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The Extensional Flow of Poly(methyl Methacrylate) and High-Impact Polystyrene at Thermoforming Temperatures

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Synopsis

The work described in the present paper was performed to establish stress–strain–time relationships at plastic sheet thermoforming temperatures. The relationships are correlated with sheet-forming "formability." Specimens of poly(methyl methacrylate) at 165°C and high-impact polystyrene at 122°C were extended to large strains at constant cross-head velocities. Initial strain rates were between 4.2×10^{-3}/sec and 1.6×10^{-1}/sec. It was found that the flow stress σ was related to the true strain ϵ and the elapsed time t by a relation $\sigma = Kt^{m'}\epsilon^n$, where K is a constant and n and m' are indices. The value of n for both materials was approximately one. The value of m' was -0.052 and -0.33 for poly(methyl methacrylate) and high-impact polystyrene, respectively. Tests were also performed in which the cross-head velocity was increased in steps. It was found that the flow stress in these tests followed the same relationship as in the constant cross-head velocity tests.

INTRODUCTION

Extensional flow of polymer melts occurs in many polymer-forming processes, for instance, fiber spinning, film blowing, flow through a die, and thermoforming of sheets.

Past work in studying extensional flow has involved some form of tensile testing under constant load,[1] constant stress,[2,3] constant strain rate,[4-9] or other.[10,11] Indirect methods, such as studying the flow from a reservoir into a die[3,12,13] or studying the drawing down of extrudate from a die[13-15] have also been used, with the advantage of being close to processing practices.

The measurement of steady-state elongational viscosities has been a prime aim; however, the nonsteady flow before the steady state sets in has also been examined; this flow involves viscoelastic and viscous components. Meissner[5] found that the stress–strain curves of a low-density polyethylene melt at 150°C showed at low strain rates an increase in the stress up to a limiting value which corresponds to an extensional viscosity. At higher strain rates, no limiting value of the stress was obtained, rather the stress–strain relation had an S-shaped curve similar to the tensile behavior of a rubber-like material. Smith[16] found, with polyisobutylene and also styrene–butadiene rubber vulcanizate, which can be considered "crosslinked molten plastics" at room temperature, that the true flow stress determined from tensile tests at constant strain rates is separable into a time effect and a strain effect.

The work described in the present paper was performed to establish stress–strain–time relationships at plastic sheet thermoforming temperatures. In a later paper,[17] the relationships will be correlated with sheet-forming "formability." The materials of interest were poly(methyl methacrylate) (PMMA) and high-impact polystyrene (HIP), and the thermoforming temperatures chosen were 165°C for PMMA and 122°C for HIP. We are not aware of any published work on the extensional flow of high-impact polystyrene at thermoforming temperatures; however, Ballman[4] reports on constant strain-rate tests on polystyrene at 300°F (149°C) and strain rates below 2.2×10^{-2}/sec. He found that steady-state (viscous) flow set in after strains of 0.2 and less. Vinogradov et al.[8] found in constant strain rate tests on polystyrene at 130°C that steady-state flow was achieved at strain rates below 6×10^{-3}/sec but not above. The maximum true strain in their experiments was about two.

Williams[10] tested poly(methyl methacrylate) in tension at 160°C and strain rates between 3.3×10^{-2}/sec to 8.3×10^{-2}/sec. He reports negligible dependence of stress on time.

EXPERIMENTAL

Materials

The investigation was conducted using $^1/_4$-in.-thick clear PMMA supplied by I.C.I. and $^1/_8$-in.-thick white opaque HIP sheets extruded by Garnite Plastics, New Zealand. Specimens machined from the sheet had the dimensions shown in Figure 1.

Apparatus

All tests were performed on a TTC Standard Instron testing machine with the Instron environmental chamber. Temperature in the environment chamber was

