Coexistence of Ductile, Semiductile, and Brittle Fractures of Elastomer-Modified Polycarbonates

WEN-BING LIU and FENG-CHIH CHANG*

Institute of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan, Republic of China

SYNOPSIS

Phenomenologically, coexistence of ductile, semiductile, and brittle fractures in an apparently identical impact testing condition for the elastomer-modified polycarbonates containing a sharper notch and at high test temperatures has been found. At the ductile–brittle transition temperature, approximately 10% of specimens fractured in the semiductile mode with impact strength about the average of the ductile and brittle modes. The fracture surface of this semiductile mode shows ductile tearing flow in the plane-stress regions near the edges and brittle crack in the plane-strain central region. This unusual semiductile fracture occurs only on the thicker specimens with a sharper notch where clear plane-stress and plane-strain are present.

INTRODUCTION

Polycarbonate (PC) is a highly ductile polymer with lower yield stress than craze stress under ordinary testing conditions and its fracture behavior has been intensively investigated. The notched PC specimens are well known to possess a distinctive ductile–brittle transition (DBT) behavior in response to numerous intrinsic and extrinsic variables such as molecular weight, molecular weight distribution, physical aging, moisture content, elastomer content, notch radius, specimen thickness, orientation, rate, and temperature.

DBT can be considered as a situation that either ductile tearing or brittle crack can possibly occur at a particular test condition. By emphasizing the temperature variable, ductile–brittle transition temperature (DBTT) is defined as a temperature (or a temperature range) that both ductile tearing and brittle crack failures are possible. DBTT has been frequently used to characterize material toughness, which is practically useful in characterizing the material's low-temperature toughness. The mechanism of this sharp transition normally found for notched PC specimens is not fully understood due to its extreme complexity and this subject has attracted great attention for practical safety reasons. Pitman et al.[1] accounted for this DBTT for PC as being a competition between shear yielding and crazing. Brown[2] reported that the yield stress and craze stress of PC are almost equal at the DBT and proposed a mixed-mode mechanism based on the specimen thickness to predict the existence of a DBT. Wu[3] emphasized the importance of the ratio of craze stress and yield stress, σ_z/σ_y, to control the mode of craze/yield behavior. The simple mechanism based on stress competition may be applicable under a uniformed stress-field condition such as typical tensile testing. However, it is certainly unable to fully explain the complex phenomenon of the DBT of a notched specimen because the stress field surrounding the crack tip is considered inhomogeneous and varies with location and the progress of crack propagation. In addition, to determine whether a notched specimen will fail as a ductile or brittle mode, the total fracture process has to be taken into consideration. In a series of investigations on the close relationship between the precrack hysteresis and DBTB for PC, we proposed the existence of a critical precrack plastic zone in determining its DBT.[4–10]

Generally, the standard notched (10 mil) PC thinner specimens ($\frac{1}{8}$ in.) fail either in a ductile mode with higher fracture energy or in a brittle mode with significantly lower fracture energy and rarely frac-

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 56, 545–555 (1995)
 CCC 0021-8995/95/050545-11

ture in a semiductile mode with fracture energy between the ductile and brittle modes. When the specimen dimension varies, such as a greater notch radius or a thicker specimen, several unusual types of semiductile modes with fracture energy between the ductile and brittle modes have been observed. Fraser and Ward[11] reported PC with small yield zone near the crack tip which has fracture toughness intermediate between the ductile and brittle modes. Dekkers and Hobbs[12] reported a fracture of certain rubber-toughened blends that showed the front section to exhibit a typical ductile mode with extensive plastic flow and clear lateral contraction, while the rear section showed a typical brittle mode. Another type of semiductile fracture was reported by Yee,[13] where the fracture surface is distinguished by a triangular flat and mirrorlike area just behind the notch. A similar phenomenon was previously reported for PC specimens with $\frac{1}{4}$ in. thickness at high temperature and a slow deformation rate.[7] We also reported the coexistence of ductile, semiductile, and brittle fractures of PC with $\frac{1}{8}$ in. thickness and 20 mil notch radius at low temperature.[14] This type of semiductile mode is very unusual where the whole fractured surface is covered with extensive but localized shear yielding and shows no sign of lateral contraction.[14] Here, we wish to report another type of a coexistence of ductile, semiductile, and brittle fractures from elastomer-modified PCs where the semiductile mode is unstable and the fracture surface shows the plane-stress ductile mode with lateral contraction on both edges and the plane-strain brittle mode in the central region.

