The Effects of Functional Azo Initiator on PMMA and Polyurethane IPN Systems. III. Tear Resistance and Crack Growth of PBD(1,2)-PU/PMMA (50%) Blends

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SYNOPSIS

The tear strength and crack growth mechanism of PBD(1,2)-PU/PMMA (50%) IPN systems were studied by the trouser tear test and single edge notched (SEN) tensile test. It was found that these blend systems showed similar structures and properties to particulate-reinforced elastomers. The tear strength was dominated by the structure of the rubber matrix. The PMMA phase increased the tearing resistance by increasing the hysteresis of the IPN systems. Chemical bonding between the PMMA-rich particle and PU-rich matrix prepared by using a reactive azo initiator inhibited the initiation of the fracture nucleus, decreased the intrinsic flaw size, and increased the tear strength. The crack growth of these IPNs was dependent on both the fracture energy available for crack propagation and the hysteresis of the material. The similar structure of these two blends resulted in the similar crack growth behavior.

INTRODUCTION

Parts I[1] and II[2] of this series described the reinforcement mechanism and mechanical properties of PU/PMMA IPN systems prepared by use of a reactive azo initiator. It had been shown that the structures of these IPNs were similar to particulate filled elastomers. The reactive initiator, which could form blocks of PMMA on the PU chains changed both the filler–matrix interface between the PMMA particles and the PU rubber matrix and the matrix structure. This paper describes the fracture properties and crack growth mechanism of low PMMA concentration (50% by weight) PU/PMMA blends by use of the same concepts that have been used in other studies of elastomers and particle-filled elastomers.

The resistance to tearing of flexible materials has been considered[3] a basic material property that depended strongly on the temperature and rate. An extension of the Griffith failure criterion[4] in which

tear energy T was defined[4] as

$$T = -(\partial W/\partial A_0)_l \qquad (1)$$

where W is the energy stored in elastic deformation, A_0 is the surface area of the unstrained tear, and subscript l denotes conditions of constant deformation. The two primary assumptions in this approach were that tear propagation resulted from the conversion of free energy to fracture energy and that this energy conversion depended on the rate of propagation rather than tear growth history.

The tearing resistance of elastomers had been extensively studied by Rivlin and Thomas.[3,5-7] Anderton and Treloar[8] and later Sims,[9] have investigated the influence of orientation of polyethylene and of polypropylene on their tearing strength. Isherwood and Williams[10] have discussed the relationship of tearing and tensile properties for a wide range of ductile materials. For multiphase polymers, Kim et al.[11] studied the tear strength of PU/PMMA IPN but no clear conclusions were given. A large number of studies of tear have been made with carbon-black-reinforced rubbers.[12,13] These results showed that the tear property was more complicated than those of gum elastomers. There was a basic resemblance to the behavior of the unfilled rubbers, but there were,

at certain rates and temperatures, superimposed regions of high tearing energy that were associated with the development of "knotty" tearing.

In the present study, tear resistance was measured in both simple trouser tear test and single edge notched (SEN) tensile test. The crack growth behaviors of the blends were studied in SEN tensile test by using a optical microscopy to measure the crack length.

EXPERIMENTAL AND CALCULATIONS

Preparation of Samples

The IPNs were prepared as described in the Paper I[1] of this series, by the interstitial polymerization of MMA monomer within a polyurethane gel. As the MMA monomer polymerization proceeded, phase separation occurred between PMMA-rich and PU-rich matrix phases. A reactive azo initiator (ABC) which could form blocks of PMMA on the PU chains was used in the systems to improve the interfaces between the two phases. Adipic acid (AA) was added in the standard initiator (AIBN) to provide the same amount of carboxyl functions, and resultant amide structures, as existed in the reactive system. The compositions of the blends were 50% PMMA by weight.

Trouser Tear Test

The trouser tear test which was described previously in Paper II[2] is shown in Figure 1. A central slit was
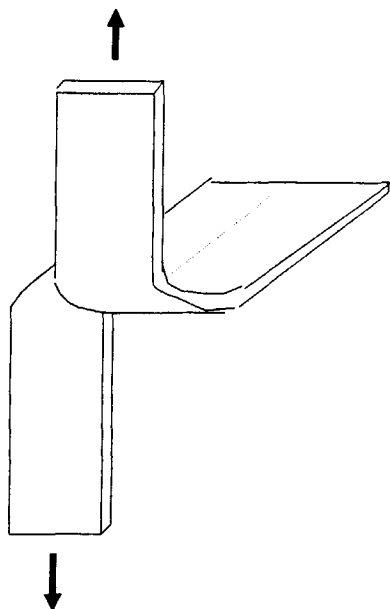

Figure 1 Trouser tear test.

made part through the thickness for all the specimens in order to guide the tear path. The tear energy for this test was given by[3,5]

$$T = 2\lambda F/t - 2bW \qquad (2)$$

where T is tear energy, λ the extension ratio in the legs, t thickness, b the width of legs, and W the strain energy density in the legs. When the extension in the leg region was negligibly small ($\lambda = 1$), i.e., when the legs were much wider than their thick, no energy was stored in the legs and eq. (2) was reduced to

$$T = 2F/t \qquad (3)$$

Equation (2) was used to calculate the tear energy for pure PU rubber because of its high extensibility. The strain energy density was determined by integration under the stress–strain relation.

It was worth noting that t was not generally the same as the sheet thickness because the tear tended to run at an angle of about 45° to the thickness direction so that it lay perpendicular to the direction of principal tensile stress. Thus, although failure appeared to result from shear stress, the tear actually followed a path at right angles to the maximum load tensile stress.

