Synergistic toughening in rubber modified blends

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(Received 10 November; revised 4 February 1987; accepted 17 March 1987)

Particle size and particle adhesion are two factors involved in the rubber toughening of glassy polymers. The role of each has been examined in the toughening of polystyrene (PS), styrene–acrylonitrile (SAN) copolymers and poly(methyl methacrylate) (PMMA). An SBS block copolymer and an emulsion rubber particle with a PMMA grafted shell were compared as modifiers for these polymers and subsequently used in combination. The styrene–butadiene–styrene (SBS) particles were irregularly shaped with dimensions of 1–5 μm, while the emulsion particles were uniform and 0.18 μm in diameter. The SBS particles toughened PS significantly, as expected, but did not improve the properties of PMMA or the SANs appreciably. The emulsion particles toughened PMMA and SANs (14.7 and 25.0% AN) with which its PMMA shell was miscible. It did not toughen PS or a SAN (6.3% AN) with which its PMMA shell was immiscible. Emulsion particle size as well as adhesion were responsible for its poor performance in the latter case. When used in combination for the matrix SAN (25% AN by weight), a synergistic toughening effect well beyond that of either additive alone was observed.

(Keywords: styrene–acrylonitrile copolymers; poly(methyl methacrylate); polystyrene; synergism; toughening; particle size; adhesion)

INTRODUCTION

Appropriate dispersal of rubber particles into glassy polymers can lead to significant toughening by inducing crazing or shear-yielding deformation mechanisms in an otherwise brittle matrix[1]. In many cases, the rubber particles are formed *in situ* during the polymerization process[1,2], or specially designed, preformed emulsion particles with grafted shells can be subsequently melt-compounded into the matrix material[1,3,4]. Alternatively, certain block copolymers with both hard and elastomeric blocks have proved to be effective impact modifiers[5,6]. Recently, blending of simple elastomers with brittle polymers using techniques to control rubber particle size[7] and to bond the rubber by either chemical or physical means to the matrix has become an important route[8–10]. The factors affecting impact performance include the amount of rubber added, the size and morphology of the particles, the degree of adhesion of the rubber to the matrix and interparticle spacing, to mention only a few. For several matrices, it has been established that the rubber particles must be above a certain critical size for effective toughening. For polystyrene, the critical size is about 1–2 μm while for styrene–acrylonitrile polymers it is about 0.1–1 μm[1,3]. Judging from the range of materials produced commercially, optimum performance is achieved using particles somewhat larger than these critical values. In spite of the great commercial importance of rubber toughening and the immense scientific literature on the subject[1,5,11,12], complete understanding of the interrelationships and optimization of the pertinent factors has not yet been achieved. This fact leaves open the possibility of important new avenues for improved rubber toughening. One example of this is the growing evidence[3,4,12–17] that a synergism in toughening can occur when two or more different rubber particle types or sizes are simultaneously incorporated into a particular matrix.

This paper explores the latter possibility using a commercial shell–core emulsion-made impact modifier and a commercial SBS triblock copolymer as the sources of rubber particles. The matrices employed include poly(methyl methacrylate) (PMMA), polystyrene (PS) and several styrene–acrylonitrile (SAN) copolymers.

MATERIALS AND EXPERIMENTAL PROCEDURES

The various glassy polymers used as the matrix in these studies are described in *Table 1*. The bulk of the experimental work, however, focused on three of these, viz. PS, PMMA and SAN 25. Rubber was incorporated into each of these matrices by addition of the block copolymer and the grafted emulsion particles described below.

The styrene–butadiene–styrene (SBS) triblock copolymer used is produced commercially by the Shell Chemical Co. under the designation Kraton 1101. This thermoplastic elastomer has been the subject of numerous studies reported in the literature, and the estimates of its composition and structure vary slightly. Most reports[18–23] give results within the following ranges: rubber content = 69 to 71% by weight; styrene endblock molecular weight = 14 000 to 16 000; and overall molecular weight = 94 000 to 106 000.

The grafted emulsion particles used are a commercial product of the Rohm and Haas Co. with the designation of Acryloid KM-680. It is a methacrylated butadiene–styrene (MBS) material normally used as an impact modifier for poly(vinyl chloride). The structure of similar products has been described[24] and the following details

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Table 1 Matrix polymers used in this study

Polymer	Abbreviation	Source	Molecular weight
Polystyrene	PS	Cosden Oil and Chemical Co. 550P	$M_n = 100000$ $M_w = 350000$
Poly(styrene-*co*-acrylonitrile) 6.3% AN	SAN 6.3	Asahi Chem. Ind. Co. Ltd	Moulding grade
Poly(styrene-*co*-acrylonitrile) 14.7% AN	SAN 14.7	Asahi Chem. Ind. Co. Ltd	$M_n = 82700$ $M_w = 181000$
Poly(styrene-*co*-acrylonitrile) 25% AN	SAN 25	Dow Chemical U.S.A. Tyril 1000	$M_n = 160000$ $M_w = 336000$
Poly(methyl methacrylate)	PMMA	Rohm and Haas V(811)100	$M_n = 52900$ $M_w = 105400$

may be taken as representative. Emulsion polymerization is carried out in three stages, with the first containing approximately 74% by weight of butadiene, 22% butyl acrylate and 4% methyl methacrylate; the second consists of styrene; and the final stage is a rigid methyl methacrylate–ethyl acrylate copolymer. The resulting emulsion particles are about 0.18 μm in diameter and contain essentially 80% rubber.

