Blends of polycarbonate with unmodified and maleic anhydride grafted ABS: fracture mechanics

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Physical blends of polycarbonate (PC) and acrylonitrile-butadiene-styrene terpolymer (ABS) at two different weight fractions were made (PC35/ABS65 and P75/ABS25). Reactive blended similar compositions of PC with maleic anhydride grafted ABS (MABS) were also made at the same compositions. The crack resistance behaviour of these two types of blends and feedstocks (PC and ABS) were studied. The generalized locus method was used to investigate the invariance of crack resistance from any set of characteristic points. PC and PC/ABS blends failed immediately after crack initiation. The modified blends (PC/MABS) exhibited failure through crack propagation after crack initiation started. The resistance to crack initiation is determined in terms of critical J-integral value (J_c). The resistance to crack propagation at maximum load point is also determined from the locus of maximum load point on the load-displacement curves. The resistance to steady state crack growth (R_p) during extensive crack propagation is determined from the total essential energy for a complete fracture. The crack resistance values for modified blends are much high compared to unmodified blends and even feedstocks. © *1999 Kluwer Academic Publishers*

1. Introduction

Polycarbonate is one of the important engineering plastics. It has excellent mechanical performance coupled with gifted transparency. It also has drawbacks which limits its engineering applications. The important drawbacks are notch sensitivity and high melt viscosity. Blending with many thermoplastics or thermoplastic elastomers are found to rectify the above drawbacks. Among them, toughening with ABS (PC/ABS blends) is well known. This alloy is in the commercial market for the past 20 years and presently the largest selling polymer alloy [1].

In commercial practice, reactive compatibilisation is followed to make this PC/ABS alloy. This technique involves addition of third components, such as costly core-shell compatibiliser to the blend system. In recent times extensive open literature has appeared on the recently publicized technique, reactive blending. A brief review of recent publications in related field is presented here.

Cecere *et al.* [2] have followed the reactive blending technique to toughen Polybutylene terephthalate (PBT) with maleic anhydride grafted ethylene propylene rubber (EPR-g-MA). A graft copolymer *in situ* generated from EPR backbone and from PBT branches acted as an interfacial agent or compatibiliser between the matrix and the rubbery dispersed phase. Horiuchi *et al.* [3] have followed the reactive compatibilisation

technique to compatibilise polyamide 6/polycarbonate blends. They used maleic anhydride grafted [styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer (SEBS-g-MA) as the reactive compatibiliser in the PA6/PC blend system. The microscale distribution is evolved because of the *in situ* melt reaction between SEBS-g-MA and amine terminal group of PA6.

Kim and Park [4] have studied the reactive blending of PC with maleic anhydride grafted polypropylene (PP-g-MA). The reaction between PP-g-MA and hydroxyl terminal group leads to the formation of PP-g-MA-g-PC compatibiliser which improves the interfacial interaction. Nelson and Subramanian [5] have studied the reactive blending of nylon 6 with MABS. They also have studied the reactive blending of nylon 6 with PP-g-MA [6]. They reported tremendous improvement in impact strength at nylon 6 rich compositions.

Kalfoglou *et al.* [7] have studied the reactive blending of PET with MABS blend system. They reported that PET/MABS test specimens showed better performance after storage for many days, whereas the PET/ABS blends showed deterioration in performance. Cimmino *et al.* [8] have studied reactive blending toughening of nylon 6 with EPR-g-MA. They assumed the formation of *in situ* compatibilisation or graft copolymer PA6-g-MA-g-EPR formation during melt blending.

Balakrishnan *et al.* [9] have followed reactive blending of PC with MABS. Morphology of unmodified

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blends showed coarse dispersions, whereas that of the modified blends showed fine and lamellar dispersion. Mechanical properties [10] of PC/MABS blends were nearly equal to or higher than those predicted by the rule of mixture and those of PC/ABS blends showed negative deviation from the rule of mixture.

