Toughening of Polycarbonate: Effect of Particle Size and Rubber Phase Contents of the Core-Shell Impact Modifier

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ABSTRACT: The toughening behavior of polycarbonate modified with core-shell type particles was investigated. The alloys were found to exhibit maximum impact strength upon addition of a modifier with a poly(butyl acrylate) rubbery core of 0.25 μm diameter. The incorporation of particles with diameter greater than 0.25 μm resulted in decreased impact strength. The influence of rubber phase contents on toughness was also studied. It was observed that the alloys exhibited maximum impact strength upon addition of 4 wt % rubber phase. Further increase in the rubber phase content resulted in reduced impact strength. Fractography of the samples showed that, below 4 wt % rubber phase content, the fracture occurs mainly by internal crazing and, from 4 wt % onward, only by shear deformation. When the effect of dual particle size distribution was analyzed, it was found that there was only a moderate increase in toughness compared with alloys containing monosized particles. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 748–755, 2005

Key words: polycarbonate; toughness; fracture; core-shell impact modifier; particle size

INTRODUCTION

Fracture toughness of polymers plays a crucial role in structural applications. Many polymers including polycarbonate (PC) have a tendency to undergo brittle fracture especially in notched impact tests. The notch sensitivity of PC is due to the change in stress state at the notch from plane stress to plane strain and the resulting change in failure mechanism from shearing to crazing. The toughness of these polymers can be improved by relieving the plane strain constraint and delocalization of the deformation. One method, which has been successful in toughening notch-sensitive polymers, is rubber toughening. Several reports on the deformation and fracture behavior of toughened polycarbonate are cited in literature.[1–10] The added elastomer particles undergo cavitation, which relieves the triaxiality at the notch and permits the matrix to deform by shear yielding. A number of factors related to the rubber components, such as particle morphology, chemical composition, particle size, etc would affect the toughness of these systems.

Core-shell elastomers are designed specifically to produce blends with good dispersion and toughness. Cheng et al.[4] studied the effect of three different elastomers on the toughness of PC and found that maximum toughness was obtained with a core-shell impact modifier. The chemical composition and crosslink density of the elastic core determine the cavitation resistance of the particle whereas the composition of the shell is chosen to provide rigidity to the particles during processing and to impart compatibility with the matrix for good dispersion and adhesion.[11,12] Yee et al.[13,14] investigated the fracture mechanism of toughened PC blends and concluded that cavitation of rubber particles occurs first, followed by the enhanced shear yielding of the matrix. It was reported by Parker et al.[15] that modifiers with greater cavitation resistance result in improved toughness. Recent studies from this laboratory have reported on the notch sensitivity of neat and toughened PC.[9]

In this article, we present the results of an extensive investigation on the toughening of PC using a core-shell impact modifier with a poly(butyl acrylate) (PBA) core and a polymethylmethacrylate (PMMA) shell. The PMMA shell of the modifier is miscible with PC.[16] Impact modifiers with varying particle size are used and their effect on impact strength is reported. The influence of rubber phase content and the incorporation of dual-sized particles are also presented.

EXPERIMENTAL

Materials

The matrix PC resin was obtained from GE (LEXAN 141). The methyl methacrylate (MMA) and *n*-butyl acrylate (BA) monomers were used after removing

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TABLE I
Recipe for the Preparation of Core Particles

		1	2	3	4	5	6
Reactor charge (g)	Water	170	150	60	120	100	200
	Seed latex	—	—	120	120	120	210
	KPS	0.1	0.54	—	—	—	—
Preemulsion charge (g)	BA	20	108	98	50	50	50
	BDA	0.2	1.08	0.98	0.5	0.5	0.5
	Water	10	54	150	75	75	75
	SDS	0.4	2.16	0.98	0.5	0.5	0.5
	AIBN	—	—	1.30	5.7	5.7	5.7
Diameter of the core particle (μm)		0.08	0.25	0.37	1.09	2.28	3.61

KPS, potassium persulfate; BA, *n*-butyl acrylate; BDA, 1,4-butanedioldiacrylate; SDS, sodium dodecyl sulfate; AIBN, azobisisobutyronitrile.

inhibitors by washing with 10% aqueous NaOH solution. Potassium persulphate (KPS), azobisisobutyronitrile (AIBN), and sodium dodecyl sulfate (SDS) were used as received. The 1,4-butanedioldiacrylate (BDA) and 1,4-butanediol dimethacrylate (BDMA) were used as crosslinking agents for the PBA rubbery core and the PMMA shell material, respectively.

