

The Significance of the Rubber Damping Peak in Rubber-Modified Polymers

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Synopsis

Dynamic mechanical properties have been used as the basis for some important conclusions with regards to the physical properties of rubber-modified high-impact polymers. This paper attempts to show that conclusions of this type should be limited to fairly narrow groupings of polymers. Since the size, shape, and position on the temperature scale of a damping peak are influenced by composition, morphology, and method of polymer preparation, the significance of the damping peak associated with the rubber phase of the polymer has probably been generalized to too great an extent. Two examples of polymer groupings are given to illustrate the need for caution in attaching significance to the dynamic mechanical properties of polymers. Also given are two fairly narrow polymer groupings to show to what extent dynamic mechanical properties can be used for a correlation with impact strength and rubber concentration.

INTRODUCTION

The measurement of dynamic shear modulus and mechanical damping over a wide temperature range has been employed for a number of years as one of the techniques used in the characterization of high polymers. In the case of rubber-modified high-impact polymers, these measurements have been used as the basis for some important conclusions.

Buchdahl and Nielsen^{1,2} have concluded that the presence of the separate rubber and polystyrene (PS) damping peaks was an indication of the existence of two separate phases. It has also been reported that the magnitude of the rubber peak is related to both the quantity of rubber present and the impact strength of these heterogeneous materials.²⁻⁹

Turley⁴ has pointed out that comparisons must be made within a given method of preparation of high-impact polystyrenes (HIPS). He showed that, for a particular styrene-butadiene copolymer rubber, polymers made by mechanical blending yielded much lower levels of rubber damping and reinforcement than in the case of solution-polymerized, i.e., in situ-grafted rubber, HIPS. For the latter, both the rubber peak and the impact strength were higher at an equivalent rubber concentration. He concluded that it was necessary to have polystyrene grafted to this rubber in order to use it most efficiently as a reinforcing agent.

Most of the successfully commercial rubber-modified polymers are grafted polymers. They are prepared by polymerizing rubber-monomer

solutions in the presence of shear agitation, particularly in the early phases of polymerization.¹⁰ This method produces a heterophase polymer in which the volume fraction of the rubber particles is increased by significant polystyrene occlusions and grafted polystyrene. In this paper, the term "rubber phase" will be used to describe the rubber with its polystyrene occlusions and grafted polystyrene; the term "rubber" or "rubber concentration" will refer to the unaltered rubber. A large reinforcing rubber phase (about 25%) can be obtained by as little as 5% rubber.¹¹

Grafted high-impact polymers, particularly the ABS polymers, may also be prepared by using a latex of partially crosslinked polybutadiene in the form of relatively large particles and polymerizing appropriate monomers in the presence of this latex.¹² It is presumed that the polymers studied in this investigation have been prepared by one of these basic processes or a combination thereof.

The purpose of this work was to examine the significance of the rubber damping peak in relation to the rubber concentration, the impact strength, and the morphology of some commercial grafted materials. Accordingly, we examined several representative, high-impact polystyrene and ABS polymers.

EXPERIMENTAL

Materials Used

High-Impact Polystyrene: Styron 456 (The Dow Chemical Company); TGD 6600 (Union Carbide Co.); Hi-Test 88 (Monsanto Co.); Elrex 422 (Rexall Chemical Co.).

ABS Polymer: Cyclocac TD-1001 (Marbon Chemical Co.); Lustran I-440 (Monsanto Co.); Tybrene 213 (The Dow Chemical Co.).

Transparent High-Impact Polymer: TH Resin (Toyo Rayon Company).

All materials were obtained directly from the manufacturer in an unpigmented form.

Compression Molding

An appropriate amount of polymer granules was placed in the $10 \times 10 \times \frac{1}{8}$ in. mold between heavy duty aluminum foil. The granules were preheated at 410°F for 5 min before applying full pressure for 2 min. The molding was slowly cooled in the press. Specimens were routed from this molding for impact testing, torsion pendulum measurements, and microscopy.

Polymer Characterizations

Although the two-phase nature of a polymeric system can be predicted from a dynamic characterization obtained with a torsion pendulum, the ambiguity associated with such a characterization (a mechanical blend of

one homopolymer with a second homopolymer, with a pure graft or with a pure block) necessitates further elucidation by such techniques as phase separation, electron microscopy, chemical analysis, mechanical properties, etc.

The gel contents of the HIPS and ABS were determined by using 1 g of polymer in 40 ml toluene and MEK, respectively. After complete dispersion, the solutions were centrifuged at $47,000 \times G$ and at $10^\circ C$. The supernatant polymer solutions were decanted, and the gel contents were determined gravimetrically. The gel-free solutions were characterized by gel permeation chromatography (GPC); the molecular weights are listed in Table I, together with the gel percentages.

