

The role of inherent ductility in rubber toughening of brittle polymers

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The plane strain fracture toughness, K_{IC} , of a series of styrene copolymers with acrylonitrile (SAN), maleic anhydride (SMA) and acrylic acid (SAA) plus blends (50:50) of poly(methyl methacrylate) (PMMA) with various SAN copolymers are reported. Relative to polystyrene, the values of K_{IC} for the copolymers increase with acrylonitrile content but decrease with maleic anhydride or acrylic acid content. The K_{IC} values for SAN copolymers are lowered by addition of PMMA but are maximum in the AN range where SAN is miscible with PMMA. The toughness of rubber modified blends of these materials correlate with the K_{IC} of the matrix.

(Keywords: styrene copolymers; poly(methyl methacrylate); rubber toughening; inherent ductility; plane strain fracture toughness; blends)

INTRODUCTION

The toughening of brittle polymers by the incorporation of a dispersed rubber phase is influenced by a number of factors: rubber content, rubber particle size and distribution, level of crosslinking in the rubber, degree of adhesion between the rubber and matrix phases, etc.¹. There has been considerable effort devoted to understanding the effects of such variables on the toughness of rubber modified plastics. In a recent study of blends of styrene-acrylonitrile (SAN) copolymers with an SAN grafted rubber, the trends with AN content dictated consideration of the inherent ductility of the matrix copolymers as one of the factors that contribute to the overall toughness of the blend², and it was proposed that the inherent ductility of SAN copolymers increases as the AN level increases. This proposal is consistent with extensive qualitative experience with ABS materials. Another recent study on toughening of styrene-maleic anhydride (SMA) copolymers raised similar issues relating to the propensity for toughening of SMA matrices³.

While it is reasonable to expect that some inherent characteristic of the matrix should play an important role in the extent to which it can be toughened, discussions on such issues are rare in the literature on rubber toughening^{4,5}. Definitive evidence for such a relationship is severely hampered by the absence of basic comparative information about the matrix polymers. It is the purpose of this paper to quantitatively compare the mode I plane strain fracture toughness, K_{IC} , of some brittle polymers, including several styrenic copolymers of various compositions, with the impact strength of blends of these materials with an appropriate rubber modifier. Based on the successful application of linear elastic fracture mechanics to brittle glassy polymers, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS)⁶⁻⁸, it is expected that evaluation of K_{IC} will provide useful

comparative information relating to the inherent ability to toughen these polymers since this quantity accurately describes the initiation of unstable fractures in such brittle materials.

MATERIALS AND METHODS

The high molecular weight moulding grade polymers used in this work are described in *Table 1*. The mechanical properties, including K_{IC} values, of polymeric materials depend on the molecular weight and molecular weight distribution⁹. Above a critical molecular weight for entanglements, however, the influence of molecular weight on K_{IC} is negligible¹⁰⁻¹². Accordingly, it is presumed that the differences in molecular weight are not a major factor and the trends found in K_{IC} values reflect effects of chemical composition.

In order to obtain an accurate K_{IC} value, it is critical to make a sharp and straight notch at the crack tip. The state of the crack, in other words, should be without crazes and reproducible if the measurement is to yield a true material property. For polymers which fail in a brittle fashion, K_{IC} values are strongly influenced by the type of notching procedure⁶. There are a number of ways to introduce a crack in a specimen, including impact razor notches and fatigue notches. Among these techniques, notches developed under various fatigue loading conditions are recognized as useful for the measurement of K_{IC} since this tends to minimize the development of craze bunches at the crack tip. Such craze bunches are usually observed in impact razor notches and result in a K_{IC} that is too high. Recently, a new technique for obtaining sharp notches in brittle polymers was developed by Bucknall¹³. In most previous procedures a new razor blade was pressed into a saw cut portion of the specimen. While this is satisfactory for ductile polymers, it gives an irregular non-planar crack tip in brittle polymers. Accordingly, as a way of solving this problem, the razor blade is slowly pressed into the

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Table 1 Polymers used in this study

