differences in structure and impact behaviors between the ECAE-processed PC and the reference PC would then be attributed to the ECAE process.

The Equal Channel Angular Extrusion Process

A servo-hydraulic driven mechanical testing system (MTS 810) was used for the ECAE extrusion through the die setup shown in Figure 1. To monitor the temperature rise within the extrudate during the extrusion process, a J-type thermalcouple (Omega GA5TC-GG-J-24-36) was imbedded at the center of the PC plate before ECAE. A digital thermometer, OMEGA DP-20, was used to acquire the temperature change during the ECAE process. The temperature profile, the plunger traveling distance, and the load needed for extrusion were recorded during the extrusion. Samples used for impact study and characterization were extruded at 100°C and at an extrusion rate of 0.25 mm/s.

The Dart Impact Test

The Dart impact tests were performed using the General Research Corp. Dynatup dart impact tester. Samples with dimensions of 101.6 × 101.6 × 3.2 mm (4″ × 4″ × 1/8″) were tested, following the ASTM-D3763 method. The test was conditioned at 25°C and a relative humidity of 50%. An impact speed of 3.55 m/s was chosen for the test.

Ballistic Impact Test

The ballistic impact tests were performed using a helium gas gun apparatus.[28] PC specimens with dimensions of 101.6 × 101.6 × 3.2 mm (4″ × 4″ × 1/8″) were firmly clamped and subjected to an impact using a fragment simulating projectile of 17 grain (1.1 g in weight) and 5.588 mm in diameter. Light screens were used as triggers for timers to record the time-of-flight of the projectile to determine the impact velocity of the projectile. Impact velocity was controlled to be approximately 215 m/s.

Fractography Observation

The fracture surfaces of the ECAE-processed samples were coated with Au-Pd and analyzed using a JSM-6400 scanning electron microscope at an accelerating voltage of 15 kV. An Olympus optical microscope (BX-60F), under transmitted mode, was used to observe the overall fracture pattern.

RESULTS AND DISCUSSION

Molecular Orientation During ECAE

Knowledge of the deformation behavior of PC during the ECAE process is critical for proper tailoring of the molecular anisotropy in the resulting extrudate. Microscopically, polymer chains have

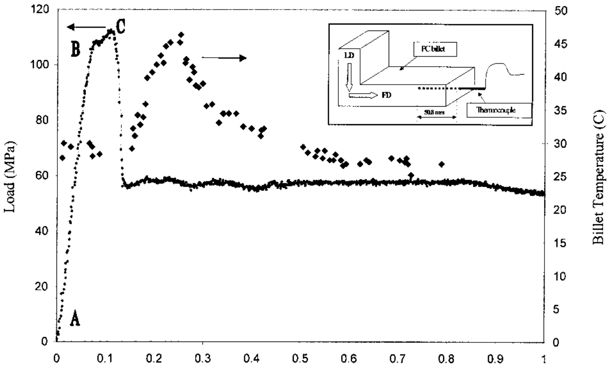


Figure 2 Load and temperature versus plunger traveling distance normalized by the billet length. The extrusion was performed at 25°C and at an extrusion rate of 0.25 mm/s. The inserted sketch on the upper right corner shows the location of thermocouple.