TABLE I
Molecular Weight Data of Commercial HIPS and ABS
(Soluble Portion)

Material	Gel, %	$\bar{M}_z \times 10^3$	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	\bar{M}_w/\bar{M}_n
Styron 456	23.1	394	209	84	2.5
Hi-Test 88	20.7	587	251	73	3.4
TGD-6600	19.4	466	252	104	2.4
Elrex 422	23.1	299	164	73	2.2
Cycolac TD 1001	33.2	164	78	34	2.3
Lustran I 440	29.5	257	108	39	2.8
Tybrene 213	13.7	379	174	50	3.5
TH Resin	15.2	200	102	45	2.3

Electron photomicrographs were obtained using the technique described by Kato.¹⁴

The torsion pendulum and the experimental method used to obtain the dynamic curves have been previously described.⁴

RESULTS AND DISCUSSION

Electron photomicrographs of the eight commercial materials studied are shown in Figures 1 and 2. These photomicrographs indicate their heterophase nature, the discreteness of the rubber phase, and the detailed morphology of this phase. The photomicrographs also indicate that the polymers of the HIPS family generally have relatively large particles ranging from below 1μ to about 5μ . The ABS family of polymers is represented by a wider spectrum of particle sizes. While Cycolac and Lustran have mostly submicron reinforcing particles, Tybrene has a particle morphology similar to that of the HIPS family. The TH Resin has a uniformly small particle size, typical of block copolymer rubbers¹⁵ when polymerized in solution.

The torsion pendulum curves are shown in Figures 3 and 4. In examining the HIPS curves, it is reasonable to assume that three materials (Styron, Hi-Test and Elrex) are modified by the incorporation of polybutadiene rubbers, as judged from the temperatures of the rubber damping peaks,

TABLE II
Impact-Dynamic Mechanical Property Correlation Data

Polymer	Butadiene rubber, %	Notched Izod impact, ^a 73°F	ft-lb/in. 0°F	Curve area, arb. units (-150°C to +20°C)	S_M (-150°C to +20°C)	S_W , dynes/cm ² (-150°C to +20°C)
Styron 456	5.6	1.50	1.10	5.27	0.960	4.90×10^8
Hi-Test 88	5.8	1.34	0.90	4.97	1.14	5.32×10^8
TGD 6600	11.9	2.03	1.13	5.17	1.03	5.08×10^8
Elrex 422	6.6	1.41	0.99	5.00	1.16	5.37×10^8
Cyclocac TD-1001	18	5.30	2.08	5.63	1.26	5.56×10^8
Lustran I-440	14	3.19	1.45	5.40	0.937	4.84×10^8
Tybrene 213	6	1.14	0.88	6.23	1.09	5.23×10^8
TH Resin	7	1.25	0.81	9.10	1.67	5.47×10^8

^a Compression-molded specimens ($3 \times 1/8 \times 1/2$ in.), notch radius 0.1 in.

(-83° , -75° , -85°C , respectively), while the TGD polymer has a rubber peak at -60°C , suggesting an SBR as the reinforcing rubber. No apparently significant differences in the sizes of the rubber peaks exist.

The dynamic mechanical properties of the ABS polymers and the transparent TH Resin (MBS-methyl methacrylate, butadiene, styrene) are of considerable interest when compared with those of HIPS. The height of the rubber peak for Lustran is surprisingly low, since it has the second

