Methyl methacrylate grafted rubbers as impact modifiers for styrenic polymers

H. Keskkula and D. R. Paul
Department of Chemical Engineering and The Center for Polymer Research, University of Texas at Austin, Austin, TX 78712, USA

and K. M. McCreedy and D. E. Henton
The Dow Chemical Company, Midland, MI 48640, USA
(Received 9 March 1987; accepted 8 June 1987)

The use of methyl methacrylate-grafted latex rubber (MMA-g) particles has been studied for the impact toughening of styrenic matrix polymers. It was found that the addition of MMA-g to mass made acrylonitrile–butadiene–styrene (ABS) and high-impact polystyrene (HIPS) significantly increases their impact strength. While the effectiveness of MMA-g for enhancing the toughness of ABS was not surprising because of the miscibility of the styrene–acrylonitrile copolymer matrix and the poly(methyl methacrylate) graft, its effectiveness in HIPS was unexpected. Also, the addition of MMA-g to brittle mixtures of ABS and HIPS restored the ductility to levels comparable with ABS or HIPS alone and beyond. This observation suggests further possibilities in the use of MMA-g for compatibilizing other brittle, immiscible polymer blends. Styrene–acrylic acid (SAA) copolymers have a high heat deformation temperature, but they are not readily toughened by the standard methods of rubber modification. However, a combination of styrene–butadiene–styrene triblock copolymers with MMA-g was found to be effective in toughening SAA copolymers. Possible reasons for the broad effectiveness of the small methyl methacrylate-grafted rubber particles in the various systems are discussed. However, an obvious need for further research is apparent for an understanding of the mechanisms of toughening in these composite polymers.

(Keywords: rubber toughening; impact strength; ABS; HIPS; styrenic polymers; rubber grafts; methyl methacrylate grafts)

INTRODUCTION

Rubber modification of brittle glassy polymers has been practised since the early 1950s with high-impact polystyrene (HIPS) and rubber-modified styrene/acrylonitrile copolymers (ABS) being important commercial examples[1-3]. More recently, various ductile, but notch sensitive engineering polymers have also been rubber-modified for improved performance[3-5], and the growth potential in this area appears to be tremendous.

Rubber modification of brittle polymers has been extensively studied for more than three decades, and a great deal is known about the nature and the mechanisms of rubber-toughening of polymers such as HIPS and ABS[1-3,6,7]. For effective use of the rubber, it is known that the rubber particles must be larger than a critical size for each of the matrix polymers, e.g. polystyrene (PS) and styrene/acrylonitrile copolymers (SAN)[1,2,5,8]. A critical volume fraction of the rubber phase is also required in order to achieve significant improvements in toughness relative to that of the matrix polymer[1,9]. The requirement of adhesion between the rubber phase and the brittle matrix is claimed by most of the literature in this field[1,5] although little has been done to quantify this issue. Grafting of the rubber phase with the matrix monomers typically leads to the required adhesion between the rubber particles and the matrix. However, there is an optimum level of grafting of the rubber phase. Excessive grafting may adversely affect the particle morphology and size in HIPS[9], while excessive grafting of small emulsion particles in ABS has an adverse effect on mechanical properties[10,11]. In addition, the rubber phase must be crosslinked to some degree, either chemically or physically as in styrene–butadiene–styrene (SBS) block copolymers, to stabilize and maintain the rubber phase morphology during melt fabrication or for optimizing mechanical properties[1,9].

Two principal mechanisms are responsible for the high ductility of rubber-toughened brittle polymers. Toughening of polystyrene involves a crazing mechanism[1] while both shear yielding and crazing mechanisms may contribute to the ductility of rubber-modified SAN. In addition, it is suggested that hole formation in small rubber particles during stressing contributes to the energy absorbing mechanisms of ABS[7,12]. Hole formation is a dilatational process as is crazing. It is generally believed, however, that shear yielding contributes most importantly to the high ductility of ABS, and it is generally regarded as more desirable than crazing for achieving superior toughness[1,5,13].