Each matrix polymer was dried for at least 12 h at 75°C before mixing. The materials were mixed with the matrix polymers in the appropriate ratios using a one inch, Killion extruder ($L/D = 30$), outfitted with a high-shear mixing screw having a compression ratio of 3:1. Each batch of about 1500 to 2000 g was run through the extruder twice to ensure good and uniform mixing. The extrudate was pelletized, dried again for at least 12 h at 75°C and subsequently injection moulded into tensile and Izod bars using an Arburg 305 moulding machine.

The tensile bars were tested on an Instron 1137 tester with a computerized data acquisition system at a crosshead speed of 0.2 in. min^{-1}, except where noted. Notched Izod impact strengths were measured according to ASTM D256-56 using a pendulum type tester. A minimum of 5 and a maximum of 10 bars were tested on each instrument. Standard deviations of 5% or less were found for stress, modulus and Izod impact values. The standard deviation for strain at break was found to be from 10 to 20% of the average value.

Transmission electron microscopy was carried out on the blends using standard techniques. Mouldings were stained in a 4% solution of OsO_4 and ultrathin slices were microtomed at room temperature. A Philips Model EM300 electron microscope was used.

PARTICLE MORPHOLOGY AND ADHESION

The MBS impact modifier and the SBS block copolymer differ fundamentally in how they disperse in the matrix and in the ultimate size and geometry of the resulting rubber particles. Using adequate mixing protocols, the MBS modifier can be dispersed so that the original emulsion particles appear discretely in the matrix. This was the case for all the matrices employed here when the mixing procedures described earlier were used. The transmission electron photographs shown in *Figure 1* illustrate this when the matrix polymer is SAN 25. The small particles are the MBS modifier. There is no significant agglomeration of these particles even at the high loadings shown. These particles are quite uniform in size and shape.

The large and irregularly shaped particles seen in *Figure 1* are the SBS copolymer. Since this polymer forms a viscous melt under processing conditions, it forms particles by drop break-up mechanisms whose final size and shape are determined by complex mixing and rheological conditions since there is no ultimate particle like that for the MBS modifier. These particles vary in size with a range from about 1 to about 5 μm. Also, the dispersion of the SBS copolymer in the SAN 25 matrix without the presence of the MBS particles can be seen in *Figure 1*. It appears that the nature and the size of the SBS particles are not affected by the MBS particles. Thus, a combination of the MBS modifier and the SBS copolymer into the same matrix, as shown in *Figure 1*, results in a bimodal distribution of particle sizes, although these two populations differ from each other in important additional ways other than just size. Similar particle morphologies can be expected for each matrix polymer mentioned in *Table 1*.

Adhesion of the rubber particles to the matrix is generally regarded as an important factor in toughening[1], although most discussions on this subject are only qualitative. For the polymer–polymer interfaces involved in the present systems some semiquantitative information is available. For the MBS particles, the outer surface is comprised essentially of PMMA chains which are effectively grafted to the rubbery core. Thus, these particles ought to adhere well to a PMMA matrix. They should also adhere well to certain SAN matrices since PMMA is miscible with styrene–acrylonitrile copolymers containing from about 9.5 to 33% AN by weight[25,25]. Based on recent studies of phase behaviour[26], the optimum composition for favourable interaction with PMMA is in the vicinity of 13 to 15% AN. As an extension of the thermodynamic investigation mentioned[26], the kinetics of adhesion development for PMMA with various SANs including PS has also been studied[27]. As expected, SANs which are miscible with PMMA do in time develop excellent adhesion when the two are juxtaposed at a temperature above their glass transitions. Owing to the stronger thermodynamic driving force for diffusion, adhesion developed most rapidly at the optimum AN level, i.e. 13 to 15%, for interaction with PMMA. SANs outside the composition window for miscibility with PMMA, including PS, also developed reasonably good adhesion to PMMA although the extent at equilibrium is clearly less than for the SANs which are miscible with PMMA.

The SBS copolymer has both polybutadiene and polystyrene phases that are orders of magnitude smaller than the SBS particles seen in *Figure 1*. The surface of these particles which contact the matrix are partly polystyrene and partly polybutadiene and the fraction of each may differ from the bulk value, depending on