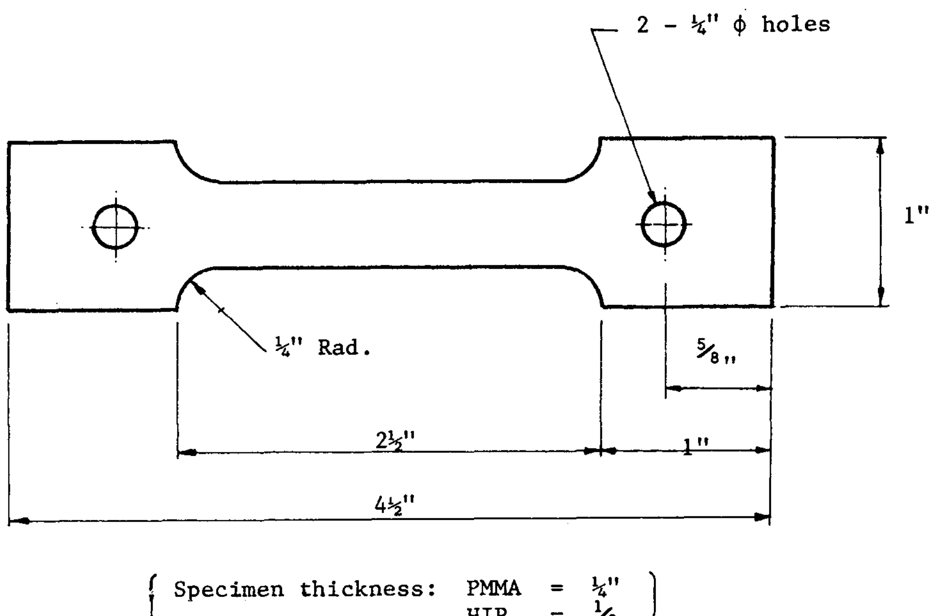

Fig. 1. Dimensions of the tensile specimens.

controlled by the Instron temperature controller. Exact temperature of the test specimens was measured using copper–Constantan wire thermocouples, taped to the specimens. In order to minimize the amount of slippage in the grips due to softening of the specimens on heating up, spring-loaded jaws were used. It was

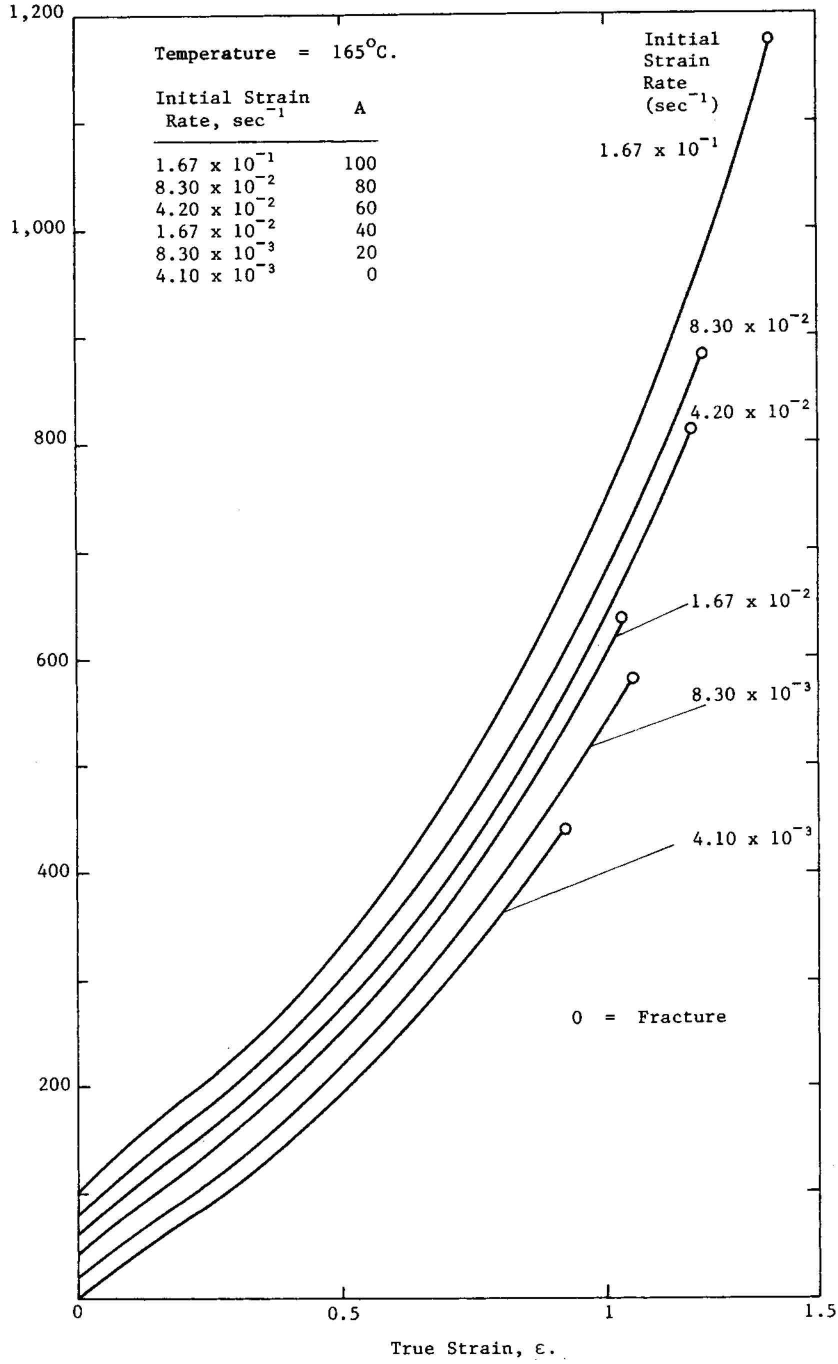

Fig. 2. Relation between true stress σ and true strain ϵ for PMMA at 165°C from constant cross-head velocity tests at initial strain rates in the range of 4.2×10^{-3} to 1.6×10^{-1}/sec.

