

Polystyrene–Polyisobutylene Network Composites from *In Situ* Polymerizations

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Synopsis

Crosslinked networks of butyl rubber [polyisobutylene (PIB) with 2 mol % unsaturation] were swelled with various amounts of styrene containing 0.25–4.6 wt % benzoyl peroxide as initiator. Polymerization of the styrene *in situ*, by increase in temperature, gave novel elastomeric composites. Scanning electron micrographs suggest phase separation which is locked in at the microscopic level, with no evidence for the particulate domains seen in the similarly prepared polystyrene–polydimethylsiloxane system. The wt % polystyrene (PS) extractible increased with increase in initiator concentration, which is consistent with decrease in the lengths of the PS chains being formed and grafted onto the PIB. Mechanical properties obtained in continuous extension showed maxima in their dependence on composition. Specifically, the ultimate strength $(f/A^*)_m$, maximum extensibility ϵ_r , energy E_r required for rupture, and permanent set $\Delta L/L_0$ generally showed maxima in the vicinity of 50 wt % PS. The shortest-chain PS samples generally showed the largest values of $(f/A^*)_m$, ϵ_r , and E_r , and the smallest values of $\Delta L/L_0$.

INTRODUCTION

In the most recent¹ of a series of studies^{1–6} dedicated to the development of novel ways of reinforcing elastomers,^{7–10} styrene was absorbed into polydimethylsiloxane (PDMS) networks and then polymerized *in situ*. The resulting materials were composites having micron-sized polystyrene (PS) particles embedded in elastomeric PDMS matrices. The relatively hard particles gave good reinforcement, with improvements in extensibility as well as in ultimate strength.²

The characteristics of the phase separation occurring in such systems depend, of course, very strongly on the chemical nature of the two components.^{10,11} It is for this reason that the present investigation extends this technique to an elastomeric matrix, polyisobutylene (PIB) $[-\text{CH}_2\text{C}(\text{CH}_3)_2-]$, which is not as different from PS $[-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-]$ as is PDMS $[-\text{Si}(\text{CH}_3)_2\text{O}-]$. In these experiments, the molecular weight of the PS is controlled by the amount of initiator used in the *in situ* polymerization. The PS–PIB composites formed in this way are first investigated using scanning electron microscopy to look for evidence of particles of PS similar to those observed in the PS–PDMS elastomers. Their mechanical properties are then determined in elongation, and the ultimate properties and permanent set thus obtained correlated with the amount and molecular weight of the *in situ* generated PS.

SOME EXPERIMENTAL DETAILS

Materials

A sample of PIB in the form of butyl rubber was generously provided by the Exxon Chemical Co. It had a number-average molecular weight of $4.6 \times 10^5 \text{ g mol}^{-1}$, and contained 2 mol % isoprene units as unsaturated sites to facilitate crosslinking. Styrene monomer (Gold label, 99 + % purity) was obtained from the Aldrich Chemical Co., and benzoyl peroxide (Bz_2O_2) from the Lucidol Corp.

Network Preparation

Bz_2O_2 dissolved in benzene was mixed into some of the PIB, and the resulting solution dried. This resulted in the incorporation of 3.0 wt % Bz_2O_2 in the PIB, which was then crosslinked by holding the mixture in a hydraulic press at approximately 12×10^3 psi and 135°C for 35 min. The resulting network sheet, which was approximately 1 mm thick, was extracted with gently stirred toluene for 3 days and then dried to constant weight. The sol fraction thus removed amounted to 9.0 wt %. The sheet was then cut into strips for the *in situ* polymerization part of the experiment.

In Situ Polymerization of Styrene

Bz_2O_2 was also used as the initiator in the polymerization, and was dissolved in three portions of the styrene to give concentrations of 0.25, 1.20, and 4.60 wt %, respectively. Weighed strips of PIB network and varying amounts of one of the styrene solutions were placed into vials, which were then filled with nitrogen, sealed, and refrigerated. After 5 days of swelling and equilibration to provide a uniform distribution of styrene, the polymerization was carried out by holding the vials at 70°C for 30 h. When the polymerization was complete, the samples were held under vacuum for 12 h to remove any unreacted styrene. The values of the wt % PS thus introduced are given in column three of Table I.

