

Crazing and the Stress Dependence of Creep in Two Glassy Polymers: Polystyrene and a Poly(styrene-Acrylonitrile) Copolymer

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Synopsis

The stress dependences of crazing and of tensile creep were studied at 30.5° and 80°C in polystyrene ($\bar{M}_v = 2.7 \times 10^6$) and in a poly(styrene-acrylonitrile) copolymer (73.5% styrene, $\bar{M}_v = 2.35 \times 10^6$) at four stresses in the interval from 0.6 to 1.5×10^8 dynes/cm². Material failure was observed in all cases for the polystyrene and in no cases for the copolymer. Crazing was found to occur at all stresses for polystyrene, the spacing between craze lines decreasing with increasing stress and temperature. A much higher stress level for the onset of crazing was found for the copolymer. An inverse stress dependence of the compliance was observed for polystyrene at 30.5°C, i.e., the compliance decreased with increasing stress. This behavior was partially reversed at 80°C below 10^2 sec and became a positive stress dependence at long times. The stress dependence of the compliance for the SAN copolymer was partially reversed at 30.5°C. At 80°C, the stress dependence was positive for stresses $\geq 0.9 \times 10^8$ dynes/cm². The present results suggest that in the copolymer there may exist an enhanced local mobility which alters the stress dependence observed in pure polystyrene and which enhances the ability of the material to deform without failure. This concept is discussed further in light of the stress dependence of the compliance and of crazing in these materials and appears to be consistent with our previous studies of the stress dependence of creep and of the stress dependence of whitening in ABS systems.

INTRODUCTION

As one of several studies of the creep behavior in unmodified and rubber-modified solid polymers, we present results of a study of the stress dependence of creep in two glassy polymers, a polystyrene and a poly(styrene-acrylonitrile) copolymer. These materials were chosen in part because they are, in at least some respects with regard to mechanical properties, representative components of acrylonitrile-butadiene-styrene (ABS) systems of the type studied previously.^{1,2} In part they were also chosen because they lend themselves to measurements of birefringence and thus provide additional means for studying impact response of ABS-type systems. (The results of the birefringence measurements are the subject of a separate paper.³)

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Although a detailed analysis of the present work could be made in terms of a rate theory concept, as was done for the ABS system,^{1,2} it was felt more desirable in view of the complex nature of the stress dependence to present the data with some rather general interpretations of the behavior.

We proceed with a brief review of the experimental procedures, which include an extremely useful step in sample conditioning for the removal of residual strains. This section is followed by a discussion of the results for the two polymers, a brief comparison with results for the previous ABS system, and some general comments and conclusions.

EXPERIMENTAL

Materials

The polystyrene used was a commercial material obtained from Monsanto Co. and designated as Lustrex HF-77-2020. It had a viscosity-average molecular weight⁴ of about 2.7×10^5 . The styrene-acrylonitrile copolymer, a Union Carbide RMD 4500 series material, contained 73.5% styrene⁵ and had a molecular weight of $2.3_5 \times 10^5$.

Sample Preparation

The polystyrene was molded at 205°C at about 600 psi for 3 min, and the copolymer, at 205°C at 700 psi for 3 min in a suitable manner to obtain bubble-free specimens. Microtensile specimens (ASTM D 1708) were prepared on a Tensile-kut apparatus using a heated wire with the sheet of polymer heated to slightly above the glass transition temperature. Samples were subsequently annealed at $90^\circ \pm 2^\circ\text{C}$ for 1 hr. Samples were checked for residual strain birefringence using crossed polarizers. The annealing procedure produced samples 90% of which were free of strain birefringence. These specimens were used throughout the investigations.

The creep measurements were carried out using the apparatus described previously.^{1,2} Temperature control was to within $\pm 0.25^\circ\text{C}$, with maximum temperature gradients of about 0.75°C . (This gradient is much too small to account for the unusual differences observed in the temperature ranges investigated.) The lowest temperature used (30.5°C) was below the lowest of those (40°C) of the ABS studies. An upper temperature of 80°C was used, a temperature high enough to observe appreciable effects on creep behavior due to nearness to the glass transition region.

RESULTS

Polystyrene Creep Behavior

Figure 1 shows the computer-generated graph of strain versus logarithmic time for polystyrene at 30°C . On an expanded scale (or by comparison of numerical data), it is clear that strain increases with increasing stress at constant time (the usually observed response). The time to break is vir-

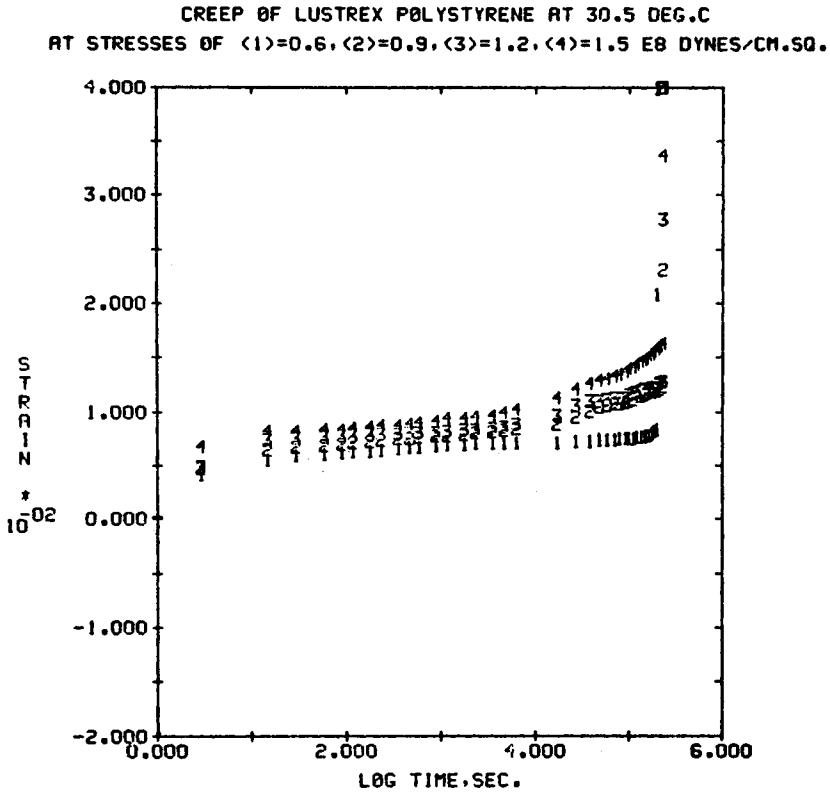


Fig. 1. Logarithmic time dependence of strain in tensile creep for polystyrene at 30.5°C at the stresses indicated. Strain magnitude to be multiplied by 10^{-2} as indicated.