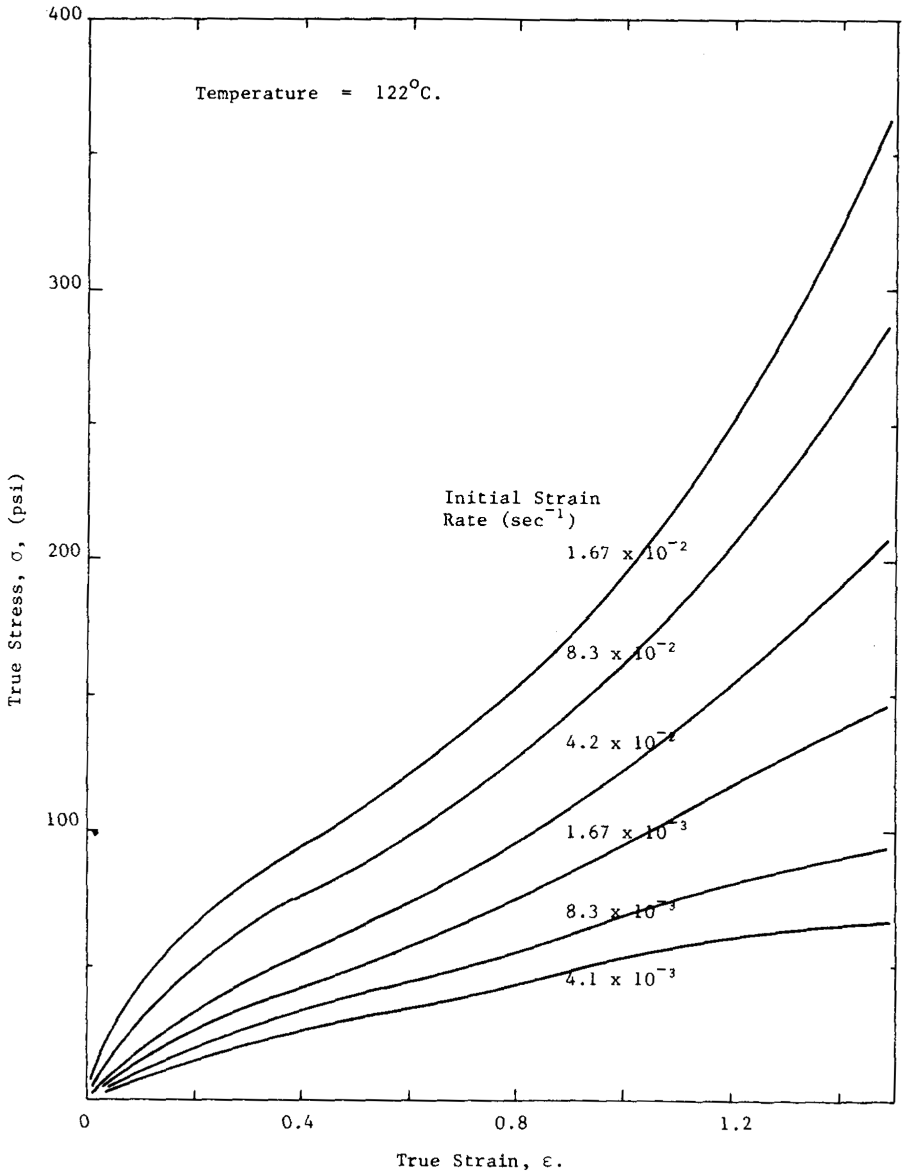

Fig. 3. Relation between true stress σ and true strain $\bullet$ for HIP at 122°C from constant cross-head velocity tests at initial strain rates in the range of 4.2×10^{-3} to 1.6×10^{-1}/sec.

found that in both materials 96% of the Instron cross-head movement was elongation of the gauge length of the tensile specimens.

Procedure

A few trial tests were required to calibrate the temperature–time relationships for different power inputs to the environmental chamber. The chamber with the necessary clamping jaws was initially heated up for about $1^1/_2$ hr. After that, the specimen was mounted. Two copper–Constantan wire thermocouples were used to measure the temperature of the specimen near the gauge length. One of