Design of engineering components requires sound understanding about the fracture behaviour of the materials under loads at various conditions. In conventional design, the material is assumed to be homogeneous and defect free, and design practices do not consider prevention of failure initiation at the defects or imperfections that will be inherently present or caused in all materials, either during fabrication or in service. So the behaviour of defects under load is of importance. In the present work, we adopted J integral method to characterize fracture toughness of blend materials. J is a path independent integral and is used to characterize fracture criteria for non-linear elastic materials. Fracture mechanics parameters for reactive blended blends (PC/MABS), physical blends (PC/ABS) and feedstocks (PC & ABS) were determined.

2. Experimental
2.1. Materials
Polycarbonate (Lexan ML 3403), extrusion grade was obtained from GE Plastics India Ltd, Vadodara, India. ABS (ABSOLAC-SP600) was obtained from ABS Industries Ltd, Vadodara, India.

2.2. Procedure
PC and ABS were pre-dried before blending at 110 and 90 °C respectively in a vacuum oven for 8 h. Maleic anhydride grafted ABS (MABS) was prepared by grafting maleic anhydride onto ABS. PC was blended at two different weight percentages of 35 and 75 with ABS using a single screw extruder with a special mixing head. The above samples have been respectively coded as P35 and P75 respectively. PC was also blended with MABS at the same weight ratios and similar conditions and these samples have been coded as MP35 and MP75. The process temperatures ranged from 220 to 240 °C. The extruded pellets of these blends were vacuum dried at 90 °C for 8 h, then used for injection moulding to make samples for fracture mechanics examination.

Injection moulded samples of $120 \times 14 \times 5$ mm were used for this study. Four initial crack lengths viz. 0.5, 1, 2 and 3.5 mm were used for all the blend materials. The cracks were made in two stages for all the notch levels except for the lowest crack level. Initially the samples were machined using a notching tool which is used to make notches to measure notched impact strength and then sharp cracks were created by pushing a sharp razor blade into the tip of the machined notch. The lowest crack of 0.5 mm was created carefully using sharp razor blade. Inherent stresses developed during injection moulding, notching and razor cutting were minimized by annealing process. The annealing of all the notched test specimens was done in a vacuum oven at 105 °C for 12 h. The specimens were stored in a dessicator for sufficient time until the measurement.

Tests were performed using a Zwick Universal Testing Machine (Zwick 1465) in flexural mode with a span length of 80 mm at a cross head speed of 5 mm/min. Load vs. load-displacement graphs were recorded and the initiation points were noted using a magnifying lens. The areas under the curves were calculated numerically. The fracture mechanics parameters were calculated from the load vs. load point displacement curves.

3. Results and discussion
The resistance to crack propagation starting from crack initiation to complete fracture was examined for the blend materials. The fracture mechanics parameters viz., critical energy for crack initiation (J_c), resistance to steady state crack growth (R_p) and resistance to crack growth at maximum load (R_{max}) were determined using the three point bending method developed by Kim and Joe [11].

Fracture toughness of the PC/ABS and PC/MABS blends was also determined using Kim and Joe's three point bending method. It is a method which determines crack growth resistance utilizing the locus of any set of characteristic points on the load versus load-point displacement curves (R-curve) of specimens which differ only in initial crack length. In general, R-curve has three sections viz. ascending, plateau and descending regions. Each region characterizes a different stage of fracture behaviour. The ascending region includes the crack initiation with increasing resistance to crack growth. The plateau region occurs when the plastic deformation zone reaches and maintains a certain size during crack growth. The descending region begins when the plastic deformation zone is confined due to specimen configuration and ends upon failure. In some cases, the R-curve consists of only ascending region. In such cases, the materials failed catastrophically, immediately after crack initiation.

Kim and Joe have used this theory successfully on less complex polymeric materials. Their work has resulted in a simple method of determining crack resistance values. Otterson *et al*. [12] have used this method to investigate compatibilisation effect on more complex nylon-6/ABS blends in terms of fracture toughness. Kumar *et al*. [13] have used this technique to evaluate toughening effect of TPU with polyacetal.

