Silicone-Toughened Poly(Styrene-co-Acrylonitrile)

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Synopsis

Uniform dispersions of high-molecular-weight poly(dimethylsiloxane) (PDMS) in a matrix of poly(styrene-co-acrylonitrile) (SAN) are prepared where the degree of crosslinking in the elastomer and its extent of grafting to the SAN matrix are controlled. This gives an impact resistant plastic at ambient and low temperatures which is resistant to outdoor exposure. The T_g of PDMS is shown to be greatly reduced when grafted to the SAN matrix. Plots of impact resistance versus shift factor a_T of the elastomer added for toughening coincide for PDMS and polybutadiene over a 150°C temperature range.

INTRODUCTION

Improvement of impact resistance in glassy thermoplastics with speciality elastomers is receiving increasing attention in order to meet requirements of performance which cannot be met by the unsaturated elastomers normally employed.[1] Important among these requirements is retention of impact resistance at low temperatures and after periods of outdoor exposure. Elastomers based on poly(dimethylsiloxane) (PDMS) are interesting candidates as toughening additives because of their well-known resistance to degradation by UV radiation and their very low glass-transition temperature (T_g). The importance of an elastomer of low T_g for impact resistance both at low temperatures and ambient is documented.[2–4]

The systems presently under consideration are terpolymers consisting of a glassy matrix of poly(styrene-co-acrylonitrile) (SAN), in which spherical particles of rubber approximately 0.05 to 1.0 μm diameter are dispersed. It is critical that the dispersed rubber phase be sufficiently crosslinked and that it adhere through grafting to the glassy matrix.[4] Generally this is done by copolymerization of the monomers in the presence of the rubber so that crosslinking and grafting take place simultaneously. Feasibility of dispersing PDMS in polystyrene to impart impact resistance was demonstrated earlier through polymerization of a suspension of styrene containing a vinyl functional PDMS.[5] Special problems arise with SAN, however, because of the insolubility of PDMS in the monomers and its high degree of incompatibility in the matrix. This magnifies the importance of grafting, which with PDMS is confounded by its reluctance to react with polymeric free radicals under normal conditions of polymerization.

The present paper describes how impact resistance in SAN can be brought at least to the level of that typically seen in poly(styrene-co-acrylonitrile)-*g*-polybutadiene (ABS) by copolymerization in emulsion of styrene and acrylonitrile in the presence of PDMS emulsion polymers. The degree of grafting is controlled by chain transfer with specified amounts of mercaptoalkyl groups along the PDMS chain while the degree of crosslinking is predetermined in the

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PDMS emulsion polymer during its formation. The extent of reaction of the polymeric free radicals would be expected to be at least four to five orders of magnitude greater at the site of the pendant mercapto groups on the siloxane chain than at the silylmethyl groups.[6] The approach thus allows observation of the effects of independently controlled crosslinking and grafting on impact resistance.

Poly(dimethylsiloxane) incorporated into SAN at the appropriate levels of grafting and crosslinking would then allow a comparison with other elastomers in terms of its relative efficiency in improving impact resistance of SAN. This is of particular interest in view of the inverse relationship found between the degree of improvement in impact resistance for various elastomers and their T_g.[3] Thus, it will be determined if PDMS, whose T_g is 40°C lower than any of the elastomers evaluated, still fits the relationship and if the results can be interpreted in terms of the relaxation time of the elastomer.

EXPERIMENTAL

Materials

Styrene and acrylonitrile were obtained from commercial sources and inhibitors were removed chromatographically prior to use. The PDMS emulsion polymers containing the specified amount of mercaptopropylmethylsiloxy repeat unit were prepared by procedures described elsewhere.[7] Crosslinking in the PDMS was introduced by admixing specified amounts of ethyl orthosilicate with the PDMS monomer prior to its polymerization. The levels of surfactants, sodium dodecylbenzenesulfonate and sodium laurylsulfate, in the emulsions were 0.3% and 0.9% by weight, respectively. Weight-average particle diameters were in the range of 0.15 μm with a distribution between 0.05 and 1.0 μm. In the absence of crosslinking number average molecular weights were 7×10^4 and weight-average molecular weights were 2×10^5 by gel permeation chromatography (GPC). A sample of commercial ABS, TD1001, was generously supplied by Ralph Arthur of Borg Warner Corporation.

Measurements

The swell ratio of the PDMS was determined by coagulation of the polymer from emulsion with an equal volume of isopropanol. The isolated polymer was washed and dried. A weighed 1 g sample w_1 was stirred with 25 g of benzene for 24 hr and then centrifuged. The supernatent solution was decanted and the weight of gel recorded w_2. The solvent was removed in a vacuum and the dried polymer weight recorded w_3. In all cases the gel fraction was $\geqslant$85%. Then swell ratio

$$q = \left(\frac{w_2}{w_3}\right)\left(\frac{\text{polymer density}}{\text{solvent density}}\right) - 1$$

Gel was determined in the terpolymer by dissolving a weighed one gram sample in 25 ml acetone. After 24 hr the insoluble material was separated by centrifugation and the supernatent solution was decanted. The insoluble materials were redispersed in acetone and again separated by centrifugation, decanted, dried in a vacuum, and weighed. Swell ratio was determined by the procedure described above.