Crack Growth Study

Crack growth measurements were carried out on thin strips of blends about 40 (length) × 10 (width) × 1 mm (thickness) (Fig. 2). A small crack, from 0.2 to 2 mm in length, was initiated in one edge of each test piece and was positioned as nearly as possible perpendicular to the surface. The test piece was then deformed in simple extension on a Minimat test machine. The load–displacement curve was recorded automatically by a computer. The crack length c was measured by use of a optical microscopy camera. The crosshead speed was about 0.2 mm/min for all specimens, which corresponded to a strain rate of 0.5%/min.

When a test piece as described above was used for both elastomers and other materials which followed a nonlinear relationship between tensile stress and elongation, the tear energy was given by[5]

$$T = 2KWc \qquad (4)$$

where W is the elastic strain energy density in the region of the test piece remote from the crack, c the length of crack, and K a function of the extension ratio, given by[7]
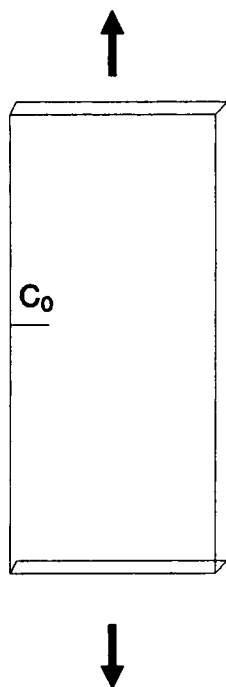
Figure 2 Single edge notched (SEN) tensile test.

$$K = \pi/(1 + e)^{1/2} \tag{5}$$

for materials subjected to a finite tensile strain e.

Recently Ahagon et al.[14] and Thomas and Kadir[15] have suggested that for rubbers which exhibit significant internal energy dissipation outside of the immediate crack tip regions, eq. (4) may still be employed. However, the stored strain energy available for crack propagation should not now be taken as the total input energy but rather as that deduced from the stress-strain relation upon retraction from the deformed state—that is, the input energy minus the hysteresis (loss) energy (elastic strain energy density).

In this study, the elastic strain energy was used to calculate the tear energy since these blends show significant hysteresis.[2] The measurement of elastic strain energy density was carried out by stretching different tensile specimens to different elongations and then allowed to retract at the same rate to the unstrained state. The same crosshead speed (0.2 mm/min) of these tear tests was used, corresponding to a strain rate of 0.9%/min.

RESULTS AND DISCUSSIONS

Tear Strength in Trouser Test

Figure 3 shows the load–displacement curves of pure PU and of PU/PMMA blends in trouser tear test.

The tear strengths of the blends with different initiators were given in Table I calculated according to eq. (3). The higher tear strength for the reactive initiator blend relative to the standard blend was possibly caused[13] by the chemical bonding between the PU/PMMA phases as shown in Paper I[1] of this series.

Higher tear strength was found in these blends than that in pure polyurethane. The PMMA particles apparently caused deviation of the tear path from a straight line, so that the tear becomes rougher and the tear strength correspondingly higher.[16,17] Figures 4(a) and 4(b) show the tear surfaces of pure PU and these blends. When the tear deviated, the rate of tear decreased and the force buildup until a new tear was initiated. The force required to start tearing was proportional to the unstrained diameter of the tip of the tear, in accordance with an equation first derived by Thomas[18]

$$T = W_b d \tag{6}$$

where W_b was the work done to break per unit volume.

The observed force necessary to propagate the tear varied widely from a maximum at tear initiation to a minimum at arrest. Since tear strength was directly dependent on tear-tip diameter, this led to a certain ambiguity in the measured strength. Most researchers have reported an admittedly qualitative propagation energy obtained by averaging the tear initiation and arrest values.[4,5,19] Others have elected to utilize only the initiation or maximum force values.[20,21] In this study, the average maximum force was chosen to calculate the tear energy.