tually independent of the stress level, suggesting that long-time creep response to the stress concentration of inherent flaws may play the dominant role in governing material failure at this temperature. This interpretation is consistent with the theoretical and experimental results of Cessna and Sternstein⁶ for poly(methyl methacrylate) (PMMA) in creep. Their results indicate a marked decrease in the dependence of the time to break, t_B , on the stress level, σ , at long times. Presumably, for a material characterized by constants somewhat different than those of PMMA,⁶ the dependence of t_B on σ could be even less, approaching a nearly constant t_B at long times.

Figure 2 shows the presence of unusual behavior in creep response. Here, in a double logarithmic plot of compliance versus time, it is evident that a stress dependence inverse to that observed in many systems obtains. That is, the strain here is less than proportional to the stress, so that at higher stress levels at constant time the ratio of strain to stress, or the compliance, decreases with increasing stress even though the strain ϵ_2 is larger than ϵ_1 for a stress $\sigma_2 > \sigma_1$. This is opposite to the stress dependence observed^{1,2} in ABS materials and is opposite to that found in poly(vinyl chloride)

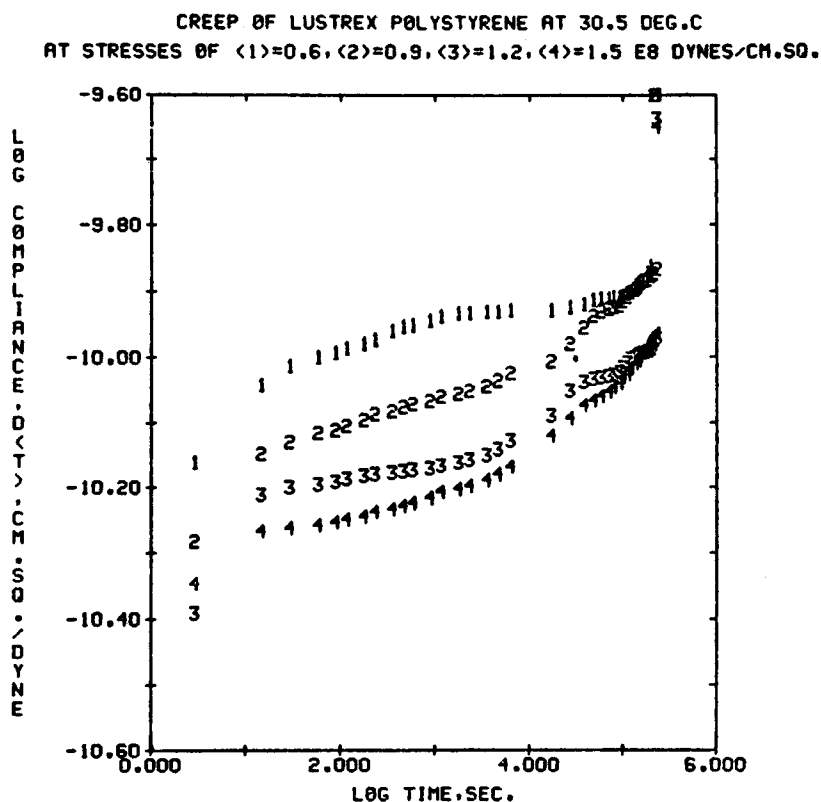


Fig. 2. Double-logarithmic plot of compliance versus time for polystyrene at 30°C at the stresses indicated.

systems by others.⁷ (We defer further discussion of these results to the next section of the paper.)

The effect of a sample temperature close to the glass transition region is indicated in the results at 80°C shown in Figure 3. Again strain is always higher at constant time at a higher stress level. Here, significantly higher levels of strain than are found at 30°C are observed before failure occurs (with the exception of the highest stress level). The level of strain at failure and the time to failure are observed to increase with decreasing stress; the strain and failure times increase from 1.7% and $10^{2.21}$ sec to 14% and $10^{5.48}$ sec as stress decreases from 1.5×10^8 to 0.6×10^8 dynes/cm². (Not shown in the published form of Figure 3 are the failures for $\epsilon_2 = 11.5\%$ at $10^{4.25}$ sec and for ϵ_1 .) Clearly, creep at the higher temperature leads to pronounced effects due to changes in the stress level, the strain at the onset of failure being lower the higher the stress.

The effect of a higher temperature on the stress dependence of the compliance is quite complex, as indicated in Figure 4. Here, the type of inverse stress dependence of the compliance observed at 30°C is found for

stress levels 1 and 2 until 10^2 sec or until a compliance of 10^{-10} cm²/dyne is attained. Thereafter, a higher compliance is observed for the sample at the higher stress level. At even higher stress levels at short times, the dependence on stress is positive, the compliance being larger for a higher stress (in the order of stresses $4 > 3 > 2$). None of the latter samples attains the compliance obtained by the sample at stress level 1 at short times. The crossover in curves 3 and 4 just prior to failure of sample 4 (difficult to discern in Figure 4) is not understood. Figure 3 indicates, however, that

CREEP OF LUSTREX POLYSTYRENE AT 80.0 DEG.C
 AT STRESSES OF (1)=0.6, (2)=0.9, (3)=1.2, (4)=1.5 E8 DYNES/CM.SQ.