Scanning Electron Microscopy

Samples approximately $1 \times 2 \times 5$ mm were cut from the PS-PIB strips and mounted in appropriate sample holders. They were then coated with gold and examined with a Cambridge 600 scanning electron microscope at a magnification of 10^4 .

Stress-Strain Measurements

The stress-strain properties of the samples were measured on an Instron Universal Test Instrument (Model 1122) with an extension rate of 2 in. min^{-1} . The nominal stress was given by $f^* \equiv f/A^*$, where f is the elastic force and A^* the cross-sectional area of undeformed sample,^{6,12,13} and the elongation by $\epsilon \equiv (L - L_0)/L_0$, where $L - L_0$ is the increase in length of the sample. The modulus at any value of ϵ was given by $(f/A^*)/\epsilon$. Measurements were carried out to the rupture points of the samples.

TABLE I
Preparative Details and Mechanical Properties
of the Network Composites

Sample preparation			Ultimate properties		
Bz ₂ O ₂ ^a (wt %)	Sample designation	PS (wt %)	$(f/A^*)_m^b$ (N mm ⁻²)	ϵ_r^c (%)	E_r^d (J mm ⁻³)
0.25	1	0.0	0.400	360	0.023
	2	13.3	0.680	400	0.036
	3	19.0	1.03	535	0.068
	4	29.0	1.51	510	0.088
	5	35.5	2.17	510	0.151
	6	48.6	2.32	270	0.087
	7	58.9	2.07	60	0.027
	8	66.1	2.76	60	0.035
	9	70.3	3.13	70	0.041
1.20	1	0.0	0.306	445	0.024
	2	15.7	0.873	560	0.064
	3	24.4	1.20	620	0.090
	4	35.1	2.21	645	0.161
	5	47.0	2.25	400	0.150
	6	57.8	2.07	160	0.038
	7	62.7	2.07	80	0.025
	8	69.1	2.18	45	0.016
	9	71.6	2.48	35	0.013
4.60	1	0.0	0.371	400	0.026
	2	19.0	0.845	490	0.053
	3	26.5	1.42	620	0.094
	4	35.6	2.66	620	0.158
	5	42.8	3.26	645	0.220
	6	48.8	4.11	600	0.297
	7	57.0	4.01	620	0.373
	8	65.7	2.01	290	0.130
	9	70.1	1.86	135	0.062

^aBenzoyl peroxide, for the styrene polymerization.

^bUltimate strength, as measured by the maximum value of the stress.

^cElongation at rupture.

^dEnergy required for rupture.

Determination of Permanent Set

Separate series of samples were prepared for these measurements. After rupture occurred in each of the samples, the two parts were put back together and the final length L_f determined. The permanent set was taken to be $100 \Delta L/L_0$, where $\Delta L = L_f - L_0$.

Extraction of Polystyrene

After the stress-strain measurements, the samples were extracted with benzene for 7 days, with occasional replacement of solvent. The samples were then dried under vacuum at 55°C to constant weight. The amount of