Preparation of impact modifier

A core-shell type particle [with a slightly crosslinked poly(*n*-butyl acrylate) rubbery core and a glassy shell composed of PMMA] was used as an impact modifier, which was prepared by seeded emulsion polymerization.[17,18] The rubbery core consisting of PBA was slightly crosslinked with BDA for maintaining its size and shape during melt blending with PC and subsequent molding of the blends. The PBA core particles of desired size (0.08–3.6 μm in diameter) were prepared by seeded emulsion polymerization in which seed particles were first formed and sequentially grown to desired size. The recipes for the preparation of the core particles and the diameter of the core particles prepared are given in Table I. The glass transition temperature (T_g) of core particles measured by dynamic mechanical testing was about -40°C. The preparation of the core-shell particles was described previously.[17,18]

Blending, specimen preparation, and mechanical tests

Core-shell particles were blended with PC pellets in a Brabender internal mixer at 220°C for 7 min. The rubber phase contents were varied from 2 to 12 wt %. The blends were compression molded into 5-mm-thick plates. The molded plates were machined into Charpy impact bars (12.6 × 5 × 120 mm). Charpy impact strength was determined using a single-edge notched specimen with a notch radius of 0.25 mm at room temperature.

Microscopy

The fracture surfaces of impact tests were subjected to a scanning electron microscope (SEM, Hitachi S-570). Specimens were coated with a thin layer of gold–palladium prior to SEM examination.

Fracture surface of impact test specimen was examined by transmission optical microscopy (TOM). A well-established polishing/sectioning technique was employed.[19,20] For this purpose, a section thin enough to transmit light was produced using a petrographic polishing technique. The fracture subsurface of the impact test specimen was examined under the bright field image using an optical microscope (Zeiss). All samples examined were from the middle part of the specimen, which satisfies the plane strain constraints according to the well-accepted fact that, in a sufficiently thick single-edged notched specimen (ASTM E399–90), the central region is in plane strain state while the surface region is in plane stress state.[21]

RESULTS AND DISCUSSION

Effect of particle size of the modifier on impact strength

The influence of the particle size of the impact modifier on the impact strength of toughened PC is plotted in Figure 1. The rubber content was varied from 2 to 12 wt %. It is clearly evident from the figure that the incorporation of modifier having a particle size of 0.25 μm (diameter of the PBA rubbery core) has resulted in a maximum impact strength irrespective of the concentration of the rubbery phase. In the case of toughened PC-containing particles with a diameter less than 0.25 μm, i.e., 0.08 μm, the impact strength is significantly improved but is still inferior to that of 0.25 μm. It can also be observed that the increase of particle size beyond 0.25 μm results in a decrease of impact strength. These results indicate that there is an optimum particle size for the impact modifier that can contribute to maximum toughening.

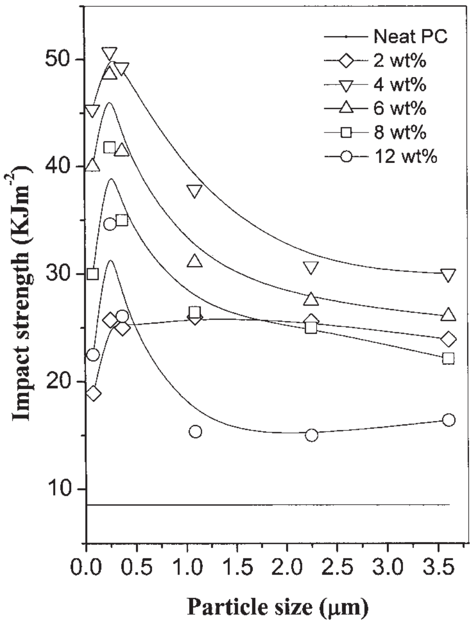

Figure 1 Impact strength of toughened PC as a function of particle size.