Samples of terpolymer were prepared for testing by mixing 70 g with 1 g of sodium stearate at 180°C and 62 rpm for 10 min on a Brabender Plasticorder equipped with a CAM mixing head. The hot sample was quickly transferred to a chase and compression molded into bars suitable for impact and tensile testing at 177°C and 34.5 MPa. Samples were aged 48 hr prior to testing.

Notched Izod impact measurements were made according to ASTM-D-256-56 where the notch is cut at 45° and 2.5×10^{-3} m deep in the bar. A windage correction was deducted from the measurement to compensate for friction. Typically an average was taken over six to ten measurements. The test stand was provided with an environmental chamber to permit testing at low temperature.

Tensile properties were obtained according to ASTM D638-72. The distance between jaws at the start of each test was 2.5×10^{-2} m and the initial length used for the calculations of modulus and elongation was 1.8×10^{-2} m. The crosshead speed was 8.5×10^{-3} m/sec. Modulus was defined as the initial slope of the stress-strain curve.

Dynamic mechanical measurements were taken in tension at 3.5 Hz on a Rheovibron tester. The sample was cooled to −150°C over a period of approximately 1 hr and data were collected as the temperature increased at about 2°C/min.

Typical Procedures for Terpolymer Preparation

Two methods were used. Method A was used where the effect of the composition of the PDMS emulsion polymer was studied. Method B gave samples of lower melt viscosity and somewhat lower impact resistance.

Method A

A solution of 144 ml distilled water, 0.012 g ferrous sulfate, 0.5 g sodium pyrophosphate, and 0.12 g of *α-D* glycose was mixed with 78 g of the PDMS emulsion (32% polymer containing 1 mol % mercaptopropyl groups and crosslinker). The emulsion was held at 65°C under nitrogen and 0.14 ml of dodecylmercaptan and 0.081 ml of cumene hydroperoxide were added. Then a mixture of 60 ml (54.2 g) styrene and 37 ml (45.6 g) acrylonitrile was metered with a syringe pump into the stirred emulsion at 65° over a period of 3 hr. After an additional 6 hr at 65°C under nitrogen the emulsion was coagulated with an equal volume of hot 2% calcium chloride. The floc was washed with water and dried overnight at 75°C. Typically 90% of the expected weight of produce was recovered. After fabrication the Izod impact resistance was 619 J/m.

Method B

A solution of 145.4 g distilled water, 0.0026 g ferrous sulfate, 0.104 g of sodium pyrophosphate, and 0.026 g of *α-D*-glucose was mixed with 71.8 g of the silicone emulsion used above (31% polymer). The emulsion was held at 65°C under nitrogen and 0.017 ml of cumene hydroperoxide was added. Then a mixture of

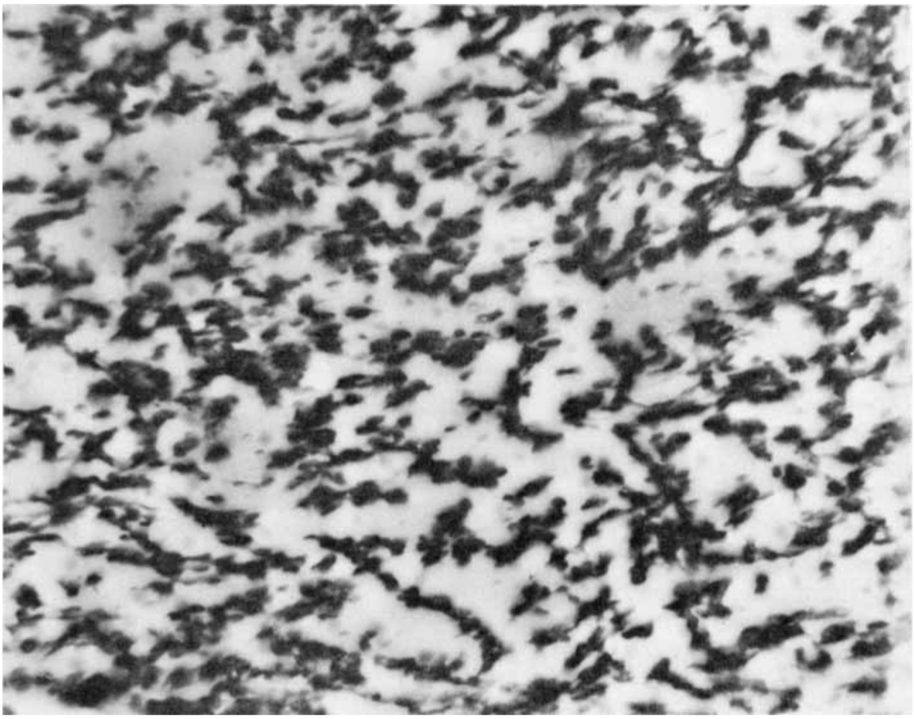

Fig. 1. Transmission electron micrograph of a thin section of SANS containing 20% of a cured PDMS copolymer with 0.56 mol % [$HS(CH_2)_3MeSiO$]. Magnification 33,000×.