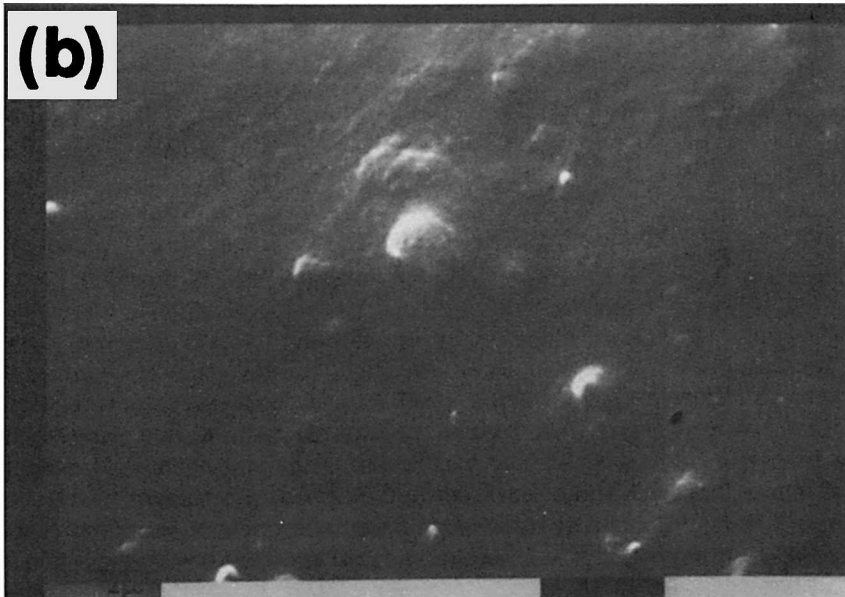
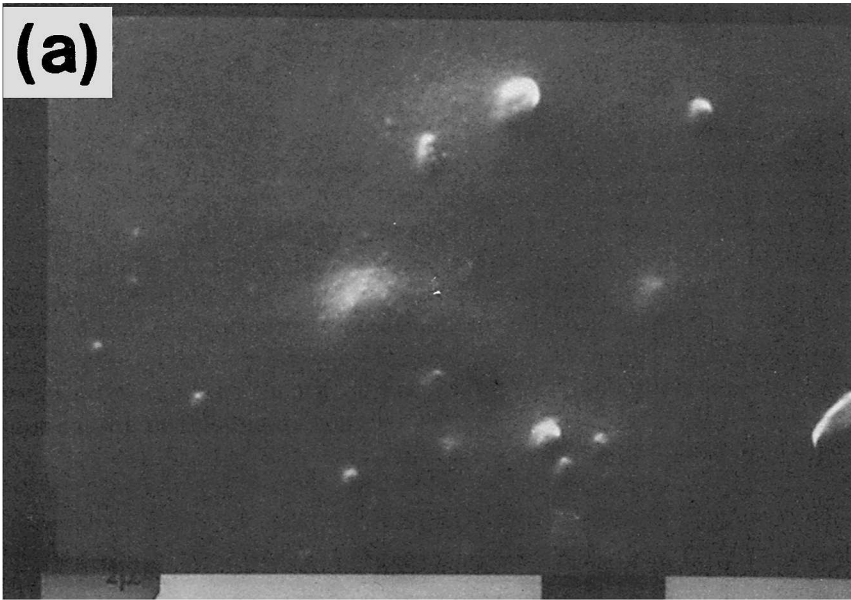


Fig. 1. Scanning electron micrographs for the PS-PIB networks prepared using 1.2 wt % benzoyl peroxide and containing (a) 15.7, (b) 35.1, (c) 57.8, and (d) 71.6 wt % polystyrene. The widths of the rectangles at the bottom borders correspond to 2 μ .

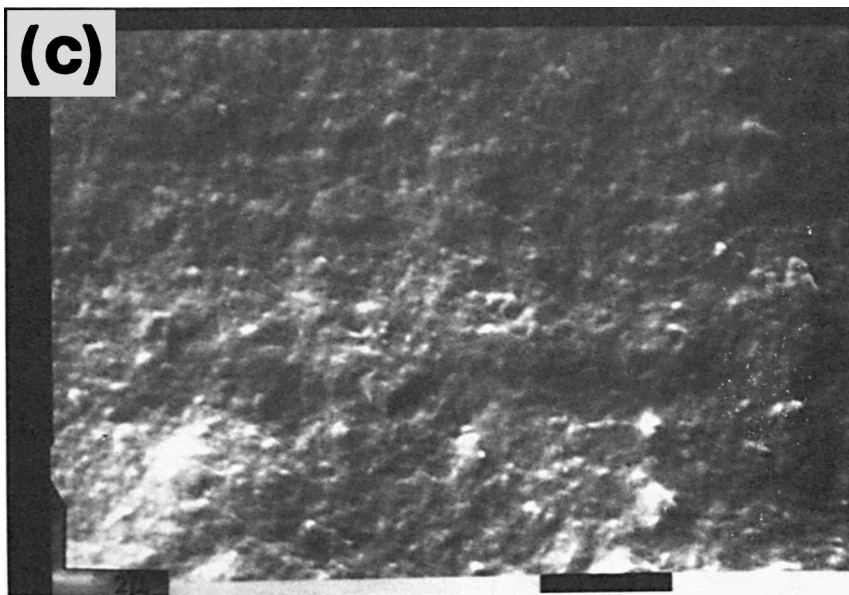


Fig. 1. (Continued from the previous page.)