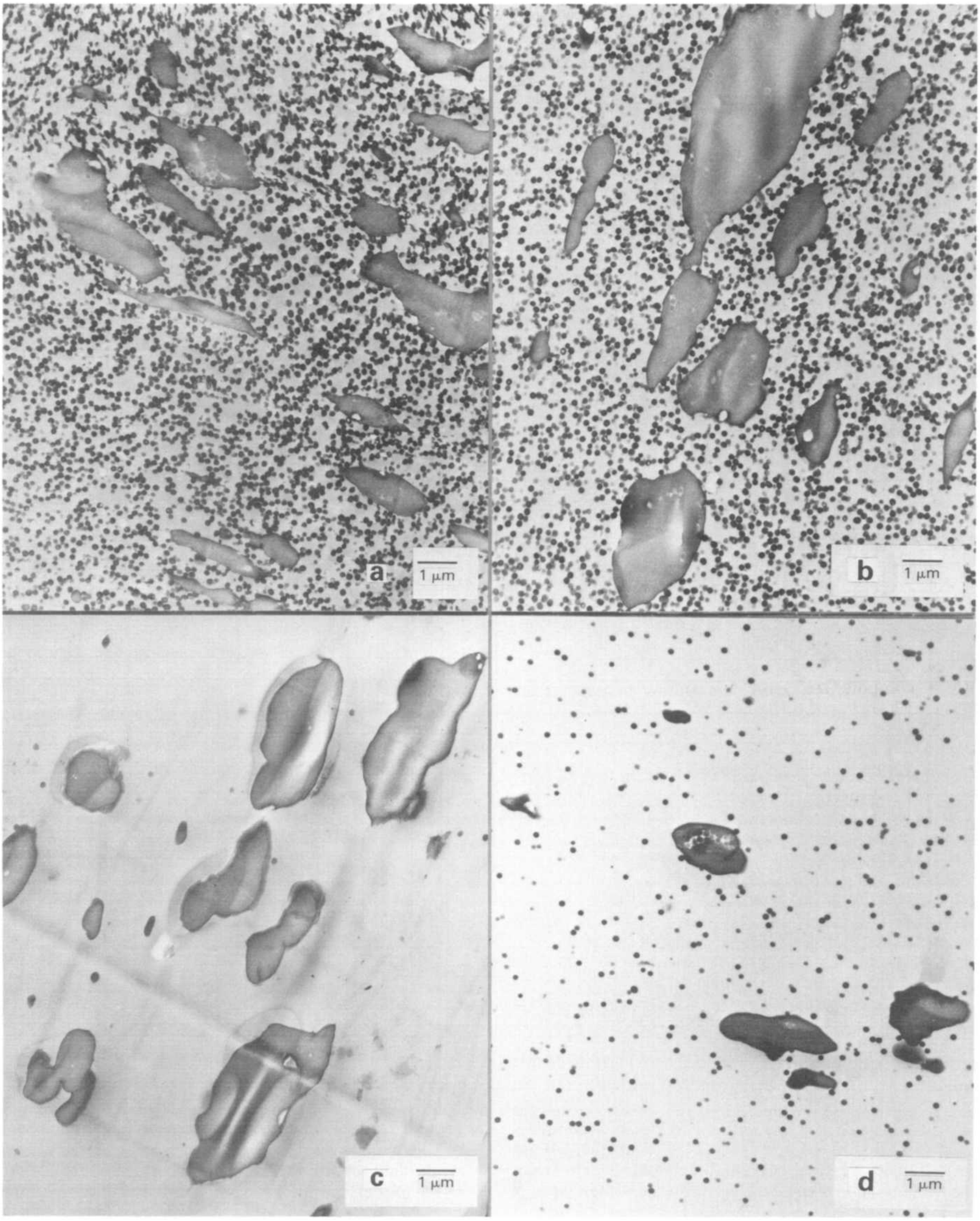

Figure 1 Transmission electron photomicrographs of SAN 25/MBS/SBS blends. (a) 50/30/20, (b) 60/30/10, (c) 70/0/30, (d) 95/3/2, (this composition was prepared by diluting (a) with SAN 25)

interactions with the matrix. Intuitively, one does not expect polybutadiene to adhere well to any of the matrix materials listed in *Table 1*. However, the styrene portions of the block copolymer should adhere well to the PS matrix. Based on the above discussion we note that there is some adhesion of PS to PMMA. While there is no published data on adhesion of PS to SAN, we would expect there to be some.

In summary, we expect the MBS particles to adhere quite well to PMMA and to the SANs within the

Table 2 Mechanical properties of neat matrix polymers

Polymer	Notched Izod impact strength (ft-lb/in)	Tensile properties: Modulus $\times 10^{-3}$ (psi)	Strength (psi)	% Elongation at break
PMMA	0.28	468	10100	5.5
PS	0.51	501	7600	2.8
SAN 6.3	0.64	485	8700	3.4
SAN 14.7	0.26	496	9100	2.1
SAN 25	0.33	542	10900	2.7