Higher tear strength in these blends may have contributed to the higher hysteresis by reaction of the PMMA phase with the PU matrix.[2,22,23] The aggregated hard segments in the PU phase may also have contributed to the hysteresis of the blends. When a crack propagates in a elastic material, its stress distribution around the crack tip usually moves with it so that the locus of maximum stress, along which the crack propagates, coincides with the crack axis. However, severe hysteresis may cause the stress distribution associated with the initial crack to remain stationary when the crack propagates in those blends which show high hysteresis. Thus, the growing crack will not follow the axis but will propagate along one or both loci of maximum stress, resulting in deviation or forking of the crack tip. The growing crack will now encounter lower and lower stress as it propagates and must therefore come to a stop unless the overall stress on the spec-
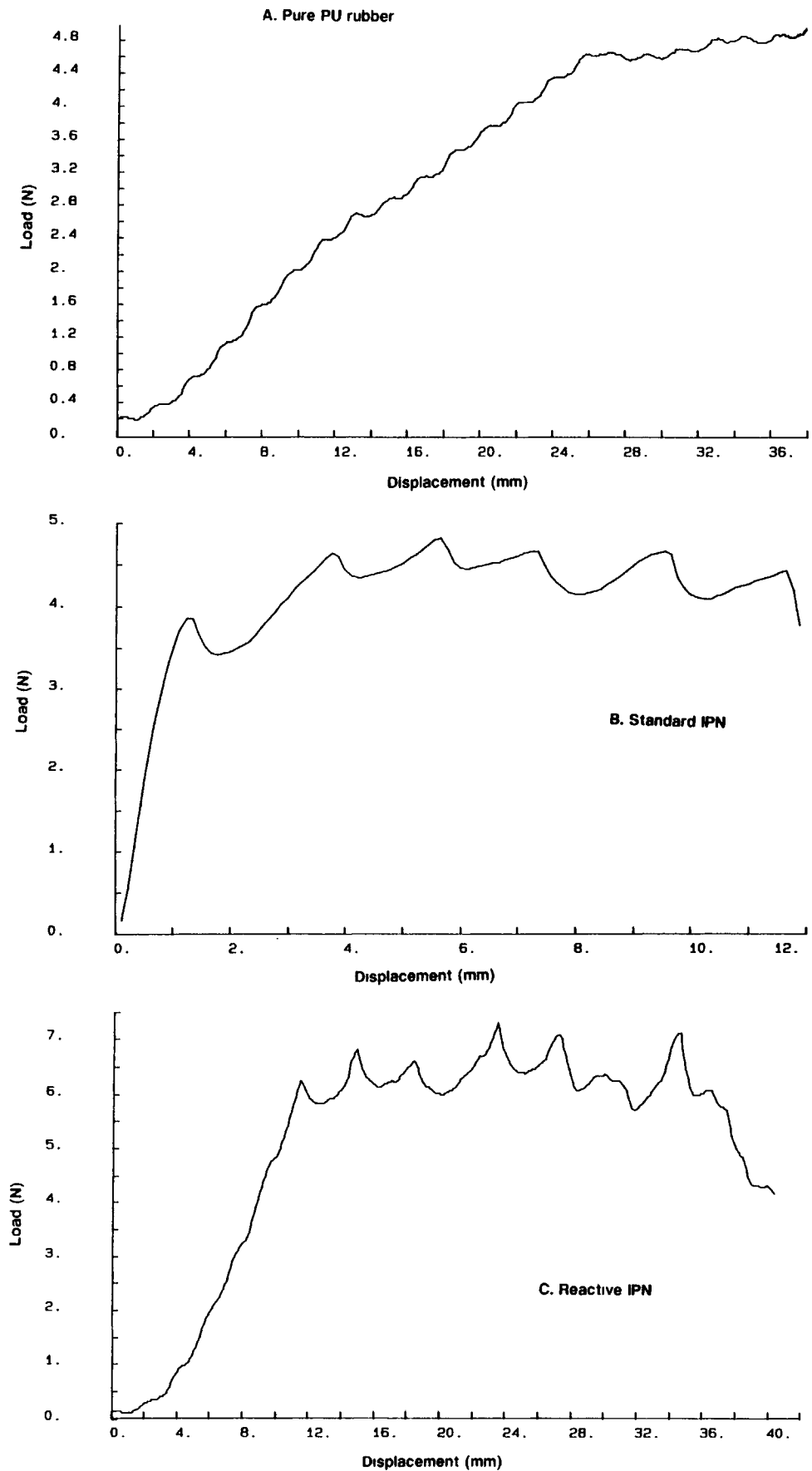
Figure 3 Load–displacement curves in trouser tear test: (A) pure PU; (B) standard PU/ PMMA (50/50) blend; (C) reactive PU/PMMA (50/50) blend.

Table I   Tear Strength and Properties of PU/PMMA (50/50) Blends

	Pure PU	Standard Blend	Reactive Blend
T (kj/m^2) (from trouser test)	4 ± 1	9 ± 3	15 ± 3
Strain energy density (kJ/m^3)	3600	6100	7500
Elastic strain energy density (KJ/m^3)	2500	820	1100
PMMA domain size (μm)	—	0.04	0.04
Hypothetical flaw size (μm)	87	750	650

imen was increased. At this high stress, the mechanisms maintaining the stationary stress distribution fail since the energy available for crack growth was far greater than that needed for stable growth and the rapid propagation phase follows. The tear deviation and the corresponding high tear energy may also result from the PMMA particle which forms barriers in the path of the tear by alignment of their aggregation and interpenetrating effect at the boundary of the PU/PMMA phases.[15,17]

Fracture Nuclei in Tension

As was noted earlier, tear strength is in many ways a fundamental measure of the strength of a material. A relationship between tear strength and tensile strength was given by Griffith's flaw concept of tensile rupture as the catastrophic growth of tearing a chance edge nick or flaw.[4] When rubbers containing rigid-particulate filler were subjected to an applied tensile stress, triaxial stresses were generated immediately above and below the filler particles.[24] These regions may act as favorable sites for the initiation and growth of internal voids and cracks. If the material was linearly elastic up to the point of rupture, with break strength σ_b and Young's modulus E, then the breaking stress and elongation at break, e_b, can be expressed directly in terms of tear strength T and the depth c of an edge nick[4]

$$\sigma_b^2 = TE/\pi c \qquad (7)$$

and

$$e_b^2 = T/\pi c E \qquad (8)$$

When the material follows a nonlinear relationship between tensile stress and elongation, a corresponding relation can be derived[5] for the elastic strain–energy density W_b at break

$$W_b = T/2Kc \qquad (9)$$

where K was given in eq. (5). The above relation could also be used for nonelastic materials when elastic strain–energy density was employed.[25]

For the PU/PMMA IPN systems, the depth c of the hypothetical flaw from which tensile initiated have been calculated by means of eq. (9), using the measured tear strength or tear energy T and *elastic* strain–energy density at break, W_b. The values obtained in this way for the depth a_0 of intrinsic flaw sizes are given in Table I. The PMMA particle sizes of these IPNs are also given in Table I. It can be seen that the average particle sizes were quite small, much less than the matrix intrinsic flaw size of about 90 μm and a value for a_0 of this size might well have been expected in these IPN systems. However, the calculated flaw sizes in these heterogeneous IPNs were in the order of hundreds of micrometers, which was in good agreement with other multiphase polymeric composites.[26] Berry[27] found that the fracture strengths of PMMA and PS were independent of the flaw size when it was smaller than its intrinsic flaw size. Obviously these large flaws were not present in the material before deformation but appeared to be formed during loading, possibly by the coalescence of microvoids or by several debonded particles. Figure 5 shows the SEM fracture surfaces of PU/PMMA IPNs. The cavitations at these fracture surfaces indicate that the PMMA particles have been removed from the PU matrix under the high stresses that developed during the rupture. These cavitations may have formed crazes or microcracks during loading and grew to the large flaw size. The smaller intrinsic flaw size in the reactive blend could have arisen from the greater chemical bonding between the PMMA particles and the PU matrix by the presence of the PMMA blocks on the PU chains, which reduced the debonding process as compared to the standard blend.