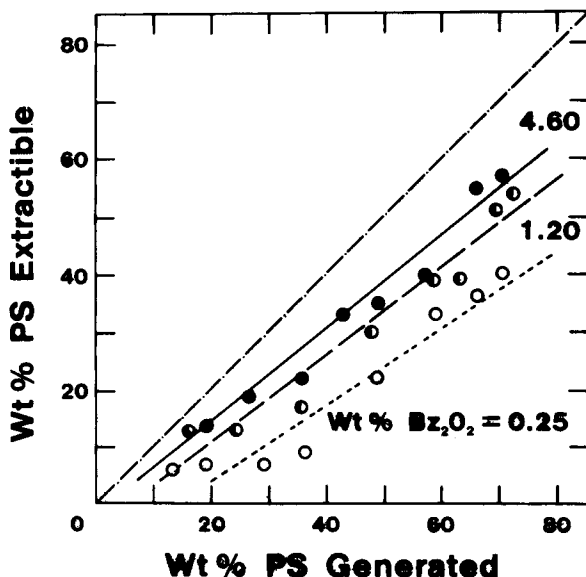


Fig. 2. The weight % polystyrene extractable from the PS-PIB networks shown as a function of the wt % PS generated in the *in-situ* polymerization initiated by 0.25 (○), 1.20 (●), and 4.60 (●) wt % benzoyl peroxide. The dashed-dotted line at an angle of 45° corresponds to the limit of 100% extractability.

polystyrene thus extracted was obtained from the sample weights before and after the extraction process.

RESULTS AND DISCUSSION

Typical scanning electron micrographs obtained at four PS concentrations are given in Figure 1. None shows any evidence for the formation of particulate PS, such as was observed in the PS-PDMS system.¹ This is presumably due to the different interactions present in the two systems. The samples, however, were opaque. This observation and the increase in surface roughness with increase in wt % PS shown in the figure attest to the occurrence of phase separation, which is locked in at the microscopic level by the PIB network structure.

Figure 2 shows the wt % PS extractable as a function of the wt % PS generated, for the three series of samples. The former is generally considerably smaller than the latter, apparently because of grafting of the PS to the PIB (presumably primarily through the unsaturated sites).^{14,15} The lowest wt % Bz_2O_2 would be expected to give the longest PS chains, including those grafted to the PIB. This would, of course, explain the observed decrease in the wt % PS extractable with decrease in Bz_2O_2 concentration.

Some typical stress-strain isotherms are shown in Figures 3 and 4. As described in Table I, samples 1-9 have increasing wt % PS. Thus, the results in these two figures document an increase in stress or modulus with increase in wt % PS, as expected.¹⁶⁻¹⁸ Typical increases for all three series of samples are shown in Figure 5. They are quite dramatic, with the samples changing from relatively soft elastomers, to tough leathery materials, to hard thermoplastics.

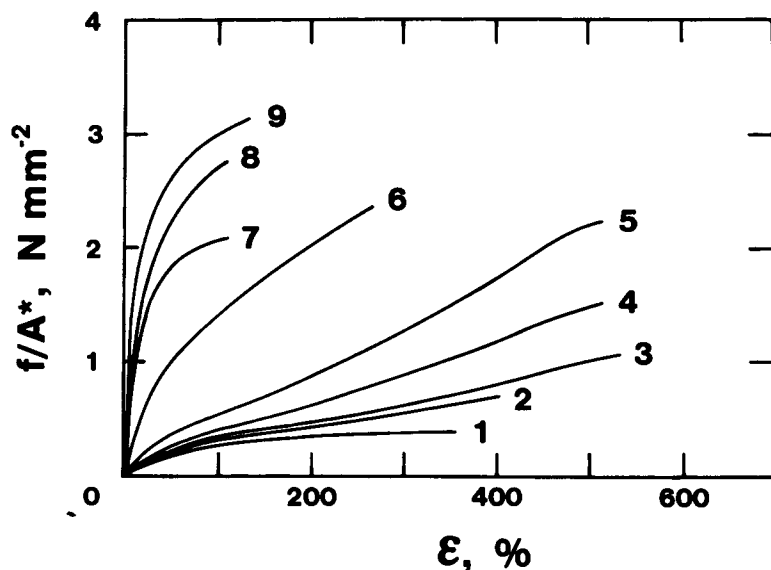


Fig. 3. Stress-strain isotherms for the samples prepared using 0.25 wt % benzoyl peroxide. The labels correspond to the sample designations given in Table I.