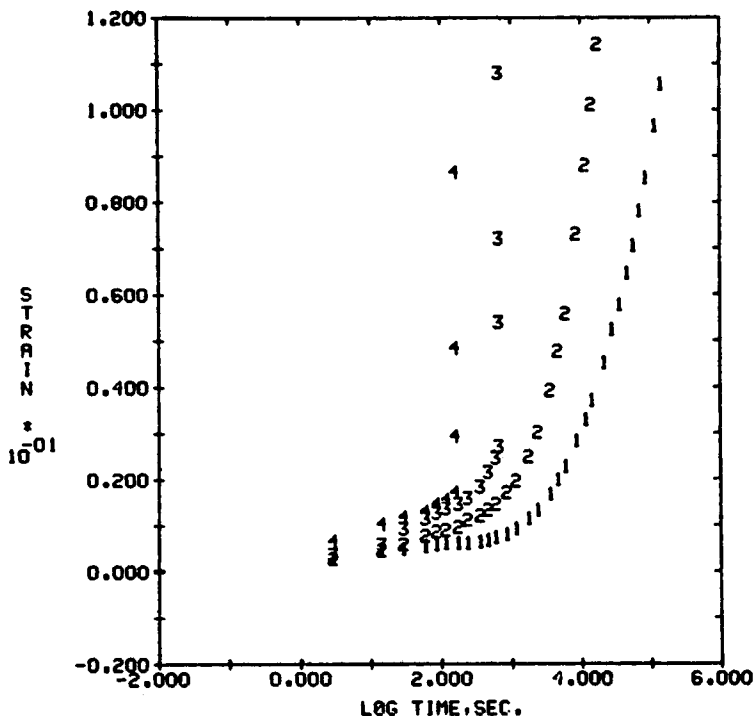


Fig. 3. Logarithmic time dependence of strain for polystyrene at 80°C at the stresses indicated. Strain magnitude to be multiplied by 10^{-1} as indicated.

the strain of curve 4 is always greater than that of curve 3. It is noteworthy that the magnitude of the compliance in Figure 4 (about 10^{-10} cm²/dyne) is nearly independent of the stress level at 90 sec. The velocity of creep just before failure increases with increasing stress, in contrast to a velocity of creep at 30.5°C nearly independent of σ . The onset of a plateau region is seen for curve 1 in Figure 4. The extent of this plateau is observed to decrease with increasing stress level, as seen more easily on a more expanded plot.

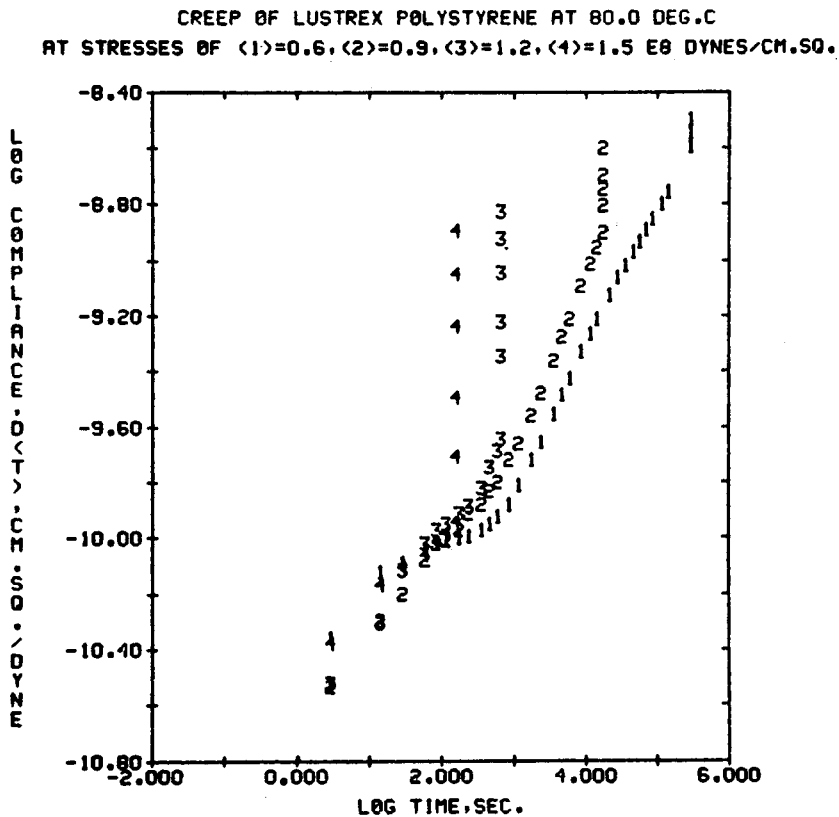


Fig. 4. Double-logarithmic plot of compliance versus time for polystyrene at 80°C at the stresses indicated.

Crazing Effects in Polystyrene

Although it is difficult to take into account quantitatively any effects of crazing on creep response, we report here experimental results of the stress and temperature dependence of crazing and of craze spacings. (Crazing was observed as a series of closely spaced lines with light-reflection properties different than those of the matrix.) These effects were taken as indirect evidence for the usual difference in the densities between crazed and non-crazed material, as commonly observed in glassy polymers.^{8,9}

Table I gives results on crazing for the two materials. The Appendix presents micrographs of samples of the two polymers. At 30.5°C, the onset of crazing probably occurs at about the lowest experimental stress level.⁴ Increasing the stress leads to sharply defined crazes of uniform spacing at the highest stress level. At 80°C, crazing is more pronounced for a given stress level than at 30°C. At the highest two stress levels, craze lines become extremely closely spaced and are so uniform as to be almost unresolvable to the eye at the highest stress level. (The effects of crazing are considered in more detail later.)

TABLE I
Stress and Temperature Dependence of Crazing
in Polystyrene and Poly(styrene-acrylonitrile)^a

$T, \sigma \times 10^{-8}$ dynes/cm ²	30.5°C	80°C
	Polystyrene	
0.6 = σ_1	slight cracks, crazes, not all the way across the sample ^b	uniform crazing ^d
0.9 = σ_2	nonuniformly spaced crazes across the sample ^c	highly crazed ^e
1.2 = σ_3	strongly crazed throughout gauge length, especially at edges	extremely close- spaced crazes ^f
1.5 = σ_4	highly crazed throughout gauge length	closest craze spacing observed
	Poly(styrene-acrylonitrile)	
0.6	no crazing	no crazing
0.9	no crazing	widely spaced crazes, cracks
1.2	no crazing	strong crazing ^h
1.5	nonuniform crazing ^g	strongest crazing for SAN ⁱ

^a Descriptions refer to samples examined at room temperature subsequent testing.

^b Craze spacing similar to that of SAN at σ_2 at 80°C.