The locus line of crack initiation points on load-displacement records is used to find the crack initiation resistance in terms of the critical J-integral value (J_c). J_c can be calculated from the following equation:

$$J_c = -(1/B)(\Delta U_c/\Delta a) \qquad (1)$$

where B is the sample thickness, a is the initial crack length, and U_c, the essential energy required to initiate the crack.

If the crack initiation point is observable and is noted on the load versus load-point deflection curve of each tested specimen, U_c is then determined from the area surrounded by the locus line of crack initiation points, the load versus load point deflection curve, and the x-axis. J_c may be found by plotting U_c per unit

thickness versus a. From Equation 1, it is seen that if U_c varies linearly with respect to a, then J_c is a constant value. The slope of this linear line represents the constant J_c.

The resistance to steady state crack propagation may be obtained in a similar way using the formula

$$R_p = -(1/B)(\Delta U_f/\Delta a) \qquad (2)$$

where U_f is the total energy for fracture.

It is also possible to determine the resistance to crack growth at maximum load (R_{max}) using the maximum load points on the load versus load-point deflection curves as characteristic points. Determination of R_{max} value depends upon whether or not the complete R-curve exhibits a point of sharp curvature between the

initiation and steady state resistances

$$R_{max} = -(1/B)(\Delta U_l/\Delta a) \qquad (3)$$

where U_l is the area surrounded by the locus line of maximum load points, the load versus load-point deflection curve, and the x-axis. The detailed procedure to determine the above parameters has been described in Otterson *et al.* [13].

Figs 1 to 6 show typical load versus load-point deflection curves obtained for feedstocks (ABS and PC), and the blends, P35, P75, MP35 and MP75 using the three-point bending method. PC and unmodified blends, P35 and P75 failed in a brittle manner, resulting in catastrophic failure immediately after crack initiation. Fracture of ABS and modified blends, MP35 and MP75 pass through crack propagation after crack initiation.
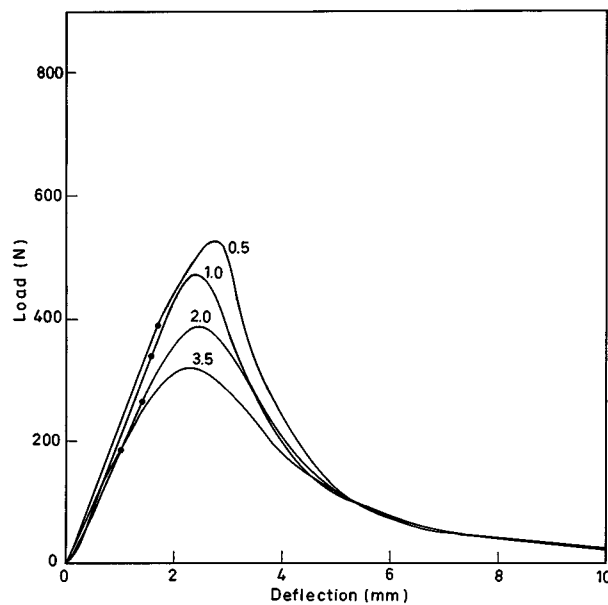

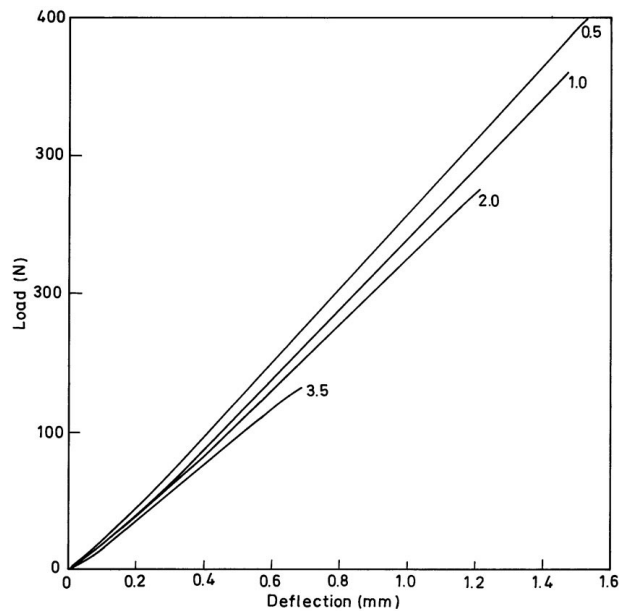*Figure 1* Load versus load-point displacement curves for ABS.