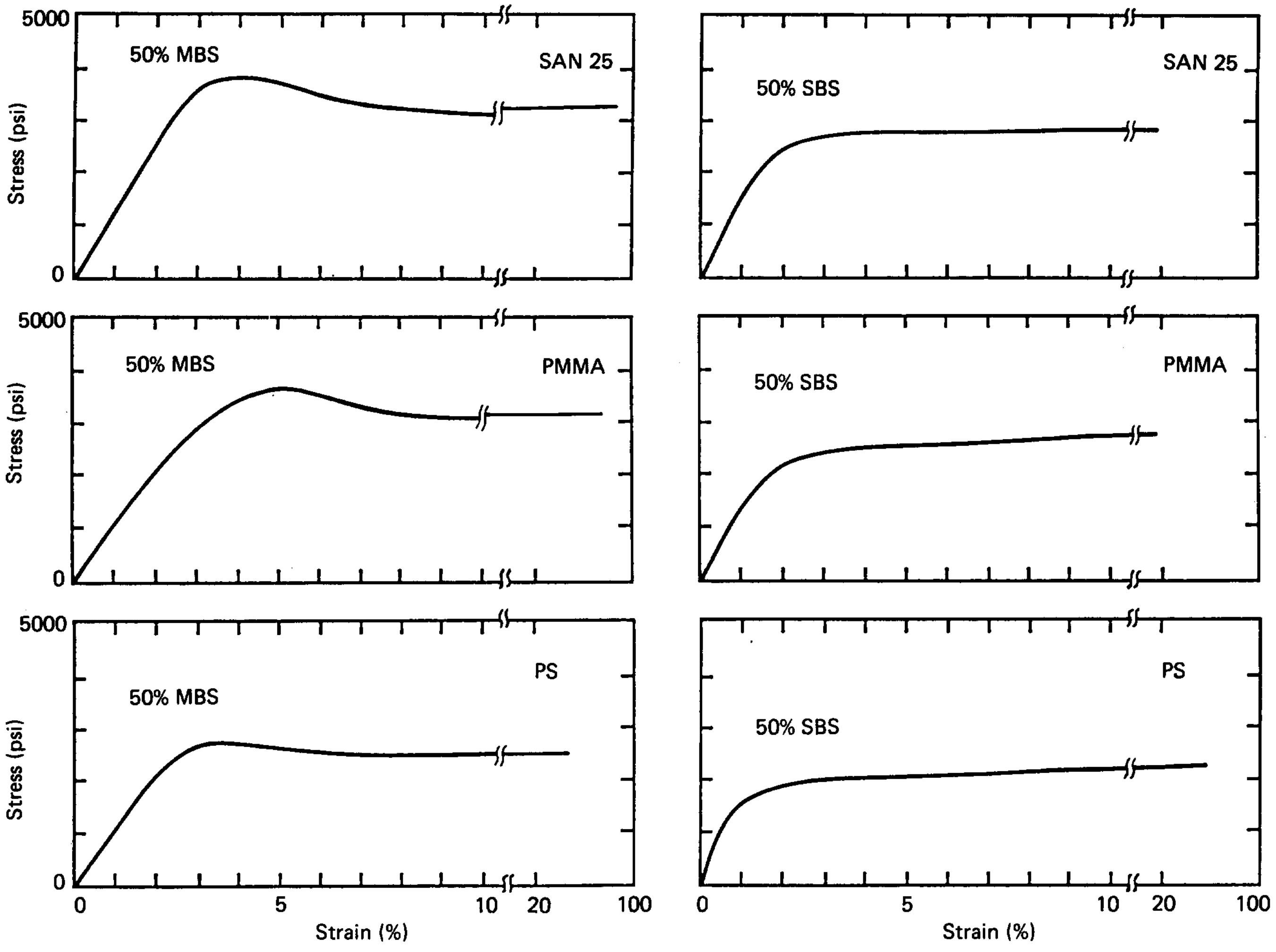

Figure 2 Stress–strain curves for SAN 25, PMMA and PS with 50% MBS and with 50% SBS

miscibility window and less well to the SANs outside this window, with adhesion being poorest with PS. On the other hand, the SBS block copolymer particles ought to adhere best to PS and less well to PMMA and the SANs. We expect that in the best cases (MBS with PMMA and SAN, SBS with PS) the MBS modifier adheres better than the SBS copolymer since the entire surface of the latter is probably not polystyrene. Clearly, MBS particles should be expected to adhere considerably better to SAN 25 than SBS particles do. In contrast, SBS particles may adhere better to PS than do MBS particles.

RESULTS AND DISCUSSION

Table 2 summarizes a variety of mechanical properties for the pure matrix polymers of interest here. Each one is relatively brittle, as the data show. However, these matrices are capable, to varying degrees, of more ductile behaviour in complex stress fields like those created around rubbery inclusions. Macroscopic manifestations of this may be seen in the representative tensile stress–strain diagrams shown in *Figure 2*, where either SBS or MBS particles alone are incorporated at high loadings into PS, SAN 25 or PMMA. For each matrix, there is a well defined yield stress which is larger than the ultimate stress at failure when MBS particles are added. However, for SBS, this well defined yield stress is absent for all matrices, and perhaps it is in some measure related to its poorer adhesion to these materials than that of the MBS modifier, although rubber particle size is an important issue as mentioned later.

Figure 3 shows the changes in Izod impact strengths as

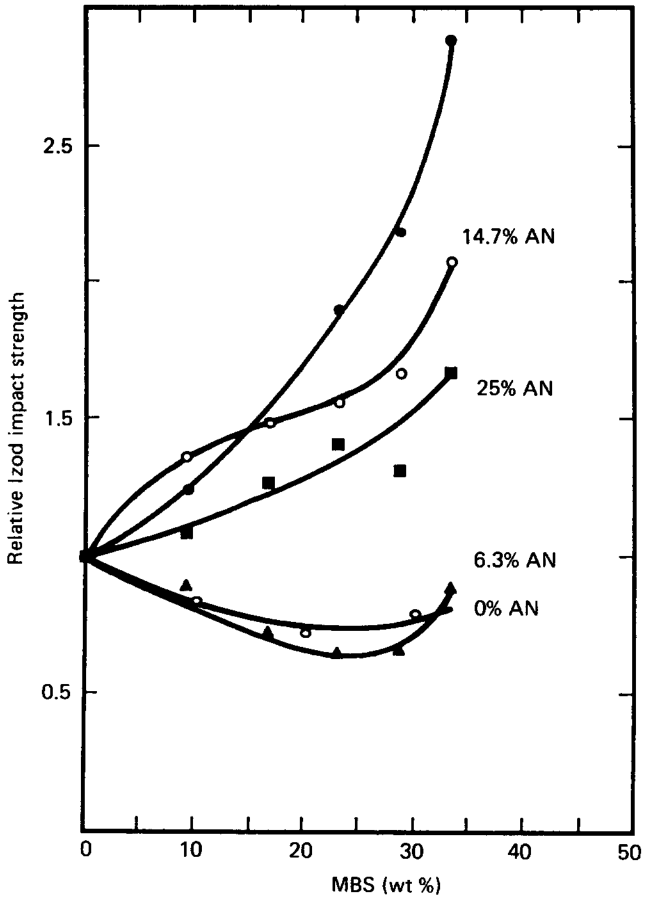

Figure 3 Izod impact strength relative to matrix value for PMMA and various SANs as a function of amount of MBS added

MBS modifier is added to each of the matrices listed in *Table 1* normalized by or relative to that of the matrix (see *Table 2*). Interestingly, toughness is improved by the addition of MBS for each matrix polymer that is miscible with the MBS shell while toughness is decreased for those matrices not miscible with the MBS shell. At first sight, this would appear to be the result of the superior particle–matrix adhesion known to occur when the shell and matrix are miscible. While this is a likely contributor, it is not the only important issue in this comparison. It is known that SANs containing AN levels of the order used in ABS materials (i.e. 25 to 28 %) are effectively toughened by small particles like the MBS modifier, whereas PS is not toughened by such small particles, as its critical particle size for toughening is about 1–2 μm. Critical particle size information is not available for SAN 6.3 or SAN 14.7, although one can expect the former to be more like PS while the latter may be more like SAN 25. So the cases of improved toughness in *Figure 3* involve both the best particle to matrix adhesion *and* an appropriate match of particle size for the matrix. The two matrices not toughened would appear to have both factors working *against* an improvement. The fact that the SAN 14.7 is toughened slightly more than SAN 25 would seem to be related to the optimal adhesion expected for the former compared to the latter[26,27] rather than a particle size effect.