Let us examine the mechanism of toughening upon addition of the modifier. The notch sensitivity of PC is attributed to the change in stress state at the notch from plane stress and the resulting change in failure mechanism from shearing to crazing.[4] Rubber particles prevent the initiation of craze inside the plastic region by decreasing mean stress by the cavitation of rubber particles. Particle cavitation is a desirable deformation mechanism since it relieves the triaxiality, thereby enabling the matrix to yield after the core-shell particles cavitate ahead of the crack tip.[15] Kayano et al.[8] reported that no cavitation could be found in brittle blends that have poor modifier distribution, which implies that a good dispersion is required for these impact modifier particles to cavitate.

Other attributes of the modifier that contribute toward the toughness also include the volume fraction of the rubber phase, its chemical composition, degree of crosslinking, particle morphology, adhesion to the matrix, and the rubber particle size.[10] Lazzeri and Bucknall[22] developed an energy-balance criterion for rubber cavitation in rubber-toughened plastics. Their model was based on the fact that the rubber cavitation should be governed by the particle volume strain and a balance between stored volume energy, void surface energy, and the work required to stretch the void biaxially. Accordingly, rubber cavitation becomes unlikely with a decreasing particle size and an increasing rubber crosslink density. They proposed that particles with a diameter less than 0.13 μm could not be cavitated. These studies imply that particles below a critical size cannot be cavitated during loading. Hence, in the case of modifiers with 0.08 μm size, the cavitation process is not as effective as with 0.25 μm particles. This is the reason why PC toughened with 0.08-μm–sized particles exhibits less improvement in impact strength compared to that toughened with 0.25 μm particles. It is also currently accepted that the effect of rubber particles itself correlates with matrix ductility and that the intrinsic properties of rubber play an important role if the cavitation of the rubber determines the yield conditions in the matrix.[23] Therefore, if the rubber cavitation does not take place, the stress condition will be unaltered and hence the modifier fails to produce maximum toughness.

It is also reported in the literature that, while in brittle polymers such as high impact polystyrene (HIPS) an increase in toughness is attained by increasing the average particle size, in ductile polymers such as polyamides and polycarbonates, a higher toughness correlates with a decreasing average particle size.[24–26] In HIPS the maximum toughness was obtained within a particle size range of 2–5 μm, for ductile polymers the maximum property was obtained with 0.3 μm particles. In general, crazing materials benefit most from relatively large particles (about 1 μm and more) and shear yielding materials are best toughened with relatively small particles (about 0.5 μm and less). Thus we can conclude that there is an optimum particle size that can impart maximum toughness, and in our system it is 0.25 μm.

Effect of dual particle size on impact strength

The impact strength of the alloy on the addition of particles with two different dimensions (diameter of the rubbery core 0.37 and 2.25 μm.) has been analyzed. The rubber phase content was kept constant at 4 wt % and the ratio of the impact modifier was varied. The effect of dual particle size on the impact strength as a function of 2.25 μm particles is plotted in Figure 2. Between the two particles, the one with lower size (0.37 μm) shows greater impact strength. Impact strength of PC alloys containing dual-sized particles is slightly improved from that of PC alloys containing only 0.37 μm particles when the content of 2.25 μm particles is in the range of 0–60%. With 70–90% 2.25 μm particle content, the alloys were fractured via a brittle or ductile mode. For brittle fracture the impact strength was rapidly decreased.

Okamoto et al.[27] and Hobbs[28] reported that dual particle size distribution of the modifier was effective in enhancing the toughness of HIPS. Fracture surface analysis of PC alloys with dual particles showed that the deformation mechanism remains the same in the single as well as dual particle–sized blends. Thus, in our system, addition of dual-sized particles was unable to produce an appreciable improvement in toughness. However, the impact strength of PC alloys containing dual-sized particles is comparatively higher than PC alloys with the same concentration of single-sized particles.

Effect of rubber phase contents on the impact strength

The effect of impact strength as a function of rubber content is plotted in Figure 3. It is evident from the figure that the system with 4 wt % rubber phase content exhibits the maximum impact strength in the whole range of particle sizes analyzed. Beyond 4 wt %, the impact strength of PC alloys reduces with rubber content.