Crack Growth Behavior

Figures 6(a) and 6(b) show the normalized load–displacement curves for different initial crack length C_0 in tests on PU/PMMA blends prepared with the standard (AIBN + AA) initiator and the reactive (ABC) initiator. When a specimen containing a crack was slowly stretched, tearing occurred at the tip of the crack when the applied force reached a
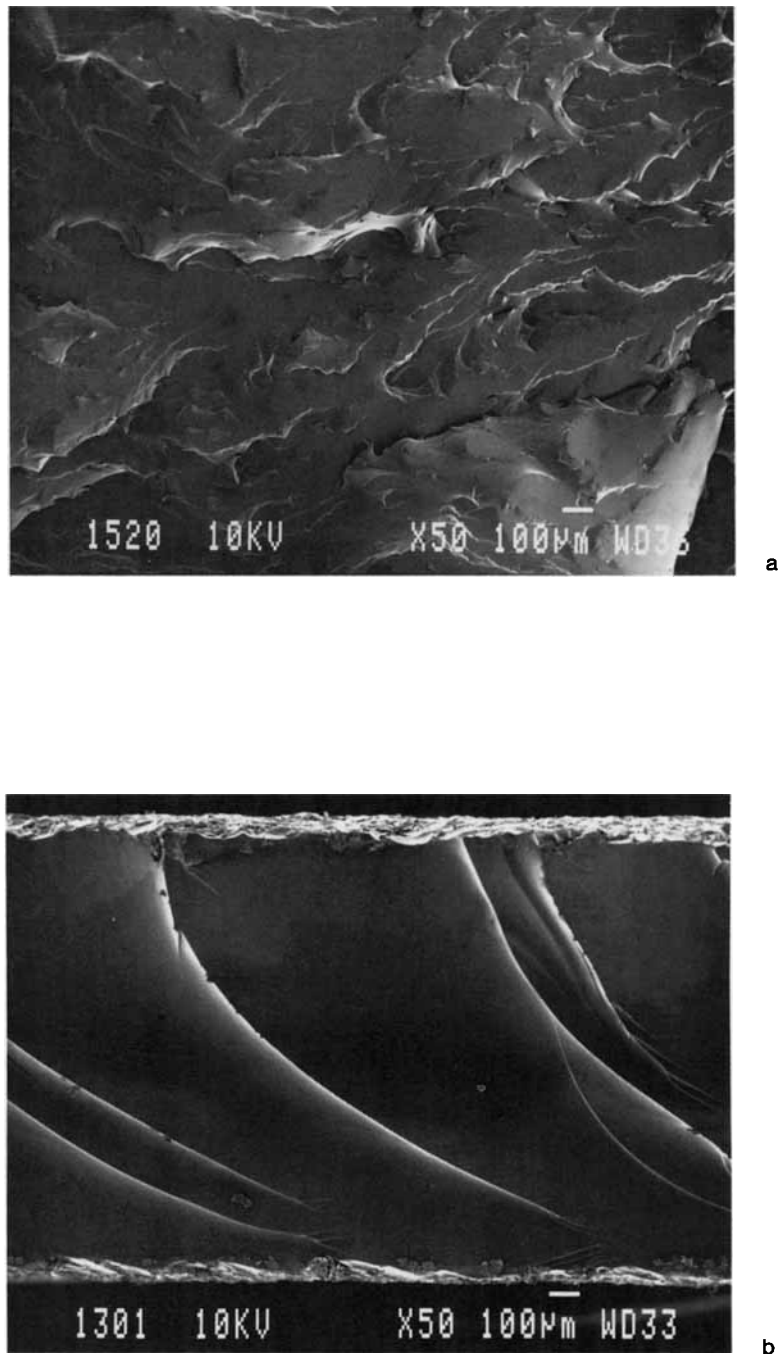
Figure 4 SEM tear surfaces in trouser tear test at low magnification: (A) pure PU; (B) PU/PMMA (50/50) IPNs.

critical value.[5] Initially, tearing continued only as long as the deformation was increasing and ceased as soon as the deformation was held constant. The amount of crack growth continued to increase during extension until, suddenly, there was a rapid increase in the length of the crack. This had been called "catastrophic" tearing.[5] The crack growth of PU/