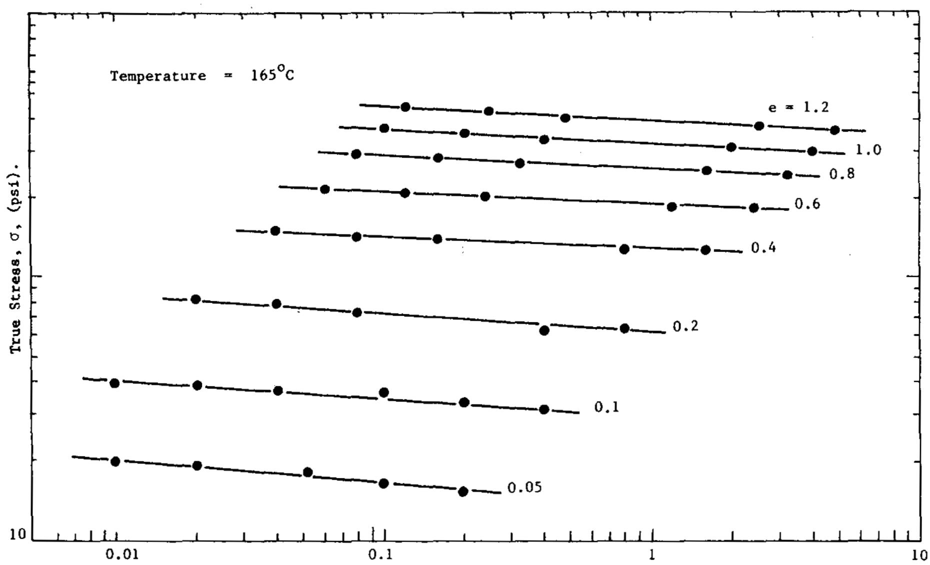

Fig. 4. Relation between true stress σ and elapsed time t for PMMA at 165°C from constant cross-head velocity tests. Each curve represents a given engineering strain e.

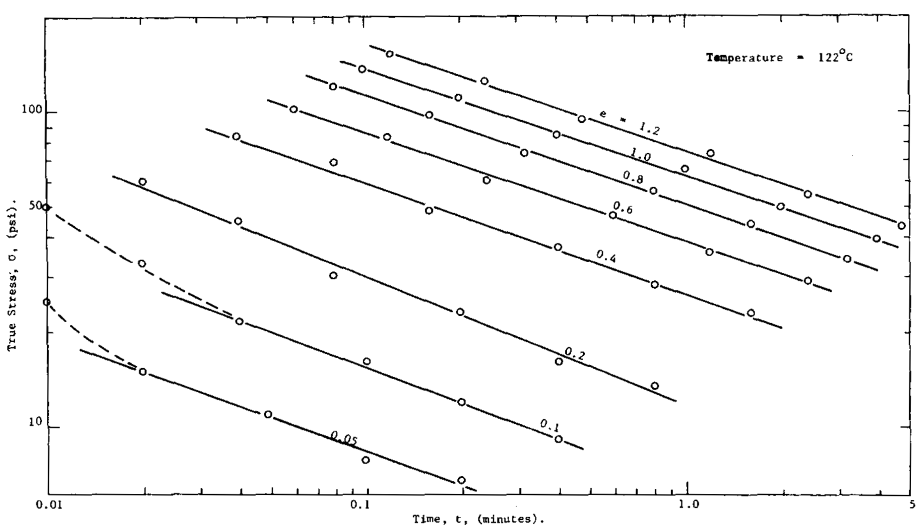

Fig. 5. Relation between true stress σ and elapsed time t for HIP at 122°C from constant cross-head velocity tests. Each curve represents a given engineering strain e.

the thermocouples was placed in a $^1/_{32}$-in.-diameter hole drilled to the midthickness of the specimen. The other thermocouple was taped to the surface of the specimen to investigate the difference in temperature between the center of the material and its surface. A heating time of roughly 25 min was arbitrarily chosen, but the exact heating time was not essential since the critical factor was the exact temperature of the tensile test specimen at testing. It was found that the temperature difference between the center of the material and its surface was less than 0.5°C.

