

Dynamic Mechanical Properties of Deformed Rubber-Modified Acrylics

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Synopsis

Rubber-modified acrylic polymers with rubber contents of 0, 1, 4, 7, 10, 13, and 16% were investigated to determine the effects of cold deformations on their mechanical and dynamic mechanical properties. A Rheovibron was used to determine damping as a function of temperature at four frequencies. A cold-rolled film and a cold-drawn film, stretched until fully crazed, were investigated. It was shown that cold deformation produces a small shift in the glass transition temperature of the rubber phase while the activation energy remains nearly unchanged. Also, the nature of the damping curve of the glassy matrix near the glass transition temperature of the matrix is altered by the appearance of a shoulder in the curve.

INTRODUCTION

The phenomenon of matrix crazing in rubber-modified high-impact polymers has been closely associated with the primary energy absorption mechanism responsible for increases in ductility in otherwise unmodified brittle glassy polymers. Kambour¹ has shown polymeric crazes to be composed of approximately equal portions of void and of bundles (100 Å to 200 Å in diameter) of oriented cold-drawn polymer. Newman and Strella² were the first to postulate that the process of microscopic cold drawing initiated at rubber particle sites was the high-energy absorption process in impact polymers. Matsuo³ has examined stained ultramicrotomed crazes in the electron microscope and has seen drawn bundles of polymer across crazes that had been initiated at rubber particle sites. Although the existence of oriented cold-drawn polymer extending across the faces of a craze has been amply demonstrated, little is known about the plastically strained molecule inside the polymer bundles.

Broutman and Patil⁴ and others^{5,6} have demonstrated the feasibility of cold rolling various polymers below their glass transition temperatures. Broutman and Patil have also tabulated the effects of cold rolling to different role reductions on the bulk mechanical properties of various polymers. In glassy amorphous polymers, it is difficult to relate changes in molecular structure to changes in bulk properties after room-temperature plastic deformation. A reasonable technique for characterizing changes in molecular

structure after deformation by crazing or cold rolling is the viscoelastic response measured by dynamic mechanical damping. Because dynamic mechanical damping is influenced by the internal molecular response, it is possible with this method to investigate changes in molecular structure due to plastic deformation.

There have been some studies in the past regarding the effects of orientation on the dynamic damping response of polymers, but none concerning the effects on damping of an amorphous glassy polymer plastically deformed below T_g . Matsuoka⁷ measured the effect of hot stretching an ABS polymer on damping and found a dilational shift of the rubber-component damping peak. Van Krevelen⁸ discusses changes in T_g peak width and temperature in PET fibers after elongations of 400% to 800%.

EXPERIMENTAL

Materials

Rubber-modified acrylic polymers were supplied by the Army Materials and Mechanics Research Center, Watertown, Massachusetts. They consisted of a grafted styrene-butadiene rubber component dispersed in a styrene-acrylonitrile-methylmethacrylate matrix. Varying rubber contents were created by "dilution" of a polymer containing an original 16% rubber to those of reduced rubber contents. The polymers tested contained 0, 1, 4, 7, 10, 13, and 16% rubber. These polymers are referred to as acrylic multipolymers (AMP), and their rubber content will be designated by abbreviations, e.g., AMP 16 and AMP 0 for 16% and 0% rubber, respectively.

Compression Molding of Sheet and Sheet Film

Sheets and sheet films were molded on a Dake Model 44-251 compression-molding machine. A sample of the bulk AMP material was placed between a 0.003-in. steel sheet shim stock located between two steel blocks of dimensions 4 in. by 4 in. Molding was done at 180°C under a load of 30,000 pounds using steel shim stock spacers at the four corners for thickness control. A lubricant, Dow Corning Silicone Mold Release Agent, was employed on the sheet shim stock to facilitate polymer flow and prevent sticking. The AMP sheet and sheet film were allowed to anneal for relief of stresses and to achieve an equilibrium structure. The anneal was accomplished by slow cooling from molding temperature to room temperature (cooling rate approximately 15°F/hr). Films 0.004 in. thick were die cut for tensile testing and razor cut for dynamic mechanical damping. Sheets 0.050 in. thick were die cut for tensile impact testing.

Compression Molding of High-Temperature Sandwich Specimens

A dynamic damping specimen in the Rheovibron II is always at a slight tension throughout the course of the test. The effect of this tension on the specimen is negligible at temperatures much below the polymer T_g , but in

the vicinity of the polymer T_g , the specimen will sag and stretch, causing the test to be discontinued. To circumvent this problem and allow measurements in the T_g range, other researchers have either lightly crosslinked the amorphous polymer or embedded a small portion of it in a material of much higher T_g . For AMP materials, it is possible to determine T_g using a sandwich specimen.

Regarding the construction of the sandwich specimen, the outer layers must consist of an acoustically inert material in the T_g temperature region of AMP materials. The sandwich specimen was therefore structured of sheet films of polycarbonate ($T_g = 145^\circ\text{C}$) + AMP ($T_g = 95^\circ\text{C}$) + polycarbonate. Intimate contact between the materials was promoted by heating the specimen to 180°C in the compression-molding machine at 10 psi and then cooling to 25°C . A damping specimen was then cut, and the AMP T_g was determined at various frequencies in the Rheovibron II.

Deformation of Films

The materials AMP 0 through AMP 16 were crazed to study the effects upon dynamic mechanical damping. Specimens were crazed by stretching the films in tension to approximately 75% of the ultimate elongation of the film. A specimen to be used for dynamic damping measurements was then razor cut from the crazed area of the tensile specimens.

Rolling of plastic films was done on a two-roll mill having 4.5-in.-diameter rolls that were 6.3 in. long. Sheet films and sheets of rectangular dimensions 0.5 in. by 3.0 in. were unidirectionally rolled between 0.003-in. sheets of steel shim stock to reductions in thickness of 20% to 25%. Specimens were then die cut or razor cut for tensile testing or dynamic mechanical testing, respectively.