TABLE I
Effect of Amounts of Mercaptan and Ethyl Orthosilicate in PDMS Emulsion Polymer on Grafting and Crosslinking in SANS

Mol % [$HS(CH_2)_3$ MeSiO]	Mol % $(EtO)_4Si$	Wt. %[a] Gel	Swell ratio of rubber: Before copolymerization[b]	Swell ratio of rubber: After copolymerization[c]
0.00	0.52	23	—	—
0.01	0.52	23	—	—
0.06	0.52	25	10.8	10.6
0.56	0.52	33	9.5	6.3
1.12	0.52	36	8.7	7.0
2.80	0.52	40	11.3	7.0
5.00	0.00	12	. . .	. . .
0.56	0.15	30	15.0	12.8
0.56	0.30	33	11.9	9.7
0.56	0.90	36	7.5	7.6

[a] Fraction of SANS insoluble in acetone; 22% rubber present.
[b] Measured in benzene on PDMS separated from emulsion.
[c] Measured in benzene on acetone insoluble gel fraction isolated from SANS.

10.8 ml (9.75 g) styrene and 6.6 ml (5.35 g) acrylonitrile was metered into the emulsion over a period of 1 hr. Stirring under nitrogen at 65°C was continued for 3.5 hr and a solution of 0.125 g of α-D-glucose, 0.0125 g of ferrous sulfate, and 0.5 g of sodium pyrophosphate was added. Then 0.081 ml of cumene hydroperoxide was added and a solution of 49.2 ml (48.7 g) of styrene, 30.4 ml (24.6 g)

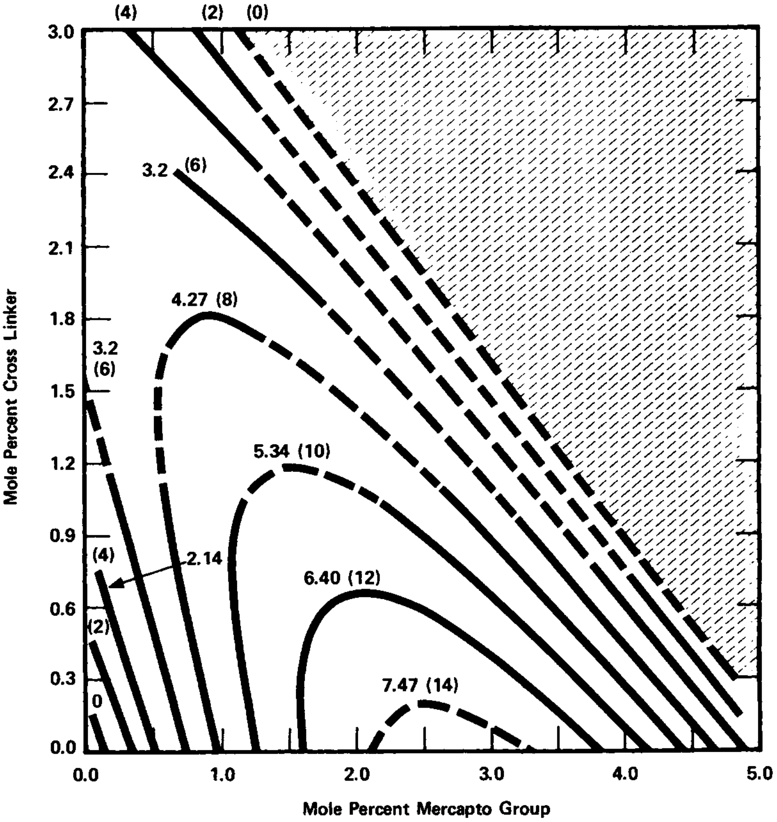

Fig. 2. Response surface for the effect of mercaptan content and degree of crosslinking in the rubber on notched Izod impact resistance in SANS containing 20 wt. % PDMS. Broken contours are extrapolations and shaded areas are unexplored. Impact strength in J/m × 10^{-2}. Data in parentheses are ft lb/in.

of acrylonitrile, and 0.14 ml of dodecylmercaptan were metered to the mixture over a period of 3 hr. Stirring at 65°C under nitrogen was continued for 3 hr and the terpolymer was isolated as above. The terpolymer showed a notched Izod impact resistance of 432 J/m.

RESULTS

Copolymerization of styrene and acrylonitrile in emulsions of mercaptan-functional PDMS gives uniform dispersions of silicone within the SAN matrix. Molded samples are white and uniformly opaque. There is no tendency to demix or exude free silicone polymer at the surface at levels as high as 40% PDMS. A transmission electron micrograph of a thin section of poly(styrene-co-acrylonitrile)-*g*-polydimethylsiloxane (SANS) is shown in Figure 1. The dark regions are particles of PDMS which do not require stain for definition. The smearing seen between particles is most probably an artifact of the method of specimen preparation since the rubber phase is still soft at −80°C where the sample is sectioned. Closer examination shows uniformly dispersed but fainter spherical particles of rubber apparently just below the surface of the section. These are close in size to the particles of the original emulsion.