The stress-strain curves for all three series of samples were also used to obtain values of ultimate strength as represented by the maximum value $(f/A^*)_m$ of the nominal stress, the maximum extensibility or elongation ϵ_r at rupture, and the energy E_r required for rupture. These results are given in the last three columns of Table I. They are seen to depend significantly on the molecular weight of the PS, as inversely related to the wt % Bz_2O_2 used to

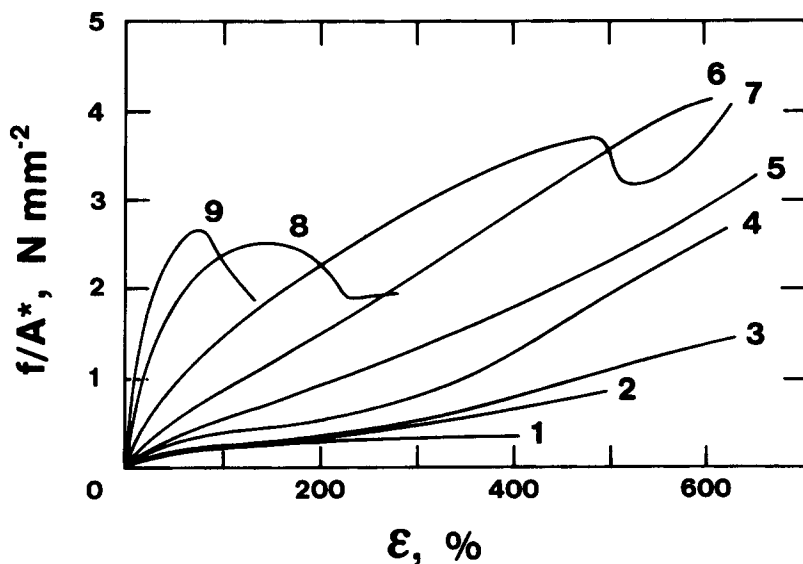


Fig. 4. Stress-strain isotherms for the samples prepared using 4.60 wt % benzoyl peroxide; see the caption to Figure 3.

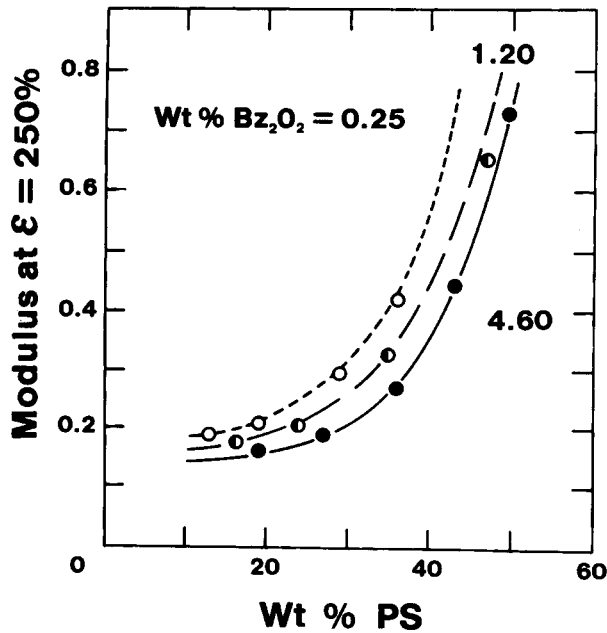


Fig. 5. Representative values of the modulus at an elongation of 250% shown as a function of the wt % PS for the three series of samples.

generate it. This is presumably primarily due to the increase in miscibility accompanying a decrease in PS molecular weight.^{11, 15, 19, 20}

These same properties are shown as a function of the wt % PS in Figures 6–8. They go through maxima in the vicinity of 50 wt % PS. The permanent set $\Delta L/L_0$ also exhibits a maxima at approximately 50 wt % PS, as is shown in Figure 9. The shortest-chain PS samples (those prepared from 4.60 wt %