However, recent observations indicate that toughening of the brittle matrix polymers such as polystyrene, styrene copolymers (with acrylonitrile, acrylic acid, maleic anhydride, etc.), and poly(methyl methacrylate) may involve other issues than those briefly outlined above. The presence of small grafted rubber particles (0.1 to 0.2μm), whose shells are either miscible or immiscible with the matrix polymer, appear to produce some unusual synergistic toughening effects for brittle matrix polymers which also contain some larger rubber particles

0032–3861/87/122063–07$03.00

Table 1 Emulsion-grafted rubber particles used in this study

	Rubber latex seed			Graft layer		
Designation	Type	% Total weight	Monomer	% Bound	% Free	% Total weight
MMA-g-1	Polybutadiene[a]	78.0	Methyl methacrylate	15.2	6.8	22.0
MMA-g-2	Polubutadiene[a]	52.9	Methyl methacrylate	18.0	29.1	47.1
MMA-g-3	Polybutadiene[a]	75.0	Methyl methacrylate	12.0	13.0	variable[c]
MMA-g-4	Terpolymer[b]	variable[c]	Methyl methacrylate	–	–	17.3 to 22.3
MMA/S-g	Polybutadiene[a]	77.7 to 82.7	MMA/S[d]	–	–	20.0
s-g	Polybutadiene[a]	80.0	Styrene	–	–	

[a] Firestone SR 6747 polybutadiene latex with volume mean particle diameter = 1190 Å

[b] Composition = 90% butadiene, 7% styrene, 3% acrylonitrile; volume mean particle diameter = 1810 Å

[c] A series of compositions with rubber contents ranging from 30.8 to 84.5%

[d] A series of compositions with ratio of methyl methacrylate/styrene spanning entire range of copolymers

of a different kind[13,14]. The purpose of this paper is to report some new results in this area and to discuss aspects of the mechanisms which may be responsible for this unusual synergism.

While the desirable features of a bimodal rubber particle distribution in ABS have been known for some time[1,9,10,15], the use of bimodal particle distribution in SAN, where the two particle populations are different both in size and kind, have only recently become known[14,16]. These systems can be synthesized by the use of mass and emulsion polymerization technologies. In this work, large rubber particles were obtained either by mass polymerization of HIPS and ABS, or by the introduction of SBS triblock copolymer rubbers. Small particles were obtained by grafting of a rubber seed latex. Methyl methacrylate (MMA) was chosen as the grafting monomer of primary interest because of its miscibility with a broad range of SAN copolymers and because of the easy and uniform dispersability of the grafted rubber in different matrix polymers; however, limited work using styrene and its copolymers with MMA was also carried out.

MATERIALS AND EXPERIMENTAL PROCEDURES

Methyl methacrylate (MMA) and styrene (S) grafted elastomers were prepared by standard emulsion grafting procedures[1,17] using a monodisperse polybutadiene rubber latex as a seed. Sodium persulphate was used as the initiator, and the monomer was added continuously until the desired composition was obtained. The grafted elastomers were recovered by freeze coagulation and dried prior to their use in blends. To characterize these materials, an extraction was performed in methyl ethyl ketone which followed by centrifugation resulted in separation of free or ungrafted polymer (formed during the polymerization described) from the grafted composite. The grafted elastomers used in this work are described in *Table 1*.

Other polymers used in this study are described in *Table 2*. Blends mentioned later were prepared on a steam heated two roll mill at about 190°C. Samples were mixed for five minutes and then compression moulded at 190°C. Notched Izod impact strengths were obtained according to ASTM procedures. More detailed procedures for the preparation of the blends and their testing are given elsewhere[17].

Table 2 Description of other polymers used in this study

Designation	Description	Source
ABS 500	A commercial mass made ABS containing 13.5% rubber; SAN matrix contains 23% AN	Dow Chemical Co.
ABS-X-1	Experimental mass made ABS containing 8% rubber; volume-average rubber particle diameter = 2.2 μm	Dow Chemical Co.
ABS-X-2	Experimental mass made ABS containing 12% rubber; volume-average rubber particle diameter = 0.85 μm	Dow Chemical Co.
HIPS	Commercial HIPS containing 6.5% rubber	Dow Chemical Co. (Styron 492)
SAA	Experimental styrene/acrylic acid copolymer (7.5% AA)	Dow Chemical Co.
SBS-1	SBS triblock copolymer $\bar{M}_w = 550\,000$, 40% styrene	General Tire Co.
SBS-2	SBS triblock copolymer $\bar{M}_w = 93\,000$, 29% styrene	Shell Chemical CO. (Kraton 1101)

Figure 1 shows transmission electron photomicrographs for blends of a high rubber content latex grafted with MMA, MMA-g-4, with PS and SAN (25% AN). It can be seen that the emulsion made particles are individually dispersed in each of these matrix polymers with no evidence of agglomeration or clumping.