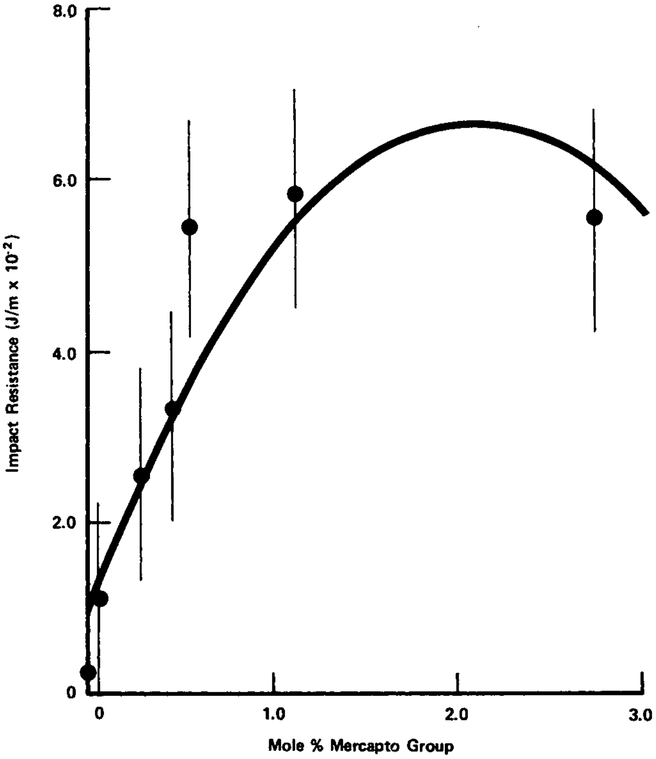

Fig. 3. Normal section of the surface in Figure 2 taken at a constant crosslinker level of 0.52 mol %. Bars represent one standard deviation on the data points.

The weight fraction of SANS insoluble in acetone in excess of the crosslinked rubber used originally indicates the degree of grafting. This is seen from Table I to be negligible unless the mercaptopropyl content exceeds 0.06 mol.%. It is also apparent from the decrease in the degree of swell in the rubber phase after copolymerization that the mercaptan group is a source of some additional crosslinking. The effect is most apparent at the highest levels of mercaptan and can be the result of interchain formation of disulfide bonds from thiol radicals formed during the copolymerization. More importantly, it can be seen from the swell measurements that the level of crosslinking in the rubber is more controlled by the amount of ethyl orthosilicate incorporated in the PDMS emulsion polymer at a constant amount of mercaptan. A minor effect on the degree of grafting can be seen as the amount of ethyl orthosilicate is increased. The slight effect might be due to entrapped chains of the SAN within or at the surface of the gelled rubber particle which were not removed by the method of extraction used here. Thus, it can be concluded that, although there may be some interdependence, the amounts of mercaptan and ethyl orthosilicate in the PDMS emulsion can be taken as indications of the degree of grafting and crosslinking in the rubber phase of SANS.

Appropriate adjustment of grafting and crosslinking in the PDMS phase give high levels of impact resistance in silicone modified SAN. The influence of each variable can be seen in Figure 2 which is a response surface representing sixteen data points where mercaptan and ethyl orthosilicate contents are varied in the

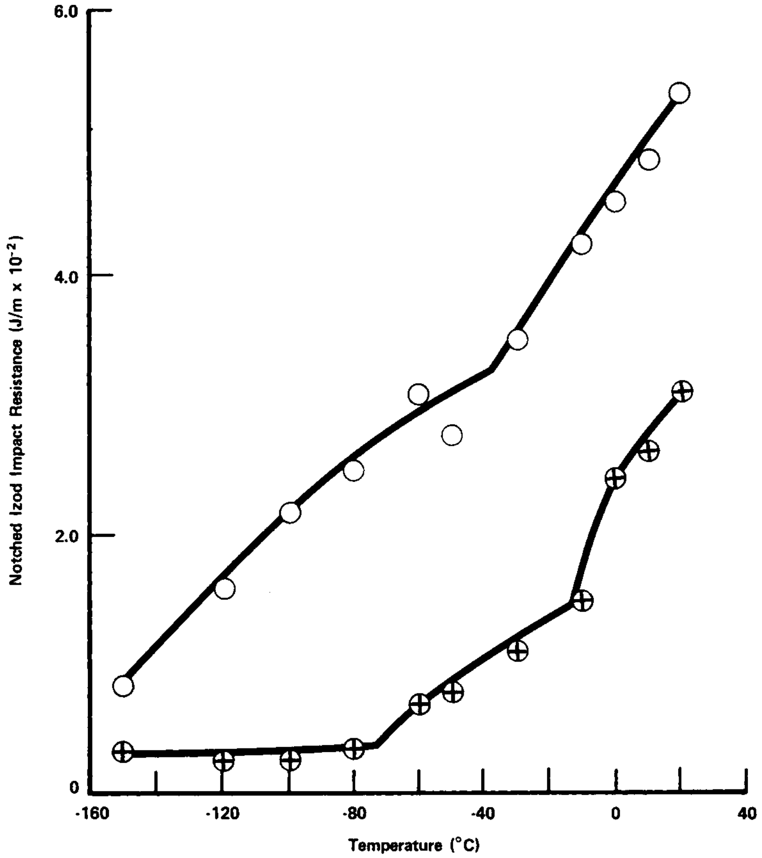

Fig. 4. Impact resistance at low temperatures. Upper curve: SANS containing 20 wt. % PDMS. Lower curve from Bucknall and Street (ref. 2) for a commercial ABS containing 20% rubber. Data points (-⊗-) were obtained in present work on a commercial ABS containing close to 20% rubber.