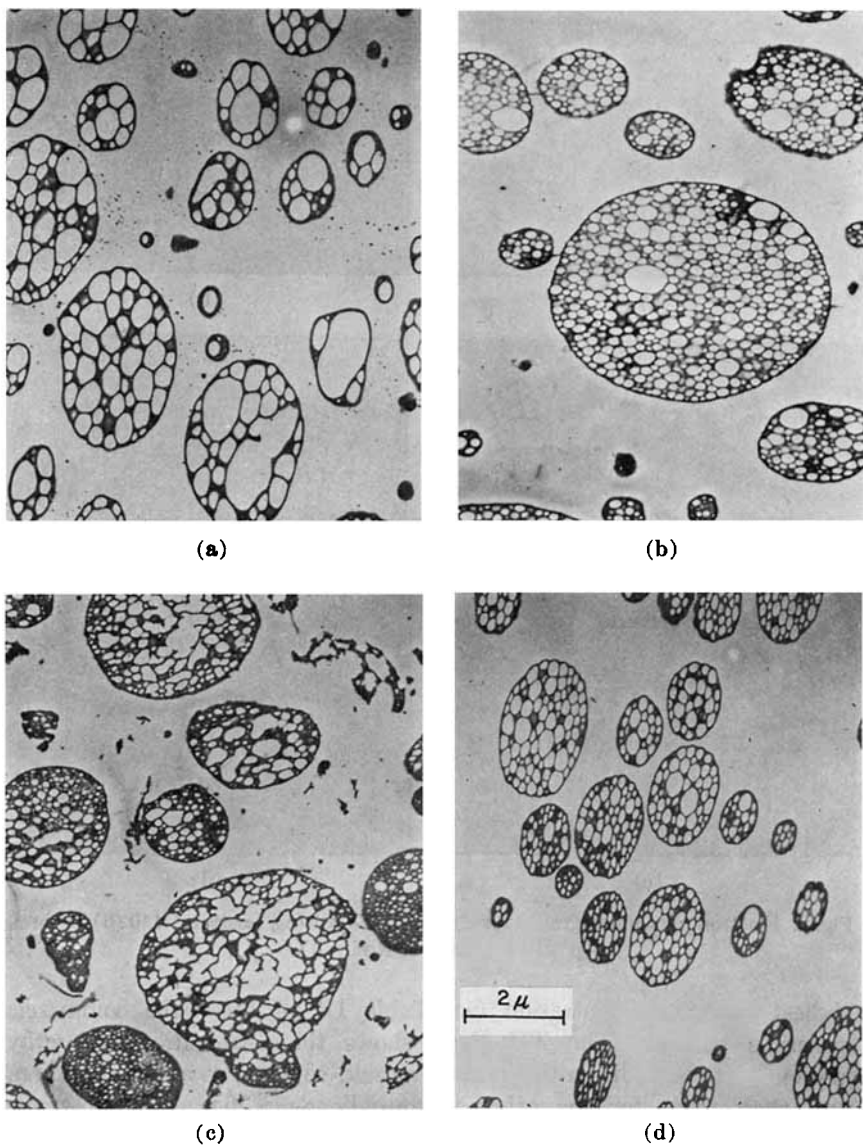


Fig. 1. Electron photomicrographs for Styron 456 (a), Hi-test 88 (b), TGD 6600 (c), and Elrex 422 (d).

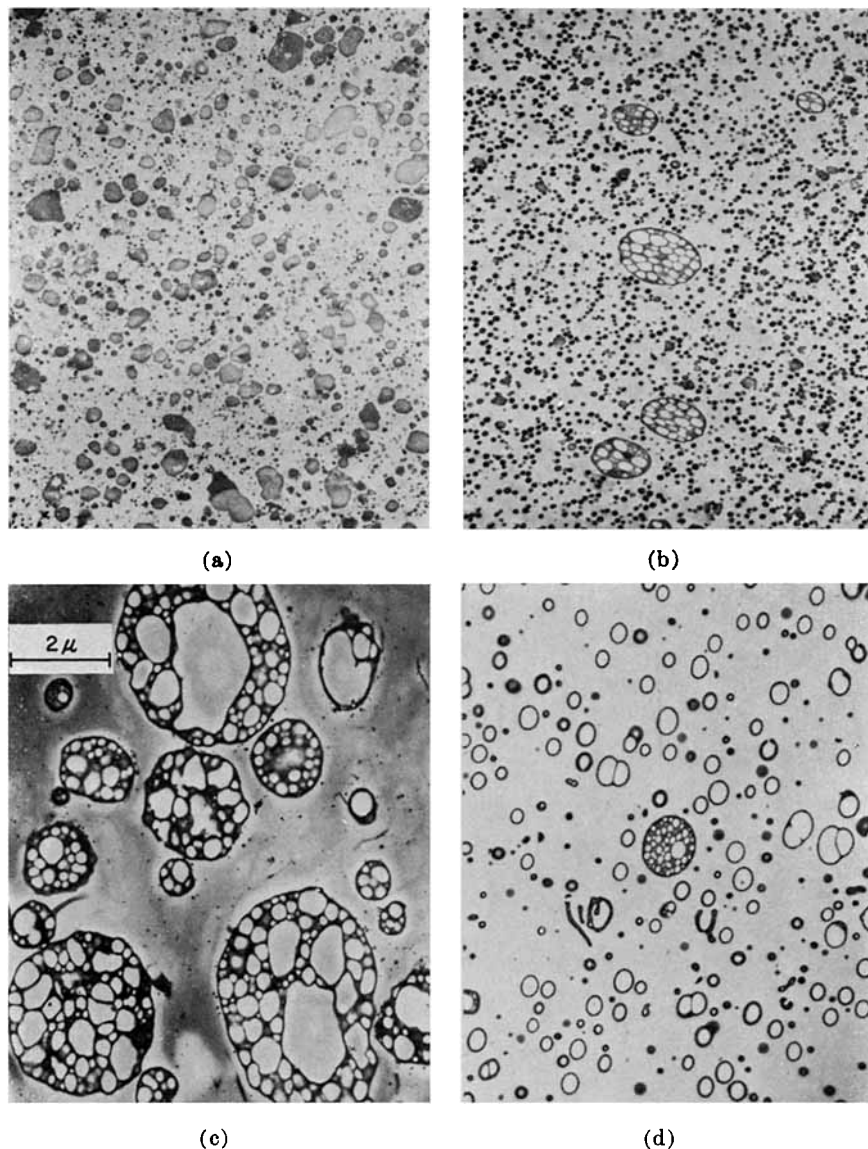


Fig. 2. Electron photomicrographs for Cylolac TD-1001 (a), Lustran I-440 (b), Tybrene 213 (c), and TH Resin (d).

highest rubber concentration (see Table II) of the eight commercial materials studied. The TH Resin shows the β -transition of methyl methacrylate in addition to the rubber peak, which is at a lower temperature than those for the other polybutadiene-modified rigid polymers. The level of damping above the glass temperature of the rigid phase is significantly higher than that for the HIPS polymers, possibly due to the effect of the acrylonitrile.