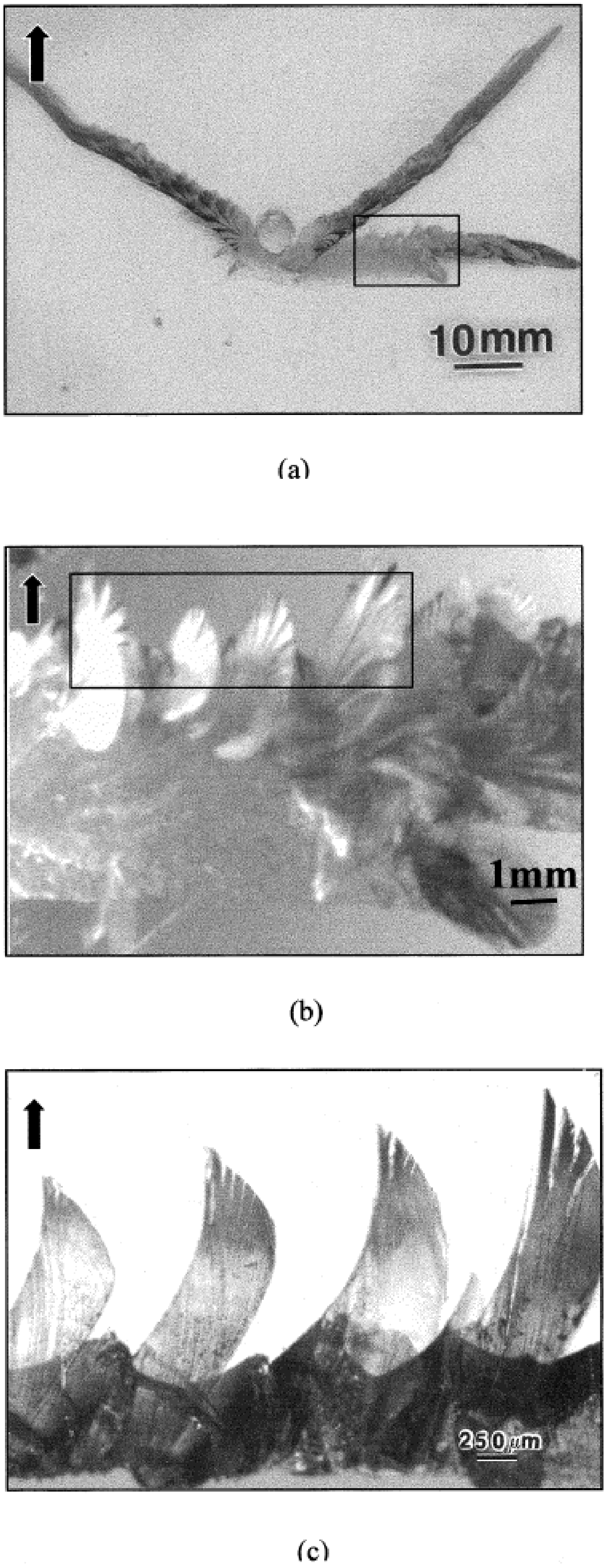


Figure 3 Optical micrographs showing the ballistic impact fracture in sample A-1. (a) Three main cracks are initiated from the point of impact. (b) Enlargement of the area marked in (a). (c) Crack tip region in (b). Arrows indicate the flow direction.

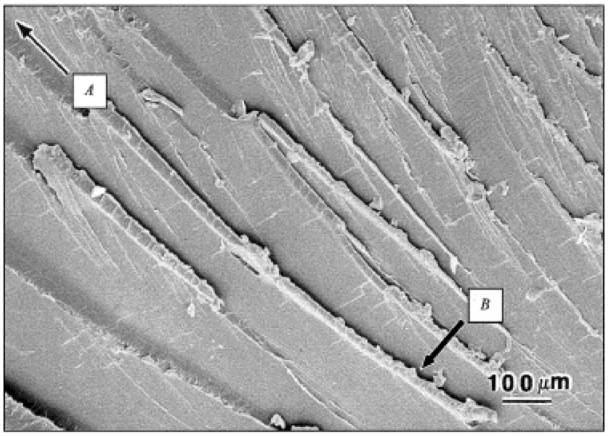


Figure 4 Scanning electron micrograph of the fracture surface for sample A-1. The striations indicate the fracture merged from different crack planes. Arrow *A* indicates the flow direction. Arrow *B* indicates the secondary fracture perpendicular to the shear plane.

to be stressed to exceed the intermolecular resistance so as to trigger segmental motion.[29,30] Molecular alignment occurs when the polymer begins to flow, which will induce an anisotropic internal resistance to resist further deformation and leads to strain hardening.[30]