^c Craze spacing < at σ_1 , > at σ_3 of SAN at 80°C.

^d Craze spacing > at σ_2 of polystyrene at 30°C.

^e More uniform crazing than for polystyrene at σ_3 at 30°C; craze spacing between that of SAN at σ_2 and σ_3 at 80°C.

^f Craze spacing less than at σ_3 for polystyrene at 30°C or for SAN at 80°C.

^g Craze spacing similar to that at σ_3 of SAN at 80°C, but crazing much less extensive.

^h Craze spacing between that at σ_2 and σ_3 of polystyrene at 30°C.

ⁱ Craze spacing greater than for polystyrene at σ_4 at 30°C; spacing between that at σ_2 and σ_3 for polystyrene at 80°C.

Styrene-Acrylonitrile

The strain-versus-logarithmic time curves for the styrene-acrylonitrile copolymer (SAN) at 30.5°C in Figure 5 indicate the usual behavior of an increase in strain at constant time for an increase in stress. In contrast to the polystyrene samples, no failures were observed for the SAN copolymer, and all experiments were terminated arbitrarily at about $10^{5.5}$ sec.

The double-logarithmic plot of compliance versus time for the SAN copolymer in Figure 6 indicates that the inverse dependence again obtains at 30.5°C, as was observed for polystyrene in Figure 2. However, the results in Figure 6 also indicate that at the highest stress level the inverse stress dependence is overcome so that the compliance at σ_4 is greater than at σ_3 . (However, the compliance at σ_4 is still less than that at σ_1 or σ_2 .) This difference from the behavior of polystyrene in Figure 2 suggests that the copolymer may have a slightly higher local mobility or ductility than the polystyrene. If this is correct, such mobility must be reflected in the dif-

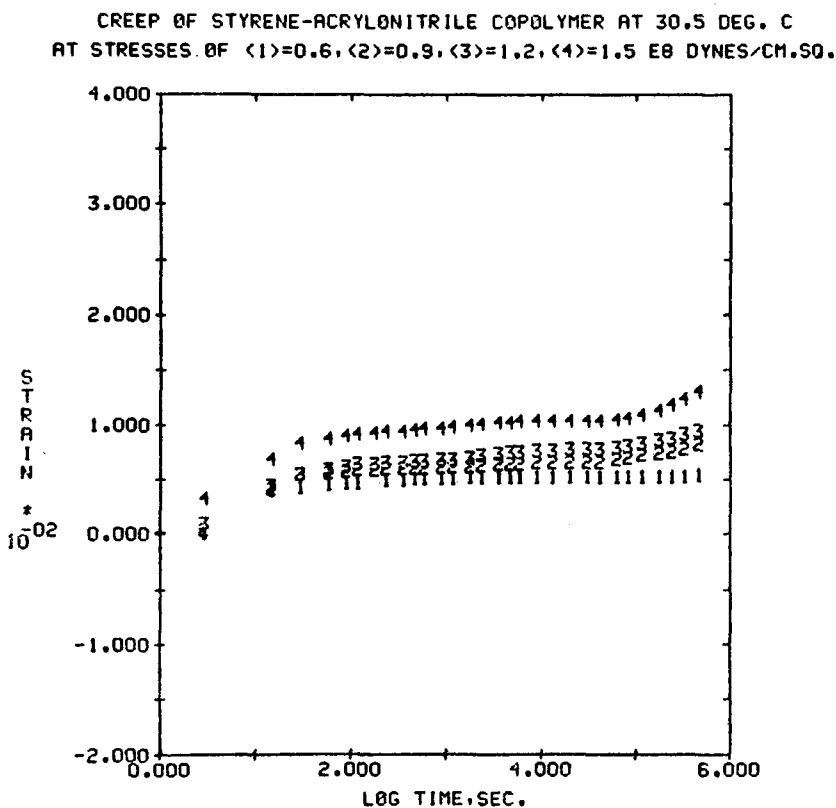


Fig. 5. Logarithmic time dependence of strain for the styrene-acrylonitrile copolymer at 30.5°C at the stresses indicated. Strain magnitude as in Fig. 1.

ferences observed in the stress dependences, since the actual compliance of the polystyrene is greater than that of the copolymer at a given stress level at 30.5°C. In this regard, it is noteworthy that the polystyrene always has some crazing present. (At σ_4 , the response of the two materials is nearly identical during the first 10^3 sec of each experiment.)

In comparing Figures 2 and 6, the reversal and the generally smaller stress dependence of the SAN copolymer may reflect effects of a stress-sensitive barrier to deformation for the copolymer, a barrier which can be biased at a sufficiently large stress level. (For a discussion of the barrier model based on a rate theory approach, see Moore and Gieniewski.¹ As outlined therein, a barrier to flow having a stress biasing or lowering of the barrier enables an increase in the displacement in response to increased stress.)

The inverse stress dependence for both polymers might be considered phenomenologically to arise from a nonlinear restoring force, or strain hardening, which would lead to a nonlinear response. The higher compliance in the case of PS might arise from dominance of the viscosity (i.e.,

CREEP OF STYRENE-ACRYLONITRILE COPOLYMER AT 30.5 DEG. C
 AT STRESSES OF $\langle 1 \rangle = 0.6, \langle 2 \rangle = 0.9, \langle 3 \rangle = 1.2, \langle 4 \rangle = 1.5 \text{ E8 DYNES/CM.SQ.}$