Impact fracture of neat PC

Let us examine the fracture surface of the neat PC and those modified with different modifier loading. The scanning electron micrographs demonstrating the fracture surface of neat PC with a notch radius of 0.25 mm are shown in Figure 4(a–c). From the Figure it can be observed that brittle fracture occurs in neat PC from internal crazes. The brittle fracture of notched PC can be explained on the basis of the slip lines field theory.

Several studies on the fracture mechanics of polymeric materials revealed that the resistance of crack initiation from the notch, i.e., toughness, is dependent on both shear yield stress and critical stress for craze nucleation. The stress-field inside the plastic deformation region ahead of the notch tip can be described by the slip lines field theory.[9,29–31] Based on this theory, for a specimen with semicircular notch, the principal stresses along the x-axis are given by

$$\sigma_1 = \frac{2}{\sqrt{3}}\sigma_T\left[1 + \ln\left(\frac{r}{\rho}\right)\right] \tag{1}$$

$$\sigma_2 = \frac{2}{\sqrt{3}}\sigma_T \ln\left(\frac{r}{\rho}\right) \tag{2}$$

and for the fully plane strain condition

$$\sigma_3 = \frac{(\sigma_1 + \sigma_2)}{2} = \frac{2}{\sqrt{3}}\sigma_T\left[\frac{1}{2} + \ln\left(\frac{r}{\rho}\right)\right] \tag{3}$$

$$\sigma_m = \frac{(\sigma_1 + \sigma_2 + \sigma_3)}{3} = \sigma_3$$

$$= \frac{2}{\sqrt{3}}\sigma_T\left[\frac{1}{2} + \ln\left(\frac{r}{\rho}\right)\right] \tag{4}$$

where σ_m is the mean stress, σ_T is the tensile yield stress, ρ is the notch radius, and r is the distance from the origin along the x-axis.

The two slip lines for the specimen with a notch radius ρ are shown in a schematic representation in Figure 5(a). The slip line refers to the elastic–plastic boundary, i.e., the inner portion of the slip line is the plastically deformed region and the outer portion is the elastic region. The mean stress around the notch tip is schematically shown in Figure 5(b). As the remote stress increases, it will induce a large plastic

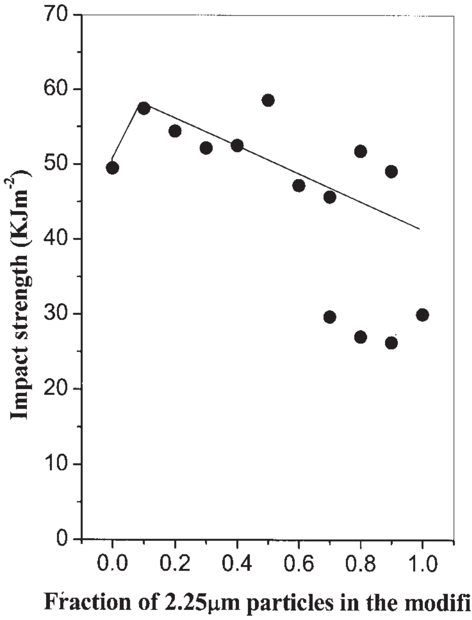

Figure 2 Impact strength of toughened PC as a function of 2.25 μm particle content in the modifier. (rubber phase content: 4 wt %).

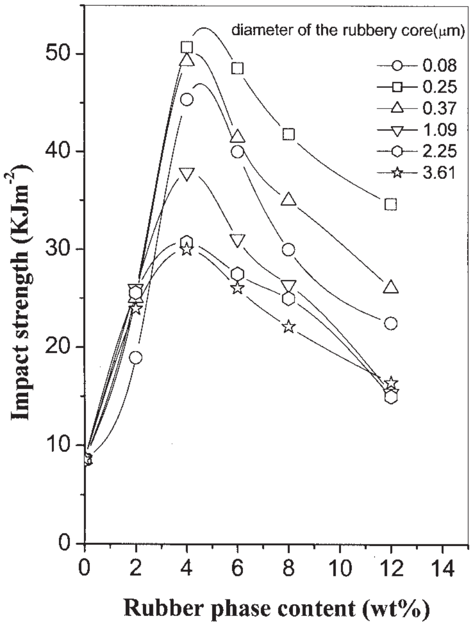

Figure 3 Impact strength of toughened PC as a function of rubber phase content.