EXPERIMENTAL

Natural-grade PC with a melt flow rate (MFR) of 15 was obtained from Dow Chemical Co. Core–shell elastomer, EXL 3330, was purchased from Rohm & Haas. Melt blending of PC and the elastomer was carried out using a 20 mm Welding Engineers twin-screw extruder with $L/D = 48$ and counterrotating intermeshing screws. The blended pellets were injection-molded into $\frac{1}{4}$ in.-thickness specimens. Specimens containing various notch radii (2.5, 5.0, 10, and 10 mil) were produced by using single-tooth cutters at ambient temperature. Standard Izod impact tests were performed by a TMI, Model 43-1, impact tester equipped with a temperature-controlled chamber. The slow-rate fracture was performed using a specially designed device dimensionally identical to an Izod impact specimen holder and the desired deformation rate was controlled by an Instron.[15]

RESULTS AND DISCUSSION

Fracture Behavior of Polycarbonates

DBT behavior is very complicated and many reasons have been put forward to explain this phenomenon and it seems clear that there is no one overriding mechanism responsible for this behavior. This is especially true when those above-mentioned semiductile fractures are taken into consideration. Most of the previously proposed mechanisms fail to give reasonable interpretation of the observed phenomena. Our previously proposed fracture mechanism based on a critical precrack plastic zone is able to explain most phenomena of those semiductile fractures.[4–7] The basic criterion for a fully ductile failure is a crack propagating within the domain of the plastic-yielded zone.

Whether a specimen will fail as a ductile mode or a brittle mode has usually already been decided before the onset of crack initiation.[6] At the onset of crack initiation, if the crack-tip plastic-yielded zone exceeds a critical level, the crack extension thereafter most likely will be contained within the plastic-yielded zone and result in a ductile failure.[4] The crack-tip plastic-yielded zone, greater or smaller, is always present either during crack blunting prior to crack initiation or during the process of crack propagation regardless of the mode of failure.

The crack growth front can be classified into a ductile tearing front and a brittle crack front. The ductile tearing front occurs when the crack growth propagates in a plastic-yielded zone above a reasonable size. Crack growth by a ductile tearing front induces a mass shear flow, with significant higher energy required. The brittle crack front occurs when the crack growth propagates in a relatively smaller plastic zone and causes only localized shear yielding with substantially lower energy consumed.

The crack growth front in a typical cracking specimen, at any particular moment, can be a combination of brittle crack front (in the central region) and a ductile tearing front (edge regions). As long as the plastic-zone front runs ahead of the crack-growing front and maintains a reasonable zone size, a fully ductile tearing will result. If the crack tip plastic-yielded zone is below the critical level at the onset of initiation, the storage strain energy release from the crack extension will lead the crack front to pass the small plastic zone rapidly and this brittle

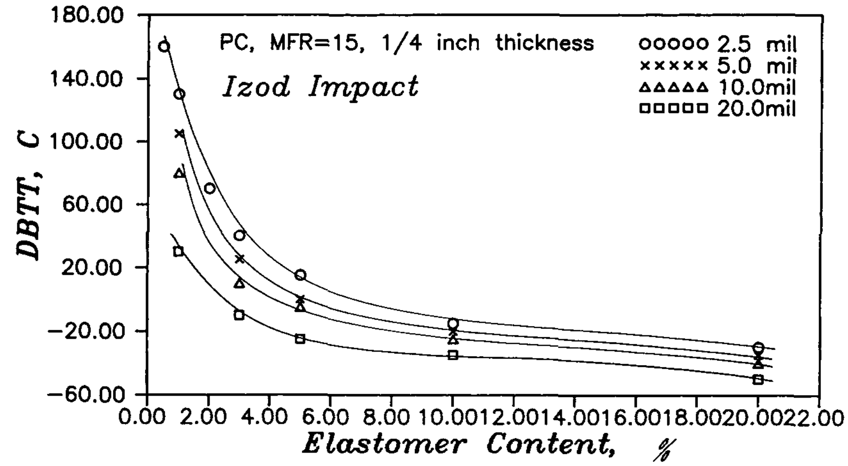


Figure 1 Effect of elastomer content on Izod impact DBTT by varying notch radius.

crack front will propagate through the whole length of the specimen and a brittle fracture occurs.