Polymer	Comonomer (wt%)	Molecular weight and viscosity	T_g (°C)	Source
PS	0	$M_n = 132\,000$ $M_w = 300\,000$	102	Dow Chemical Co.
SAN6.3 ^a	6.3	$M_n = 121\,000$ $M_w = 343\,000$	103	Dow Chemical Co.
SAN14.7	14.7	$M_n = 83\,000$ $M_w = 182\,000$	105	Asahi Chemical Industry Co. Ltd
SAN20	20	$M_n = 88\,000$ $M_w = 178\,000$	107	Dow Chemical Co.
SAN25	25	$M_n = 77\,000$ $M_w = 152\,000$	107	Dow Chemical Co.
SAN30	30	$M_n = 81\,000$ $M_w = 168\,000$	109	Dow Chemical Co.
SAN34	34	$M_n = 73\,000$ $M_w = 145\,000$	110	Asahi Chemical Industry Co. Ltd
SAN40	40	$M_n = 61\,000$ $M_w = 122\,000$	110	Asahi Chemical Industry Co. Ltd
SAN58	58	–	116	Monsanto Co.
SAN68	68	–	112	Monsanto Co.
SMA2 ^b	2	$\eta = 3.92 \text{ cP}^d$	103	Dow Chemical Co.
SMA14	14	$M_n = 90\,000$ $M_w = 180\,000$	128	Arco Chemical Co. (Dylark 332)
SMA25	25	$\eta = 4.73 \text{ cP}^d$	149	Dow Chemical Co.
SAA3 ^c	3	–	107	Dow Chemical Co.
SAA8	8	–	118	Dow Chemical Co.
PMMA		$M_n = 52\,900$ $M_w = 105\,400$	108	Rohm & Hass V(811) 100

^aSAN, styrene-acrylonitrile copolymer

^bSMA, styrene-maleic anhydride copolymer

^cSAA, styrene-acrylic acid copolymer

^dViscosity of a 10 wt% solution in methyl ethyl ketone at 25°C

saw cut at a temperature $\sim 10^\circ\text{C}$ below the glass transition temperature (T_g). In order to press a razor blade into the specimen, a 70 g weight was placed on the specimen and left in position overnight. After removing the razor blade and the weight, the notched specimen was annealed for 1 h and cooled slowly to room temperature by turning the heater off. This procedure is particularly effective for relieving induced stresses and consequently is expected to produce more consistent results in K_{IC} for brittle polymers.

Specimens for testing were machined from a 20.3×20.3 cm sheet prepared by compression moulding. Thick specimens (0.635 cm) were used in order to ensure plane strain conditions in accordance with ASTM E 399 (ref. 14). The single edge notched (SEN) specimen geometry is shown in Figure 1. Measurements of maximum tensile load of these specimens were made using an Instron tester at a cross-head speed of $0.127 \text{ cm min}^{-1}$. At least six specimens were tested for each polymer, and mean values of maximum loads were used for calculation of K_{IC} . The following equation was used to calculate the stress intensity factor for SEN specimens¹⁵:

$$K_{IC} = \frac{P}{Wt} (\pi a)^{1/2} Y \left(\frac{a}{W} \right) \quad (1)$$

where P = maximum load, W = specimen width, t =

specimen thickness, a = crack length and

$$Y \left(\frac{a}{W} \right) = 1.12 - 0.23 \left(\frac{a}{W} \right) + 10.6 \left(\frac{a}{W} \right)^2 - 21.7 \left(\frac{a}{W} \right)^3 + 30.4 \left(\frac{a}{W} \right)^4 \quad (2)$$

Based on the K_{IC} values, the fracture energy, G_{IC} , values were calculated using the relationship: $K_{IC}^2 = EG_{IC}/(1 - \nu^2)$, where Poisson's ratio, ν , was taken as 0.35 for all SAN copolymers¹⁶ and Young's modulus, E , was taken from a previous study².