PMMA blends can be divided into four regions (Fig. 7): crack blunting, crack initiation, stable crack growth, and catastrophic crack growth. Rivlin and Thomas[5] also showed a similar phenomenon in gum natural rubber. A comparison of the load–displacement curves of a PU/PMMA sample which contained a crack and another sample without crack
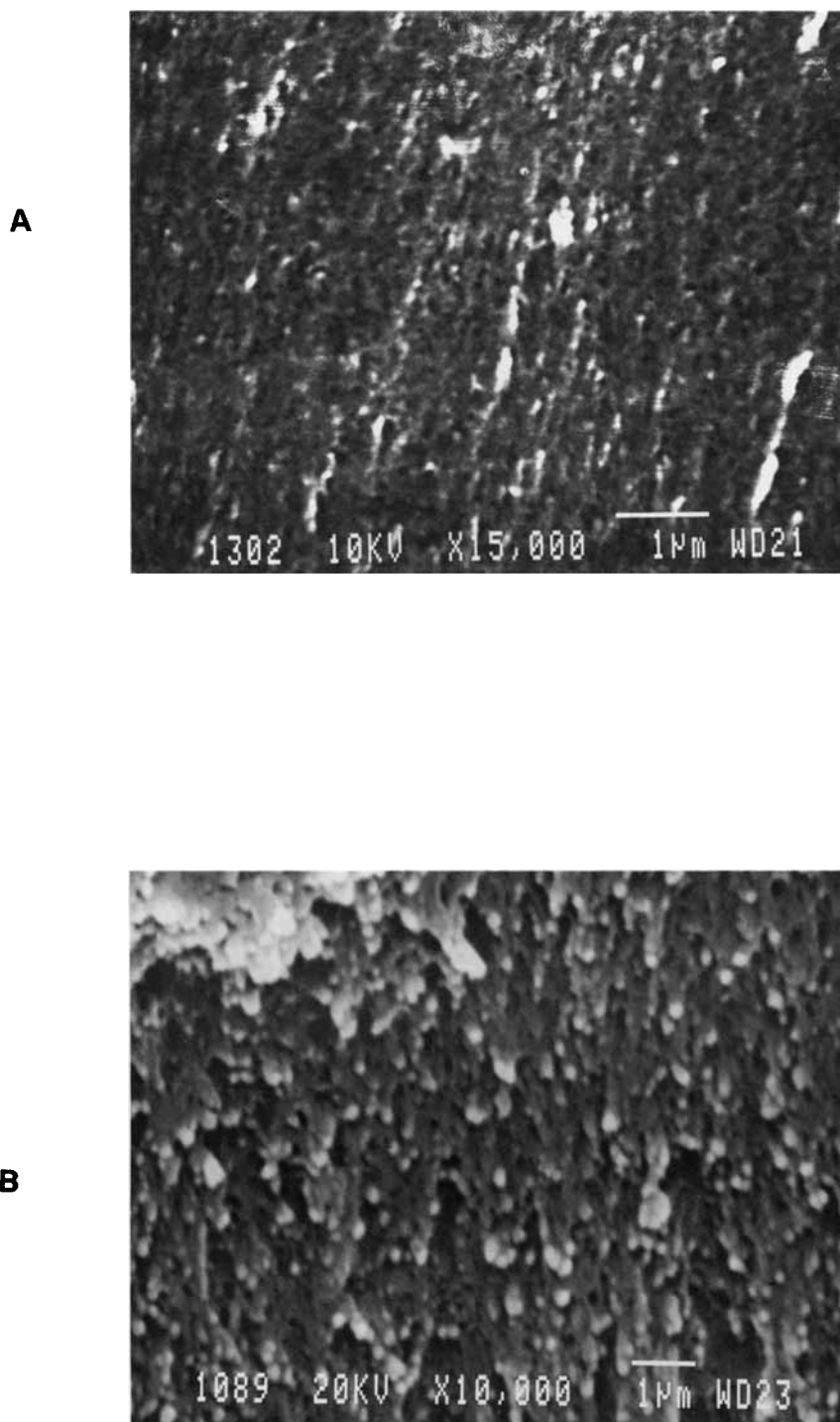
Figure 5   Fracture surfaces of PU/PMMA IPNs: (A) PU/PMMA (50/50); (B) PU/ PMMA (20/80).

showed that even a very small crack decreased the maximum load and extension ratio significantly, and the crack initiation became much easier relative to pure gum natural rubber[5] (Table II). This may relate to the heterogeneity produced in the blends by PMMA particles. For heterogeneous materials, such as filled rubbers and strain-crystallizing rubbers, the crack initiation site was near the filler particles or crystallinity.[24] This may explain the lower T_0 values in these blends as compared to pure PU, which was
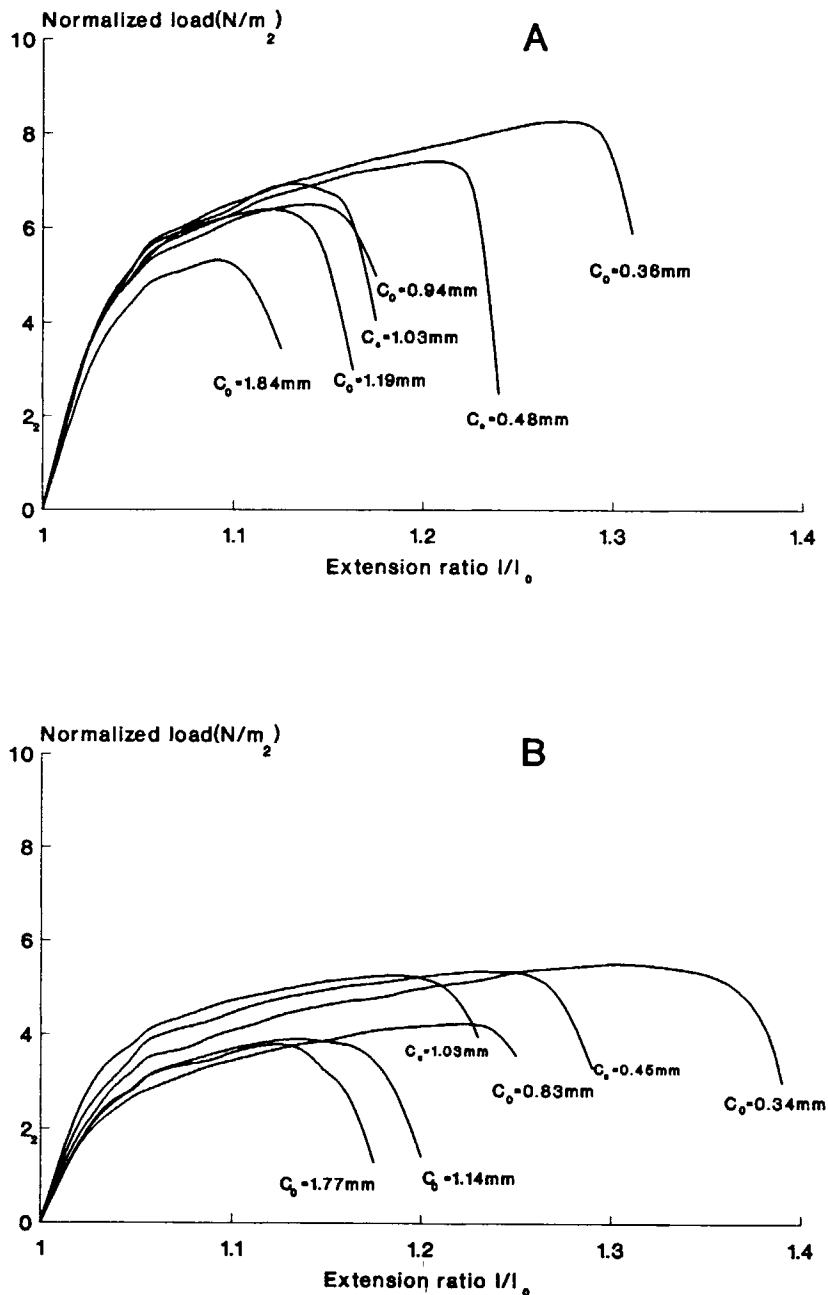
Figure 6   Normalized load–displacement curves of PU/PMMA (50/50) blends in SEN test: (A) standard blend; (B) reactive blend.