PDMS emulsions used to prepare SANS. Silicone, 20 wt. %, is used in this series. The contours defining the surface represent notched Izod impact resistance and are associated with a standard deviation of ±128 J/m. Broken contours are considered reasonable extrapolations while shaded areas represent unexplored regions. Broken contours adjacent to the unexplored regions are probably distorted because of a scarcity of local data. The curve in Figure 3 is a section taken normal to the response surface where data exists at a constant level of crosslinker, ethyl orthosilicate, in the PDMS emulsion polymer. Bars on the data point represent the standard deviation in impact resistance. In some cases impact resistance as high as 747 J/m were observed on individual test bars when crosslinking and grafting were near optimum.

The response surface shows that excessive crosslinking can be detrimental. The area giving the highest impact resistance is indicated where about 2.5 mol % mercaptan functionality is present in PDMS with little or no added crosslinker. Much of the required crosslinking probably arises from the previously mentioned interchain disulfide bonds which can form in the silicone rubber phase during the copolymerization. It is also of interest that Figure 2 indicates significant impact resistance at high levels of crosslinker and low levels of mer-

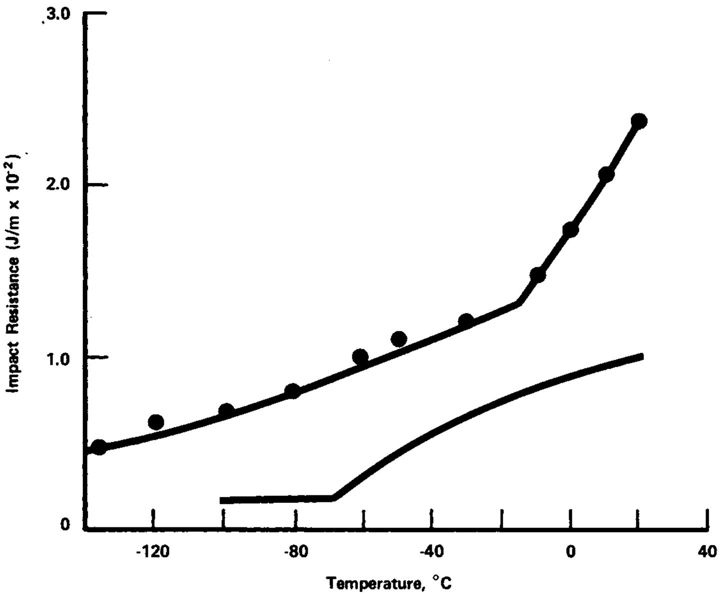

Fig. 5. Impact resistance at low temperature for SANS containing 10 wt. % PDMS. Lower curve from Bucknall and Street (ref. 2) for ABS with 10 wt. % rubber.

captan functionality in the PDMS. This effect was seen in independent work[8] where SANS made from pre-gelled PDMS emulsions containing methylvinylsiloxane repeat units and no mercaptan gave impact resistance in the range of 267 J/m. The rubber phase in these examples were highly crosslinked and showed relatively low degrees of grafting. It is postulated that in this situation enough adhesion to the matrix could be attained through entanglement of the SAN chains in the matrix with the PDMS chains at the surface of the crosslinked rubber particles. Such entanglements while not permanent might be expected to be more persistent at higher degrees of crosslinking in the rubber particle.

Silicone modified SAN showed significantly higher impact resistance than a commercial ABS at comparable levels of rubber, Figures 4 and 5. Although the commercial materials were made presumably by the emulsion process[9] and showed the same type of morphology[10] as SANS, comparisons should be qualitative as the molecular weight of the rubber in the commercial material which reportedly influences impact resistance[3] was unknown. It can still be seen however that a greater portion of impact resistance is retained by SANS as temperatures fall below ambient.

The most surprising observation was the absence of brittle failure in SANS at temperatures well below the T_g for PDMS (−120 to −125°C). Evidence of tough failure and whitening at the fracture in broken samples were seen at the limit of the experiment, −150°C. Typically embrittlement is seen 5 to 10°C above T_g for the rubber in ABS as shown in the lower curves, in Figures 4 and 5 that were taken from the literature.[2] Data obtained on ABS in the present work were superimposed on the curve for ABS with 20% rubber taken from the literature in Figure 4 to verify the present observation and method of measurement.

A dynamic mechanical spectrum of SANS from −150 to 100°C, Figure 6, also showed unusual features. Little indication is seen of the transitions expected