In some cases, tensile stress–strain diagrams give an adequate picture of toughness and some features like elongation at break parallel other measures such as the notched Izod test. *Figure 4* compares the response of these two quantities as MBS and SBS modifiers are individually added to SAN 25 and PMMA matrices. The correlation between the two measures of toughness is only qualitative at best, so the conventional notched Izod quantity is used primarily for the remainder of these discussions. Clearly, for SAN 25 and PMMA, the MBS modifier improves the Izod impact strength more than does equivalent amounts of the SBS block copolymer. The size of the SBS particles are right in the range needed for toughening a PS matrix, whereas the MBS particles are much too small. As mentioned earlier, the SBS particles very likely adhere better to PS than do MBS particles. Therefore, the PS matrix favours the SBS as an impact modifier for *both* reasons.

On the other hand, the addition of relatively large amounts of SBS to PS causes impressive toughening, as seen in *Figure 5* and noted previously in the literature for related block copolymers designed specifically for this purpose[5,28]. As noted before, addition of the MBS modifier does not toughen PS. *Figure 5* also shows the effect on Izod impact strength of combinations of SBS and MBS at fixed percentage of total modifier or matrix phase. Toughness decreases as SBS is replaced by MBS.

In contrast to the response of PS shown in *Figure 5*, an impressive synergism is seen in *Figure 6*, when SBS and MBS are used in combination for an SAN 25 matrix. Here, we see at fixed levels of total modifier a maximum toughness for certain proportions of the two. As noted earlier, similar synergisms have been reported previously[3,4,12–17], but none of these previous cases involved such large departures from additivity. Alone, the SBS material does not toughen SAN 25. The MBS modifier is better than SBS, due partly to its superior adhesion to SAN 25; however, it fails to provide the toughness found in commercial ABS materials, which probably stems in part from the fact that the MBS particles are smaller than the optimal range for this matrix.

A similar but far less pronounced synergism is seen when PMMA is the matrix. Curves for PS and for SAN 25 matrices are shown for comparison in *Figure 7*.

For the sake of completeness and to make some useful points, *Figure 8* shows pertinent information from tensile stress–strain diagrams for three matrices plotted *versus* the proportion of SBS and MBS at three total modifier levels. For this discussion, we focus on the elongation or strain at break determined at 0.2 in. min^{-1}. For SAN 25, the trends in *Figure 8* approximately parallel those seen in Izod values in that similar synergisms exist, although details differ considerably. For PS, the trends in elongation at break parallel those of Izod impact strength very well except at 50 % total modifier. These data suggest that 50 % MBS is considerably better than 30 or 40 % and nearly the same as 50 % SBS. However, when the tensile test is done at higher strain rates, as seen in *Figure 9*, there is a considerable loss in toughness according to this index whereas there is far less decline in the value for 50 % SBS in PS. Thus, the high toughness for 50 % MBS seen here is an artefact of the very low testing rate used in determining the tensile stress–strain curve. Finally, we mention that the elongation at break does not suggest any significant synergism when PMMA is the matrix, which is in reasonable accord with the Izod data.

While the mechanical behaviour of the blends with a single rubber modifier seems to be readily explained by