about 0.8 kJ/m^2. Table II shows the elastic strain–energy density and tear energy of the two PU/PMMA blends at crack initiation point with different initial crack length. It can be seen that the tear energy at this point (T_0) was about 170–220 J/m^2 for standard blend and 100–170 J/m^2 for reactive blend. The relatively high T_0 in standard blend may be attributed to the rigid matrix structure in this blend than that in the reactive blend.

Rivlin and Thomas[5] have shown that the growth of a crack by catastrophic tearing can be described by an energy criterion. Lake and Lindley[28] have shown further that the small growth of a crack Δc before catastrophic tearing occurs was also determined by the energy (T) available for crack propagation. After studying several different types of rubbers, they concluded that[29] the relation between crack growth rate and tearing energy was an intrinsic
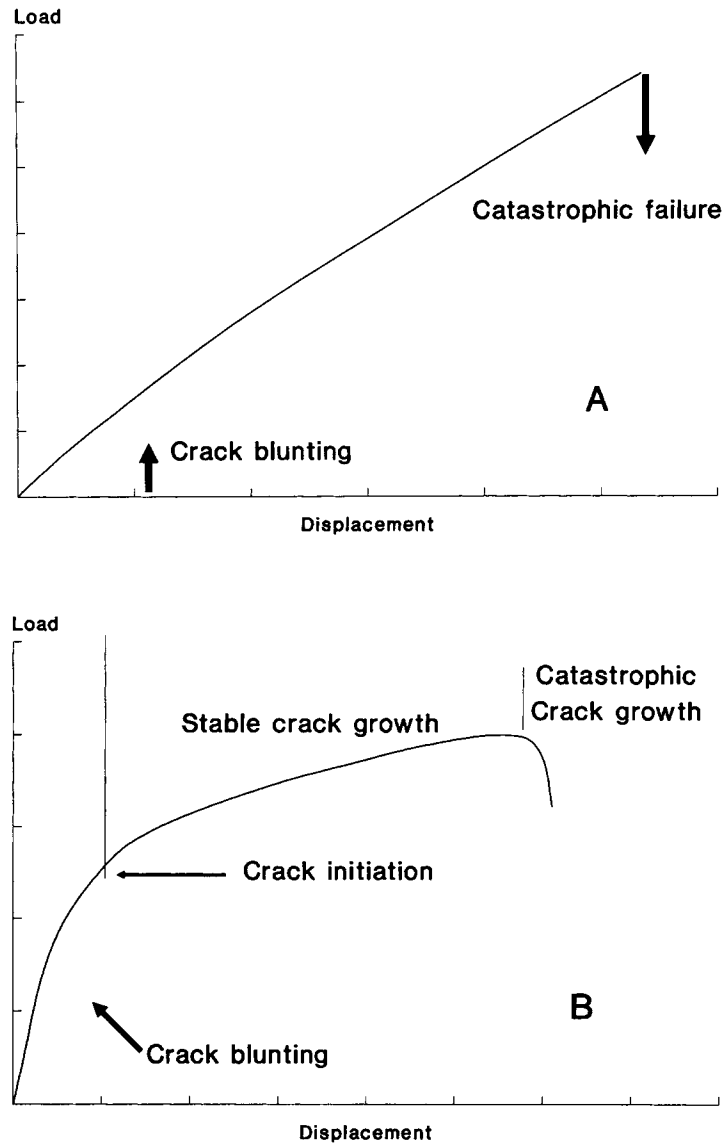
Figure 7 Schematic shows the crack growth behavior in SEN test: (A) pure PU; (B) PU/PMMA (50/50).

property of the material. Figures 8 and 9 show plots of crack growth rate ($\Delta c/dt$) and crack growth (Δc) against tearing energy T on a logarithmic scale. The following approximate relationships were obeyed by these data:

$$\Delta c/\Delta t = T^n/G_1 \qquad (10)$$

and

$$\Delta c = T^m/G_2 \qquad (11)$$

where G_1, G_2, n, and m were material constants given in Table III. It can be seen that the blends

have similar crack growth constants to those of natural rubber which undergoes crystallization on stretching[30] (Table IV). Therefore, the PMMA in the PU rubber phase and crystallinity in natural rubber gave similar effects. Greensmith[12] and Thomas[31] also found that the effect of crystallinity on natural rubber and carbon black filler on elastomers showed a similar effect. The smaller n and m and larger G_1 and G_2 values in PU/PMMA blends and natural rubber compared to vulcanized SBR rubber indicated a higher tear resistance to crack growth than that of vulcanized SBR rubber.