RESULTS AND DISCUSSION

Modification of mass made ABS

Dow ABS 500 is a commercial ABS material made by a mass or bulk polymerization process. It contains 13.5% rubber and has a notched Izod impact strength of 128 Nm m^{-1} at room temperature. As can be seen in *Figure 2*, addition of MMA grafted latex rubber particles (MMA-g-1; see *Table 1*) causes a large increase in the notched Izod impact strength for this material. At a total rubber content of 23%, the notched Izod value is 684 Nm m^{-1}. An equally dramatic increase was noted when the impact strength was measured at −17.8°C (80 vs. 438 Nm m^{-1}).

Tensile properties of these blends are also affected but to a much lesser degree. At 20% and 30% total rubber

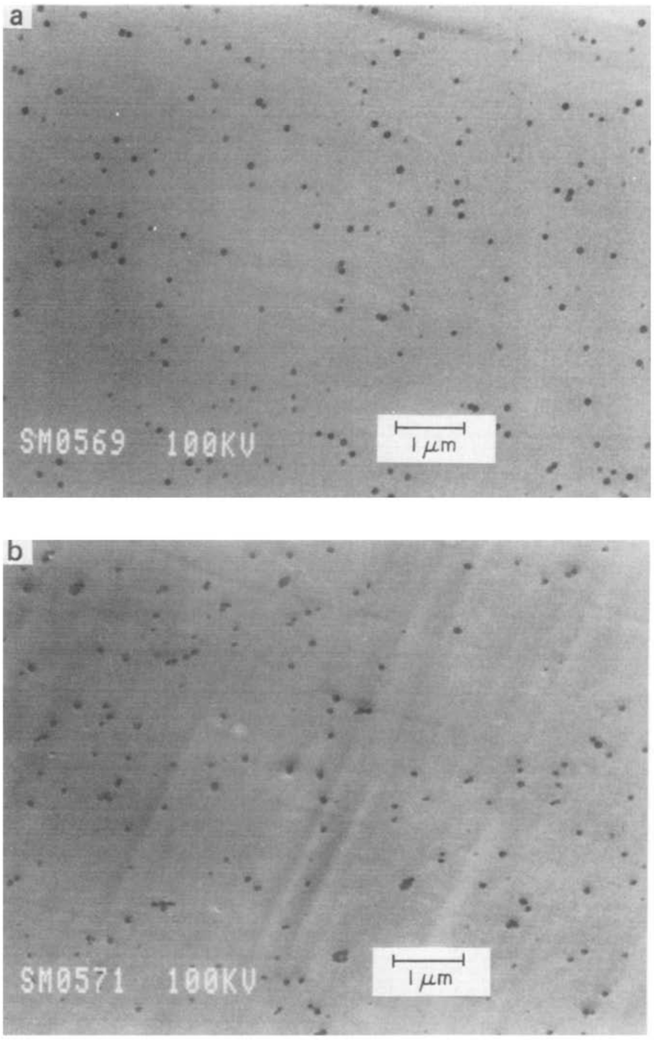

Figure 1 Dispersion of MMA-grafted rubber (1 %) in (a) SAN and (b) PS matrix

level, the ABS 500 based composites have tensile yield strengths of 35.6 MPa and 27.9 MPa, tensile rupture strengths of 29.2 MPa and 21.4 MPa and tensile moduli of 1930 MPa and 1448 MPa, respectively. While the heat deformation temperature of the blends containing MMA-g was not changed, the melt flow rate, *MFR*, was reduced significantly. The *MFR* (Condition I ASTM D1238) for the ABS 500 is 3.6 g/10 min which was reduced to 1.8 and to 0.12 g/10 min for blends containing 20 and 30 % total rubber. This decrease in *MFR* is not unexpected, since it has been known for some time that the addition of small gel particles to a thermoplastic polymer increases its melt viscosity at low shear rates. Rosen[18] also pointed out that melt processability may be improved due to reduced die swell and elastic strain energy.