Dynamic Mechanical Property Correlations

Dynamic mechanical property data of rubber-modified rigid polymers have been related both to the concentration of rubber present in the polymer and to impact strength. Normally, the height of the rubber peak, the area under the rubber peak, or the extent of the modulus drop associated with the rubber peak are considered for these correlations.

Rubber Concentration

The size of the rubber peak for each polymer, as the area under the damping curve from -150°C to $+20^{\circ}\text{C}$, is given in Table II along with notched Izod impact strength. The butadiene rubber concentration, as determined by infrared analysis, is also given for these polymers. For TGD, which is judged to be made with SBR, the value given assumes a 23/77 weight ratio of styrene/butadiene.

The larger rubber peaks are associated with those polymers having rubber particles containing large rigid phase occlusions. The two high-impact ABS polymers, Cycolac and Lustran, have particularly small rubber peaks with regard to the rubber concentrations in these polymers.

No correlation within the HIPS series or the ABS series was possible between the rubber peak area and the rubber concentration.

Impact Strength

Notched Izod impact strength data on compression-molded specimens (at 73°F and 0°F) are summarized in Table II. This measurement for impact strength was chosen primarily because of the limited availability of some of the polymers. A more satisfactory approach would have been in supplementing these data with dart drop measurements or providing additional Izod data at various notch radii. However, since compression moldings, which are nearly isotropic, were used, reasonably satisfactory assessment of the relative toughness of these materials is believed to be represented by these data.

When comparing the notched Izod impact data with the areas under the damping curves from -150°C to $+20^{\circ}\text{C}$, a procedure similar to that used by Wada and Kasahara,¹⁶ it is evident that no correlation is possible.

Relaxation Strength

The extent of the modulus drop in the glass transition region of the rubber phase has been suggested as an indication of impact strength.^{16,19} The relaxation strength as defined by McCrum¹⁷ should therefore be a measure of impact strength. The relaxation strength,

$$S_M = (G_{T_1} - G_{T_2})/G_{T_2}$$

where G is the dynamic shear modulus, T is the temperature, and $T_1 < T_2$, was determined for each of the eight polymers under study. The results

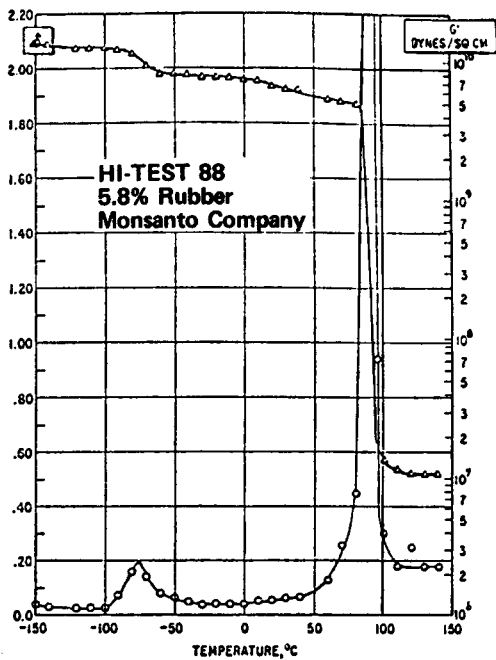
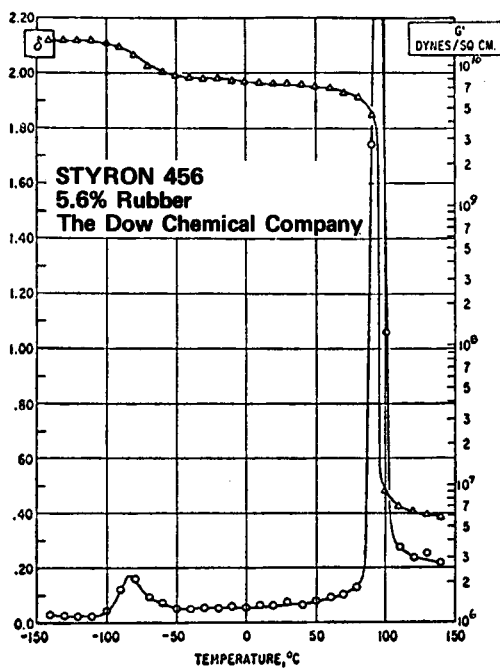


Fig. 3 (continued)