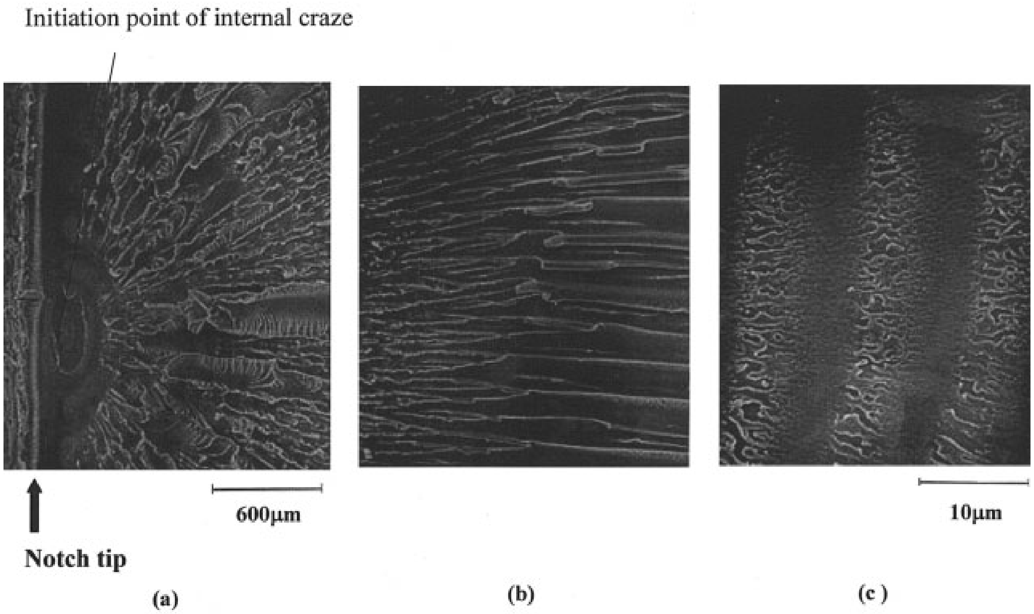

Figure 4 Fracture surface of neat PC: (a) around notch tip; (b) crack propagation region; (c) higher magnification of (b).

deformation, i.e., the plastic deformation zone grows outward. The stress will be maximum at the elastic–plastic boundary and, when the mean stress reaches the critical value for craze initiation, the internal crazing will occur at the elastic–plastic boundary. The internal craze initiates away from the notch tip as shown in Figure 5(b).

Lai and Van der Giessen[32] studied the crack-tip plastic zones in glassy polymers using a constitutive model that incorporates their typical softening and hardening behavior. Their studies revealed that the distribution of mean normal stress is intimately related to the pattern of plastic deformation in front of the crack. The maximum stress was found to occur near the tip of the plastic zone where shear bands cross, i.e., at some distance ahead of the tip. It was also observed that the distribution of hydrostatic stress responsible for the crazing is intimately related to the plastic deformation in front of the crack tip. To characterize possible deformation patterns near sharp crack tips, Jeong and coworkers[33] conducted four-point bending tests of double- notched pure epoxy and rubber-toughened epoxy specimens and observed plastic deformation in the form of slip lines in both cases. Furthermore, they constructed theoretical slip lines for pressure-sensitive perfectly plastic materials, which showed good agreement with the slip lines observed in the pure epoxy specimen studied.