Tensile Testing

The determination of stress-strain properties of annealed and cold-rolled specimens of materials AMP 0 through AMP 16 was conducted on specimens whose dimensions are specified by ASTM 1822-68 Type L.⁹ The use of these specimens was necessitated because sheet films were molded discs of only 3 in. in diameter. The annealed specimens and the cold-rolled specimens were all tested at room temperature at a cross-head rate of 0.1 in./min. For modulus of elasticity measurements, a gauge length of 0.5 in. was employed between the pneumatic clamps in the Instron testing machine.

Measurement of Dynamic Damping and Dynamic Modulus

The determination of the dynamic mechanical damping and dynamic modulus was conducted on a Rheovibron II for annealed, cold-rolled, and crazed AMP 0 through AMP 16. Measurements were taken every 4° from -120°C to $+84^\circ\text{C}$. For the T_g matrix determination, measurements were taken on sandwich specimens from 80°C to 100°C at 1° intervals. For calculation of molecular motion relaxation energies of activation,

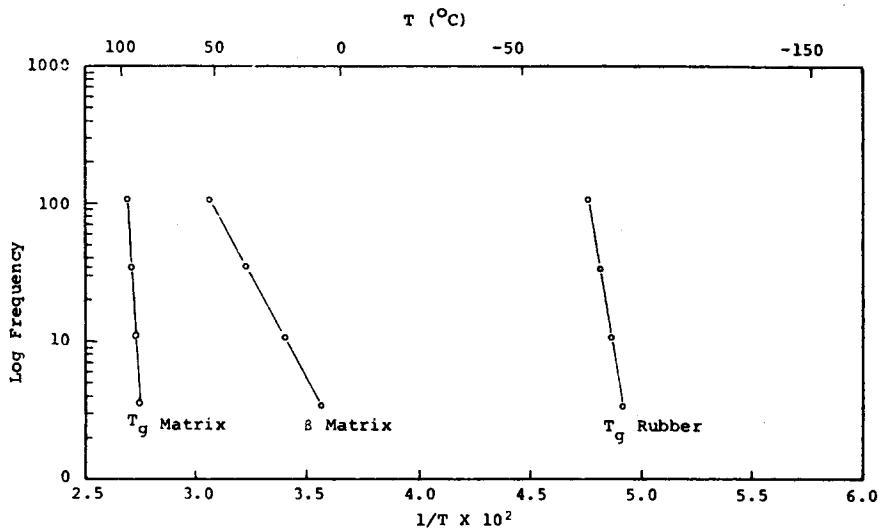


Fig. 1. Experimental data for AMP 7 used to obtain activation energies of molecular relaxations.

measurements were made at frequencies of 3.5, 11, 35, and 110 Hz. Measurements were taken at 1°C intervals for the T_g rubber and the T_g matrix peaks. For the broader β -matrix peak, measurements were taken at 4° intervals. A typical plot from which activation energies were determined is shown in Figure 1 for AMP 7.

RESULTS

Tensile Properties

The appearance of annealed tensile specimens after fracture is shown in Figure 2. All specimens are seen to exhibit shear banding across and crazing throughout the gauge length. With increasing rubber content, the shear banding and crazing progresses from slight to incomplete to complete. In AMP 16, it is observed that crazing has taken place so thoroughly that any indication of shear banding has been completely masked.

Shown in Figure 3 is the appearance of cold-rolled specimens after fracture in tension. In comparison with the annealed specimens in Figure 2, the chief effect of the cold rolling was to reduce the shear banding and crazing in the respective specimens. As with the annealed specimens, there is an increase in crazing with increasing rubber content.

The load elongation curves for the specimens exhibited in Figures 2 and 3 are shown in Figures 4 and 5. These curves assist greatly in the explanation of the appearance of the crazed polymers broken in tension. A number of effects due to increasing rubber content may be noted. As shown in Figure 6, the modulus of elasticity decreases linearly with increasing per cent rubber. In Figure 7, the effect of rubber content on the yield point has

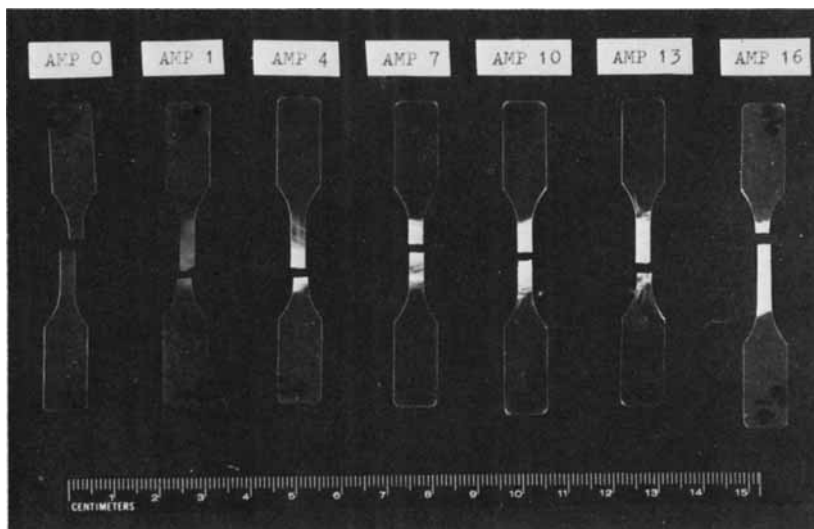


Fig. 2. Appearance of annealed AMP 0 through AMP 16 after fracture in tension at a strain rate of 0.2 in./min.