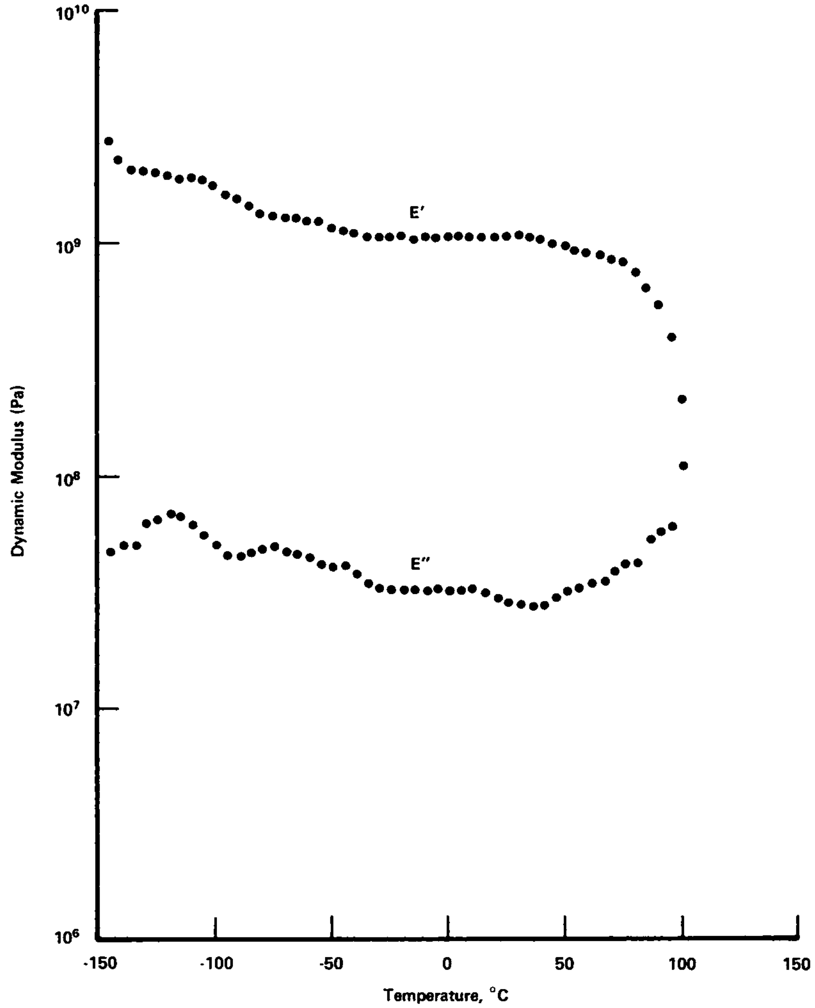

Fig. 6. Dynamic mechanical spectrum at 3.5 Hz showing storage modulus E' and loss modulus E'' for SANS with 20% PDMS.

in PDMS at −40 to −60°C for melting and at −120 to −125°C for T_g. The slight inflections seen are minor compared with those in ABS with a comparable amount of polybutadiene. Figure 7 shows spectrum for ABS where a strong maximum is apparent in loss modulus E'' at −75°C, the expected T_g for the rubber phase. The position of this maximum agrees well with that previously published for the same material.[10]

A shift to lower temperature of the loss maximum at T_g for the grafted rubber particles at decreasing total rubber content in ABS has been interpreted elsewhere as arising from increased thermal stresses and modulus in the matrix surrounding the particles.[11] It was proposed in ref. 11 that for ABS the increased modulus of the matrix at low rubber content prevents relief of thermal stresses which dilate the rubber particles and subsequently lower T_g of the elastomer. The effect of low rubber content might alternatively arise if the elastomer used were highly incompatible with the matrix and hence less effective in reducing

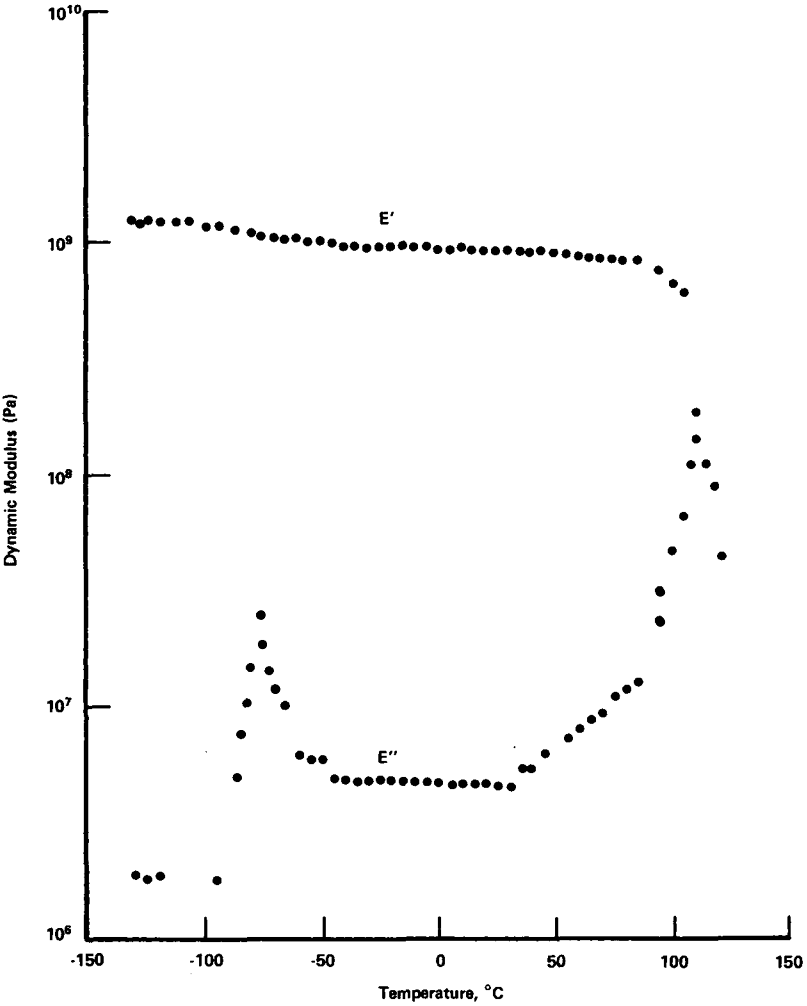

Fig. 7. Dynamic mechanical spectrum at 3.5 Hz for a commercial ABS containing close to 20% rubber.