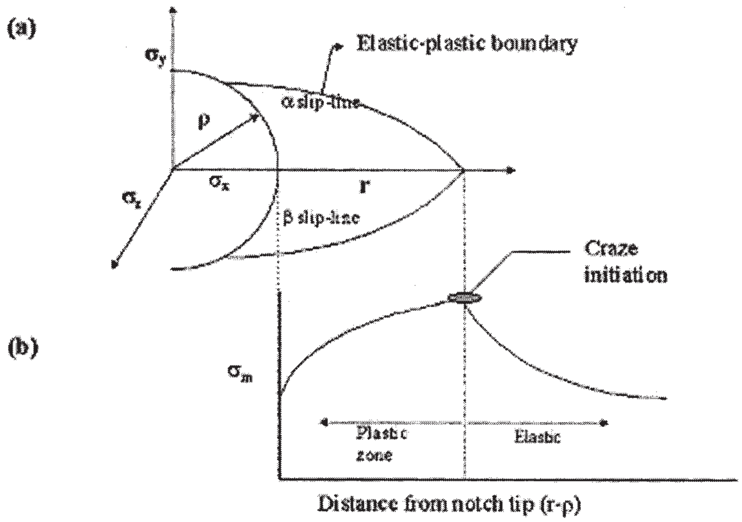

Figure 5 Schematic diagram illustrating the mean stress field around the notch tip.[9,29–31]

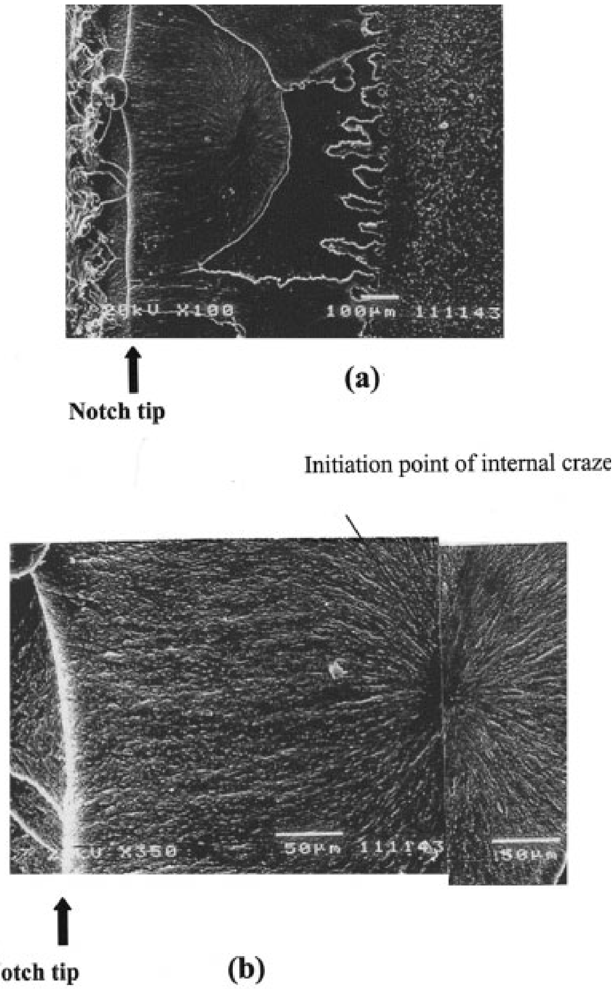

Figure 6 SEM micrographs of fracture surface of toughened PC (rubber phase content: 2 wt %, particle size: 0.25 μm); (b) is the higher magnification of (a).

For neat PC, the critical mean stress for the development of internal crazes is less than shear yield stress. Therefore, as stated by the theory, we can see that, for neat PC, the internal crazes are nucleated at the tip of the local plastic zone. When the mean critical stress is reached, the plastic zone initiated at the notch tip reaches a certain critical size and nucleation of internal craze occurs at the zone tip. Once internal craze is initiated in the specimen, catastrophic fracture will follow.

Impact fracture in toughened PC

An SEM micrograph of the fracture surface of PC toughened with a core-shell impact modifier having 2 wt % rubber content with a particle size of 0.25 μm is shown in Figure 6. The micrograph clearly indicates that, even with 2 wt % rubber content, the impact fracture of PC follows the mechanism of internal crazing. The fracture of other PC alloys with 2 wt % rubber content also followed the internal crazing route irrespective of the particle size. Consequently, it can be noted that, for PC toughened with modifier having 2 wt % rubber content, the impact strength is not significantly improved (Fig. 3). The fracture surface morphology of impact-modified PC with 4 wt % rubber content is shown in Figure 7. The scanning electron micrographs do not show any sign of crazing and the maximum toughness is observed for PC alloys with 4 wt % (rubber content) loading for all the particle sizes studied.