PC with a standard notch (10 mil) and a thinner specimen ($\frac{1}{8}$ in.) always results in either ductile or brittle fracture, with essentially none in between. When the notch radius and/or specimen thickness is increased, competition of the crack growth front and the plastic-zone front becomes more complicated; several unusual types of semiductile fracture may result. The Type I semiductile mode is a ductile fracture in the front section and a brittle crack in the rear section and this type of fracture has been reported on certain rubber-toughened blends.[12] The Type I phenomenon has never been found in PC or PC-related blends. This Type I fracture can be interpreted as the crack-propagating front exceeding the plastic-zone front in the middle of the fracture process. In other words, the ductile tearing front initially formed shifts into a brittle crack front in the middle of the crack propagation. Type II semiductile fracture comes from PC with a greater notch radius at low temperature where the whole fractured surface is covered with extensive but localized shear yielding. This Type II fracture can be explained as the propagating crack front running side-by-side with the plastic-zone front. The crack growth front of this Type II fracture is neither the ductile tearing nor the brittle crack front; it is an intermediate type of crack growth front with characteristics of both ductile tearing and brittle crack fronts. Type III semiductile fracture has a brittle crack in the front section and ductile tearing in the rear section, which has been briefly mentioned previously.[7] Type III fracture is the reverse of Type I, which can be interpreted as the initially formed brittle crack front changing to a ductile tearing front in the middle of the crack growth.

When the specimen thickness is increased from $\frac{1}{8}$ to $\frac{1}{4}$ in. and the notch radius is reduced to 2.5 mil, the crack-growing pattern will become even more complex. At the DBT, clear plane-strain and plane-stress zones are present, the initially formed crack growth front possessing a brittle crack front in the central region and a ductile tearing front on both edges. This combination crack growth front may propagate independently and results in an unusual fracture with a brittle crack in the central region and a ductile tearing crack on both edges. We classify this type of failure as a Type IV semiductile fracture.

Effect of Notch Radius and Elastomer Content

The effect of notch radius on thinner PC specimens has been reported previously.[14,16,17] Figure 1 shows the plots of elastomer content vs. DBTT by varying the specimen notch radius for PC specimens with $\frac{1}{4}$ in. thickness. Figure 1 clearly demonstrates that the presence of an elastomer is able to reduce notch sensitivity. An elastomer-toughening mechanism involves the promotion of mass shear yielding for ductile fracture and the enhancement of localized energy dissipations for brittle fracture.[18] The mechanism for DBT has been proposed based on the critical precrack plastic zone.[4-7] Elastomer in the PC matrix diverts part of the input energy into inelastic plasticity and reduces the elastic strain energy to strain the existing crack tip.[6] Therefore, the presence of an elastomer is able to delay the onset of crack initiation and allows the precrack plastic-yielded zone to exceed the critical level. The crack extension thereafter will be contained within the domain of the plastic-yielded zone and results in a ductile fracture. A smaller notch radius creates a greater stress concentration and plane-strain state which will cause earlier crack initiation and therefore higher DBTT.

Coexistence of Ductile, Semiductile, and Brittle Fractures

Figure 2 shows the plots of impact strength vs. temperature for PC and various elastomer-modified PC. Coexistence of ductile, semiductile, and brittle fractures at the DBTT was found only for the elastomer-modified PC. The observed DBTT decreases with increasing elastomer content in the blend, as would be expected. The DBTT is believed to be a temperature range rather than a single temperature, as shown in Figure 2. The neat PC fails essentially in all brittle modes, even at temperatures above its T_g (153°C). The impact strength of the semiductile fracture is not very consistent and only the average values are shown in the plots. To obtain the probability of each mode of fracture at the DBTT and the detailed fracture morphologies, a large number of apparently identical specimens were tested at the DBTT and the results are summarized in Table I and Figures 3–5. The definite classification of these three modes of fractures is rather difficult due to the extremely complex fracture nature to be shown later. The semiductile fracture makes up of about 10–12% from all three transition temperatures while the probability of the corresponding ductile and brittle modes are fairly comparable (40–50% each).