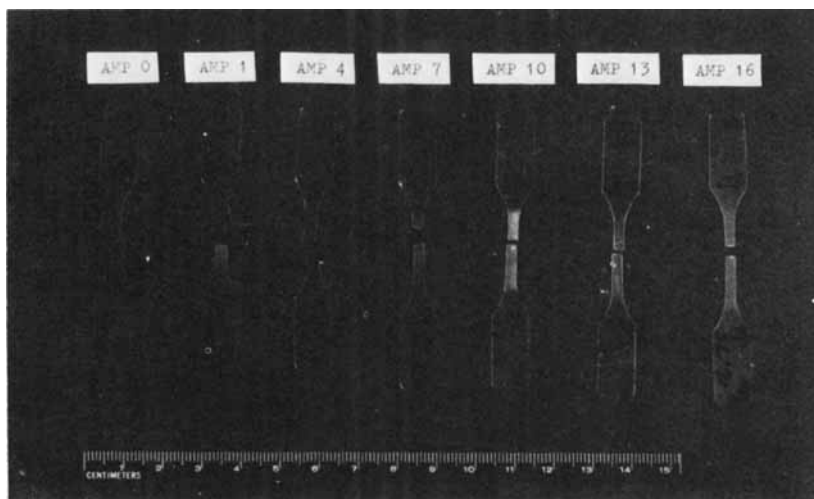


Fig. 3. Appearance of cold-rolled AMP 0 through AMP 16 after fracture in tension at a strain rate of 0.2 in./min.

been plotted. A linear relationship between increasing rubber content and decreasing yield stress is displayed for the annealed polymers.

AMP 0 and AMP 1 exhibit a yield point but are so brittle that they have no ability to draw. From AMP 4 through AMP 16, a trend toward increasing elongation to failure with increasing rubber content is observed. It is noted, though, that throughout the entire elongation the drawing stress (the stress after yield while the polymer is elongating) remains rela-

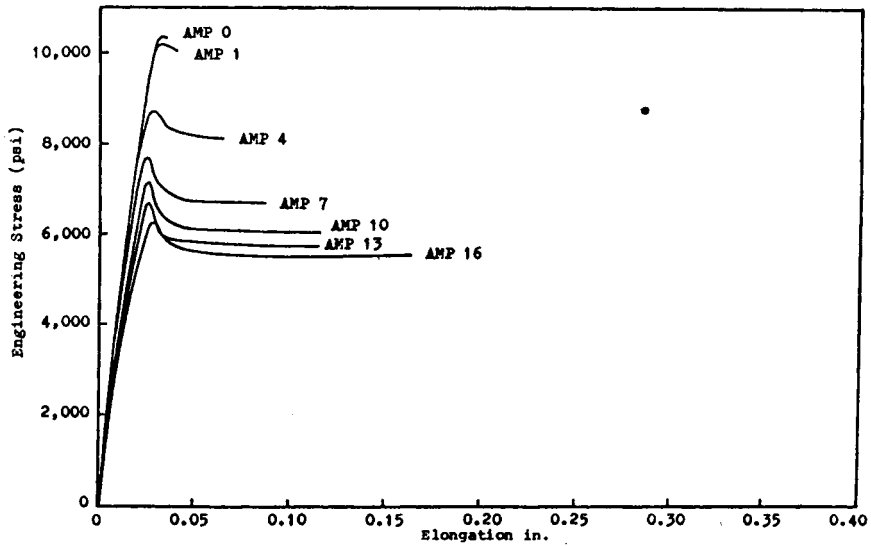


Fig. 4. Load elongation curves for annealed AMP 0 through AMP 16 specimens.

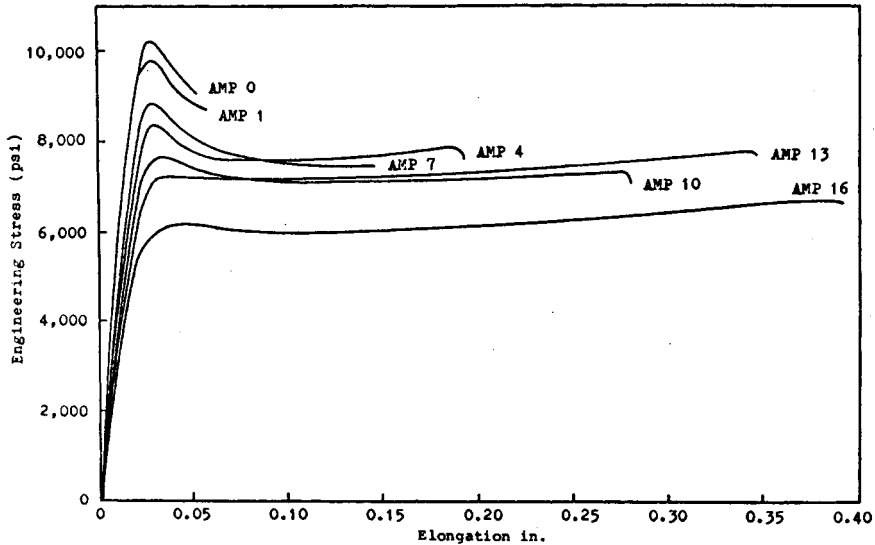


Fig. 5. Load elongation curves for cold-rolled AMP 0 through AMP 16 specimens.

tively constant and does not increase with increasing elongation. Shown in Figure 5 are the load elongation curves for the cold-rolled AMP polymers. A number of effects are noted in comparing the curves in Figure 5 with those of the annealed specimens in Figure 4. The yield point in the cold-rolled specimens is broader and not as sharply defined as in the annealed specimens. In the cold-rolled polymers, AMP 0 and AMP 1 exhibit some degree of ductility because they draw slightly beyond the yield point. All