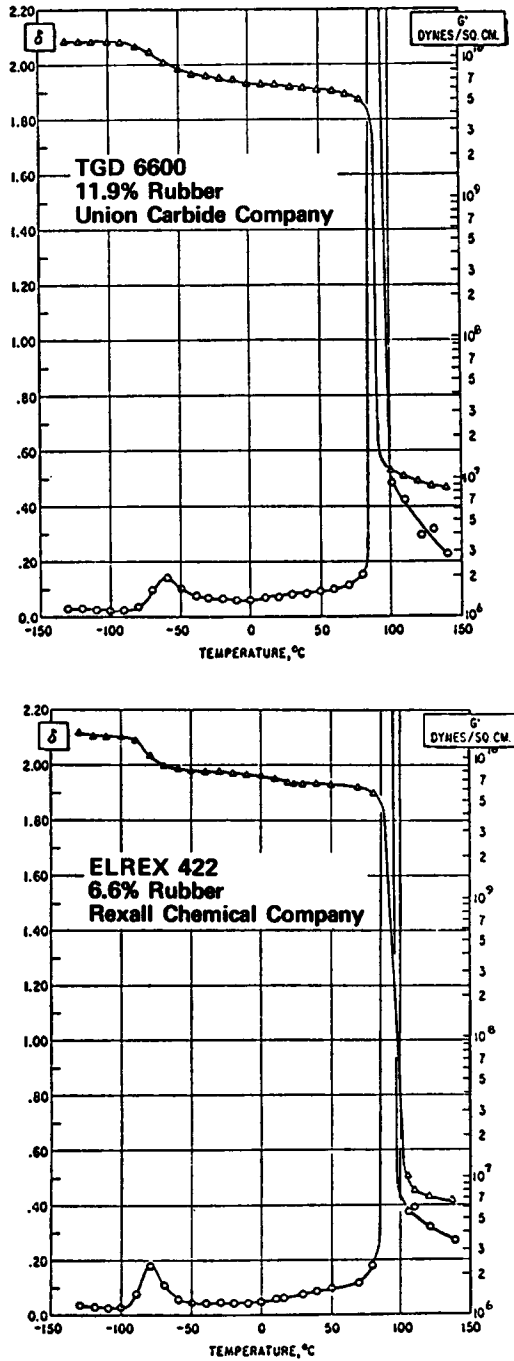


Fig. 3. Dynamic mechanical curves for polymers as shown. The one high temperature damping point for each material that appears to scatter could well be an indication of the $T_{1,1}$ transition of polystyrene.¹⁸

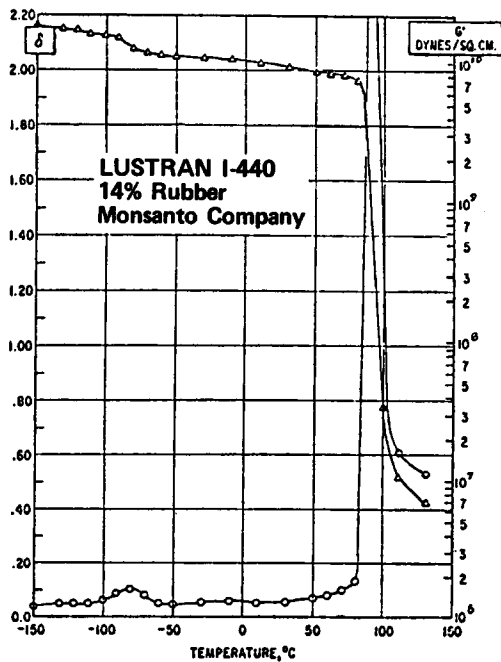
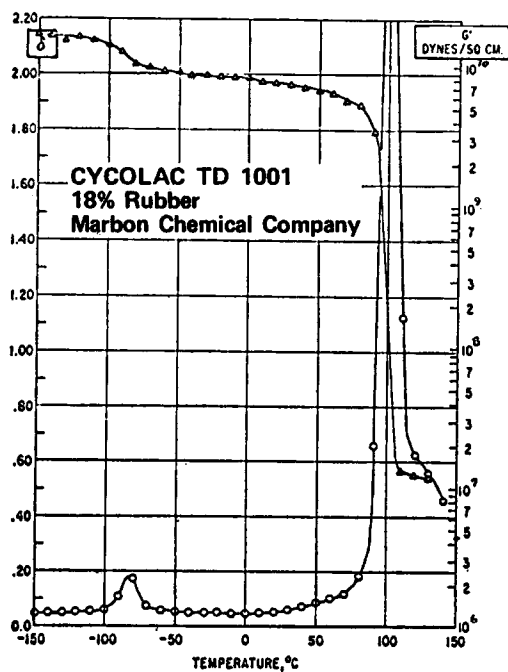


Fig. 4 (continued)