The addition of MMA grafted latex rubber particles (MMA-g-3) to two experimental ABS materials having fairly uniform rubber particle size distributions with volume-average particle diameters of 0.85 μm (ABS-X-2) and 2.2 μm (ABS-X-1) led to a significant improvement of their toughness even when small amounts of MMA-g were added. This method of improving toughness is particularly useful since there are limits to both the rubber concentration and the ultimate impact strength of the mass polymerized products. The data in *Figure 2* show that the composite blends containing a combined rubber concentration of 13.5 % (same as ABS 500) have impact strengths of about 187 and 342 N m m^{-1}. In this comparison, the mass product with 8 % rubber and a particle size of 2.2 μm appears to be most effectively modified. While all three of the mass made ABS polymers are further toughened by the addition of the small MMA grafted rubber particles, it is apparent that the ABS polymer with the largest particles and the lowest original rubber content shows the strongest improvement in toughness upon adding small (~0.12 μm) MMA grafted rubber particles. The rate at which the notched Izod impact strength increases in *Figure 2* with total rubber content is considerably greater than what can be expected for increased content of large rubber particles of the type formed in the original mass made ABS materials. Furthermore, addition of the small MMA grafted rubber particles alone to an SAN matrix produces only modest gains in toughness as noted before[13]. Therefore, the large increases shown in *Figure 2* represent a significant synergism in toughening stemming from the simultaneous presence of both types of particles[17].

The interaction or miscibility of the graft layer of the small rubber particles with the matrix polymer may be expected to play a role in their ability to toughen based on simple notions of adhesion. This effect is illustrated in *Figure 3* where ABS 500 has been blended with a series small rubber particles (MMA/S-g) where the graft layer consists of a random copolymer of methyl methacrylate and styrene. The Izod impact strengths for these composites containing 23 % total rubber, at −17.8°C and 22.8°C are plotted *versus* the percentage styrene in the grafted polymer layer. PMMA is miscible with the SAN

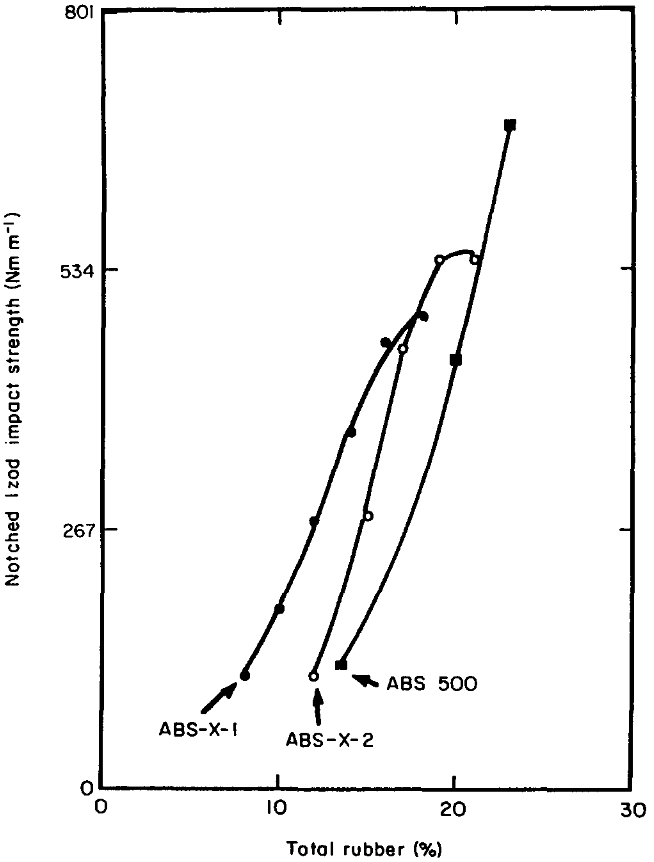

Figure 2 Effect of the addition of MMA-grafted rubber particles on the notched Izod impact strength of mass made ABS