The higher tear resistance to crack growth in

Table II Elastic Strain Energy Density and T_0 of PU/PMMA (50/50) Blends in SEN Test

Sample No.	c_0 (mm)	Extension Ratio	Elastic Energy Density (kJ/m^3)	T_0 (kJ/m^2)
A. Standard IPN				
137	0	1.6	820	—
137	0.36	1.01	15	0.033
137	0.48	1.05	74	0.22
137	1.03	1.02	30	0.19
142	0.94	1.02	30	0.17
142	1.19	1.02	30	0.22
142	1.84	1.01	15	0.17
B. Reactive IPN				
136	0	1.85	1100	—
136	0.36	1.04	46	0.096
136	0.48	1.03	35	0.096
136	1.03	1.02	23	0.15
141	0.83	1.03	35	0.17
141	1.14	1.02	23	0.16
141	1.77	1.03	35	0.38

these blends was attributed to local energy dissipation at the crack tip.[18] This energy dissipation may arise from both hysteresis and bond rupture. When a test piece of PU/PMMA blend containing a crack was extended, the stress at the crack tip increased until the blend was at the point of breaking. Up to this point the stress at the tip was governed by the extension stress–strain curve. If the extension of the test piece continued, the crack began to grow, causing relaxation of a region of highly strained blend around the crack tip. This relaxation was governed by the retraction stress–strain curve and influenced the stress at the new tip. Since these blends were hysteresial in the highly strained state, the stress at the tip may have been substantially less than would have been the case if the they were perfectly elastic. This effect can explain why a crack does not propagate indefinitely once crack start growing. Thus, the amount of crack propagation which did occur depended on the hysteresial properties of the material. The greater the hysteresis, the more difficult it was for the crack to propagate. It appeared that the addition of the PMMA into the PU matrix increased the hysteresis ratio and resulted in a high tear resistance.

The crack growth constants G_1 and G_2 in eq. (10) and (11) were dependent on the oxygen concentration of the atmosphere in which the test was conducted.[32] Greater resistance to tearing (larger G_1 value) in sulfur vulcanized SBR rubber (Table III) had been attributed to labile sulfur bonds that break and reform to release internal stresses. It appears that these constants in IPNs also related to their high hysteresis ratio of the materials. The similar G_1 and G_2 values for the two PU/PMMA blends confirmed their structure similarity.

The different initiators which produced different interfaces between PU rubber matrix and PMMA particles and different matrix structure of the blends did not produce any remarkable effect on the crack growth behavior of the blends, even though their mechanical properties were different. These initiators did not significantly influence the relation of crack growth and tear energy but modified the tear-
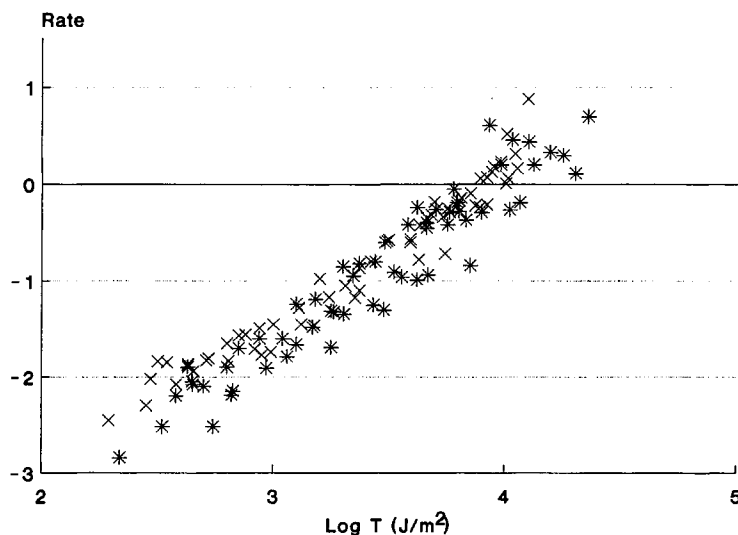

Figure 8 Crack growth rate $(\Delta c/\Delta t)$ vs. tearing energy (T) of PU/PMMA blends in SEN test: (X) reactive IPN; (*) standard IPN.
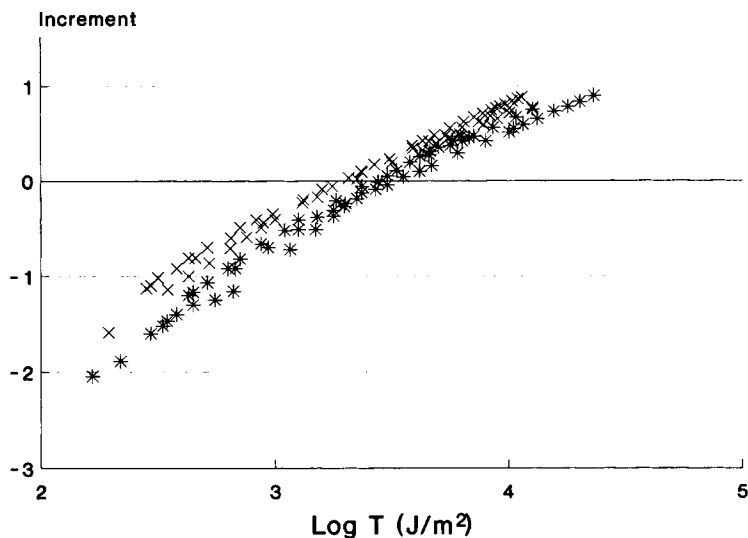
Figure 9 Crack growth increment Δc (mm) vs. tearing energy (J/m^2) of blends in SEN test: (X) reactive IPN; (*) standard IPN.