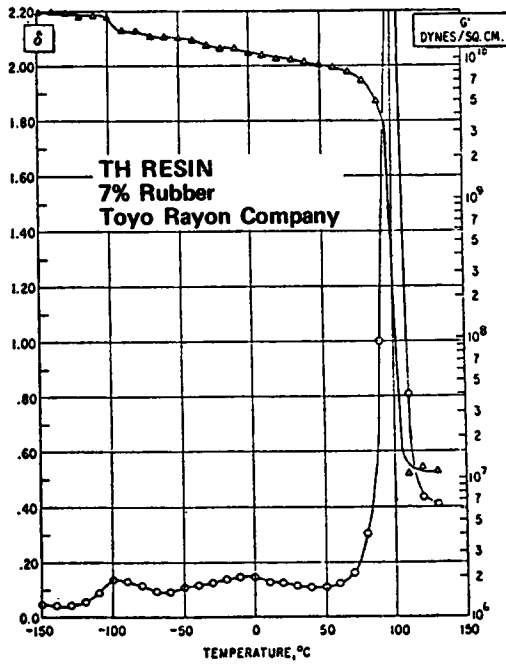
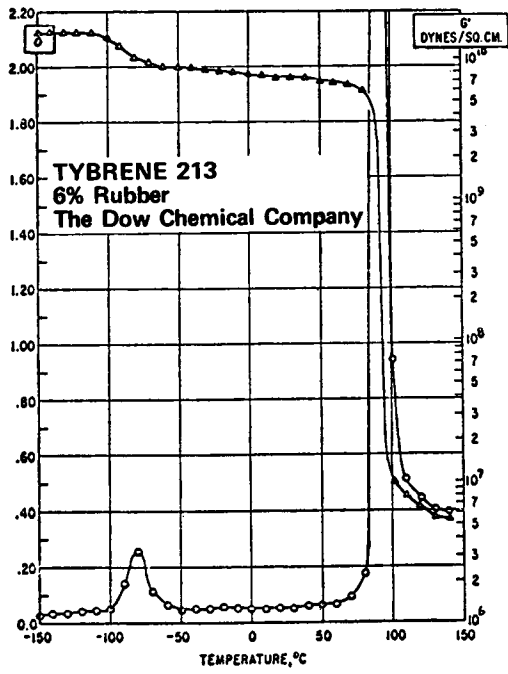
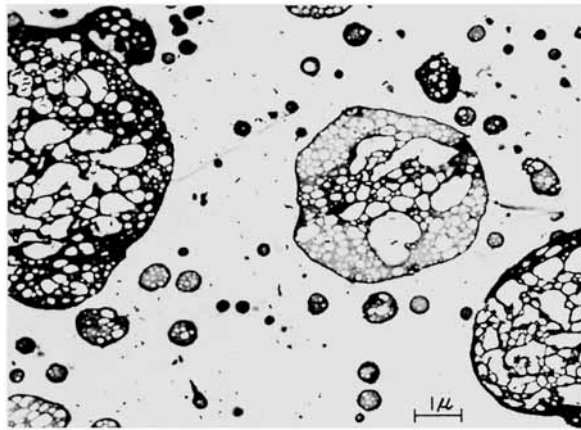
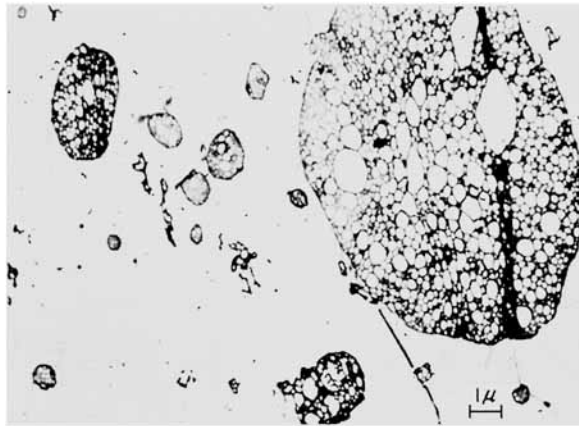


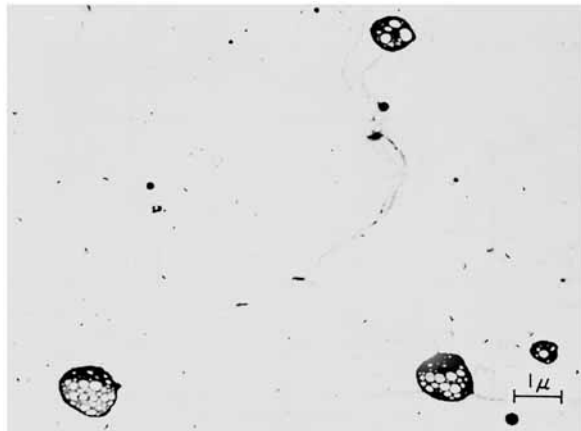
Fig. 4. Dynamic mechanical curves for polymers as shown.



(a)

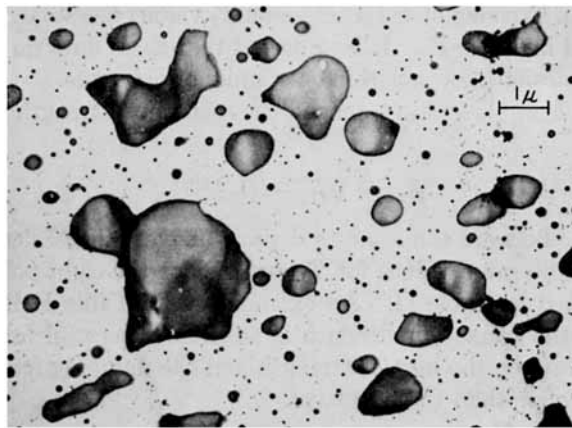


(b)

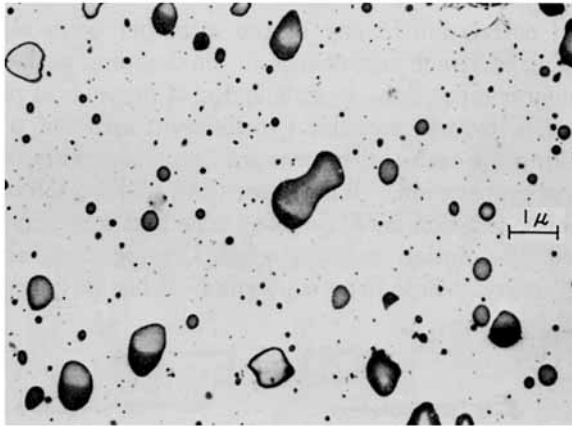


(c)