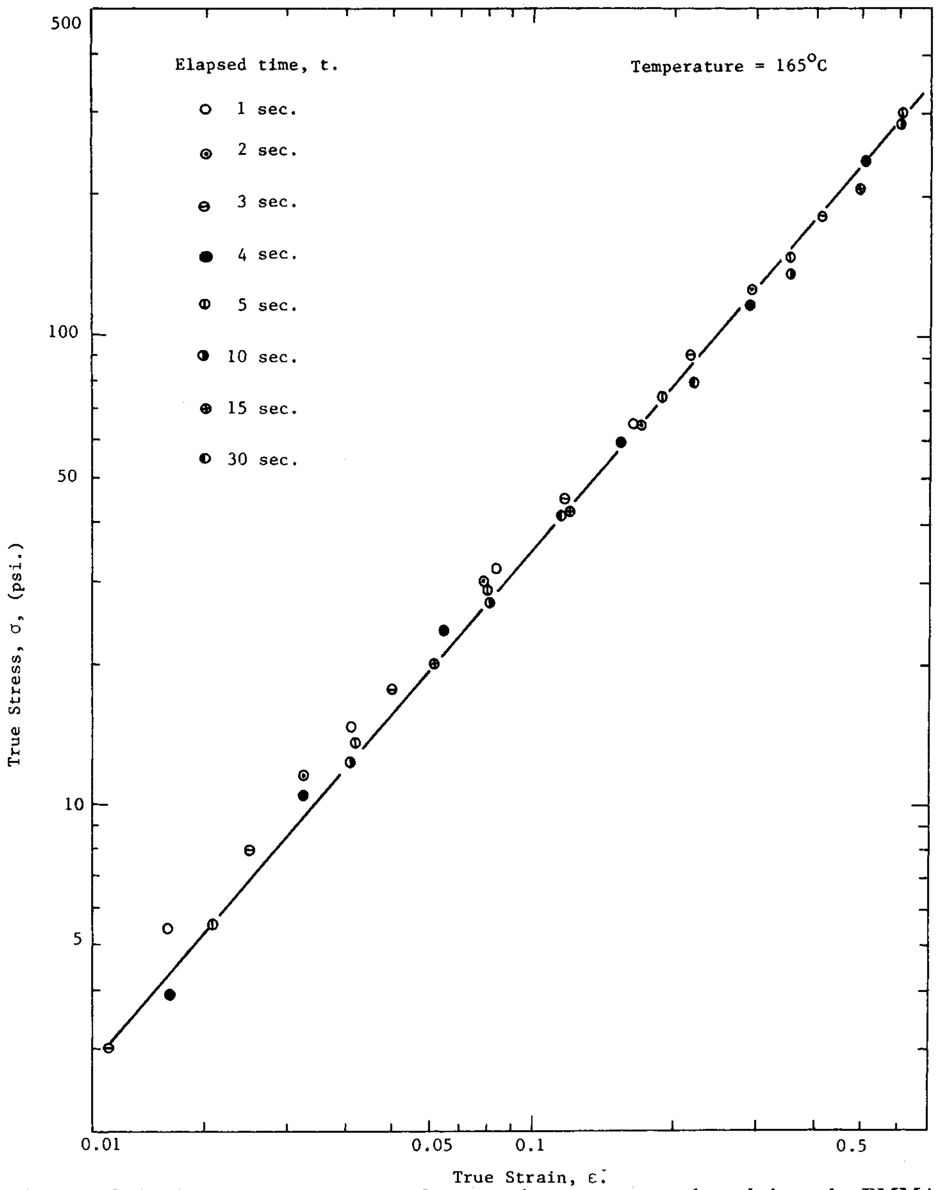

Fig. 6. Relation between true stress σ and true strain ϵ at constant elapsed time t for PMMA at 165°C. Data are from constant cross-head velocity tests.

The tensile testing of the materials followed a parallel procedure to the calibration of the environmental chamber. When the chamber was heated up, the specimen was quickly set up in the grips. With the two thermocouples taped to the surface about 1 in. apart along the gauge length, the specimen was heated to the exact required temperature which was the temperature at which the thermoforming experiment described in a following paper was carried out.[17] For PMMA specimens, this was 165°C, and for HIP, 122°C. Initial strain rates ranging from 4.2×10^{-3} to 1.6×10^{-1}/sec were used. At least four specimens were tested at any one cross-head speed. Two of the specimens were tested at