Figure 2 shows the load history and temperature experienced by the specimen during various stages of a typical ECAE process conducted at 100°C and at an extrusion rate of 0.25 mm/s. These processing stages are plotted against the plunger traveling distance normalized by the length of the extrudate. From point A to point B

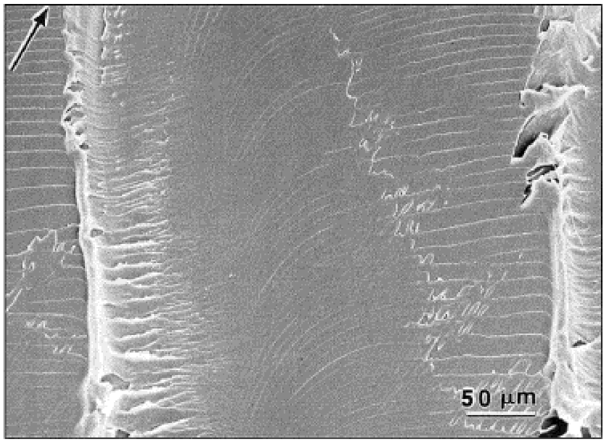


Figure 5 Enlarged scanning electron micrograph taken of a shear-plane induced crack in sample A-1. The fine striations indicate fracture perpendicular to the shear plane. The arrow indicates the flow direction.

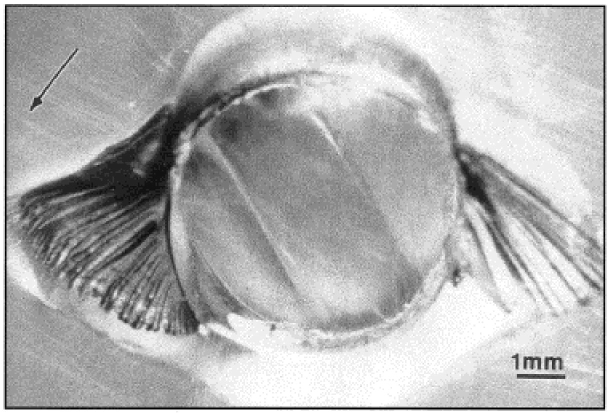


Figure 6 Fracture pattern of sample C-2 after ballistic impact. Arrow indicates the flow direction.

in Figure 2, the deformation is mainly elastic. The onset of plastic deformation occurs from point B to point C, during which molecular orientation takes place. Molecular chains begin to flow and orient along the maximum shear direction after point C. Beyond that, the molecular orientation is stabilized and reaches a final orientation.

It has been shown in our previous work that, after one ECAE pass, the molecular chains are orientated along the maximum shear direction, i.e., at an angle of 28° counterclockwise away from the flow direction.[19] The molecular orientation leads to the formation of weak shear planes. The forces that hold the orientated molecules together are weak secondary bonds. The orientated molecules that are adjacent to each other appear to be still entangled. As for the C-2 ECAE process, the shear plane orientation direction is 40° counterclockwise away from the flow direction. The overall molecular orientation is less anisotropic than that of sample A-1.

A portion of mechanical energy stored is dissipated in the form of heat during the extrusion process. As a result, an increase of up to 25°C in temperature was observed (Fig. 2). The temperature rise facilitates the yielding and the local scale molecular motion of PC during the extrusion.

Ballistic Impact Test

Figure 3(a) shows the fracture patterns of PC before and after the ECAE process for sample A-1. Large radial cracks initiating from the vicinity of impact are apparent. Propagation of the main crack occurred at an angle of about 28° away from the flow direction [Fig. 3(a)], which corresponds to the weak shear planes formed by the weak interfaces between oriented molecules.[19] In addition to the formation of the main crack, microcracks parallel to the flow direction, but normal to the shear plane, are also observed in sample A-1 [Fig. 3(b) and (c)]. This suggests that secondary weak planes are also formed between the orientated molecular chains.