modulus of the matrix which might be expected of PDMS. This could reduce T_g of the PDMS in SANS in a manner similar to the polybutadiene in ABS but to a much greater extent because of the lower temperatures. The weak transition seen in Figure 6 and the absence of brittle failure in SANS below the expected T_g for PDMS seen in Figures 4 and 5 can therefore be due to the true T_g being beyond the range of temperatures observed. Extrapolations of the curves for SANS in Figures 4 and 5 implies an effective T_g of grafted PDMS in a SAN matrix of approximately −170°C.

A weak maximum in E'' at −80°C not usually found in PDMS is seen in Figure 6. Similar inflections above T_g have been associated in radial butadiene-styrene block copolymers with the longest relaxation times for reptating molecules of free polybutadiene.[12] A small amount of nongrafted PDMS is possible in the present system and the inflection seen at −80°C might be attributed to similar

TABLE II
Tensile Properties of SANS

Material	Tensile strength at rupture, MPa	Elongation at rupture, %	Young's modulus, MPa
SANS (20% PDMS)	39.4	21	883
SANS (10% PDMS)	49.0	7	1062
ABS (ca. 20% rubber)	33.1	15	786

TABLE III
Accelerated Weathering of SANS[a]

Material	Izod impact resistance, J/m	
	Initial	After exposure
SANS[b]	496	325
SANS[c]	469	277
ABS[c]	336	122

[a] Three months exposure in Arizona at Desert Sunshine Exposure Tests, Inc. EMMAQA, of compression molded bars 0.125 in. thick for the notched Izod impact test (see Experimental).

[b] Contains 20% PDMS, no additives.

[c] Contains 20% rubber and 0.2% each of Tinuvin P, Tinuvin 770 and Irganox 1010 added prior to molding.

phenomena. A relatively high-loss modulus in SANS over the entire range of temperature as compared with ABS at similar levels of rubber can also be seen in Figure 7. The difference, an order of magnitude, is inexplicable but might at least in part be associated with the high interfacial tension at the surface of the PDMS particles and the SAN matrix.

Tensile properties at failure, Table II, of the sample with 20% PDMS are somewhat greater than a sample of ABS with a comparable amount of rubber. The higher tensile modulus parallels the effect of higher E' for SANS seen in Figures 4 and 5. This can be interpreted as less interpenetration of the PDMS in the SAN matrix because of its lower solubility parameter than polybutadiene. A more clear definition of the phases might be expected to give higher modulus in the case of PDMS.[13]

Stability at high temperature was apparent in extrusions of SANS made at 280°C which showed no discoloration or tendency to bubble. The upper limit for ABS appeared close to 220°C where foaming and discoloration were severe. Data in Table III illustrate the durability of SANS to outdoor weathering. Two thirds of the impact resistance was retained in samples with no pigment after three months exposure while one third was retained in ABS. Both SANS and ABS showed a tendency to assume a yellow color after the exposure even when antioxidants and ultraviolet screens were present.

DISCUSSION

Correlations of the impact resistance in rubber toughened plastics with test temperature, while previously interpreted in terms of an activation energy for crazing in the glassy matrix[4] can also be considered in terms of the relaxation processes occurring within the elastomer particles during the time span of the impact test. Plots of log[impact resistance] versus $1/T$ gave two independent linear correlations where the slope for ABS was 3.5 times that for SANS. Such widely diverging correlations would not be expected if crazing in the glassy matrix were the primary temperature-activated process that gives rise to impact resistance. On the other hand a ratio of approximately 3.5 is obtained from the activation energies calculated from the shift factors a_T for polybutadiene and PDMS.[14,15]

An approach based on a_T can be considered if it is assumed that the generally accepted mechanism of multiple crazing for rubber toughening holds,[16] if the elastomer does not alter the inherent character of the glassy matrix and if the test temperatures are at least 50°C below T_g of the glassy matrix. Then if the chief role of the elastomer particle is to initiate crazing in the matrix through its relaxation under stress, the number of crazes should be proportional to the rubbery strands undergoing relaxation at a given temperature and rate of testing. This can be expressed as a_T calculated from the general Williams-Landel-Ferry (WLF) equation where T_g of the elastomer is taken as the temperature of reference.[17] This gives the ratio of the primary relaxation time of the elastomer at the test temperature to that of the elastomer in the glassy state. Since the amount of energy absorbed by the test sample relates to the number of crazes,