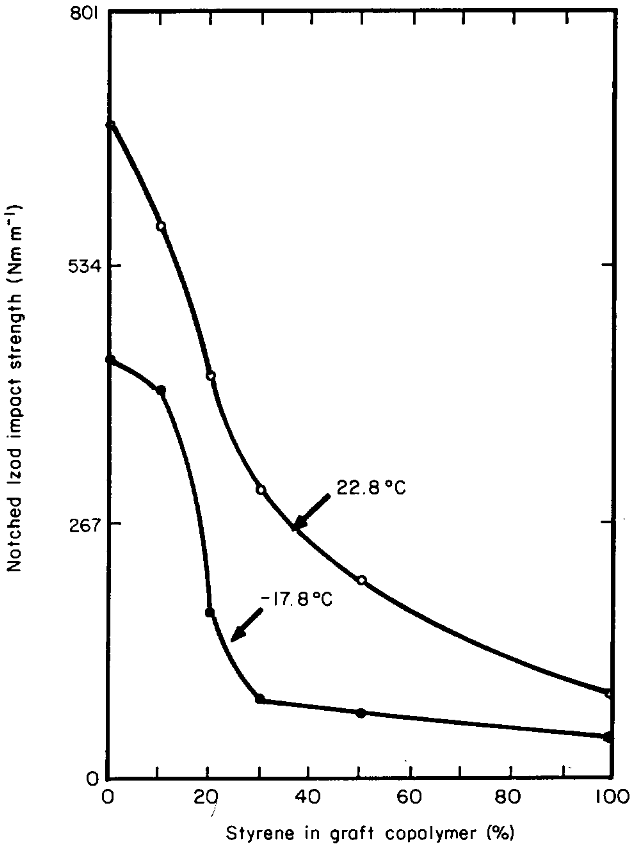

Figure 3 Effect of graft composition (S/MMA ratio) on the notched Izod impact strength of graft blends with ABS 500; total rubber content: 23%

matrix of the ABS 500[19]; whereas, PS is not miscible with the SAN[20]. At some styrene content, the MMA/S copolymer will cease to be miscible with the SAN; although, the exact composition boundary between miscibility and immiscibility has not been reported in the literature. The pure MMA graft significantly increases the toughness of ABS 500 as expected from the previous discussion while a pure styrene graft reduces its toughness. As styrene is incorporated into the graft copolymer, the notched Izod values for the composite decreases gradually at 22.8°C while at −17.8°C a more abrupt decline occurs between 10 and 20% styrene. The latter may reflect the expected transition in miscibility; however, the dispersability or the tendency of the higher styrene content grafts to agglomerate is an issue that requires further examination. Nevertheless it appears from these results that miscibility or perhaps adhesion of the graft layer with the matrix polymer is one of the requirements for synergistic toughening by the addition of small rubber particles.

The amount of monomer grafted to the small rubber particles is also an important factor affecting their ability to further toughen ABS as shown in *Figure 4*. In this case, ABS 500 has been blended with a series of grafted rubber particles (MMA-g-4) where the fraction that the graft layer contributes to the total particle mass has been systematically varied. To form a common basis for comparison, the composites were formulated to achieve a constant total rubber content of 20%. Composites without any graft layer, i.e. the seed rubber, are not expected to be useful for toughening as suggested by the broken line. However, the notched Izod values are about constant from the lowest fraction of graft layer shown in *Figure 4* (15.5% combined graft and free PMMA) up to about the 50% level. Beyond this, the toughness falls off rapidly. The causes for this loss in effectiveness may stem from several factors. Michler[11] has pointed out that as the extent of grafting to an emulsion made rubber particle is increased, the effective elastic modulus of the particle will also increase. At some point the difference in moduli of the matrix and the composite particles is too small to create an effective stress concentration required for toughening. It appears that the smaller the rubber particle is, the more detrimental an excessively thick graft layer will be.

Modification of polystyrene and HIPS

MMA grafted rubber particles can also be used advantageously for toughening compositions where polystyrene is the matrix polymer even though PMMA and PS are not miscible. However, recent studies[21] have shown that reasonable levels of adhesion can be developed at PMMA–PS interfaces. The lower curve in *Figure 5* shows that significant toughening of polystyrene is not achieved until the rubber content reaches about 20% when MMA-g-1 is added to polystyrene. However, more dramatic toughening is realized when MMA-g-1 is added to the HIPS described in *Table 2* as shown by the upper curve in *Figure 5*. Similarly excellent toughness is achieved by the addition of both the MMA grafted rubber particles and 5% of either of the SBS block copolymers described in *Table 2* (see single points in *Figure 5*). The cases shown in *Figure 5* provide further examples of