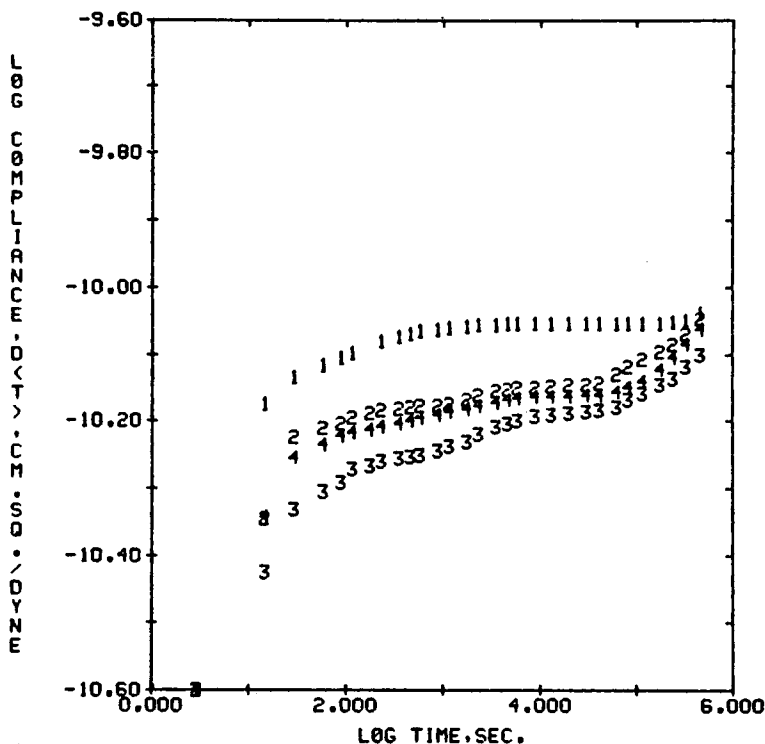


Fig. 6. Double-logarithmic plot of compliance versus time for the styrene-acrylonitrile copolymer at 30.5°C at the stresses indicated.

lower viscosity) in determining creep response and/or from the onset of crazing.

From a general phenomenological viewpoint, one could use a model composed of a stress-sensitive Voigt element to characterize the retarded response, in series with a Maxwell element containing a nonlinear spring element. This model would contain the inverse dependence of the compliance on stress for the two polymers; but in the case of SAN, the barrier to response would be lowered at the appropriate stress level leading to the normal stress dependence of the compliance.

As suggested above, the differences might also be an indication of effects of the crazing phenomenon which would give rise to the combined creep response of two materials of rather different moduli in series. Crazing effects must be considered here since crazing occurs in SAN at σ_4 but not at σ_3 (see Table I). If the compliance of the crazed material were large and its stress dependence were positive, this could give rise to the reversal at the highest stress level. This would still not account for the "inverse" stress dependence observed in the two materials, however. Since orienta-

CREEP OF STYRENE-ACRYLONITRILE COPOLYMER AT 80 DEG.C
 AT STRESSES OF $\langle 1 \rangle = 0.6$, $\langle 2 \rangle = 0.9$, $\langle 3 \rangle = 1.2$, $\langle 4 \rangle = 1.5$ EB DYNES/CM.SQ.

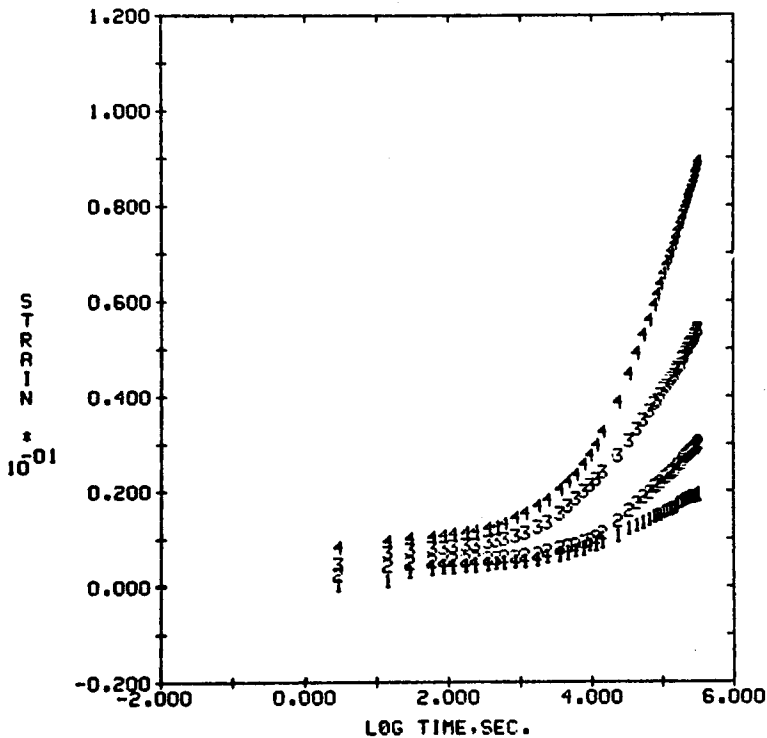


Fig. 7. Logarithmic time dependence of strain for the SAN copolymer at 80°C at the strains indicated. Strain magnitude as in Fig. 3.

tion of material in the stress direction would increase the modulus, a dependence of the degree of orientation on stress might account for this inverse dependence. Experiments to determine this stress dependence have not, to our knowledge, been carried out. Birefringence measurements in creep would be useful in this regard. (Our results³ at constant strain rates are not directly applicable since interconversion of the rheo-optic functions requires use of as yet undeveloped theory.)

Figure 7 indicates the time dependence of strain for the SAN copolymer at 80°C at the four stresses. The effect of the high temperature is seen in larger strains as compared to Figure 5. At a given time, strain again increases with increasing stress. The strain magnitude is strongly stress dependent at long times. Again, no failures were observed. Strain magnitudes are less than for polystyrene (Fig. 4) at 80°C.

Figure 8 gives a double-logarithmic plot of compliance versus time for the SAN copolymer at 80°C. The strong stress dependence at short times is not in the inverse order, but follows the dependence typical of most systems. At about 10^2 to $10^{2.5}$ sec, the stress dependence reaches a minimum, similar

CREEP OF STYRENE-ACRYLONITRILE COPOLYMER AT 80 DEG.C
 AT STRESSES OF (1)=0.6, (2)=0.9, (3)=1.2, (4)=1.5 E8 DYNES/CM.SQ.