Detailed analysis of the fracture surfaces reveals that cracks initiate along the weak shear planes, followed by the formation of secondary microcracks along the secondary weak planes (Figs. 4 and 5). Because the molecular chains are aligned parallel to each other on the shear planes, the fracture surface is rather smooth. The spacing between the weak shear-plane induced cracks is estimated to be about 20 μm for sample A-1 (Fig. 4). The characteristic spacing between the weak shear-plane cracks, however, has been found to be a strong function of extrusion rate, the number of passes and the internal diameter of the die chamber.[23]

In the case of sample C-2, in which the specimen is processed by rotating 180° around the loading direction at the second pass, the global deformation of the extrudate is restored. As a result, a more isotropic structure is obtained compared with sample A-1. In fact, sample C-2 exhibits ductile response upon impact (Fig. 6). It is noted that microcracks (and/or crazes) are initiated in the vicinity of the impact in sample C-2. However, cracks do not continue to propagate in sample C-2. As a result, the brittle crack propa-

Table I Dart Impact Test Results[a]

PC	Deflection at Maximum Load (cm)	Crack Initiation Energy (E_i) (J)	Crack Propagation Energy (E_p) (J)	Total Energy (E_t) (J)
Reference	1.6	56.3	4.4	60.7
A-1	1.5	57.5	19.8	77.3
C-2	1.6	57.9	7.9	65.8

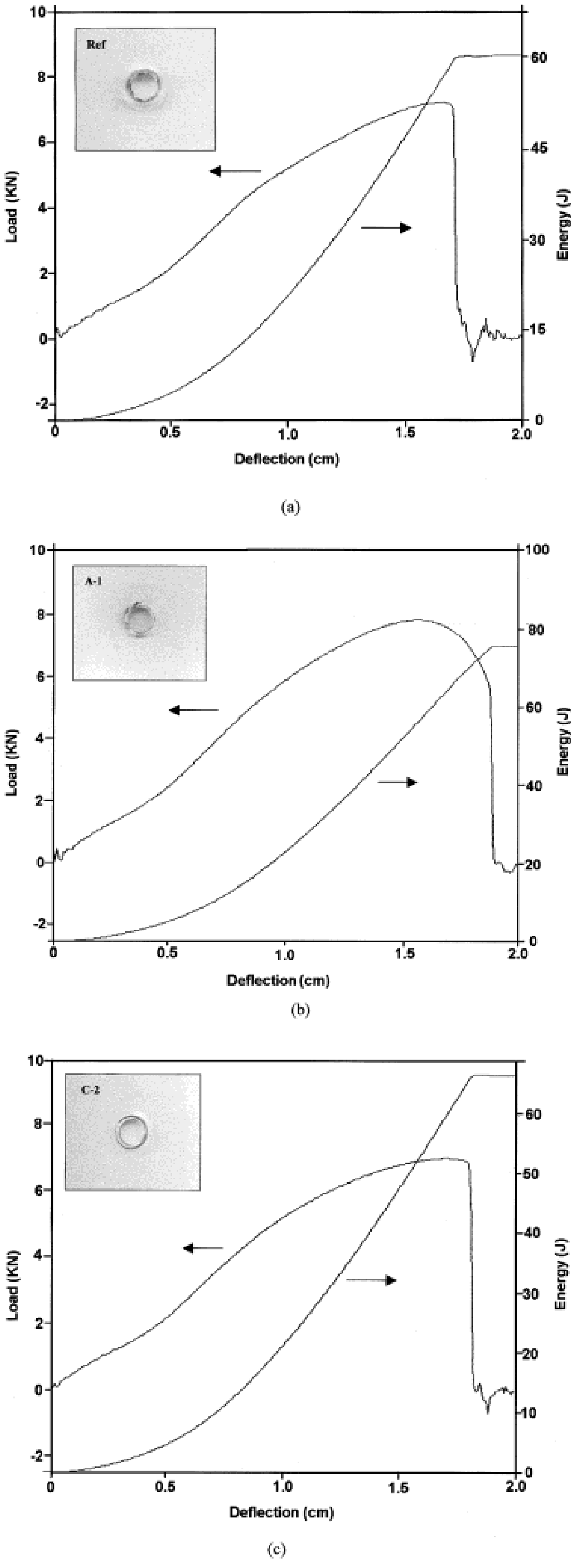
[a] Impact velocity: 3.54 m/s.