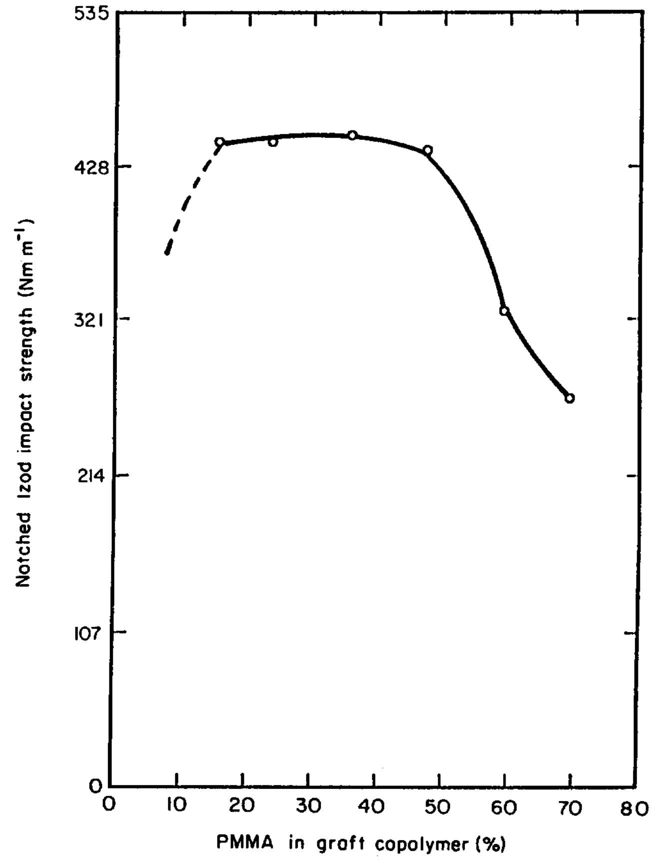

Figure 4 Effect of PMMA in the graft copolymer (including free PMMA) on the notched Izod impact strength of graft blends with ABS 500; total rubber content: 20%

synergism mentioned earlier when dual rubber particles are employed.

It should be pointed out that the particular MMA grafted rubber used here is effective for use with matrix polymers with which PMMA is not miscible only because it has a low free PMMA content (see MMA-g-1 in *Table 1*). When a similar material, MMA-g-2, having 29.1% free PMMA was added to HIPS no improvement in toughness resulted. This free PMMA apparently forms separate domains with the PS matrix and due to the mechanical incompatibility of PMMA and PS brittle fracture results. However, a similar problem is not encountered when MMA-g-2 is added to ABS 500 since the free PMMA is miscible with the SAN matrix and no such phase separation occurs.

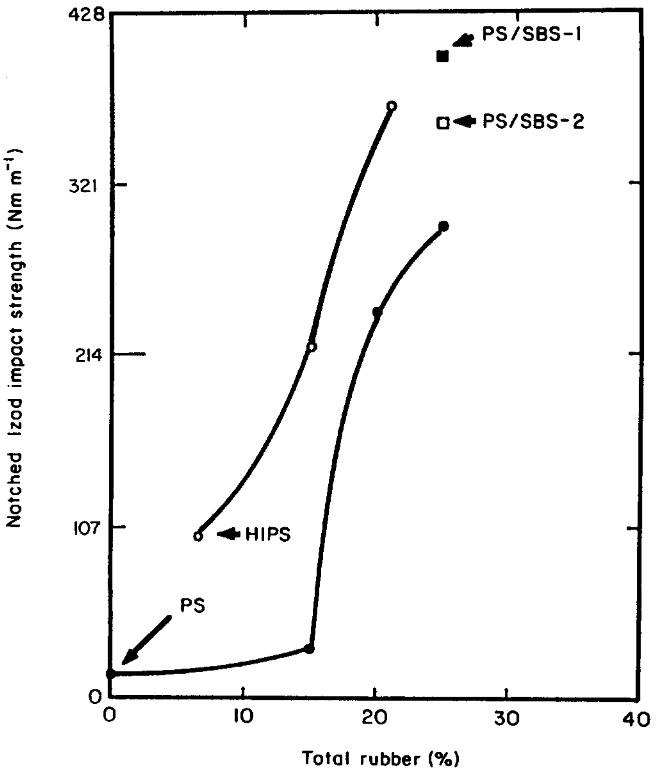

Figure 5 Effect of total rubber concentration on the notched Izod impact strength in PS and HIPS blends with MMA grafted rubber and S/B/S triblock copolymers