Table I Impact Strengths (J/M) for $\frac{1}{4}$ In., 2.5 Mil, Notched Specimens at DBTT Temperatures

A. 2.0% elastomer at 70°C
a. Brittle: Ave = 195 (40%)
166, 168, 170, 173, 181, 192, 192, 199, 203, 207, 209, 211, 211, 211, 226
b. Semiductile: Ave = 416 (10%)
318*, 383, 437, 527
c. Ductile: Ave = 821 (50%)
640*, 679, 683, 754, 786, 792, 796, 796, 816, 833, 854*, 865, 871, 887, 897, 907, 927, 949
B. 1.0% elastomer at 130°C
a. Brittle: Ave = 152 (51%)
117, 121, 122, 124, 124, 126, 128, 128, 128, 132, 132, 137*, 139, 156, 158, 159, 160, 170, 170, 170, 170, 173*, 192, 213, 213, 218*
b. Semiductile: Ave = 480 (12%)
344*, 405, 461, 527*, 534, 609*
c. Ductile: Ave = 822 (37%)
713*, 718, 762, 769, 784, 790, 805, 807, 811, 811, 811, 833, 852*, 854, 854, 865, 891, 906, 982
C. 0.5% elastomer at 150°C
a. Brittle: Ave = 141 (41%)
128, 130, 132, 143, 145, 149, 162
b. Semiductile: Ave = 607 (12%)
552*, 662*
c. Ductile: Ave = 982 (47%)
811, 833, 877, 918*, 1057, 1107, 1109, 1147

Specimens with SEM photograph denoted by *.

SEM Morphologies

The SEM morphologies are selected from the specimens with an asterisk shown in Table I. Figure 3 shows selected fracture surfaces for the PC/2% elastomer blend fractured at the DBTT (70°C). Figure 3(A) is the fracture surface from a selected specimen with impact strength of 318 J/M, which shows a small ductile tearing zone near the crack tip and a pair of leaflike ductile zones with lateral contrac-

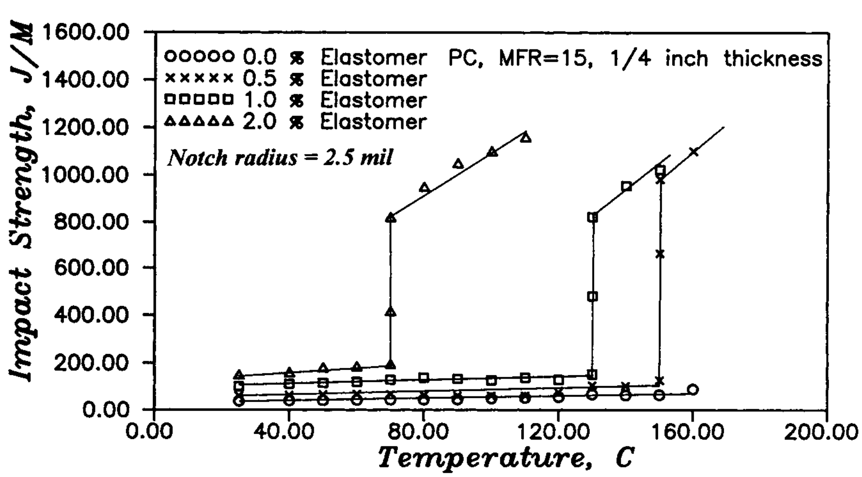


Figure 2 Plots of impact strength vs. temperature for PC and elastomer-modified PCs.

A

B

C

Figure 3 Selected fracture surface SEM micrographs of PC/2% elastomer blend at 70°C: (A) I.S. = 318 J/M; (B) I.S. = 640 J/M; (C) I.S. = 854 J/M.