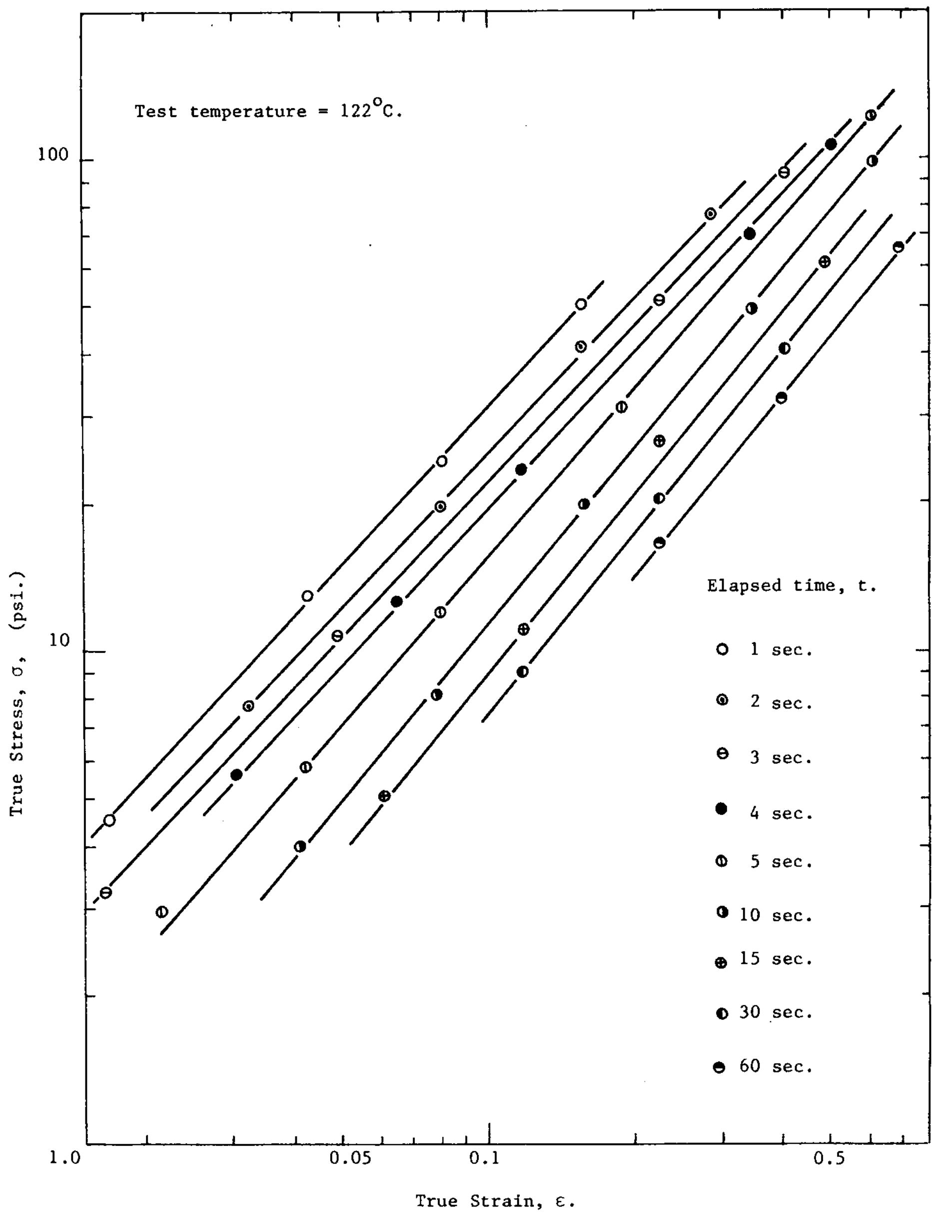

Fig. 7. Relation between true stress σ and true strain ϵ at constant elapsed time t for HIP at 122°C. Data are from constant cross-head velocity tests.

the exact mentioned temperature while the other two were tested at temperatures 1°C above and 1°C below this exact temperature to ensure that the tests were correctly conducted. All tests were duplicated if necessary. At various extensions, engineering stress temperature plots were drawn to ensure that the stress at the required temperatures lay about halfway between the stress of temperatures 1°C above and 1°C below the required temperatures. True stress–true strain curves for the materials at the required temperatures were then calculated from the load–extension curve at the required temperatures. Very