ing energy and corresponding crack growth rate. The reason may include the following: (1) the crack growth behavior of the blends was dependent on the interfaces between the PU/PMMA phases.[24] Both blends had similarly strong filler/matrix interfaces by bonding by chemical reactions. From the DMTA data,[2] it appeared that this chemical bonding between the filler and the matrix in the reactive blend did not have a significant effect on the interface. (2) The similar elastic strain energy density–strain relation of the two blends (Fig. 10) gave similar crack growth behavior even while their hysteresis behavior was different. These similarity of elastic strain energy–strain relation may have arisen from the similar matrix structure of the two blends.

CONCLUSIONS

1. The structure and mechanical properties of PU/PMMA IPN systems at low PMMA load were similar to the particulate reinforced elastomer and strain-crystallizing elastomers.
2. Lower tear strength in the standard blend

relative to the reactive blend was caused by chemical bonding. Tear deviation appeared to be the mechanism of the high tear resistance.

3. Chemical bonding between PMMA particle and PU rubber matrix may have prevented the debonding process and decreased the intrinsic flaw size at catastrophic tear.
4. The crack growth behavior of the blends was determined by the energy available to crack propagation and the hysteresis of the blend. The similar structure of these blends gave the similar crack growth behavior.

SUMMARY

The data presented in Papers I, II, and III of this series show that the reactive initiator (ABC) produced enhanced chemical bonding between the polyurethane-rich (PU) phase and the poly(methyl methacrylate)-rich (PMMA) particles, which were dispersed in the rubber matrix. However, in many cases, this chemical bonding was dominated by a

Table III Crack Growth Constants of PU/PMMA (50/50) Blends

	Standard Blend	Reactive Blend
n	1.87 ± 0.3	1.66 ± 0.3
G_1	4×10^6	1.7×10^6
m	1.34 ± 0.4	1.39 ± 0.24
G_2	5×10^4	2×10^4

Table IV Crack Growth Constants of GUM Vulcanized Rubbers[a]

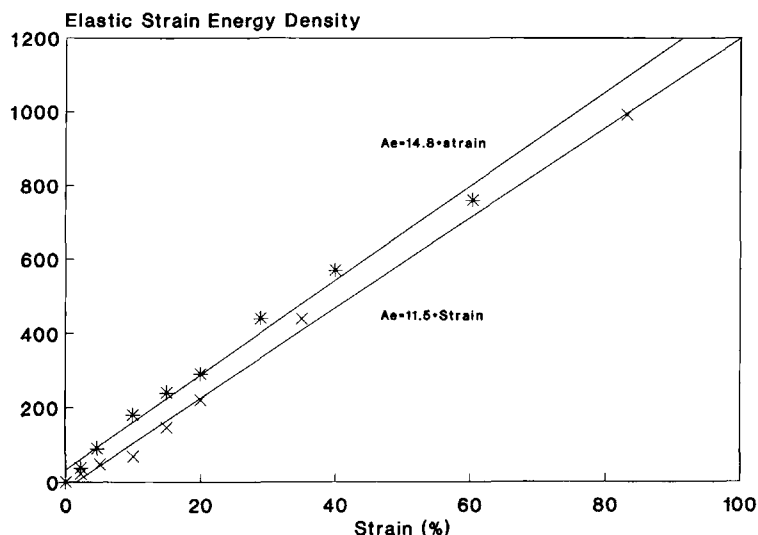|	SBR (Polysar)	Natural Rubber
n	4	2
G_1	60	—
m	4	2
G_2	—	2×10^5

Figure 10 Elastic strain energy density (kJ/m^2) vs. strain (%) of 50/50 PU/PMMA blends in tensile test.

chemical reaction between the urethane functions of the PU and the ester functions of the PMMA. The occurrence of this bonding had been shown by infrared spectra most clearly in specimens that had been heated to 120°C and higher and in the DMTA tests where these PMMA-rich phases and/or interphases exhibited transitions in 20/80 compositions that were significantly higher than the transition of PMMA and, in 50/50 compositions, were between those of PU and of PMMA. The development of these structures occurred more completely in the ABC bonded PU/PMMA materials. The PMMA-rich particles in both ABC and AIBN systems acted to reinforce the elastomeric PU matrix.

The PMMA bonded to PU by ABC appeared to produce a composition with fewer *hard segments* than normal PU materials. The chemical attachment of the PMMA may have acted by introducing a new *soft segment* or by breaking up some of the normal hard segments present in the PU. The introduction of a diacid (adipic) into either the ABC or AIBN systems increased the *hard segment* (amide) content of the PU with the resultant increase in moduli and tensile strength with less elongation at break in both systems.

The enhanced chemical bonding between the PMMA and the PU by the use of ABC decreased the hysteresis ratios of these materials, producing a longer elongation at break and enhancing the tear resistance to crack growth. This bonding also helped prevent the debonding process and decreased the intrinsic flaw size at catastrophic tear with the product becoming less prone to catastrophic tearing.

Introducing the PMMA phase into the PU phase

significantly increased the hysteresis of these IPNs and made the fracture more ductile. A modified Thomas–Rivlin fracture analysis successfully predicted the crack growth behavior. The reactive initiator, however, did not produce any remarkable effects in the crack growth behaviors.

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