RESULTS AND DISCUSSION

Styrene copolymers

A number of K_{IC} values for PS have been reported in the literature. Due to variations in polymer source, sample preparation and test conditions, the reported values vary considerably. For example, Marshall *et al.*⁶ reported values in the range of 1.1–1.4 $\text{MPa m}^{1/2}$ depending on test speed, while Lee *et al.*¹⁷ reported a value of 1.94 $\text{MPa m}^{1/2}$. The present value of 1.72 $\text{MPa m}^{1/2}$ (Figure 2) falls within the range of values that have previously been reported. Variations are most likely due to the notching process. Because of the nature of the notching process used in this study, specimens may

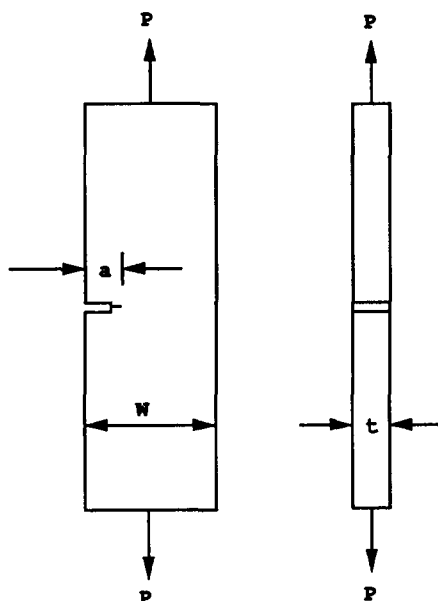


Figure 1 Single edge notched specimen. $W = 2.54$ cm, $t = 0.635$ cm, $\left(\frac{a}{W}\right) = 0.2$

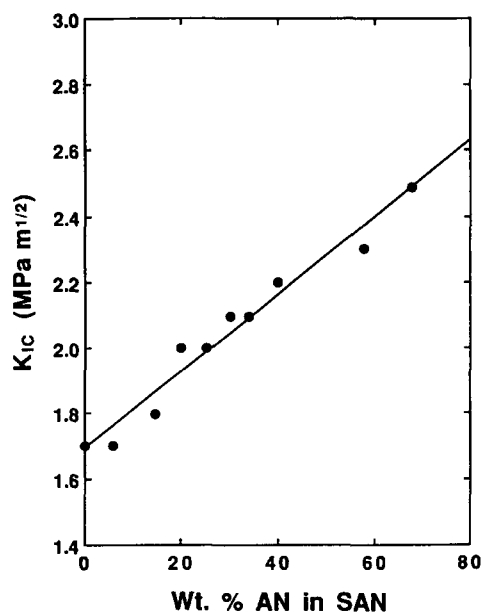


Figure 2 Effect of acrylonitrile content on K_{IC} for SAN copolymers

experience physical ageing in the sub- T_g range used. To examine any possible effect of this on the measured K_{IC} values, specimens of SAN25 were notched at a temperature 10°C higher than T_g for 1 h. The K_{IC} value from this specimen was $1.93 \text{ MPa m}^{1/2}$ which is comparable to that ($1.99 \text{ MPa m}^{1/2}$) obtained by the procedure described in the Experimental section. Accordingly, physical ageing does not seem to significantly affect the K_{IC} values obtained. Our value of K_{IC} ($1.45 \text{ MPa m}^{1/2}$) for PMMA is comparable to others reported in the literature^{6,17}. These comparisons provide some evidence for the reliability of the present method. Comparison of values measured by the same method should be even more meaningful. The results for the various SAN copolymers tested in this work are shown in Figures 2 and 3. As seen, K_{IC} increases significantly as AN content increases. The relation is essentially linear

with only modest scatter. Linear regression analysis gives a correlation coefficient of 0.96. The G_{IC} values shown in Figure 3 were calculated from K_{IC} as mentioned earlier. Since the Poisson ratio was not measured for each SAN, Figure 3 only serves as a guide to the dependence of this parameter on AN content. These measurements support the hypothesis outlined in our previous paper² that the propensity for toughening of SAN copolymers increases with AN content.