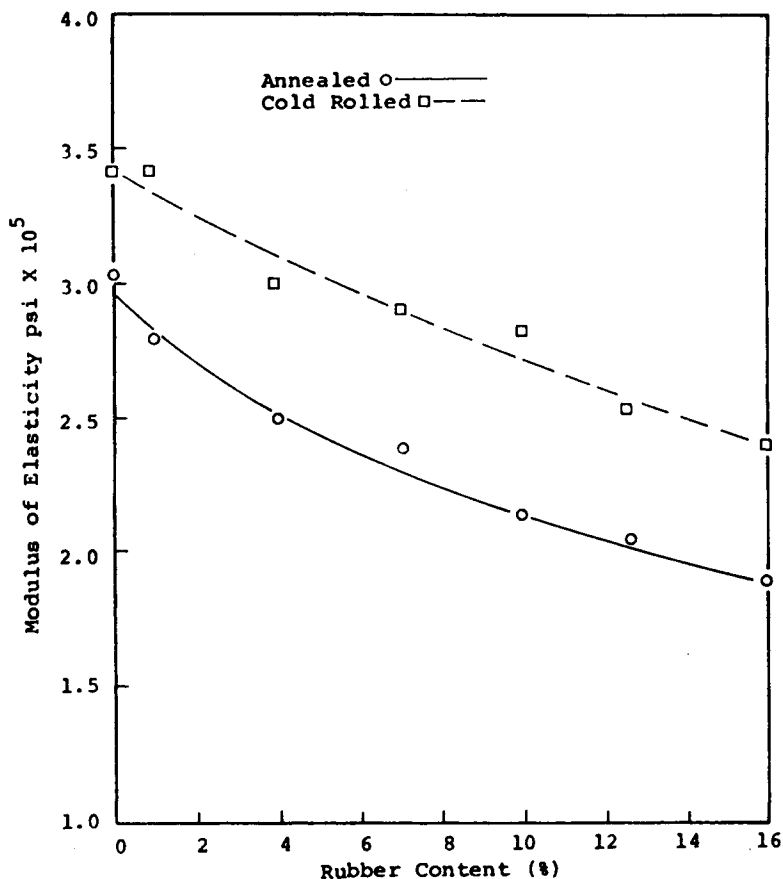


Fig. 6. Effect of rubber content of the modulus of elasticity for annealed and cold-rolled AMP polymers.

cold-rolled AMP polymers exhibit considerable increases in elongation to failure over the annealed AMP polymers. In the cold-rolled polymers AMP 13 and AMP 16, the yield point has disappeared, whereas in the annealed polymers AMP 13 and AMP 16, a distinct yield point was exhibited. In Figure 7, the effect of rubber content on the yield stress of annealed and cold-rolled polymers is shown. In all cold-rolled polymers, the yield stress is higher than in the annealed polymers. Figure 6 shows the effect of rubber content on the modulus of elasticity for annealed and cold-rolled AMP polymers. In all polymers, the modulus has increased over that of the annealed specimens.

Dynamic Mechanical Properties

Before considering the effect of the rubber component on the dynamic mechanical properties, it will be useful to examine the dynamic mechanical properties of the unmodified matrix polymer, otherwise referred to as AMP 0.

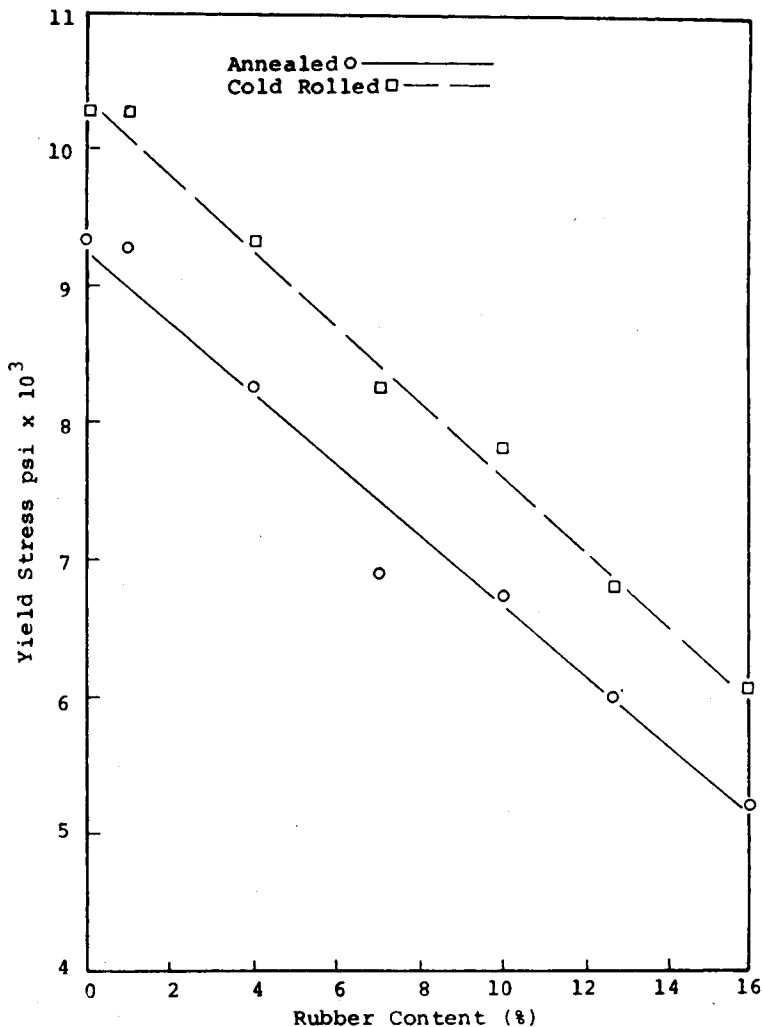


Fig. 7. Effect of rubber content on the yield stress of annealed and cold-rolled AMP polymers.

Figure 8 represents the dynamic mechanical damping versus temperature at frequencies of 3.5, 11, 35, and 110 Hz for AMP 0. Starting from the lowest temperature, an increasing $\tan \delta$ is observed climaxed by a peak at 0°C at a frequency of 3.5 Hz. This peak, which is referred to as the β -matrix peak, is associated with the strong β -transition of the poly(methyl methacrylate) component of the matrix.¹⁰ This peak is very much temperature-rate dependent as demonstrated by a large shift toward T_g over the frequency range of 3.5 Hz to 110 Hz. From this shift, the activation energy of the peak may be determined. The average activation energy for the β -matrix peak for all AMP polymers is shown in Table I to be 16.7 kcal/mole.