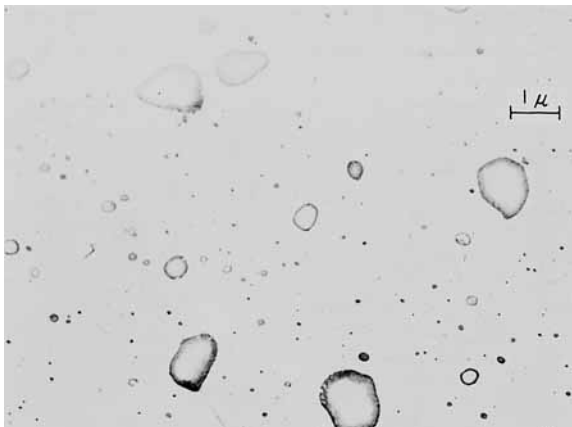
Fig. 5. Electron photomicrographs of solution-polymerized, SBR-modified polystyrene: (a) 10% rubber; (b) 5% rubber; (c) 2% rubber.



(a)



(b)



(c)

Fig. 6. Electron photomicrographs of mechanically blended SBR-PS: (a) 15% rubber; (b) 10% rubber; (c) 5% rubber.

are based on a T_1 value of -150°C and a T_2 value of $+20^\circ\text{C}$. These data are also listed in Table II. It is apparent that these data do not correlate with impact strength, even within one family of polymers.

Wada and Kasahara¹⁶ have defined the relaxation strength in a different form:

$$S_w = (G_{T_1} - G_{T_2})^2 / G_{T_1}$$

where the symbols are the same as defined above. The calculated values of S_w , using the same values for T_1 and T_2 , for the eight polymers under study are listed in Table II. An examination of Table II indicates that this form of the relaxation strength is no more successful for obtaining a correlation between the impact strength and the damping for either of the series of polymers than the first form.

Correlations in Narrow Polymer Groupings

The lack of correlation in any of the attempts given above suggests caution in trying to attach significance to the damping peaks for polymers having dissimilar compositions, morphologies, or methods of preparation.

In this section, we will consider two different series of polymers; the polymers making up each series have similar components, morphologies, and methods of preparation. We will see that, within each of these series, some degree of correlation is obtainable. The first series consists of polymers prepared by solution polymerization, having 2, 5, and 10% of a random 23/77 styrene-butadiene copolymer rubber in polystyrene. The

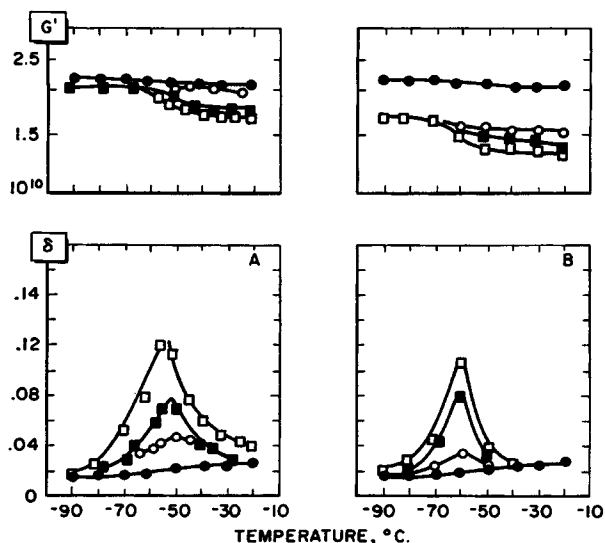


Fig. 7. (A) Dynamic mechanical curves for polystyrene, (●) and three solution-polymerized, rubber-modified polystyrenes: (○) 2% SBR; (■) 5% SBR; (□) 10% SBR. B. Dynamic mechanical curves for polystyrene, (●) and three mechanically blended, rubber-modified polystyrenes: (○) 5% SBR; (■) 10% SBR; (□) 15% SBR.