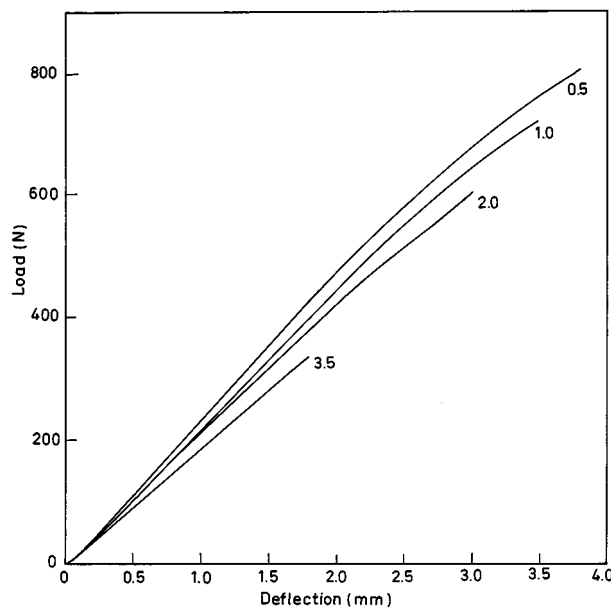*Figure 2* Load versus load-point displacement curves for PC.

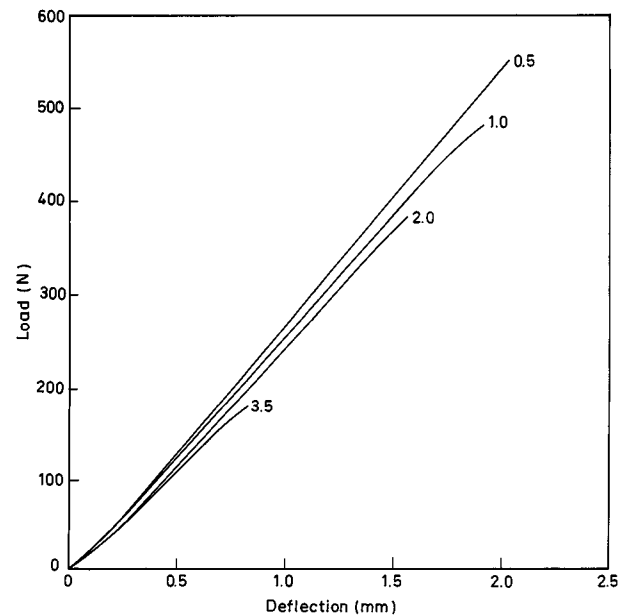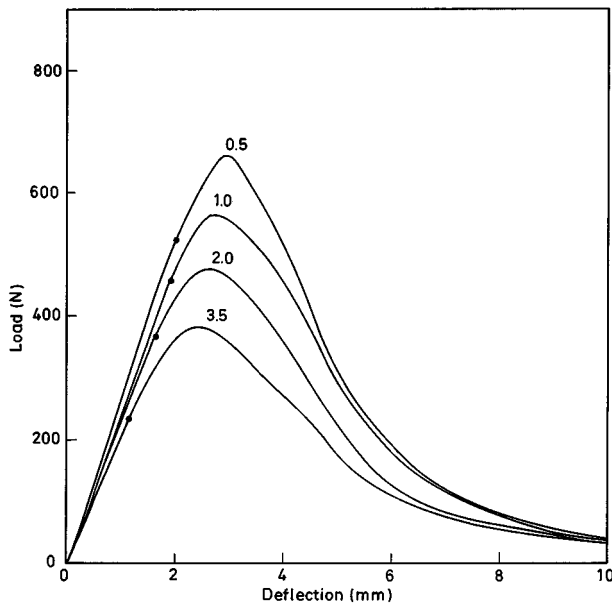*Figure 3* Load versus load-point displacement curves for P35.