Figure 4 shows the effect of comonomer content on the fracture toughness of SMA and SAA copolymers. Contrary to SAN copolymers, addition of maleic anhydride and acrylic acid as comonomers with styrene reduces the K_{IC} value. It is noted that only 2% of MA in the copolymer results in a dramatic reduction in K_{IC} . As shown elsewhere^{3,18}, SMA copolymers are not effectively toughened by incorporation of grafted rubber particles even when the grafted chains are miscible with the matrix. It is of interest to compare the notched Izod

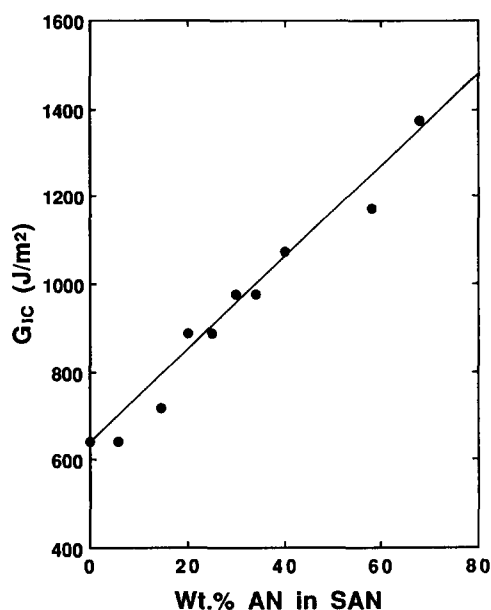


Figure 3 Effect of acrylonitrile content on G_{IC} for SAN copolymers (Poisson ratio assumed to be 0.35)

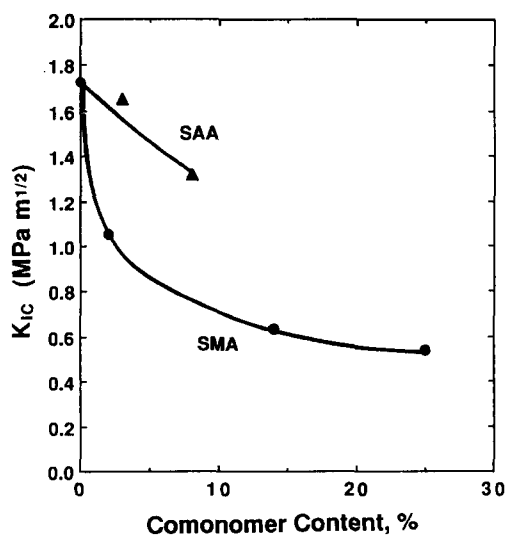


Figure 4 Effect of comonomer content on K_{IC} for SAA and SMA copolymers

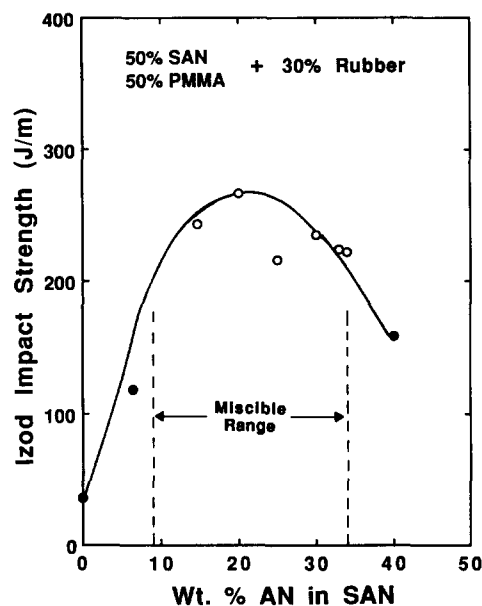


Figure 5 Notched Izod impact strength of SAN/PMMA blends containing 30% rubber as a function of acrylonitrile content of SAN copolymer. Matrix components: (○) miscible; (●) immiscible