gation observed in sample A-1 does not occur in sample C-2. Further analysis reveals that these microcracks (and/or crazes) still initiate at an angle from the flow direction (Fig. 6), indicating that different extent and nature of molecular orientations are induced through the route-C ECAE process.[19]

Dart Impact Test

Compared with the ballistic impact test, the instrumented falling dart impact test is capable of providing the quantitative energies required for crack initiation (E_i) and crack propagation (E_p).[31] The sum of these two energy values ($E_t = E_I + E_p$) reflects the extent of energy absorption of a tested material upon impact.[27] The energy for crack initiation (E_i) is defined by the energy consumed by the specimen up to the maximum load. The energy for crack propagation (E_p) is obtained by subtracting E_i from E_t. Because there is no notch or precrack imposed on the specimen, the majority of the fracture energy is presumably associated with crack initiation.

The impact load and fracture energy as a function of deflection for the reference PC and samples after A-1 and C-2 ECAE are shown in Table I and Figure 7. These results indicate that E_i remains unchanged after both A-1 and C-2 ECAE processes. The reason for this is that under high strain rate conditions, the molecular chains do not have enough time to respond to the impact load. As a result, all three samples show similar E_i values. The energy needed for crack propagation, however, is quite different among the three samples. This indicates that the improved impact resistance in the ECAE-processed PC is mainly attributed to molecular anisotropy, which makes the specimen more effective in diverting crack propagation. As a result, a higher impact fracture resistance can be achieved after the ECAE process. This finding, although logical, is somewhat unexpected. At this point, we are still uncertain about the exact reason(s) for the improvement in E_p. The dynamic mechanical spectroscopy[19] investigation on orientated PC indicates that the transition between α and β relaxation is greatly facilitated after the A-1 and C-2 ECAE processes;



(a)

(b)

(c)

Figure 7 Dart impact results for (a) reference PC, (b) sample A-1, and (c) sample C-2. Optical clarity is apparent after ECAE based on the micrographs shown on the upper left corner of each Figure.

especially the onset temperature for α-relaxation is decreased significantly. This implies that the long chain motion associated with glass transition is more pronounced after A-1 and C-2 ECAE processes. The facilitation of the long chain molecular motion may help improve the impact fracture toughness.[2] Significant work is still needed to fundamentally understand the nature of molecular scale motion in molecularly orientated polymers.

As discussed above, it is clear that the novel ECAE process is effective in orientating molecular chains in glassy polymers. The unique advantage of ECAE is that it not only improves the quasi-static fracture toughness in both the flow and transverse directions,[19,23] but also improves impact strength of polymers. Furthermore, as indicated by the optical micrographs in Figure 7, there is no change in optical clarity of PC after ECAE. This feature enables ECAE to have useful applications for the fabrication of many anti-impact components, such as fighter-jet canopies, vehicle structures, windshields, police shields for personnel protection, and anti-theft transparencies. Moreover, the ECAE technique can be easily incorporated into the conventional polymer processing setup without much capital investment.[32] Significant use of ECAE to fabricate polymer components for various engineering applications is expected.

CONCLUSION

The ECAE process is an effective process in facilitating molecular orientation of polymeric materials without changing their physical dimensions and optical properties. After the ECAE process, molecular chains are preferentially orientated along the maximum principal shear direction. The effect of molecular anisotropy on the impact strength of PC was examined. Both the route-A and route-C processed specimens have a higher impact strength than that of the reference PC, which suggests that the ECAE process is useful for applications in which impact resistance is desired.

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