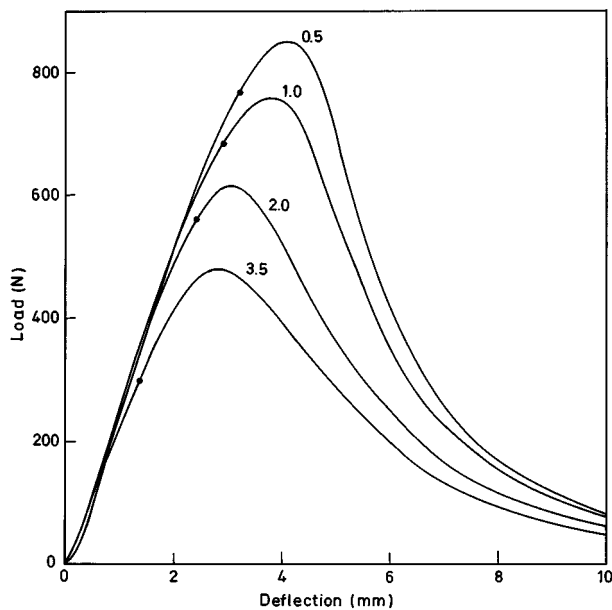*Figure 4* Load versus load-point displacement curves for P75.

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Figure 5 Load versus load-point displacement curves for MP35.

Figure 6 Load versus load-point displacement curves for MP75.

TABLE I Crack resistance values for PC, ABS and blends

Blend materials	Fracture toughness (kJ/m^2)		
	J_c	R_{max}	R_p
PC	75.62	—	—
P35	17.67	—	—
P75	32.31	—	—
MP35	26.68	36.12	74.07
MP75	65.74	82.12	124.56
ABS	13.85	17.43	25.82
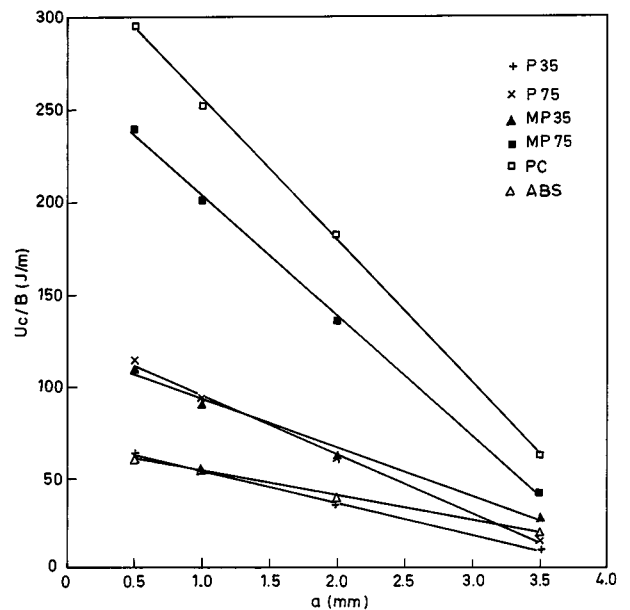
Figure 7 U_c/B versus initial crack length a.
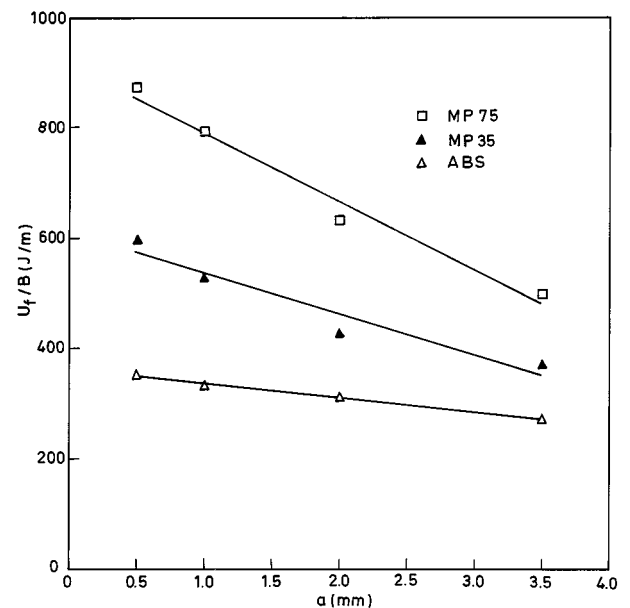
Figure 8 U_f/B versus initial crack length a.