impact values of rubber toughened SAN and SMA copolymers using the same impact modifier^{2,3}. The impact modifier used was a commercial product of the Sumitomo Naugatuck Co. The material contains equal amounts of a butadiene based rubber and SAN (AN content = 22.5 wt%). About 40% of the total SAN is bound to the rubber and the remainder is free SAN. The SAN graft of this modifier should be miscible with the SAN and SMA matrices used here^{2,3}. While SAN copolymers toughened with this modifier give impact strengths up to 500 J m^{-1} , SMA copolymers at high rubber loadings show only $\sim 100 \text{ J m}^{-1}$. The ability of SAN and SMA copolymers to be toughened by this impact modifier parallels the K_{IC} trends shown in Figures 2 and 4. These results show that SAN copolymers are inherently more ductile (i.e. more easily toughened) than PS, while the SMA copolymers have lower inherent ductility and can be less effectively toughened than PS. SAA copolymers have lower K_{IC} values than PS and are not likely to be as readily toughened as PS or SANs. Indeed, attempts to toughen styrene-acrylic and methacrylic acid copolymers, using several combinations of rubbers, have yielded only moderate increases in impact strength¹⁹⁻²¹.

The trends shown in Figures 2 and 4 may be reasonably explained in terms of the flexibility and mobility of the polymer chains. The rigidity of maleic anhydride units in SMA copolymer and the strong hydrogen bonding of acrylic acid units in SAA copolymer no doubt inhibit ductile deformation in such polymers. Plastic deformation is well known to be limited by hindrance to side group and main chain motions²². In such circumstances, breaking of atomic bonds prevails and low fracture energy is expected. In the case of SAN the dipole interaction between acrylonitrile units provides strong cohesive forces while permitting greater degrees of freedom for plastic deformation than the more specific hydrogen bonds in SAA copolymer.

A number of amorphous glassy polymers, other than SMA or SAA copolymers, have a low capability of being

effectively toughened by the addition of impact modifiers. Such polymers usually have a high heat deformation temperature. Styrene copolymers with α -methylstyrene and *p*-*t*-butylstyrene serve as examples²¹. Numerous efforts have been made to develop tough styrenic polymers with heat deformation temperatures higher than that of PS; however, there has been only limited success^{23,24}. The reasons for the difficulty in toughening such polymers may be manifold, but one definite possibility appears to stem from their rather low inherent ductility. It should also be pointed out that the widely used epoxy resins for engineering applications are often rubber modified but only a modest increase in impact strength is achieved²⁵. K_{IC} values²⁶ for unmodified epoxy resins are $\sim 0.5 \text{ MPa m}^{1/2}$. This is consistent with the notion that brittle polymers with a low inherent ductility cannot be modified to a high level of toughness.

SAN/PMMA blends

PMMA is difficult to toughen by the addition of grafted rubber particles and it has a K_{IC} value of $\sim 1.45 \text{ MPa m}^{1/2}$. To further investigate the importance of the inherent ductility of the matrix, blends of PMMA with various SANs were used. It is well-known that PMMA and SAN are thermodynamically miscible when the AN levels in the copolymer are $\sim 9\text{--}33\%$ ²⁷⁻²⁹. The strongest interaction between the two polymers occurs when the SAN contains 13–20% AN, as judged by the lower critical solution temperature behaviour of the blends²⁹. In another study, adhesion of SAN/PMMA blends to the SAN grafted rubber was measured by a lap shear test, and it was found that SAN20/PMMA gives the strongest adhesive bond³⁰.

Matrices were formed by blending equal parts by weight of PMMA with SAN copolymers containing varying levels of AN. An SAN (22.5% AN) grafted emulsion rubber was added to these matrices in an amount to achieve 30% rubber in the final blend². All blends were prepared by compounding in a single screw extruder as described previously². Notched Izod values for these blends (Figure 5) show that a maximum impact strength is reached when the SAN component in the matrix contains 20% AN. As might be expected the matrices based on homogeneous mixtures of PMMA and SAN lead to the highest levels of impact strength as seen in Figure 5. The peak Izod impact strength occurs when the SAN in the matrix contains $\sim 20\%$ AN. No doubt the heterogeneity of PMMA/SAN blend matrices that are outside the miscibility window is a factor in their mechanical behaviour.