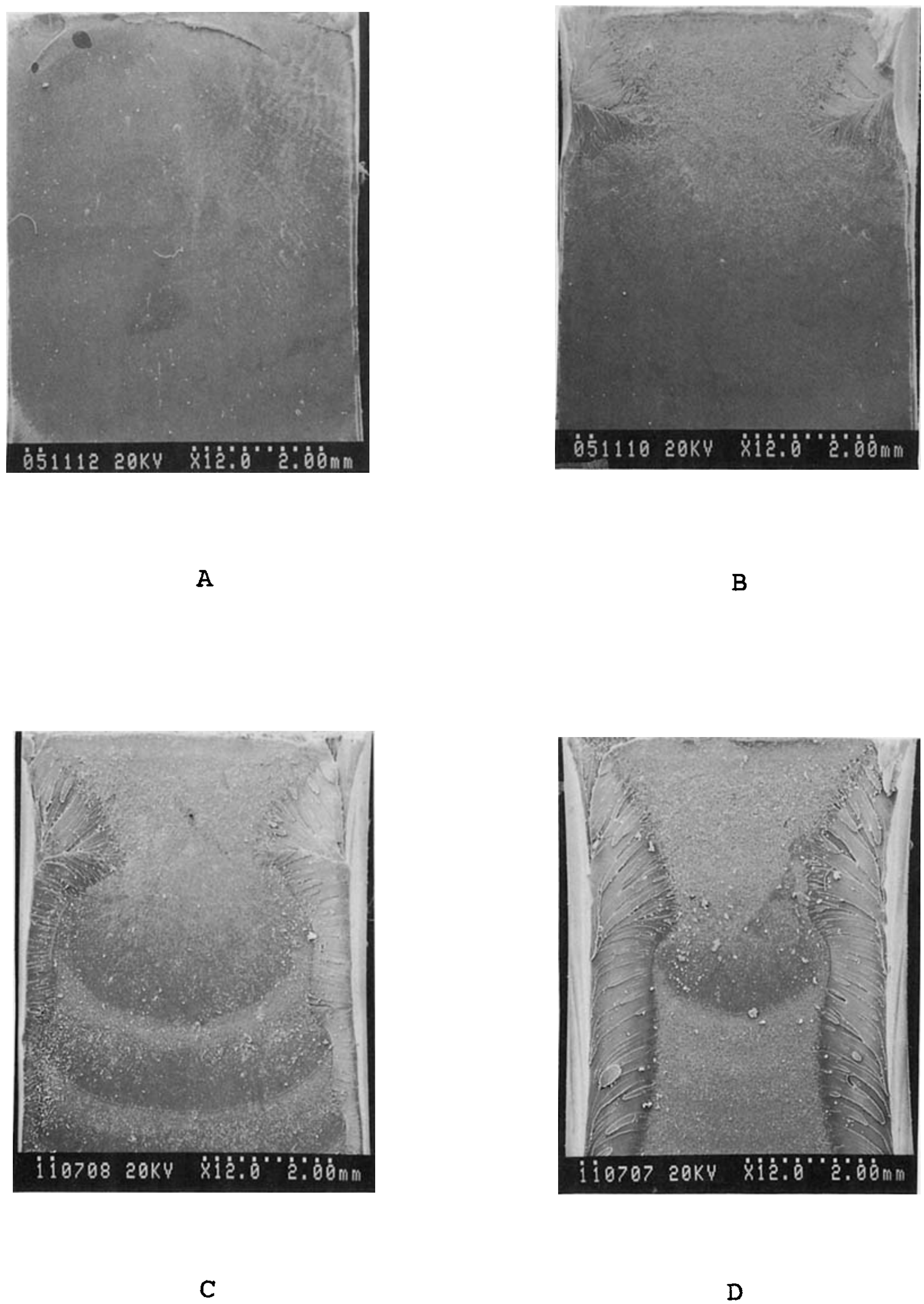


Figure 4 Selected fracture surface SEM micrographs of PC/1% elastomer blend at 130°C: (A) I.S. = 137 J/M; (B) I.S. = 173 J/M; (C) I.S. = 218 J/M; (D) I.S. = 344 J/M; (E) I.S. = 527 J/M; (F) I.S. = 609 J/M; (G) I.S. = 713 J/M; (H) I.S. = 852 J/M.