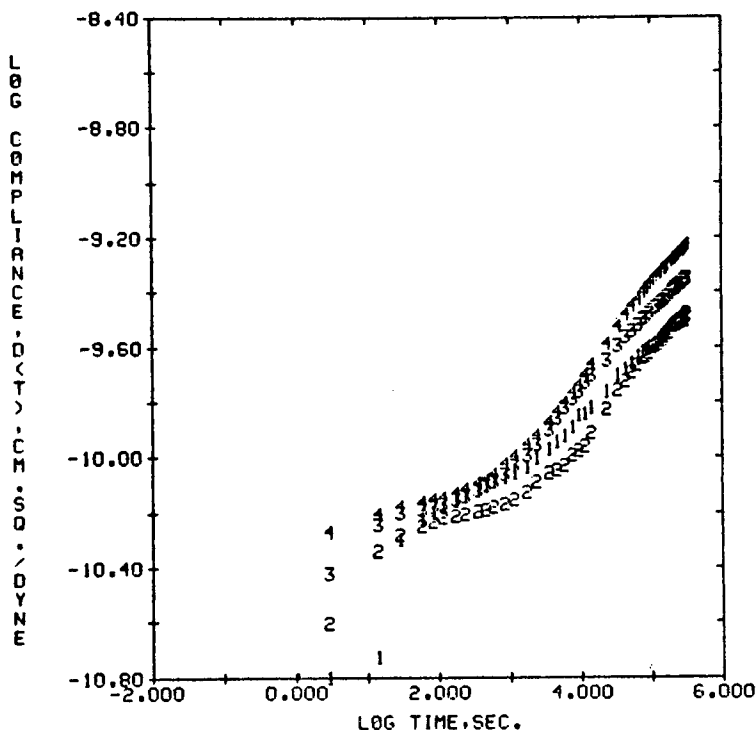


Fig. 8. Double-logarithmic plot of compliance versus time for the SAN copolymer at 80°C at the stresses indicated.

to the behavior observed for polystyrene in Figure 4. Beyond about $10^{1.8}$ sec, an inverse stress dependence appears for curves 1 and 2. This unusual behavior may indicate that two mechanisms are operative at the two lowest stress levels—one at very short times with the usual stress dependence, another at longer times with an inverse dependence. Complicating the response overall is the generally positive stress dependence of the compliance, as judged by comparing only curves 2, 3, and 4; the effects of crazing almost certainly play an important role, as discussed below. At best, interpretation of the long-time stress dependence of curves 1 and 2 is difficult and rather uncertain.

If only times larger than 10^2 sec are considered, it appears that the general effect of an increase in temperature is to decrease the stress at which the onset of positive stress dependence occurs.

Crazing in Poly(styrene-Acrylonitrile)

As indicated in Table I and in the Appendix, the stress effects on crazing are remarkably different for SAN than for polystyrene at these stress levels.

Crazing begins only at σ_4 at 30°C and at σ_2 at 80°C in SAN. The role of these effects must be considered in general in the reversal of the stress dependence for the SAN material. From the temperature dependence of the stress for the onset of crazing we can obtain a rough estimate of α_g , the thermal expansion coefficient of the glassy polymer.¹⁰ For SAN, this appears to be about $0.5 \times 10^{-4} \text{ deg}^{-1}$, about one half the magnitude of α_g we estimate from published data¹⁰ for poly(methyl methacrylate). This difference is probably not significant in view of the uncertainty in our estimate of the stress for the onset of crazing. At present we have no information on the time dependence for the onset of crazing nor on the stress and temperature dependence of creep in a system with a single well-defined craze.

We have, however, estimated times for the onset of crazing for several stress levels in PS at 30.5°C, based on results of Ziegler and Brown.¹¹ Our calculations predict crazing times of $10^{4.57}$, $10^{3.42}$, and $10^{2.81}$ sec at σ_2 , σ_3 , σ_4 , respectively, crazing not being predicted at σ_1 . This is reasonable since the stress for the onset of crazing decreases with increasing temperature and according to the above investigators,¹¹ would occur for a temperature of 30.5°C at about $0.8_6 \times 10^8$ dynes/cm² for a slightly different polystyrene (Styron 666). Crazing at 80°C would be predicted to occur almost instantaneously. (Our experimental apparatus was not designed to study the onset of crazing, however, and we have no experimental tests of our estimates.) We note that cyclic stress-strain measurements have been made on a single polycarbonate craze by Kambour, however.⁸ From information provided by Kambour,^{8,9} we estimate that, for the SAN copolymer with a void content of 60% in crazed regions,⁹ the modulus of the craze should be between 0.15 and 0.25 that of the bulk polymer. Thus, strain magnitude should be influenced significantly for a reasonably finite ratio of crazed to noncrazed material. Finally, we note that the temperature dependence described above for times larger than 10^2 sec is consistent with the observed temperature dependence of the critical stress required for the onset of crazing in poly(methyl methacrylate),¹⁰ as implied in our discussion of α_g .

CONCLUSIONS

Results of a study of the stress dependence in creep on polystyrene and on a SAN copolymer indicate that an inverse stress dependence exists for the compliance for polystyrene at 30.5°C. This is partially reversed at 80°C at times below 10^2 sec and becomes a positive stress dependence at long times. The stress dependence of the compliance for the SAN copolymer is partially reversed at 30.5°C. At 80°C, the stress dependence is positive for stresses larger than or equal to 0.9×10^8 dynes/cm². A complicated behavior is observed when results for this lower limit are compared with a level $\frac{2}{3}$ its magnitude. (An always positive stress dependence was observed in earlier work on an ABS material.^{1,2}) Material failure was ob-