Modification of styrene–acrylic acid copolymers

Styrene/acrylic acid copolymers (SAA) have high heat deformation temperatures, but they are brittle. They are easily melt fabricated because the interchain hydrogen bonding responsible for the high heat distortion temperature is no longer effective at fabrication temperatures[22]. Even though there are many applications for tough polymers with a high heat deformation temperature, only limited examples of such toughened styrenic polymers are described in the literature[14,16].

The results shown in *Table 3* indicate that a dual rubber system is more effective for toughening SAA than any other single source of rubber examined there. Note that the PMMA grafted to the rubber, MMA-g-1, is miscible with SAA[23] whereas the polystyrene in the SBS block copolymers or on the graft, S-g, is not expected to be miscible with SAA. All single sources of rubber give impact strengths of less than 53 Nm m^{-1} while at the same total rubber content several combinations involving MMA-g-1 as one of the sources produce impact strengths over 160 Nm m^{-1}. There appears to be a limiting concentration of MMA-g-1 needed to produce such levels of toughness as seen by the cases where total rubber content was reduced from 23 to 19% (with essentially a fixed amount of S-g) resulting in the notched Izod values falling from 203 to 80 Nm m^{-1} (rows 4, 5 and 6 in *Table 3*). Significant toughening is not observed when 5% SBS block copolymer is used in combination with MMA-g-1; however, raising the SBS content to 10% produces a more impressive gain.

Compatibilization of ABS/HIPS blends by MMA-g

Polystyrene and SAN are not miscible, so it is not surprising that their toughened counterparts, HIPS and ABS, form blends with poor mechanical properties as shown in *Table 4*. However, addition of MMA-g to ABS/HIPS blends restores toughness. In fact at 20% MMA-g, the impact strength of the ternary blend is greater than that of either HIPS or ABS as seen in *Table 4*. At 30% MMa-g, an impressive impact strength of 278 Nm m^{-1} is obtained. The last two rows in *Table 4* show similar comparisons for slightly different ABS and MMA-g materials.

Figure 6 is a transmission electron photomicrograph which shows the complex morphology of the material described in the last row of *Table 4*. Interestingly, most of the MMA-g particles are located at the interface between

Table 3 Synergism in impact modification of styrene/acrylic acid (SAA) copolymers with dual rubber systems

SAA	Composition (%) MMA-g-1	S-g	SBS-1	SBS-2	Total rubber (%)	Notched Izod (Nm m^{-1})	*MFR*[a] (Cond. I) g/10 min	Vicat H.D.[b] (°C)
80.6	19.4	–	–	–	15	10.04	2.0	121
67.9	32.1	–	–	–	25	20.08	–	–
69.8	–	30.2	–	–	25	22.59	–	–
71.5	12.4	16.1	–	–	23	85.34	0.05	–
71.5	15.4	13.1	–	–	23	95.38	0.15	–
71.5	9.4	14.1	–	–	19	37.65	0.11	–
75.6	19.4	–	5	–	20	15.06	0.6	121
70.6	19.4	–	10	–	25	47.69	0.2	121
75.6	19.4	–	–	5	20	10.04	1.1	120
70.6	19.4	–	–	10	25	40.16	1.5	119

[a] Melt flow rate
[b] Heat distortion temperature

Table 4 Effect of MMA grafted rubber on the impact strength of ABS/HIPS blends

Composition (%)			Total rubber (%)	Notched Izod impact strength (Nm m^{-1})
MMA-g[a]	HIPS	ABS[b]		
0	100	0	6.5	101
0	0	100	13.5	128
0	50	50	10.0	21
10	45	45	16.9	59
20	40	40	23.8	187
30	35	35	30.7	278
0	50	50[c]	9.25	12
10[d]	45	45[c]	15.0	69

[a] MMA-g-1 except where noted
[b] ABS-500 except where noted
[c] ABS-X-2
[d] MMA-g containing 76.6% rubber