The crack initiation points of these ductile-failed samples are shown as black dots on each curve.

The total energy required to initiate the crack (U_c) was determined and plotted in accordance with Equation 1 for the set of specimens in which crack initiation could be observed. The ultimate failure points in the R-curve for brittle samples are considered as crack initiation points as well, since they failed immediately after crack initiation. The resulting plots for all the samples are shown in Fig. 7. The slopes of each of these plots represent J_c for each material and these values are given in Table I.

The total energy for fracture (U_f) for each specimen was determined and plotted in accordance with Equation 2. These plots are shown in Fig. 8. The slopes of these plots represent R_p for each material and these values are given in Table I. The total energy up to maximum load (U_l) for each specimen was determined and

plotted in accordance with Equation 3. These plots are shown in Fig. 9. The slopes of these plots represent R_{max} and these values are given in Table I.

Reactive blending of PC/MABS blends has dramatic synergistic effect on fracture properties of these blends. Crack initiation energy values of modified blends are
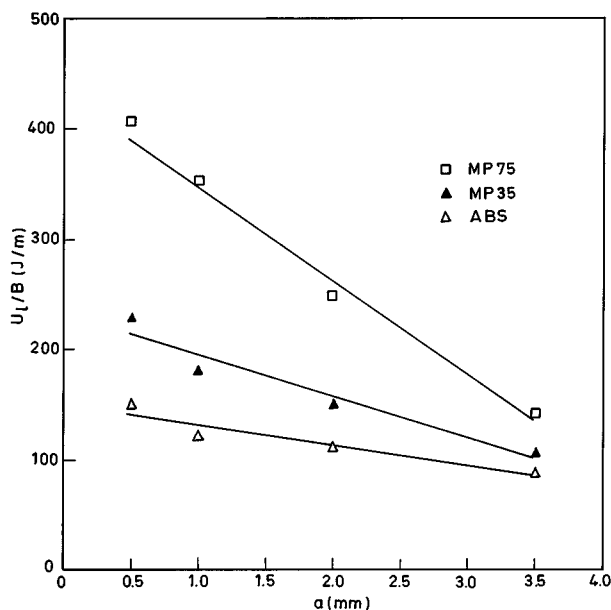
Figure 9 U_1/B versus initial crack length a.

at least proportional to the additivity values of initiation/fracture energy value of PC and initiation energy value of ABS. The experimental fracture energy values (R_p) for these blends are much higher than the weighted average values. This suggests that tremendous improvement in fracture toughness is observed in the case of modified blends. Crack initiation/fracture energies of unmodified blends are generally less than those of modified blends at similar PC weight percent levels. Probably the coarse dispersion and PC deterioration in unmodified blends are responsible for the poor fracture values [9 and 10]. Fracture energy of MP75 (124.5 kJ/m^2) blend is much higher than that of PC (75.62 kJ/m^2).

4. Conclusions

(1) The fracture pattern for PC and, PC/ABS blends are the catastrophic failure after crack initiation whereas that of ABS and, PC/MABS blends exhibited steady crack propagation after crack initiation until failure.

(2) The crack growth in modified blends includes crack propagation after crack initiation, characteristic of ductile material. Unmodified blends failed immediately after crack initiation, characteristic of brittle material.

(3) The fracture energy values for modified blends are much higher than those of unmodified blends. The fracture energy for MP75 is nearly four times higher than that of P75 while the crack initiation energy for MP75 is twice the value for P75.

(4) Such a large increment in the case of modified blends could be because of the finer and lamellar type morphology development whereas the morphology in the case of unmodified blends is coarse.

(5) The fracture energy value for MP75 blend (124.56 kJ/m^2) is much higher than that of PC (75.62 kJ/m^2).

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