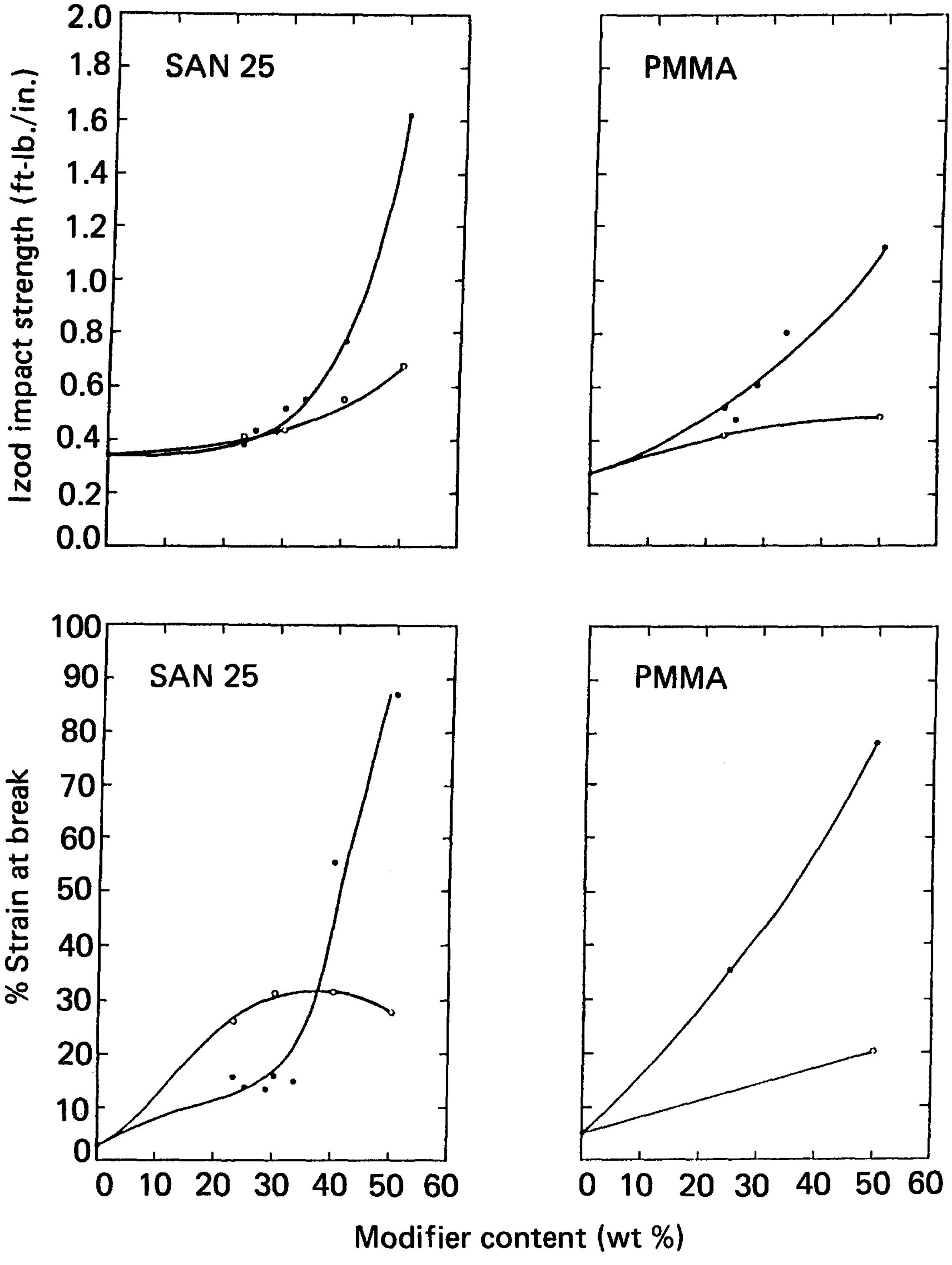

Figure 4 Comparison of measures of toughening for MBS (●) and for SBS (○) in SAN 25 and PMMA

the above discussion, the synergistic deformation behaviour of the modified SAN by the use of the dual rubber system requires further discussion. As pointed out in the Introduction, the use of rubbers with a bimodal particle size distribution for an increased efficiency in toughening of various brittle polymers has been reported[14]. In most cases, these modifiers of various sizes are grafted rubbers that adhere well to the matrix. In this case, however, while the small particles adhere well to the matrix, the large SBS particles are expected to have poorer adhesion. These large particles are not effective as impact modifiers for SAN (*Figure 6*). It may be suggested that the cause for the unexpected toughness of the modified SAN is related to a fortuitous combination of effective craze initiation, controlled growth and, most importantly, termination.

It is expected that a large number of crazes are readily initiated at the SBS particles, as adhesion is not required for the craze initiation at the stress concentration locations[29]. The process of craze growth without craze breakdown[30] and subsequent craze termination are clearly related to the small MBS particles. A most likely contribution of the small particles to the termination process is their ability to initiate shear bands which can terminate growing crazes[31]. It may also be possible that a high concentration of small particles at the craze tip may

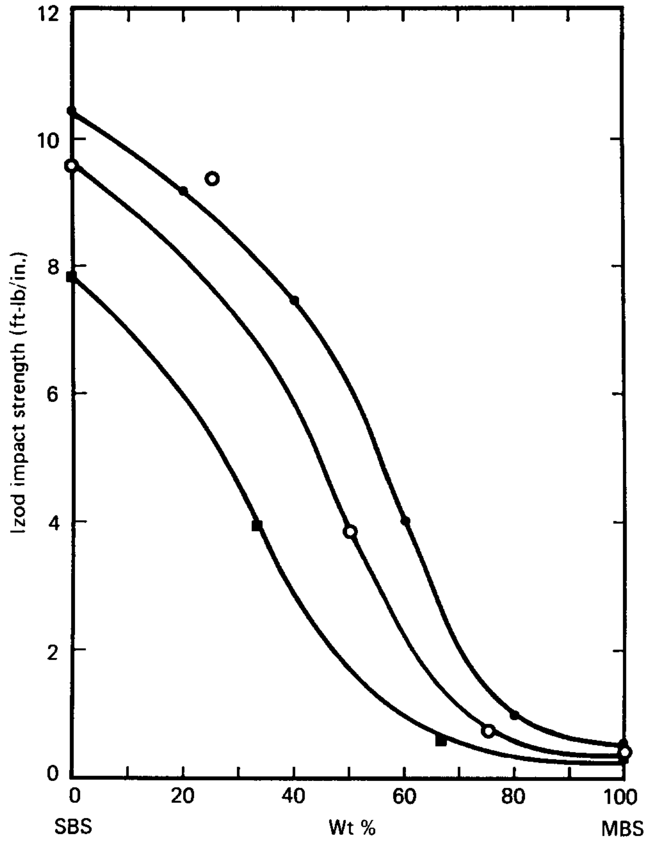

Figure 5 Impact strength for a PS matrix with combinations of MBS and SBS at fixed levels of total modifier content: ■, 30%; ○, 40%; ●, 50%

interact with the growing craze stress field to impede its further progress. In the consideration of both of these termination mechanisms, minimum mean distance between the small particles or mean free path[32] may be of considerable importance for the understanding of the contribution of the small particles to the craze termination mechanism.