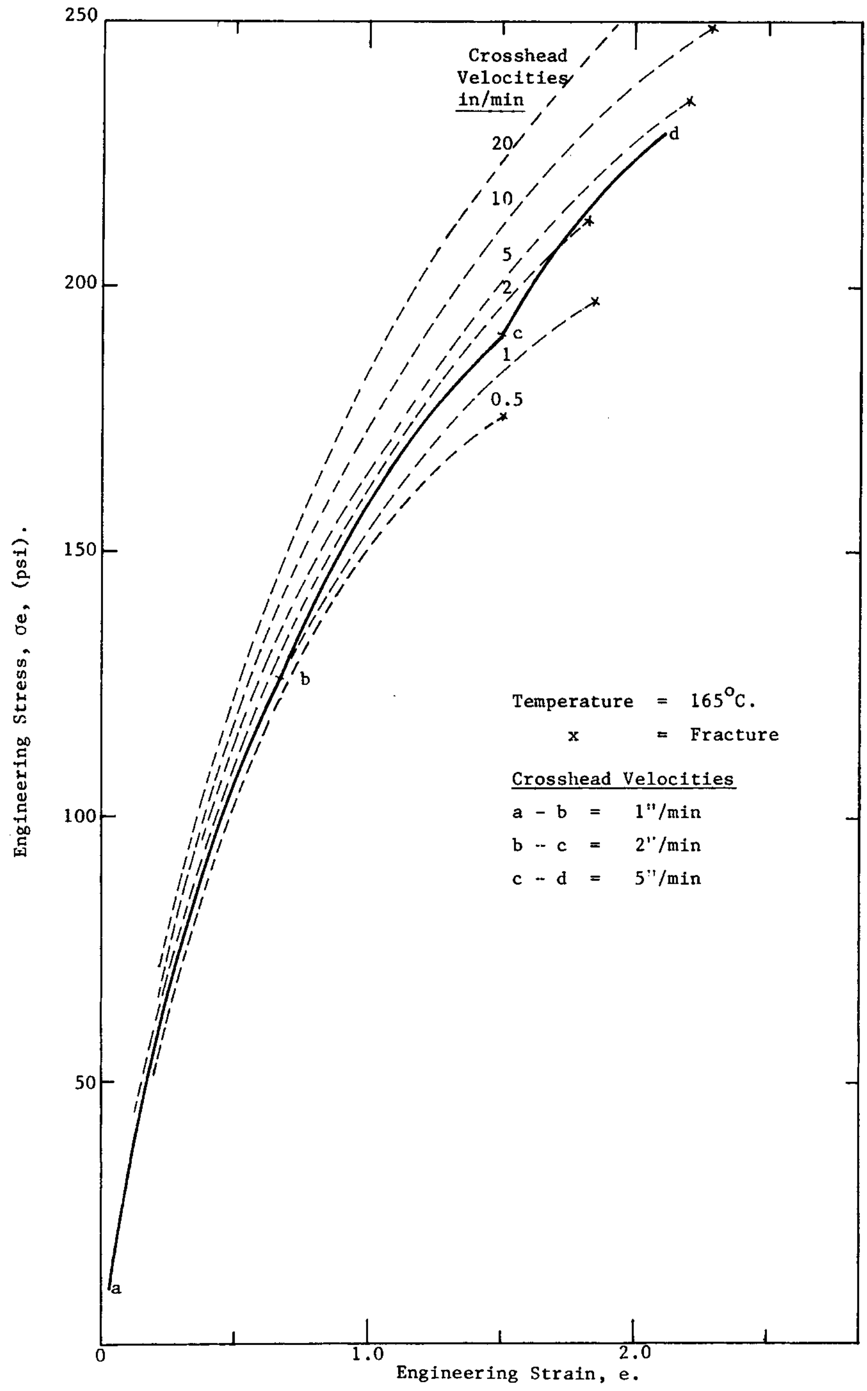

Fig. 8. Relation between engineering stress σ_e and engineering strain e for PMMA at 165°C from step-speed tests. Constant cross-head velocity data are shown dotted.

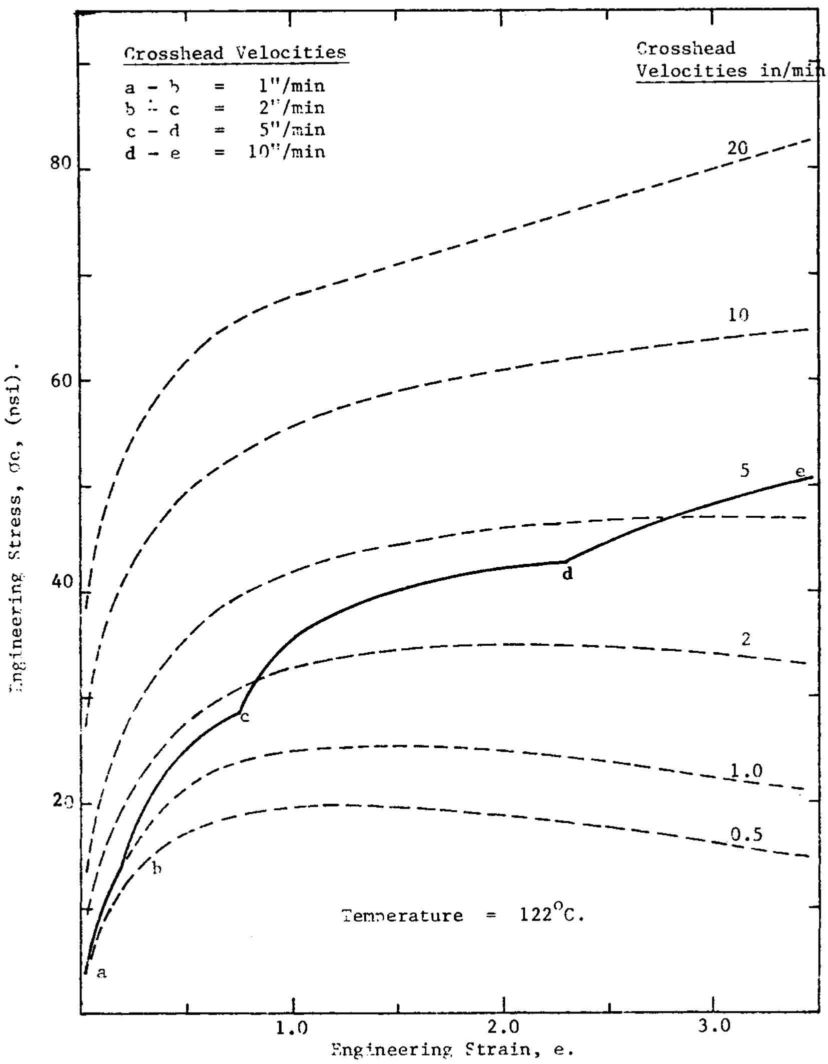

Fig. 9. Relation between engineering stress σ_e and engineering strain e for HIP at 122°C from step-speed tests. Constant cross-head velocity data are shown dotted.

little scatter was observed in the stress–strain curves for the specimens tested at the required temperature and cross-head speed. In calculating true stress, an effective Poisson ratio of $^1/_2$ was assumed. True strain was calculated from the cross-head movement since, as mentioned above, 96% of the total cross-head movement was elongation of the gauge length.