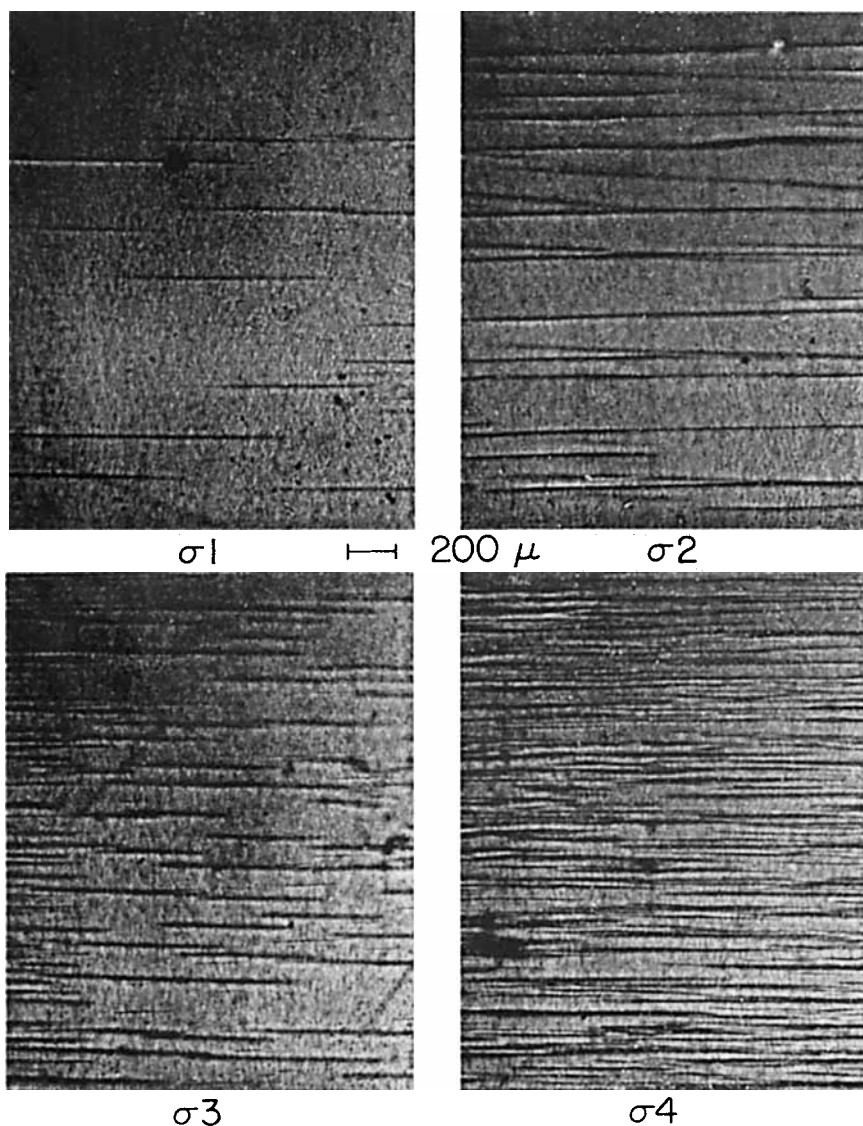


Fig. A-1. Photomicrographs of polystyrene samples at 25°C after elongation at 30.5°C at the stress levels defined in the text.

served in all cases for the polystyrene and in no cases for the SAN copolymer. The present results suggest that, although in the copolymer there may exist an enhanced local mobility which alters the stress dependence observed in pure polystyrene and which enhances the ability to deform without failure, this has to be considered in combination with the stress dependence of the onset of crazing. These results suggest that ABS is in some respects an extreme example of this trend in mobility and that the butadiene

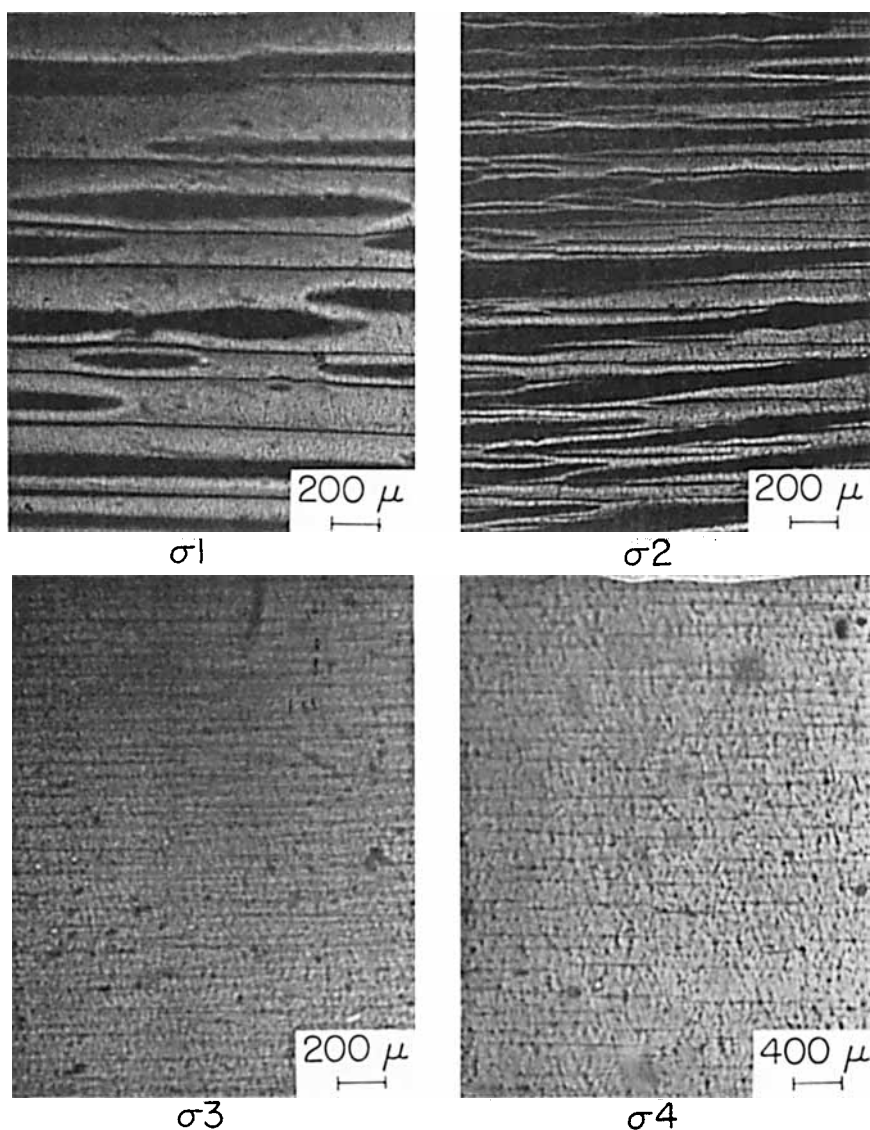


Fig. A-2. Photomicrographs of polystyrene samples at 25°C after elongation at 80°C at the stress levels defined in the text.

component provides additional mobility which leads to the experimentally observed always positive stress dependence and to deformation without failure.^{1,2} This may be provided through very local yielding around the rubber particles, analogous in some respects to crazing. In this regard stress whitening was observed to occur in ABS at stresses greater than 1.1 but less than 1.8 at 50°C, and at stresses greater than 0.9 but less than 1.8 at 80°C, in units of 10^8 dynes/cm². Thus, crazing (and whiten-