E

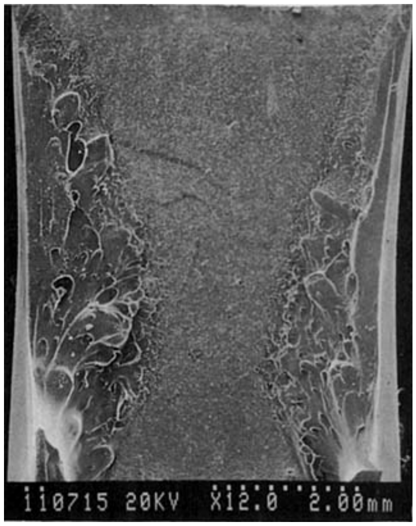
F

G

H

Figure 4 *(Continued)*

tion on both edges. The rest brittle fracture zone can be divided into the rough light-colored front zone and the flat darker-colored rear zone. The rough light-colored zone is indicative of slower crack growth with relatively more localized surface shear yielding and consumes more energy than does the darker flat zone. Figure 3(B) shows the characteristics of a typical ductile fracture except the presence of a triangular brittle zone near the end of the specimen. This is probably due to the increase of the plane-strain nature of the deep notch effect and such an effect will appear repeatedly later. This type of



A

B

C

Figure 5 Selected fracture surface SEM micrographs of PC/0.5% elastomer blend at 150°C: (A) I.S. = 552 J/M; (B) I.S. = 662 J/M; (C) I.S. = 918 J/M.

fracture is similar but not quite the same as the Type I semiductile mode described earlier. This triangular brittle zone in the rear section is surrounded by the ductile tearing zone. This particular specimen has an impact strength of 640 J/M, which is somewhat higher than a typical semiductile fracture but lower than a fully ductile fracture. Figure 3(C) shows the fracture surface of a typical ductile fracture where the whole surface is covered with a mass shear flow with a clear lateral contraction.

Variations of fracture patterns for the PC/1.0% elastomer blend at the DBTT (130°C) are probably the most interesting series among all. Figure 4(A)–(H) illustrates some selected fracture morphologies ranging from the brittle to the semiductile to the ductile mode with impact strength being progressively increased. Figure 4(A) shows a typical brittle fracture where most of the surface is covered with a flat and darker mirror zone except for a pair of small ductile zones near the crack tip. Figure 4(B) is very similar to Figure 3(A) except that the size of the leaflike ductile zones near the crack tip is increased. In addition, the light-colored rough zone is also increased. Figure 4(C) shows that the leaflike ductile zones grow inward and extend in the direction of crack propagation to form two narrow ductile tearing bands. In the central brittle region, at least two crack termination bands are present near the rear section of the specimen. That means that the brittle crack propagating rate may vary with time by alternative shifts of the rough and the flat zone in this specimen. Figure 4(D) shows a clear brittle crack in the central region and ductile tearing with lateral contraction on both sides, which belongs to the typical Type IV semiductile mode that we mentioned previously.[6,7] The sum of the ductile tearing surface area is comparable to that of the brittle crack region. The brittle region also shows a crack termination band near the middle of the crack growth path. Figure 4(E) and (F) show that the ductile zones extend inward in the middle of the crack growth path and leave two triangular brittle zones near the crack tip and the end. Figure 4(G) shows the close-up of the ductile zones and the triangular brittle zone in the rear section has now disappeared. The impact strength of this specimen is 713 J/M, which is considered as a ductile fracture. Figure 4(H) shows the surface covered with extensive shear flow. The impact strength of this specimen is 852 J/M, which is considered to be a fully ductile fracture.

Figure 5(A)–(C) show the fracture morphologies of the PC/0.5% elastomer blend where the testing temperature (DBTT) is very close to the glass transition temperature of PC. Both Figure 5(A) and (B) show a clear brittle zone in the central region and ductile tearing on both edges. The texture of the ductile tearing zones near the T_g shows much more shear flow, which is quite different compared with previous ductile fracture specimens tested below the T_g. Figure 5(C) shows that the triangular brittle zone has almost disappeared and has been replaced with a high-flow ductile tearing zone.