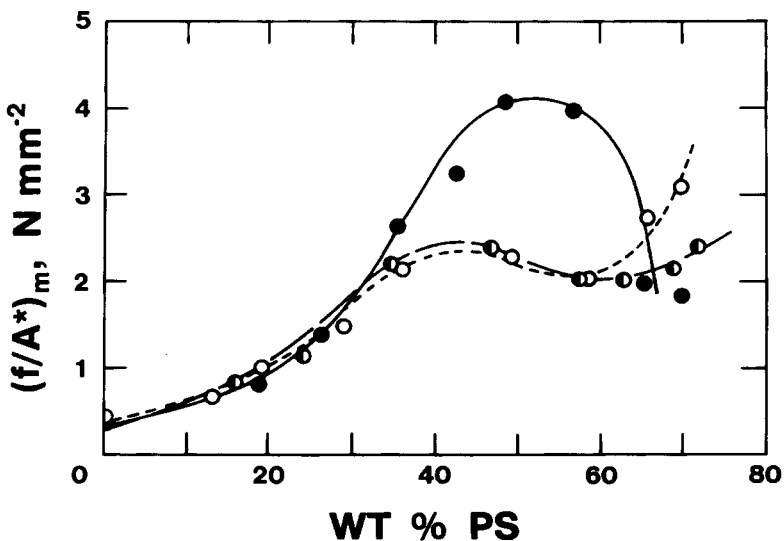


Fig. 6. The ultimate strength as represented by the maximum value of the reduced stress shown as a function of the wt % PS; see the caption to Figure 2.

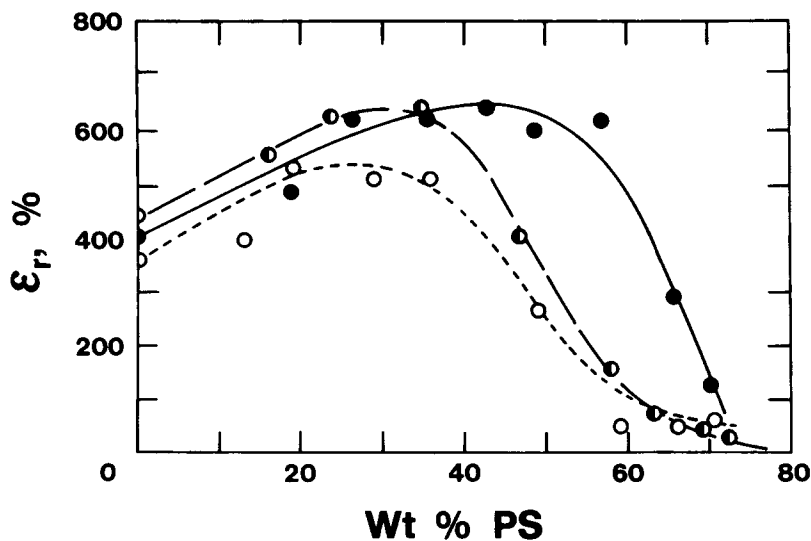


Fig. 7. The maximum extensibility or elongation at rupture shown as a function of the wt % PS; see the caption to Figure 2.

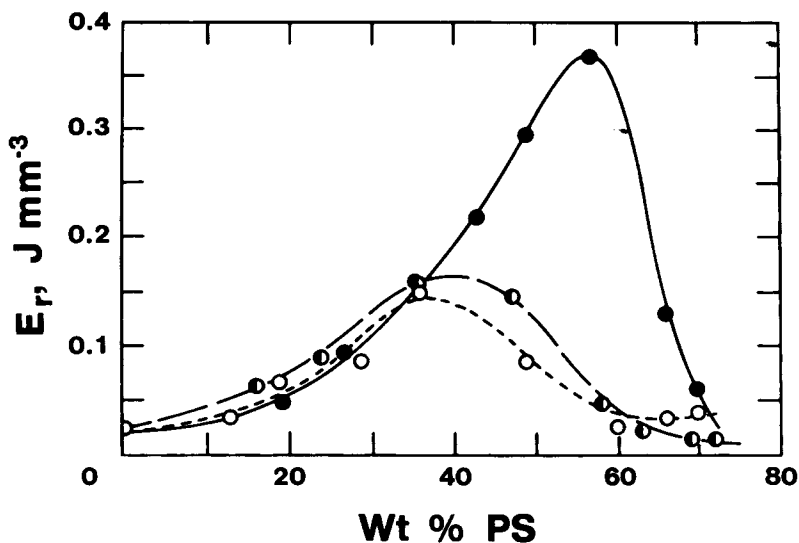


Fig. 8. The energy required for rupture shown as a function of the wt % PS; see the caption to Figure 2.