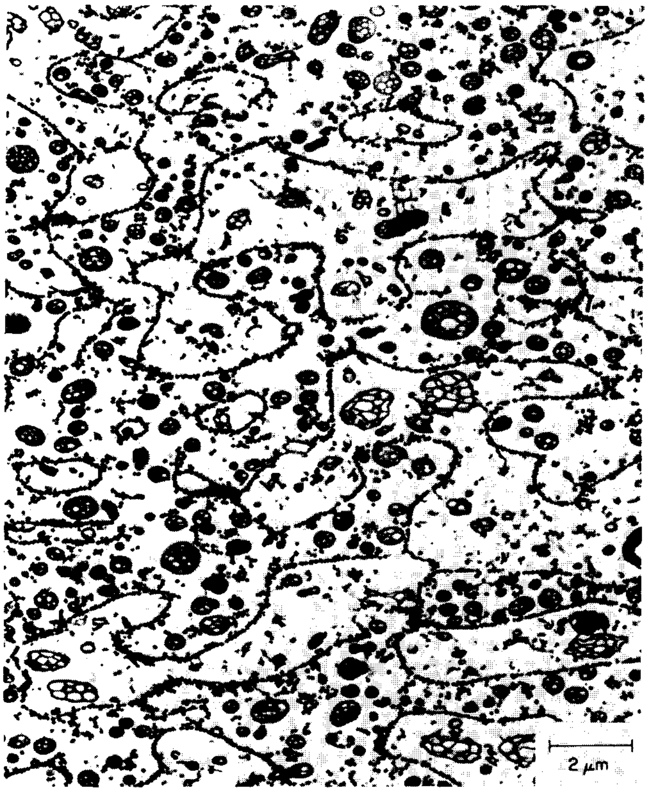

Figure 6 Transmission electron photomicrograph of a ternary blend of HIPS, ABS 500- and MMA-grafted rubber; HIPS domains are characterized by rubber particles with large occlusions, while ABS domains have more compact rubber particles; submicron solid graft particles are at the domain interfaces

the PS and SAN matrix with very few of the small particles located in either of these phases. Upon more intensive melt mixing, the MMA-g particles become more uniformly dispersed. A subsequent paper[24] will elaborate on the formation of these unusual morphologies.

SUMMARY

A qualitative summary in *Table 5* shows the effectiveness of the small (0.1 to 0.2 μm) MMA-grafted rubber particles in combination with larger rubber particles from HIPS and ABS or those from SBS block copolymers. It was noted that both the small as well as the large particles may have a strong or a poor interaction with the matrix polymer, as judged by the miscibility of the graft layer with the matrix polymers. Based on the effectiveness of MMA-g and the strong synergism shown in some of the examples, as well as the variability of the apparent interaction or adhesion of the particles to the matrix, it is apparent that further study of the mechanisms for toughening in these systems should be pursued. It appears that, generally, the large particles are responsible for multiple craze initiation. This observation seems to be valid whether the graft and block polymer segments of particles are miscible or immiscible with the matrix polymers. The small particles at some *critical concentration* or *critical interparticle distance* for each of the different matrix polymers appear to control the craze growth rate and ultimately the craze termination. It is likely that the small particles cause the formation of shear bands in some matrix polymers which may be responsible for craze termination and the ultimate toughening. Alternatively, the overlapping of stress-fields around the small particles may cause the rupture of the particles which in turn may be responsible for the control of the craze termination process. The role of the small MMA-g particles in establishing the ductility of the brittle HIPS–ABS blends is not readily understood and more work is required here. Mechanical dilatometry and microscopy studies should lead to an improved understanding of the mechanisms for the type of synergisms described here for the toughening of brittle polymers.

Table 5 Qualitative summary of the effectiveness of small MMA-g particles for toughening of brittle matrix polymers containing large rubber particles

Source of large rubber particles	Matrix polymer	Graft layer miscibility with matrix		Effectiveness of impact modification
		Large particles	Small particles	
ABS-mass	SAN	Yes	Yes	Excellent
SBS	SAN	No	Yes	Good[a]
HIPS	PS	Yes	No	Good
SBS	PS	Yes	No	Excellent
SBS	SAA	No	Yes	Good
S-g[b]	SAA	No	Yes	Good

[a] Ref. 13
[b] S-g particles agglomerated during melt blending

ACKNOWLEDGEMENT

The authors wish to thank The Dow Chemical Company for their support.

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