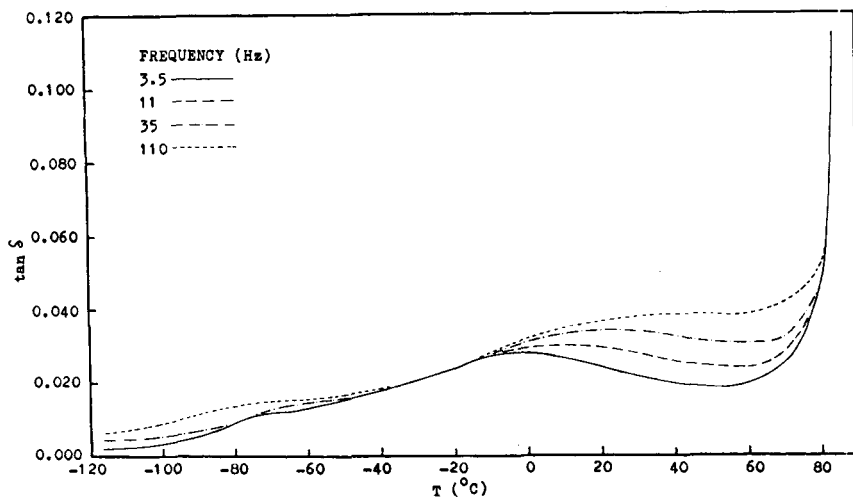


Fig. 8. Plot for AMP 0 of $\tan \delta$ vs. temperature at frequencies of 3.5, 11, 35, and 110 Hz.

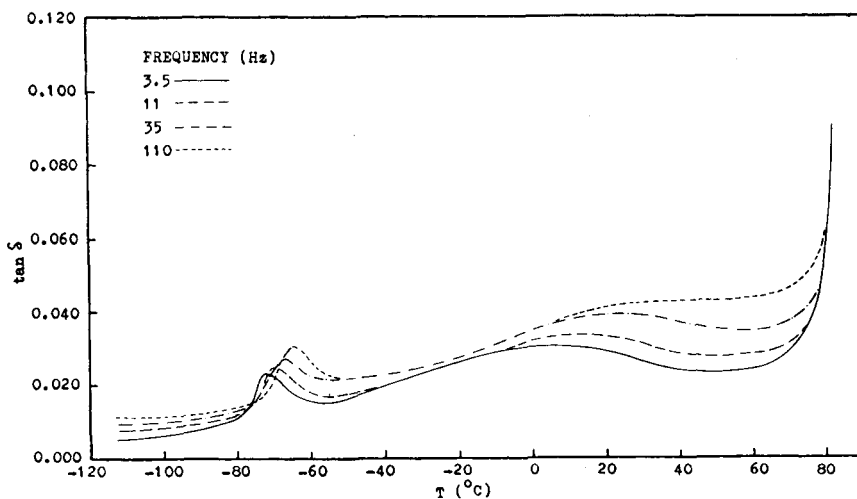


Fig. 9. Plot for AMP 7 of $\tan \delta$ vs. temperature at frequencies of 3.5, 11, 35, and 110 Hz.

Through the use of the sandwich specimen, the T_g of the matrix has also been experimentally determined to be 90.5°C . This T_g appears to correspond with that of the styrene-acrylonitrile component of the matrix as previously reported for an ABS polymer.¹¹ The average activation energy of this peak for AMP polymers has been calculated and is shown in Table I to be 137.1 kcal/mole.

The effect of increasing rubber content on the damping properties of AMP polymers is typically shown in Figure 9. The only significant difference between this curve and the damping curve of AMP 0 is the appearance of a low-temperature damping peak at, on the average, -70°C at a fre-

TABLE I
Annealed AMP Polymer Temperature-Frequency Peaks and Activation Energies

AMP	Temperature-frequency peak, °C				Activation energy, cal/mole
	3.5 Hz	11 Hz	35 Hz	110 Hz	
Rubber T_g Peak					
0	—	—	—	—	—
1	—	—	—	—	—
4	-71.8	-69.7	-66.4	-63.0	32,800
7	-70.6	-69.0	-67.5	-64.3	53,500
10	-69.8	-68.4	-67.0	-64.2	56,100
13	-69.9	-68.4	-66.8	-64.3	58,400
16	-69.0	-67.6	-65.7	-63.2	52,600
				Average	50,700
Matrix β -Peak					
0	0	9	22	35	17,500
1	2	11	28	40	14,700
4	0	12	20	35	18,000
7	4	19	20	45	16,500
10	4	15	30	50	18,000
13	4	17	34	50	14,700
16	6	11	38	50	17,500
				Average	16,700
Matrix T_g Peak					
0	90.0	92.5	95.0	96.5	134,200
1	88.5	91.6	94.1	96.5	121,300
4	90.3	92.6	94.0	96.8	140,200
7	90.0	91.0	95.0	96.8	126,600
10	91.8	92.4	94.5	96.5	149,300
13	88.4	91.1	92.5	95.5	143,400
16	90.4	92.5	94.5	97.0	144,700
				Average	137,100

quency of 3.5 Hz. This peak can then be attributed to the styrene-butadiene rubber component. The intensity in terms of peak height versus content has been plotted in Figure 10 and shows a linear correlation. A 4°C to 5°C shift in the peak is also observed as the frequency is increased from 3.5 Hz to 110 Hz. The average activation energy of this peak for annealed AMP polymers has been calculated and is shown in Table I to be 50.7 kcal/mole. It appears that the addition of the rubber component does not affect either the activation energy of the β -matrix peak nor the T_g matrix peak.