Values of K_{IC} were measured for the 50:50 blend matrices of PMMA and SAN, and the results are shown in Figure 6 as a function of percentage AN in the copolymer. There is an interesting parallel between the trends in impact strength (Figure 5) and in K_{IC} (Figure 6). There is, in fact, a maximum in K_{IC} at 20% AN; however, it should be noted that the addition of PMMA to SAN copolymer significantly decreases the K_{IC} values relative to that of neat SAN (Figure 2). The maximum value of K_{IC} for SAN/PMMA blends is only $1.76 \text{ MPa m}^{1/2}$, a value that is comparable to that of PS ($1.72 \text{ MPa m}^{1/2}$). The heterogeneities in the blends outside the miscibility region no doubt influence the K_{IC} observations in a way that is not easily interpreted.

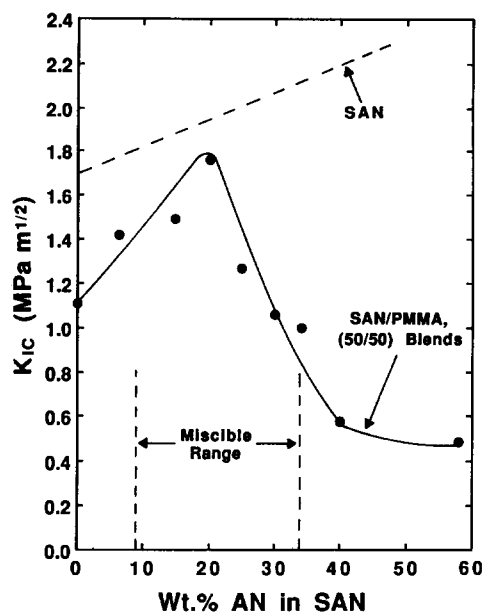


Figure 6 K_{IC} value for 50/50 PMMA blends with SAN copolymers as a function of AN content of SAN. Broken line shows K_{IC} values of SAN copolymers

CONCLUSIONS

The inherent ductility of a series of styrene copolymers with acrylonitrile, maleic anhydride and acrylic acid as well as PMMA and SAN/PMMA blends was evaluated by measuring their plane strain critical stress intensity factor K_{IC} . It was found that K_{IC} increases with AN content in SAN but decreases with maleic anhydride and acrylic acid content. Even a small amount (~2%) of maleic anhydride causes a significant drop in K_{IC} relative to PS.

The inherent ductility of brittle polymers as measured by K_{IC} seems to be an important factor in determining the propensity of the polymer to be rubber toughened. Of course, rubber particle size and adhesion between the rubber phase and the matrix play important roles as well.

In Table 2 we compare values of K_{IC} for three homogeneous matrices with impact strength of their blends with the same SAN grafted butadiene based emulsion rubber. The SAN graft adheres well to all three matrices. There is a five-fold variation in notched Izod values of the blends stemming from inherent differences in these matrices. Blend toughness correlates well with the K_{IC} values of the matrices. This provides at least a partial demonstration that the level of attainable toughness of rubber modified polymers is limited by the inherent ductility of the matrix polymer.

ACKNOWLEDGEMENTS

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Table 2 Comparison of K_{IC} values for various selected matrix systems and the toughness of their rubber toughened blends^a

Matrix polymer	K_{IC} (MPa m ^{1/2})	Notched Izod impact strength (J m ⁻¹) ^a
SAN34 ^b	2.10	500 (ref. 2)
SAN20/PMMA ^c	1.76	266 (This work)
SMA14 ^d	0.64	100 (ref. 3)

^aAll blends contain 30% rubber to which SAN22.5 was grafted (see text for further details)

^bIn a series of SAN copolymers of varying AN content, SAN34 gave maximum toughness

^cFor blends of PMMA with various SAN copolymers, SAN20 gave maximum toughness

^dIn a series of SMA copolymers of varying MA content, SMA14 gave maximum toughness

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