Effect of Strain Rate

The well-known time–temperature equivalence of viscoelastic thermoplastic materials has received extensive investigation through creep or stress-relaxation but relatively fewer investigations have been on the fracture behavior of notched specimens. By applying the general principle of the time–temperature relation, the approach of using reduced impact velocity has been demonstrated to be a viable method to study polymer fracture behavior.[15] All the above data are from high-speed Izod impact tests (3 m/s) and the neat PC fails essentially all in brittle modes even at temperatures above the T_g (Fig. 2). However, a similar semiductile mode (Type IV) fracture from neat PC can be obtained by reducing the strain rate (10 mm/min) at 80°C, and the selected SEM micrographs are shown in Figure 6. Figure 6(A) is the fracture surface of a typical brittle fracture under a slow strain rate (100 mm/min) where a large flat mirror zone is present near the crack tip. By further reducing the strain rate to 10 mm/min, the viscoelastic nature of PC results in a different type of fracture. Figure 6(B) is the fracture surface from a specimen fractured at 10 mm/min, which is also considered as a brittle fracture but shows the initial stage of forming the familiar triangular brittle zone near the crack tip. Figure 6(C) is from another specimen fractured under the same conditions as that of Figure 6(B) (strain rate at 10 mm/min), where the surface contains a clear brittle zone in the central region and two ductile tearing zones with lateral contraction on both edges. This is a typical Type IV semiductile mode fracture as are those from the elastomer-modified PCs.

CONCLUSIONS

Coexistence of ductile, semiductile, and brittle fractures in an apparently identical impact testing condition for the elastomer-toughened PCs with a sharper notch has been identified. The presence of both plane-stress and plane-strain in the sharper-notched specimens makes it possible to fracture by

A

B

C

Figure 6 Selected fracture surface SEM micrographs of neat PC at 80°C and slow strain rates: (A) strain rate = 100 mm/min; (B) strain rate = 10 mm/min; (C) strain rate = 10 mm/min.

ductile tearing in the plane-stress-edged regions and by a brittle crack in the plane-strain central region simultaneously. This semiductile fracture also occurs on neat PC under a considerably slower strain rate. The impact strength of these semiductile fractures is inconsistent and fluctuated between ductile and brittle modes. This unusual type of semiductile fracture occurs only on thicker ($\frac{1}{4}$ in. or greater) specimens with the definite presence of plane-stress and plane-strain. This report provides additional information on the complex fracture behavior of PC under various intrinsic and extrinsic variables.

This study was financially supported by the National Science Council, Republic of China, under Contract Number NSC 79-0405-E009-02.

REFERENCES

1. G. L. Pitman, I. M. Ward, and R. A. Duckett, *J. Mater. Sci.*, **13**, 2092 (1978).
2. H. R. Brown, *J. Mater. Sci.*, **17**, 469 (1982).
3. S. Wu, *Polym. Eng. Sci.*, **30**, 72 (1990).
4. F. C. Chang and H. C. Hsu, *J. Appl. Polym. Sci.*, **43**, 1025 (1991).
5. F. C. Chang and H. C. Hsu, *J. Appl. Polym. Sci.*, **47**, 2195 (1993).
6. F. C. Chang and H. C. Hsu, *J. Appl. Polym. Sci.*, **52**, 1891 (1994).
7. F. C. Chang, in *Handbook of Advanced Materials Testing*, Marcel Dekker, New York, 1994, p. 539.
8. H. C. Hsu and F. C. Chang, in *Proceedings of the 13th ROC Polymer Symposium*, Taiwan, 1990, p. 796.
9. C. D. Teng and F. C. Chang, in *Proceedings of the 1991 Annual Conference of Chinese Society for Material Science*, Taiwan, p. 474.
10. F. C. Chang and H. C. Hsu, in *Preprints China–Japan Bilateral Symposium on Polymer and Materials*, Guangzhou, 1990, p. I.13.
11. R. A. W. Fraser and I. M. Ward, *J. Mater. Sci.*, **12**, 495 (1977).
12. M. E. J. Dekkers and S. Y. Hobbs, *Polym. Eng. Sci.*, **27**, 1164 (1987).
13. A. F. Yee, *J. Mater. Sci.*, **12**, 757 (1977).
14. F. C. Chang and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 1615 (1992).
15. F. C. Chang and M. Y. Yang, *Polym. Eng. Sci.*, **30**, 543 (1990).
16. G. Allen, D. C. W. Morley, and T. Williams, *J. Mater. Sci.*, **8**, 1449 (1973).
17. J. T. Ryan, *Polym. Eng. Sci.*, **18**, 264 (1978).
18. F. C. Chang, J. S. Wu, and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 491 (1992).

Received November 16, 1993
Accepted September 22, 1994