In Figure 11, the effect of cold rolling on the dynamic mechanical damping is displayed for the unmodified AMP 0 polymer. There are three basic effects that can be readily noted. The first effect is the decrease in the intensity of the β -matrix peak occurring at 0°C. It was no longer possible to obtain the activation energy of this peak because the exact temperature

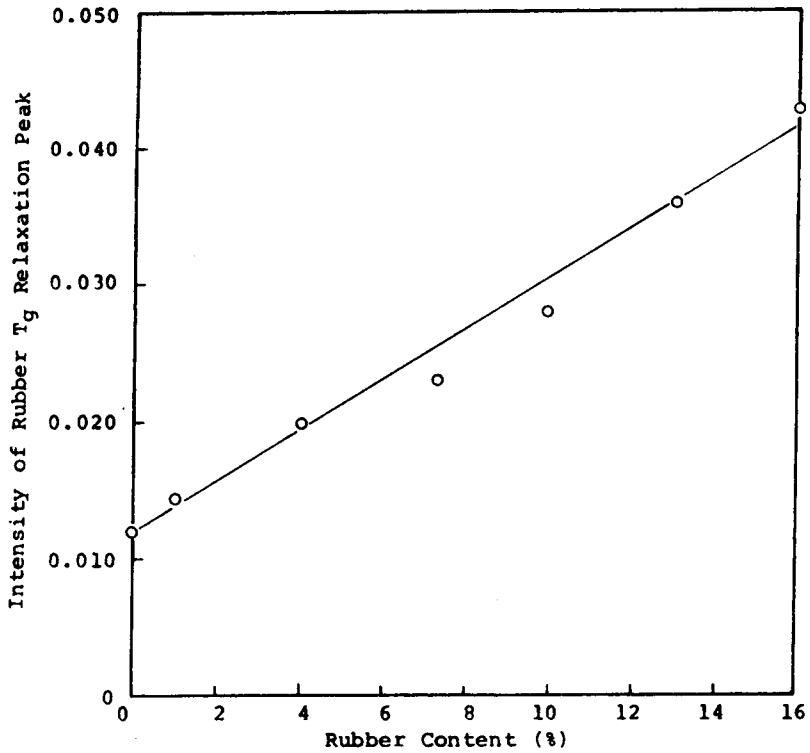


Fig. 10. Effect of rubber content on the intensity of the rubber T_g relaxation peak.

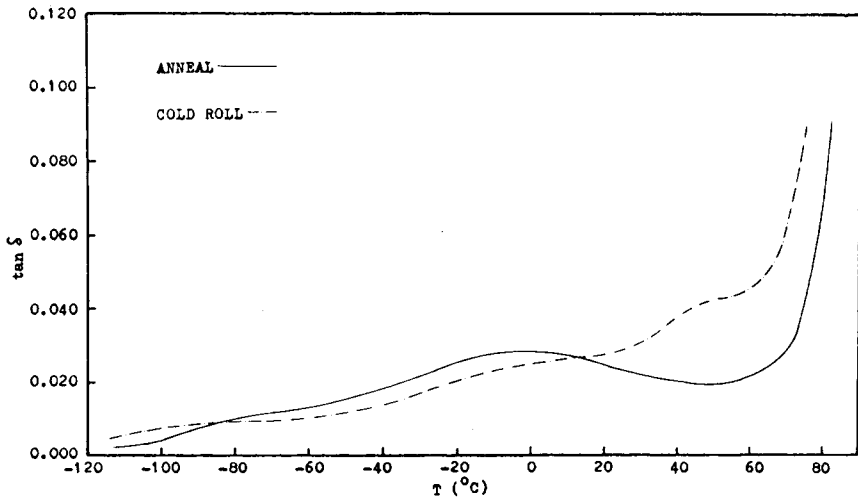


Fig. 11. Plot for AMP 0 of $\tan \delta$ vs. temperature for annealed and cold-rolled specimens at 3.5 Hz.

TABLE II
Cold-Rolled AMP Polymer Temperature-Frequency Peaks and Activation Energies

AMP	Rubber T_g peak, °C				Activation energy, cal/mole
	3.5 Hz	11 Hz	35 Hz	110 Hz	
0	—	—	—	—	—
1	—	—	—	—	—
4	-69.1	—	—	—	—
7	-65.7	-64.3	-62.4	-59.7	53,300
10	-67.0	-65.0	-62.4	-61.1	51,900
13	-67.0	-65.1	-61.7	-60.4	43,800
16	-68.4	-65.7	-64.3	-62.4	48,900
				Average	49,500

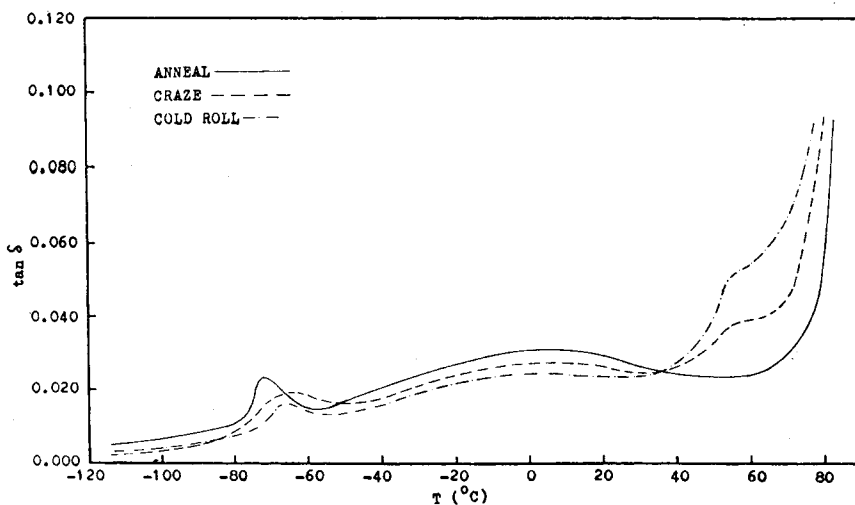


Fig. 12. Plot for AMP 7 of $\tan \delta$ vs. temperature for annealed, crazed, and cold-rolled specimens at 3.5 Hz.

at which the peak occurred could no longer be accurately determined. This was found to be true for tests on all subsequent AMP polymers also. The second effect of cold rolling was the appearance of a "shoulder" at a temperature that was higher than the β -matrix peak and lower than the T_g of the matrix peak. This shoulder might be considered to be a peak, but its proximity to the T_g peak does not allow a clear definition of its appearance. The third feature is the shift to a lower temperature by about 4°C of the rise in $\tan \delta$ associated with the T_g of the matrix peak.