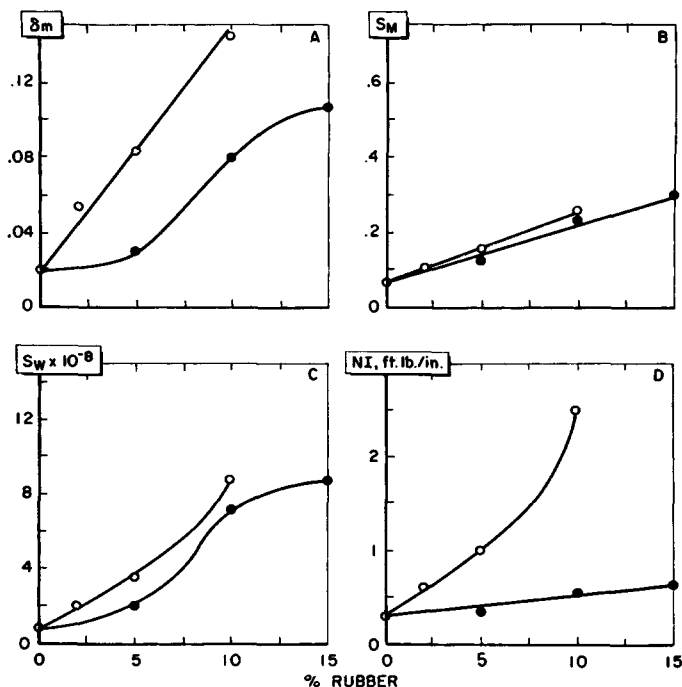


Fig. 8. Relationships between percent rubber and damping peak height (A), relaxation strength (McCrum) (B), relaxation strength (Wada and Kasahara) (C), and notched impact (D): (●) polystyrene; (○) solution polymers; (●) mechanical blends.

second series was prepared by mechanically blending polystyrene with 5, 10, and 15 wt-% of the same copolymer rubber used in the first series. Styrene homopolymer is included in both series as a reference.

The electron micrographs for these two series of polymers are given in Figures 5 and 6. Figure 5 shows that the series of solution polymers, in addition to having similar compositions and methods of preparation, also have similar morphologies; the rubber particles of each polymer contain many polystyrene occlusions. Figure 6 shows that the series of mechanical blends, in addition to having similar compositions and methods of preparation, also have similar morphologies; the rubber particles of each polymer contain no polystyrene occlusions.

The dynamic curves for these two series of polymers are given in Figure 7. Only the temperature regions between -90°C and -20°C are shown. It is apparent from the damping curves that both the peak heights and the areas under the curves increase with increasing rubber content. It is also obvious from the modulus curves that there is an increasing softening effect with increasing rubber content.

Correlations were attempted between per cent rubber and notched impact strength, peak height, relaxation strength as defined by McCrum, and relaxation strength as defined by Wada and Kasahara. Correlations were

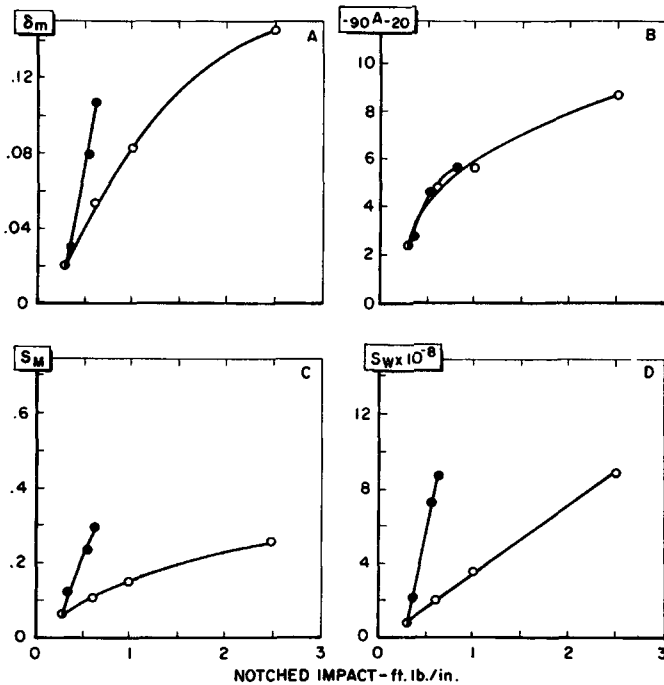


Fig. 9. Relationships between notched impact and damping peak height (A), area under the damping curve from -90° to -20°C (B), relaxation strength (McCrum) (C), and relaxation strength (Wada and Kasahara) (D): (○) polystyrene; (○) solution polymers; (●) mechanical blends.

also attempted between notched impact strength and peak height, area under the damping curve from -90°C to -20°C , and the two forms of relaxation strength. These curves are shown in Figures 8 and 9.

In all four plots of Figure 8, there are increases in the functions plotted along the ordinates with increasing rubber content. Figures 8A, B, and C show that, within a narrow, well-defined series of polymers having similar compositions, morphologies, and methods of preparation, the damping peak or the modulus dispersion can provide an indication of the rubber content. Figures 8A and D indicate that the efficiency of grafted rubber is considerably higher than that of blended rubber.

In all four plots of Figure 9, there are increases in notched impact strength accompanying the increases in the function plotted along the ordinates. These four plots indicate that, for a series of polymers as defined above, the dynamic properties also provide an indication of impact strength.

CONCLUSIONS

It has been shown that some of the traditionally held views with regard to the rubber peak size as relating to rubber concentration and impact strength may be complicated by additional considerations such as com-

position, morphology, and method of preparation. When polymers are grouped with these complications in mind, it is possible to show relationships between rubber concentration or impact strength and the dynamic mechanical properties.

Also, it can be concluded that the presence of a low-temperature damping peak in a rigid polymer gives an indication of a two-phase system. However, while the presence of such a damping peak seems necessary for toughening, its size in general does not appear to be related to the actual degree of toughening, except within a fairly narrow family of similarly prepared polymers.

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