In the case of rubber-toughened PC, the critical stress for rubber cavitation or interfacial debonding is presumably less than that for the internal crazing. Hence, when mean stress reaches a value for internal cavitation, rubber particles are cavitated or the interfacial failure occurs at the interfaces. With the development of voids, the constraint of strain in a direction perpendicular to the maximum principal stress would be relaxed because the material containing voids inhibits the transmission of load. Therefore, the mean stress does not reach the critical level for craze initiation. As a result, internal crazing cannot occur for toughened PC. Thus the rubber particles prevent the initiation of the craze in the plastic region by decreasing the mean stress through cavitation of rubber particles or interfacial failure as well as by inducing matrix shear deformation. Hence we can conclude that toughened PC fails by shear deformation whereas the neat PC fractures via internal crazing.

The plastic deformation region ahead the notch tip of the toughened PC consists of two zones, which can be schematically represented by Figure 8. Region 1 is the intense yielded region and region 2 is the shear yielded region. The optical micrographs of the shear yielded and intense yielded region are shown in Figures 9(a) and (b). Shear bands interconnecting the core-shell particles are clearly observable in the shear yielded region. But the intense yielded region does not

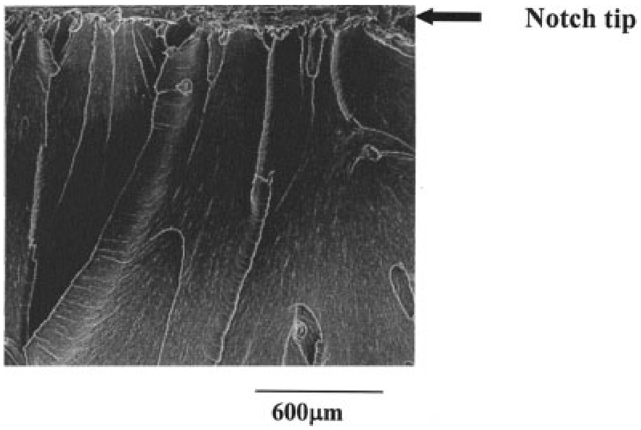

Figure 7 SEM micrograph of fracture surface of toughened PC (rubber phase content: 4 wt %, particle size: 0.25 μm).

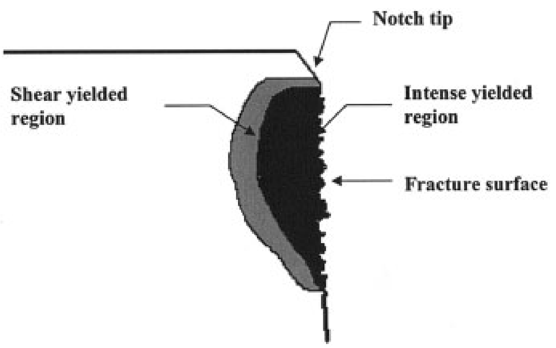

Figure 8 Schematic illustration of the deformation zone ahead of the notch tip for toughened PC.

contain any shear bands, since the whole matrix is deformed homogeneously. With the successive loading, in the shear yielded region the matrix will be severely deformed, gradually resulting in the disappearance of shear bands forming the intense yielded region. As can be seen in Figure 9(b), almost all of the rubber particles are debonded at the interface and the matrix around the particles is homogeneously deformed in the intense yielded region.

From the above results we can suggest that, by the addition of 4 wt % rubber, the toughness of PC is enhanced by suppressing the crazing and inducing shear deformation. Figure 3 shows that addition of the modifier with rubber content beyond 4 wt % decreases the toughness of the alloys. This observation can be explained on the basis of several factors: As the rubber content is increased, the inclusions will begin to interact after moderate amounts of plastic strain. With further deformation, the diameter of the ligaments between the inclusions is reduced due to void growth, which in turn reduces their load carrying capacity. This will finally result in decreased impact strength. In our system, after the incorporation of 4 wt % rubber content, the alloys fracture by shear deformation only. Thus the addition of 4 wt % rubber content seems to be sufficient for altering the stress state. When fracture is not initiated by internal craze, impact strength is decreased as rubber content is increased. The reason for the decrease of impact strength can be attributed to the decrease of strain energy density, plastic deformation zone, yield stress, and modulus upon further increase of rubber content.