Shown in Figure 12 is the typical effect of the rubber component on the dynamic damping properties of a cold-rolled AMP 7 polymer. The effects of cold rolling on the rubber T_g peak were found to be the following. The temperature at which the peak occurs is increased 2°C to 5°C. The intensity of the peak is diminished from its original height. The activation energy of the T_g rubber peak is 49.5 kcal/mole as shown in Table II.

TABLE III
Crazed AMP Polymer Temperature-Frequency Peaks and Activation Energies

AMP	Rubber T_g peak, °C				Activation energy, cal/mole
	3.5 Hz	11 Hz	35 Hz	110 Hz	
0	—	—	—	—	—
1	—	—	—	—	—
4	—	—	—	—	—
7	-64.3	-63.0	-61.7	-59.7	65,200
10	-65.0	-64.9	-63.6	-60.4	66,300
13	-69.7	-67.7	-65.7	-62.8	43,300
16	-65.0	-62.5	-61.7	-59.7	56,700
				Average	57,800

Shown additionally in Figure 12 is the effect of crazing on the dynamic mechanical damping. In general, the effects on the matrix are the same as for the cold-rolled polymers, although not as severe. In all polymers, the β -matrix peak is reduced in intensity, although not to as great a degree as that of the cold-rolled polymer. There is a shoulder formed between the β -matrix peak and the T_g of the matrix peak, but its intensity is not as great as that for cold-rolled AMP polymers. There is, in all polymers, a shift to a lower temperature by about 2°C of the rise in $\tan \delta$ associated with the T_g matrix peak. In all polymers, there is an upward shift of the T_g rubber peak of 2°C to 4°C in temperature. The peak intensity for crazed polymers has been reduced, but in comparison with that of the cold-rolled polymers it has been diffused or broadened to a greater degree. The average activation energy for crazed AMP polymers of the rubber T_g peak, as shown in Table III, is 57.8 kcal/mole.

DISCUSSION

The results for the change in mechanical properties due to the effect of the addition of a rubber component agree, in general, with those of others, for example, Matsuo and Imasawa.¹² They have found a reduction in tensile strength and modulus and an increase in elongation with increasing rubber content. Boyer et al.¹³ have found an increase in impact strength with an increase in the percentage of the rubber component. In this study, the effect of increasing the rubber content from 0% to 16% has the following effects on the properties. Figure 6 shows the modulus of elasticity being reduced from an original value of 3×10^5 psi to a value 30% less than that. Figure 7 shows the yield stress being reduced by 45% from an original value of 5.1×10^3 psi. The load elongation curves in Figure 4 show the elongation to failure being increased by a value of 600% from an original value of 0.03 in. Figure 2 shows that the increase in the elongation to failure, or the ductility, is also associated with an increase in the amount of crazing present at failure.

The annealed AMP polymers were cold rolled to a roll reduction 25%. As discussed by Broutman and Patil,⁴ there will be a general enhancement of mechanical properties due to the orientation of the polymer. The property enhancement will only be in the direction parallel to that of the cold rolling. The changes in properties must be related to a specific polymer. For the AMP polymers, the changes in properties from those of the annealed AMP polymers were the following. Figure 6 shows the modulus of elasticity increasing in general by 70%. Figure 7 shows the yield stress increasing in general by 11%. The load-elongation curves for cold-rolled AMP polymers in Figure 5 shows the elongation to failure increasing by approximately 100%. Although there is an increase in the elongation to failure, Figure 3 shows a decrease in the amount of crazing present in comparison anneal AMP polymers.

The changes due to cold rolling are generally resolvable in terms of having increased the amount of covalent bonding available in the direction of cold rolling. There appears to be an anomalous result, though, with regard to the decrease in the amount of crazing and the increase in the ductility as seen in elongation to failure. With cold rolling, the potential for elongation and orientation in the crazed material has decreased because the material has now been already partially oriented. This accounts for the decrease in the amount of crazing. But the increase in the ductility must be accounted for by the decrease in the notch sensitivity of the material due to the presence of the oriented polymer chains. The oriented polymer chains serve to blunt or restrain catastrophic cracks from propagating across the bulk material. This, then, is the reason for the increased ductility at the roll reduction of 25%. It must be considered, though, that if the roll reduction is continually increased, a point will be reached at which the ability to orient, the mechanism of ductility, will be exhausted and ductility will decrease.

The appearance of a well-defined rubber T_g damping peak in Figure 9 demonstrates that the rubber component exists as a discrete phase in the brittle glassy matrix. This result is not unusual and agrees with similar conclusions by Boyer et al.¹³ and Matsuo et al.¹⁴ and other researchers.

The dynamic damping of the unmodified, or AMP 0, matrix in Figure 8 displays a strong β -transition at 0°C at a frequency of 3.5 Hz. As demonstrated by Deutsch et al.,¹⁰ this peak is due to the secondary transition of the poly(methyl methacrylate) component of the matrix. The activation energy determined was 16.7 kcal/mole, which agrees well with a value of 18 kcal/mole as found by Deutsch et al.¹⁰ The T_g of the matrix occurs at 90.5°C at a frequency of 3.5 Hz. The activation energy of 137.1 kcal/mole and the temperature at which the peak occurs agree with the results of Moore and Giewnewski.¹¹ This peak is associated with the acrylonitrile-styrene components of the matrix and the activation energy is in agreement with that determined by Moore and Giewnewski of 111 to 147 kcal/mole in creep measurements.