Hobbs[14] found similar synergism in HIPS blends containing a bimodal distribution of particle sizes. He also proposed a numerical model relating craze termination to rubber particle size to explain the phenomenon. He assumed that the large rubber particles retard craze growth. Morbitzer *et al.*[4] also examined the use of small and large particles in ABS materials. While the small particles improved the toughness only slightly, the larger particles improved the impact strength significantly. When used in combination, an even greater impact strength was observed. These authors suggested that the larger particles initiated crazes due to a lower initiation stress, and the smaller particles act as a reinforcing agent by bending the craze path. The presence of small particles also influences the yielding process, such that shear bands are likely to be formed in addition to the crazes. As discussed above, this is what appears to be happening in SAN 25, since the large SBS particles do not appear to have any beneficial effect without the MBS particles.

CONCLUSION

The results of this study show the combined effects of particle size and adhesion on the toughening of polymer glasses. The MBS modifier is more efficient for modifying

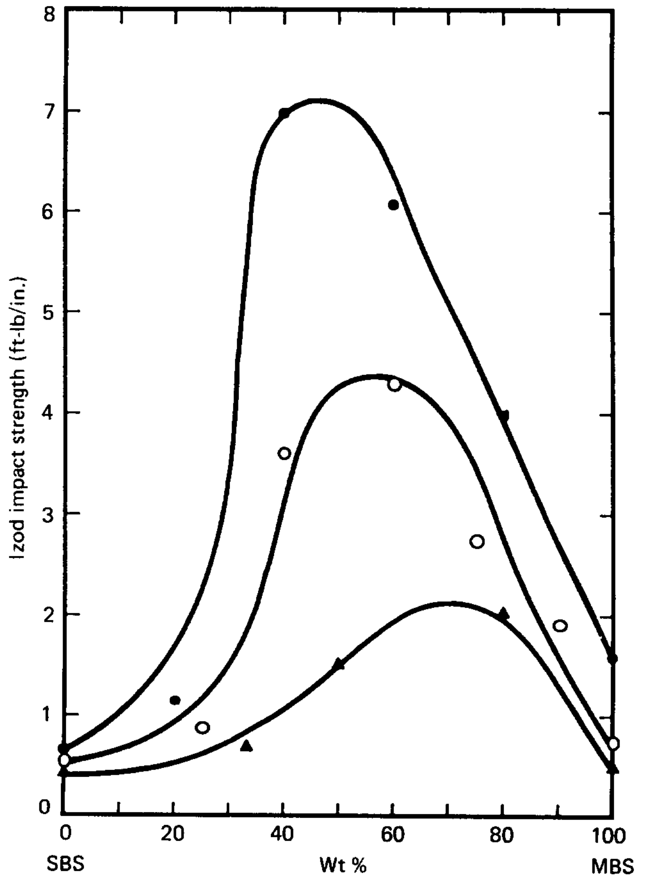

Figure 6 Izod impact strength of SAN 25 for combinations of SBS and MBS at various total loadings of modifier: ▲, 30%; ○, 40%; ●, 50%. Note synergism when the modifier is a mixture of SBS and MBS

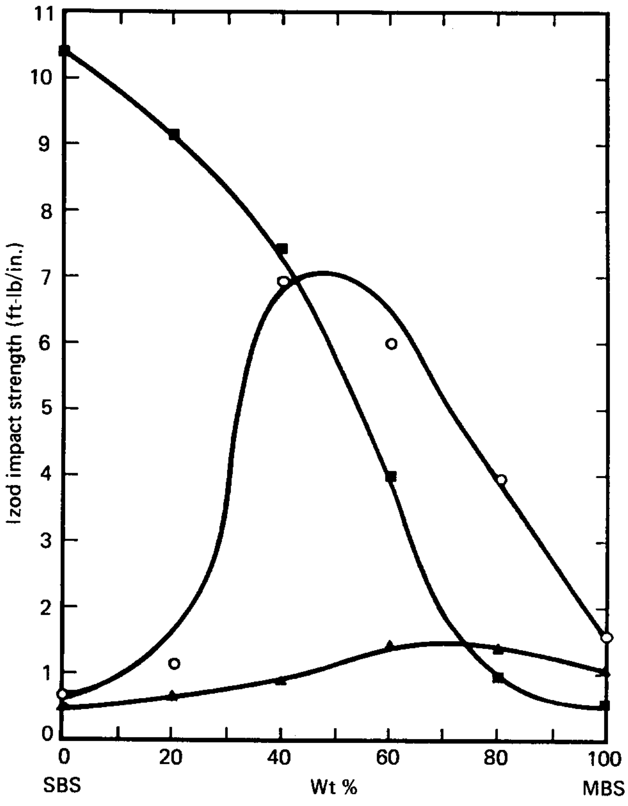

Figure 7 Comparison of combinations of MBS and SBS for toughening of various matrices: ○, SAN 25; ▲, PMMA; ■, PS. Total modifier held constant at 50% by wt