The plastic deformation zone is increased when the rubber content is increased up to 4 wt %. However, with further increase in rubber content, the plastic deformation zone is reduced, which may be due to the decrease in strain at break at high rubber contents. In addition to these aspects, the yield stress and modulus decrease at high rubber contents, which in turn will reduce the stress transfer. Hence the crack propagates without a large deformation of the matrix component near the crack tip, which results in decreased impact strength. Therefore it can be stated that there is an optimum rubber phase content that can impart maximum toughness for the notched PC. The optimum rubber phase content therefore refers to the least content of rubber that can suppress the internal crazing in PC alloys and thereby induce them the maximum toughness.

CONCLUSION

To improve its notched impact strength, polycarbonate was modified using core-shell rubber particles with a polybutyl acrylate core and a polymethyl methacrylate shell. The impact strength was maximum with an optimum particle size (diameter of the

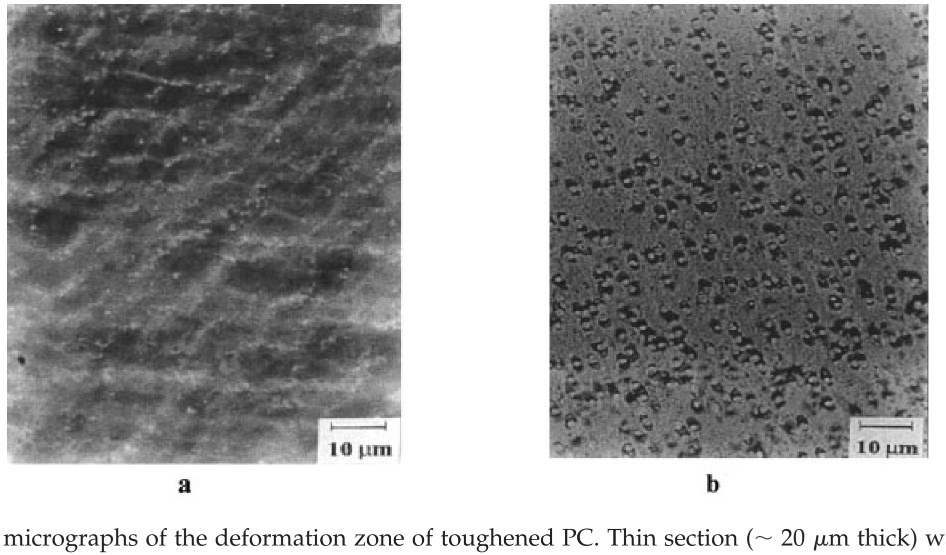

Figure 9 Optical micrographs of the deformation zone of toughened PC. Thin section (~ 20 μm thick) was taken from the fracture subsurface. Rubber content: 4 wt %, particle size: 30.61μm: (a) shear yielded region (b) intense yielded region.

rubbery PBA core) of the modifier, which was found to be 0.25 μm. For those particles below the optimum size, the improvement in toughness was less, which may be attributed to the inability of the smaller particles to undergo cavitation. The incorporation of modifiers with dual particle size resulted in marginal improvement in toughness compared with alloys containing monosized particles. The effect of rubber phase contents on the impact strength revealed that the system exhibited maximum impact strength when the rubber phase content was 4 wt %. The fracture surface analysis showed that internal crazing occurs only in those PC alloys with a rubber content less than 4 wt %. When the rubber phase content was more than 4 wt %, fracture in the alloys took place via shear deformation. The increase of rubber content above 4 wt % resulted in decrease of strain energy density, plastic deformation zone, yield stress, and modulus, which ultimately leads to reduced toughness at high rubber contents. This demonstrates that there is an optimum particle size (diameter of the rubbery core) and rubber phase content of the modifier that can impart maximum toughness for the notched polycarbonate.

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