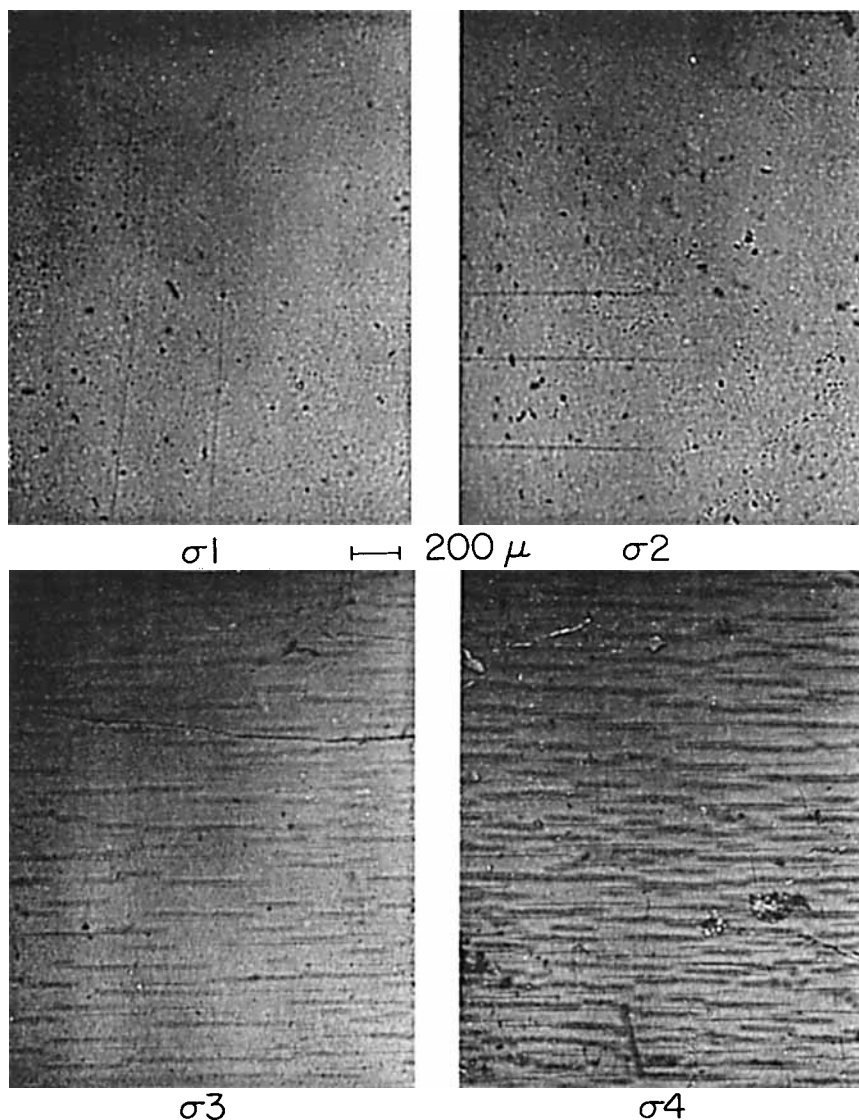


Fig. A-3. Photomicrographs of poly(styrene-acrylonitrile) samples at 25°C after elongation at 80°C at the stress levels defined in the text.

ing) occurs at increasing stresses at a given temperature in the series styrene, SAN, ABS.

As shown in a recent paper,³ some local mobility is always present since orientation as observed from birefringence studies occurs before yielding in the ABS systems studied. The present results in creep are used³ in derived calculations for comparison with birefringence data obtained at constant strain rates.

Appendix

Figures A-1 to A-3 are photomicrographs of samples of PS and SAN subsequent to creep. Photomicrographs of the latter for creep at 30.5°C were omitted since crazing occurred only at σ_4 .

These transmission photomicrographs were taken with the plane of polarization of the incident light perpendicular to the direction of the craze lines. No analyzer was used. Focusing could be carried out in a manner such that crazes could be rendered easily visible on either the front or the rear face of a sample. In several of the figures, crazes on the rear face of the sample are in focus. (See Figures A-2 at σ_1 and σ_2 , for example.) This results in an exaggerated width of the now out-of-focus upper-face crazes. These results indicate that although crazes extend through a sizable part of the sample depth, a given craze is not likely to extend to the other face of the sample.

In all three figures, the number of craze lines per unit length of sample (in vertical direction) increases as σ increases. The relationships of spacings for the different stress levels are described in Table I. A larger field of view indicates that in some cases the number of crazes per unit length is larger at the sample edges than at the center. This is easily seen, for example, at σ_3 and σ_4 for PS at 30.5°C, and at σ_2 at 80°C. Figure A-3 is an example of front-focusing. The darker horizontal shadows depict out-of-focus crazes near the rear face of the sample.

No specific numbers for craze spacings have been included because it was felt that observation of the photomicrographs, themselves, would be far more instructive and because the craze patterns are complex. It is quite evident that extremely small spacings between craze lines can occur in polymers, as in Figure A-2 at σ_4 .

References

1. R. S. Moore and C. Gieniewski, *Macromolecules*, **1**, 540 (1968).
2. R. S. Moore and C. Gieniewski, *Polym. Eng. Sci.*, **9**, 190 (1969).
3. R. S. Moore and C. Gieniewski, *J. Appl. Phys.*, **41**, 4367 (1970).
4. P. G. Kelleher, private communication, 1969.
5. L. T. Pappalardo, private communication, 1969.
6. L. C. Cessna, Jr., and S. S. Sternstein, *Fundam. Phenomena Mater. Sci.*, **4**, 45 (1967).
7. R. D. Andrews and Y. Kazama, *J. Appl. Phys.*, **38**, 4118 (1967).
8. R. Kambour and R. W. Kopp, *J. Polym. Sci. A-2*, **7**, 183 (1969).
9. R. Kambour, *J. Polym. Sci. A*, **2**, 349 (1964).
10. S. S. Sternstein, L. Ongchin, and A. Silverman, *Appl. Polym. Symposia*, **No. 7**, 175 (1968).
11. E. E. Ziegler and W. E. Brown, *Plast. Technol.*, **1**, 341 (1955).

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