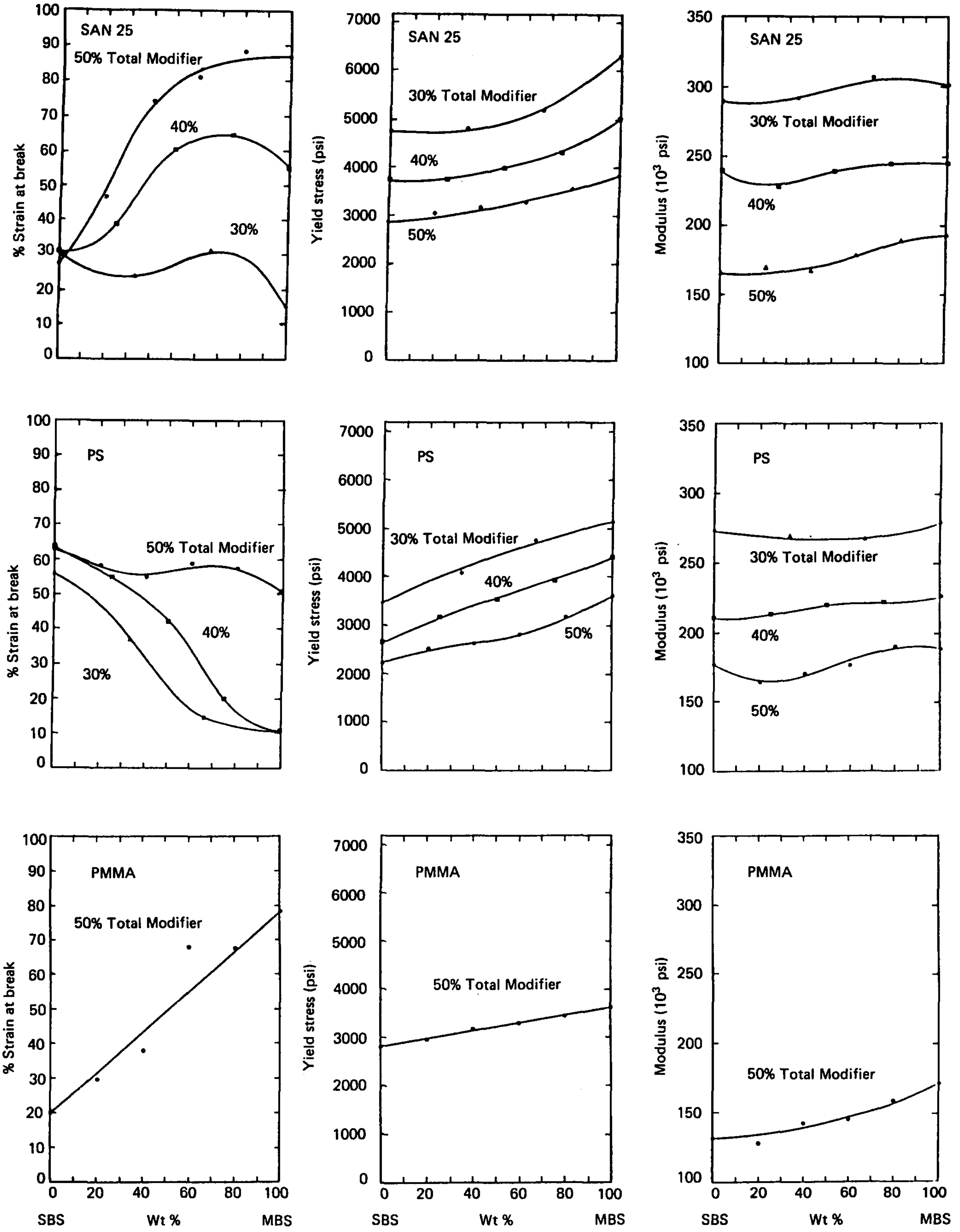

Figure 8 Effect of MBS and SBS combinations on tensile stress–strain characteristics for three matrices at various total modifier contents

PMMA and SAN than PS, while the SBS copolymer toughens PS better. The MBS modifier appears to be better at toughening SAN matrices with which its PMMA shell is miscible, although particle size considerations must also be taken into account.

A synergistic toughening effect was observed for SAN 25 containing both MBS and SBS particles. A similar but less pronounced effect was seen for PMMA. PS properties decrease rapidly as MBS particles replaced SBS particles in the matrix.

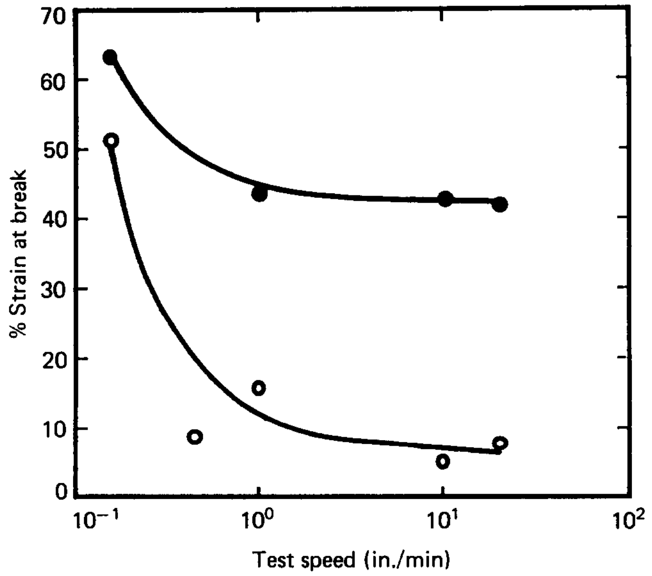

Figure 9 Effect of tensile test speed on per cent elongation at break for PS containing 50% SBS (●) and for PS containing 50% MBS (○)

A complex mechanism of craze initiation, propagation and termination is apparently responsible for the toughening of SAN. We speculate that the small MBS particles create shear bands that interact with the crazes initiated at the SBS particles. Due to the high loading of the MBS particles, the mean free path between the particles is small, which means that they could also interact with the crazes directly to cause termination.

Independent of the mechanism involved, the phenomenon is interesting and somewhat unexpected. We believe further study is in order to determine the mechanism in the hope of applying this knowledge to other systems.

ACKNOWLEDGEMENTS

The authors wish to thank Dow Chemical Co., Rohm and Haas Co., Cosden Oil and Chemical Co. and Asahi Chemical Industries Co. Ltd for supplying the materials used in this study. Special thanks are due to R. H. Weese for many helpful discussions and contributions. Transmission electron microscopy was carried out by M. Dineen of the Dow Chemical Company. This work was supported by the US Army Research Office. M.E.F. acknowledges fellowships from the IBM Corporation and the Phillips Petroleum Company.

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