The rubber T_g peak occurs at -70°C at a frequency of 3.5 Hz and has an activation energy of 50.7 kcal/mole. As shown in Figure 10, there is a linear relationship between the percentage of the rubber component in the respective AMP polymer and the intensity of the damping of the rubber T_g peak. This result concurs with that of Boyer et al.¹³ for any series of similarly prepared rubber-modified polymers. This result, though, cannot be generalized in comparing one commercial polymer to another because the method of preparation greatly affects the intensity of the rubber damping peak.

The changes in the dynamic damping response of AMP polymers due to cold rolling are the following. Shown in Figure 12 are the three basic changes in the dynamic damping curve for the unmodified, or AMP 0, polymer. The first effect is a reduction in the intensity of the β -relaxation peak. The second is the appearance of a new "shoulder" or peak at a temperature above that of the β -matrix peak and slightly below that of the T_g matrix peak. The third effect is a shift to a lower temperature of the rise in damping associated with the T_g of the AMP 0 polymer.

The changes due to cold rolling in the AMP polymer damping curve are similar to those occurring in other polymers such as polycarbonate.¹⁵ The reasons for these changes are not well understood at the present time, but some explanations will be offered. The changes as reported in this study are also similar to those occurring in polymers that have been rapidly quenched from the melt state. This indicates that the effects of two entirely different treatments may be similar in the end result. Broutman and Patil⁴ have shown the presence of residual stresses in quenched or cold-rolled polycarbonate. These residual stresses may be a macroscopic phenomenon of microscopic stresses in the polymer chains. If indeed this is true, there may be a "locking out" of some β -segmental motion in the process of stiffening the polymer chains. This would account for the reduction in the intensity of the β -molecular relaxation peak. Many of these smaller segments might then remain in the strained state until enough thermal energy is applied to the segments to relax to their former state. This relaxation, then, would manifest itself as a new peak occurring at a higher temperature. This would account for the appearance of a new "shoulder" just below the T_g matrix relaxation peak. The shift in the damping curve at the T_g of the matrix could be either a shift in the matrix T_g or a broadening of the matrix T_g . This could be accounted for by either the additional energy stored in the strained polymer chains or the addition of free volume to the matrix which will also produce a lowering of the matrix T_g .

The final effect to be noted in regard to cold rolling is with respect to the rubber T_g peak. This relaxation peak has been reduced in intensity and shifted upward by 2°C to 4°C . The effect of orientation on the glass transition of natural rubber has been studied by Shen and Johnston, and they have surveyed the literature only to find no consistently agreeable

data.¹⁶ The explanation offered by this study is that the modulus and strength of the stretched rubber has increased, thereby requiring a higher activation energy or a higher temperature to activate this relaxation. As considered previously, the strained segments may lose some mobility thereby reducing the intensity of the relaxation.

In crazing, the same effects are found to occur for dynamic damping as with cold rolling. This is reasonable since the crazing involves an orientation process. The only difference will be the appearance of a wide range of orientation process. The only difference will be the appearance of a wide range of orientations which will cause, as seen in Figure 12, a broadening of the damping spectrum at the T_g of the rubber phase. All other effects can be related to the discussion in the cold-rolling explanation section.

CONCLUSIONS

1. For annealed AMP polymers, increasing the rubber content from 0% to 16% has the following effects on the mechanical properties: (a) the modulus of elasticity is reduced by 30% from an original value of 3×10^5 psi; (b) the yield stress is reduced by 45% from an original value of 5.1×10^3 psi; (c) the drawing stress is reduced by 27% (at AMP 4) from an original value (at AMP 4) of 7.5×10^3 psi; (d) the elongation to failure has increased 600% (there has also been a corresponding increase in the amount of crazing in the fracture specimens).

2. Annealed AMP polymers were cold rolled to a roll reduction of 25%. In comparing cold-rolled AMP polymers to annealed AMP polymers, the effects on the mechanical properties were (a) an increase in the modulus of elasticity of 17%; (b) an increase in the yield stress of 11%; (c) an increase in the drawing stress by 17%; (d) an increase in the elongation to failure by 100% (although crazing in the direction of cold rolling had been greatly reduced).

3. For annealed AMP polymers, the molecular relaxation activation energies can be determined by temperature-frequency measurements. The activation energies are (a) 50.7 kcal/mole at approximately -70°C for the rubber T_g peak; (b) 16.7 kcal/mole at approximately 2°C for the β -matrix peak; (c) 137.1 kcal/mole at approximately 90°C for the matrix T_g peak. The effect of increasing rubber content was a linear increase in the intensity of the rubber T_g peak.

4. Changes in the dynamic damping response of AMP polymers due to cold rolling are the following: The rubber T_g peak is reduced in intensity and the location of it is shifted to a higher temperature by 2°C to 4°C . The β -matrix peak is reduced in intensity while at the same time a new "shoulder" α peak appears between the β -matrix peak and T_g matrix peak. The rise in dynamic damping associated with T_g in the annealed polymer is shifted to a lower temperature, thereby indicating a lowering of the T_g or a possible broadening of the T_g peak. The lowering in intensity of the β -matrix peak and the appearance of the shoulder peak near T_g are associated

with a strain induced locking out of the β -molecular relaxation in some main chain segments. These segments will then require additional thermal energy supplied at a higher temperature to relax to their normal unextended state. This relaxation will manifest itself as a shoulder slightly below the T_g matrix peak.

5. Crazing in AMP polymers is reduced by cold rolling. Crazing affects the dynamic damping of AMP polymers in the same manner as does cold rolling, but the effects are not as intense since the overall degree of orientation is not as great.

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