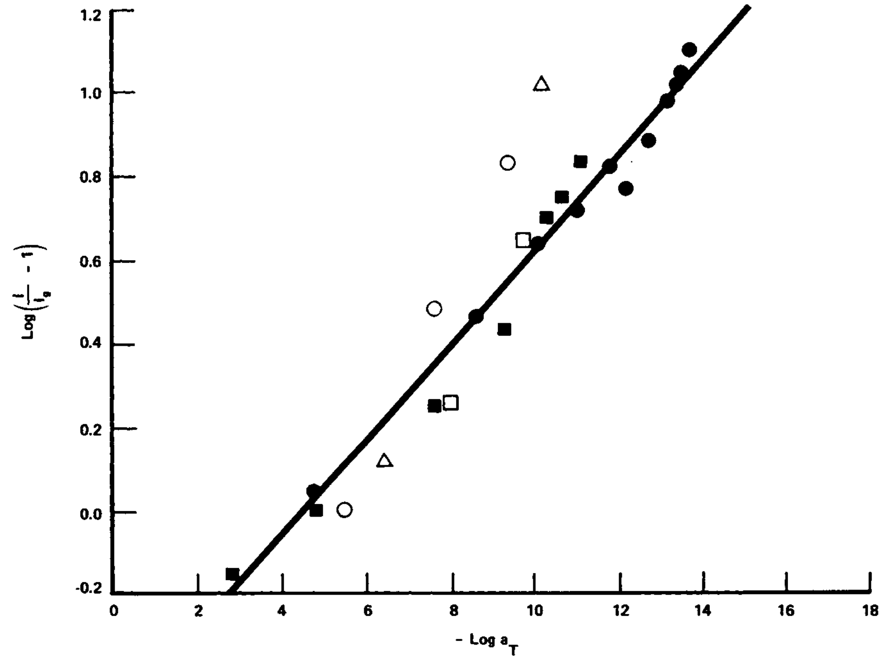

Fig. 8. Plot of impact resistance vs shift factor for the elastomer in rubber modified SAN: (-●-) SANS; (■) ABS. Open data points are based on data from three different elastomers given in ref. 4.

impact strength should vary inversely with a_T for the elastomer phase. This implies that the degree of craze initiation or impact resistance in rubber toughened SAN can be reduced to a single time-temperature scale. A common plot of impact strength versus $1/a_T$ should accommodate data taken at any rate of testing, temperature or with any type of rubber suitably dispersed in the SAN. In the present work the rate of testing is presumed constant.

The contribution to impact resistance from rubber relaxation would be $(I - I_0)/I_g$, where I is the observed impact resistance at test temperature, I_0 is the impact resistance at test temperature of the glassy matrix with no rubber modifier, and I_g is the impact resistance of rubber modified SAN at T_g of the rubber. If I_0 approximates I_g the above term reduces to $I/I_g - 1$ were I_g is a measurable quantity. The T_g of the elastomer and I_g are not adjustable parameters and are determined by interpolation of the data from Figure 4. Figure 8 is a plot of $\log(I/I_g - 1)$ versus $-\log a_T$ based on the data of Figure 4 for both SANS and ABS. Here I_g was 37.3 J/m, T_g for PDMS was 103°K, and T_g for polybutadiene in ABS was 203°K. Considering the inherent error in impact measurement the plot is remarkably close to linear and the data for SANS and ABS nearly coincide. The correlation coefficient is 0.987. It is of interest that even data for three different elastomers from ref. 4 where Charpy instead of Izod impact resistance was measured fall close to the correlation in Figure 8.

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References

1. N. Platzer, *Chem. Technol.*, **7**, 634 (1977).
2. C. B. Bucknall and D. G. Street, SCI. Monograph No. 26, Society of Chemical Industry, London, 1967, p. 272.
3. E. M. Hagerman, *J. Appl. Polym. Sci.*, **13**, 1873 (1969).
4. M. Matsuo, A. Ueda, and Y. Kondo, *Polym. Eng. Sci.*, **10**, 253 (1970).
5. J. C. Saam, S. E. Lindsey, A. W. Duncan, and J. R. Falender, *SPE J*, **29**, 58 (1973).
6. J. C. Saam and D. J. Gordon, *J. Polym. Sci., A-1*, **8**, 2509 (1970).
7. D. R. Weyenberg, D. E. Findlay, J. Cekada, Jr., and A. E. Bey, *J. Polym. Sci., Part C*, **27**, 27 (1969); Also U.S. Patent No. 3,294,725 (1966) and U.S. Patent No. 3,532,729 (1970).
8. U.S. Patent No. 3,898,800 (1975).
9. U.S. Patent No. 3,238,275 (1966).
10. H. Keskkula, S. G. Turley, and R. F. Boyer, *J. Polym. Sci.*, **15**, 351 (1971).
11. L. Morbitzer, D. Kranz, G. Humme, and K. H. Ott, *J. Appl. Polym. Sci.*, **20**, 2691 (1976).
12. G. Kraus and K. W. Rollman, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 385 (1977).
13. L. E. Nielsen, *Rheol. Acta*, **13**, 594 (1974).
14. E. Maekawa, R. G. Mancke, and J. D. Ferry, *J. Phys. Chem.*, **69**, 2811 (1965).
15. D. J. Plazek, W. Dannhauser, and J. D. Ferry, *J. Colloid Sci.*, **16**(2), 101 (1961).
16. See C. B. Bucknall, *Toughened Plastics*, Applied Science Publishers, London, 1977, p. 189.
17. M. Williams, F. R. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 370 (1955).

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