Bz_2O_2) generally showed the largest values of $(f/A^*)_m$, ϵ_r , and E_r , and the smallest values of $\Delta L/L_0$. Of this series, the ones having compositions in the vicinity of 50 wt % PS have the best balance of mechanical properties. They might therefore be of considerable commercial interest.

It is a pleasure to acknowledge the financial support provided by the Army Research Office under Grant DAAL03-86-K-0032 (Materials Science Division) and the National Science Foundation through Grant DMR 84-15082 (Polymers Program, Division of Materials Research). We also wish to thank Mr. E. G. Clark for performing the scanning electron microscopy.

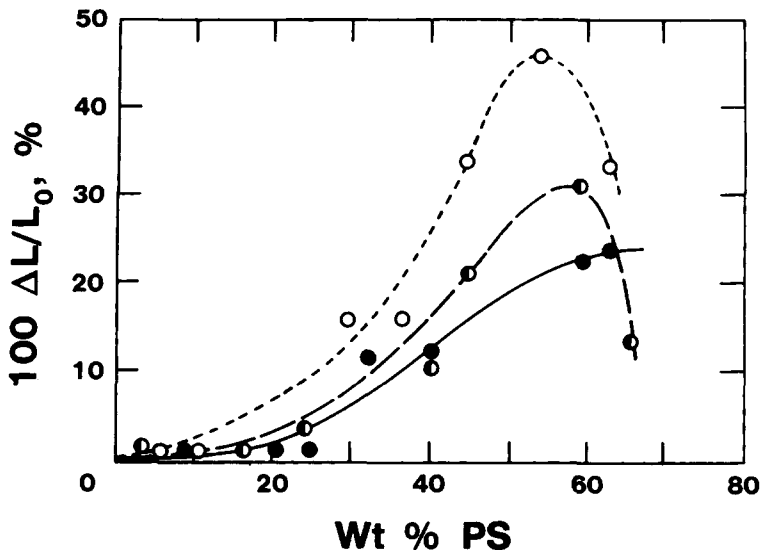


Fig. 9. The permanent set shown as a function of the wt % PS; see the caption to Figure 2.

References

1. F.-S. Fu and J. E. Mark, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 2229 (1988).
2. J. E. Mark, *Br. Polym. J.*, **17**, 144 (1985).
3. S. J. Clarson and J. E. Mark, *Polym. Commun.*, **28**, 249 (1987).
4. G. B. Sohoni and J. E. Mark, *J. Appl. Polym. Sci.*, **34**, 2853 (1987).
5. J. E. Mark, in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, J. D. MacKenzie and D. R. Ulrich, Eds., Wiley, New York, 1988.
6. J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer*, Wiley-Interscience, New York, 1988.
7. B. B. Boonstra, *Polymer*, **20**, 691 (1979).
8. E. L. Warrick, O. R. Pierce, K. E. Polmanteer, and J. C. Saam, *Rubber Chem. Technol.*, **52**, 437 (1979).
9. Z. Rigbi, *Adv. Polym. Sci.*, **36**, 21 (1980).
10. P. J. Corish, in *Science and Technology of Rubber*, M. Morton, Ed., Academic, New York, 1978.
11. *Colloidal and Morphological Behavior of Block and Graft Copolymers*, G. E. Molau, Ed., Plenum, New York, 1971.
12. J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
13. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Clarendon, Oxford, 1975.
14. G. Riess, C. Beslin, J. L. Locatelli and J. L. Refregier, in *Polymer Science and Technology, Vol. 10, Polymer Alloys*, D. Klemperer and K. C. Frisch, Eds., Plenum, New York, 1977.
15. D. S. Campbell, in *Developments in Block Copolymers—2*, I. Goodman, Ed., Applied Science, New York, 1985.
16. M. Shundo, T. Hidaka, K. Goto, M. Imoto, and Y. Minoura, *J. Appl. Polym. Sci.*, **12**, 975 (1968).
17. M. Morton, *J. Elastoplast.*, **3**, 112 (1971).
18. K. Satake, K. Shinki, T. Teraoka, and S. Ibe, *J. Appl. Polym. Sci.*, **15**, 2807 (1971), and pertinent references cited therein.
19. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 805, 815, 825 (1985).
20. J. D. Moore, *Polymer*, **12**, 478 (1971).

Received March 4, 1988

Accepted June 16, 1988