RESULTS AND DISCUSSION

Figures 2 and 3 show the true stress–true strain curves at various cross-head velocities for PMMA at 165°C and HIP at 122°C. Unlike HIP, which can be stretched without breaking to an engineering strain greater than four, it was found that PMMA specimens fractured. The stress and strain at fracture in-

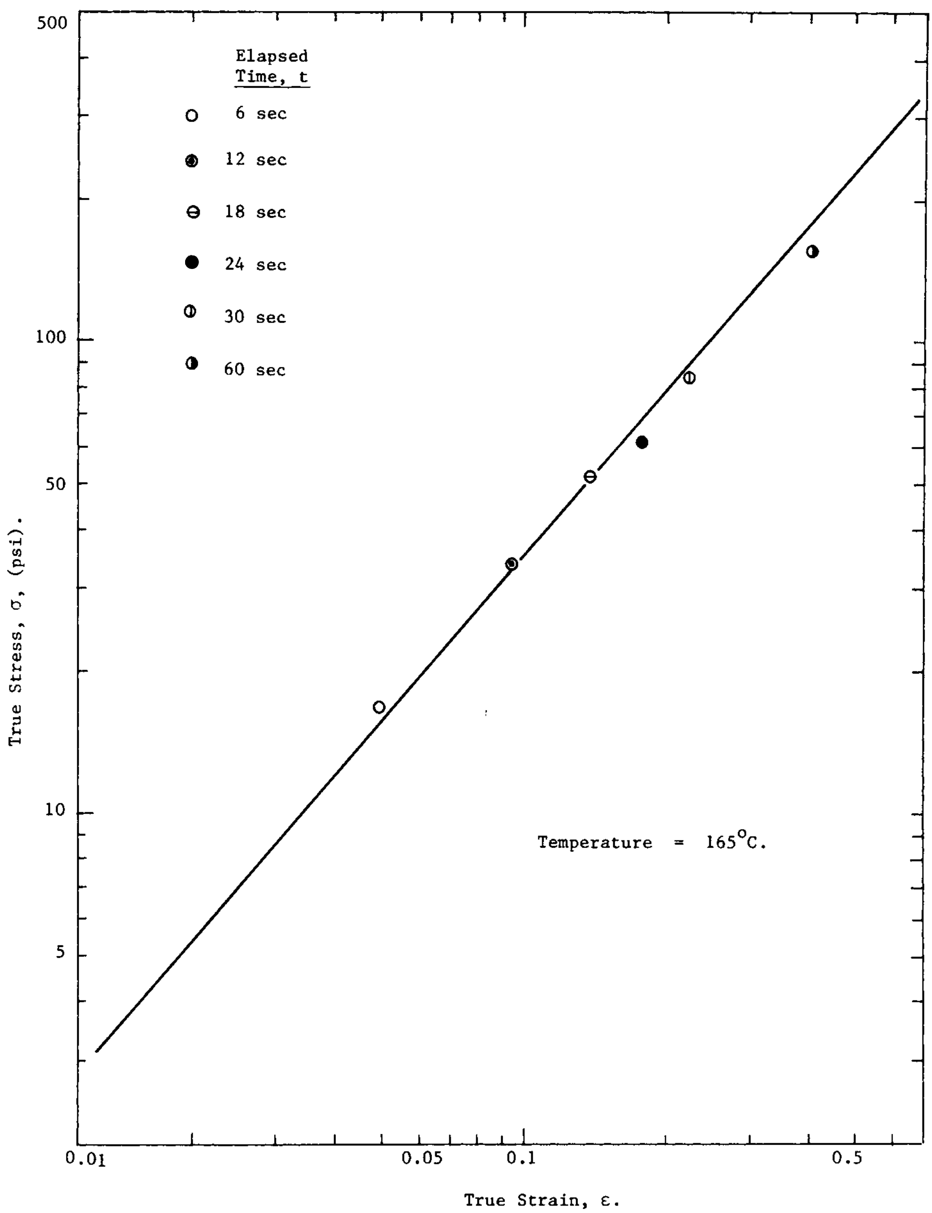

Fig. 10. Data points of true stress σ and true strain ϵ at constant elapsed time t for PMMA from step-speed change test. The line shown is that of Fig. 6.

creased with increasing cross-head speed. Such a dependence of fracture on strain rate has been observed in rubbery materials by others.[18–20]

After fracture, the two halves of the PMMA specimen retracted almost to the initial gauge length. The deformation of HIP, however, seemed to be less recoverable.

The stress–strain results were analyzed along similar lines to those followed by Smith[16] with amorphous elastomers. The logarithm of the true stress is plotted against the logarithm of the elapsed time at constant engineering strain in Figures 4 and 5 for PMMA and HIP, respectively. The logarithm of the true stress

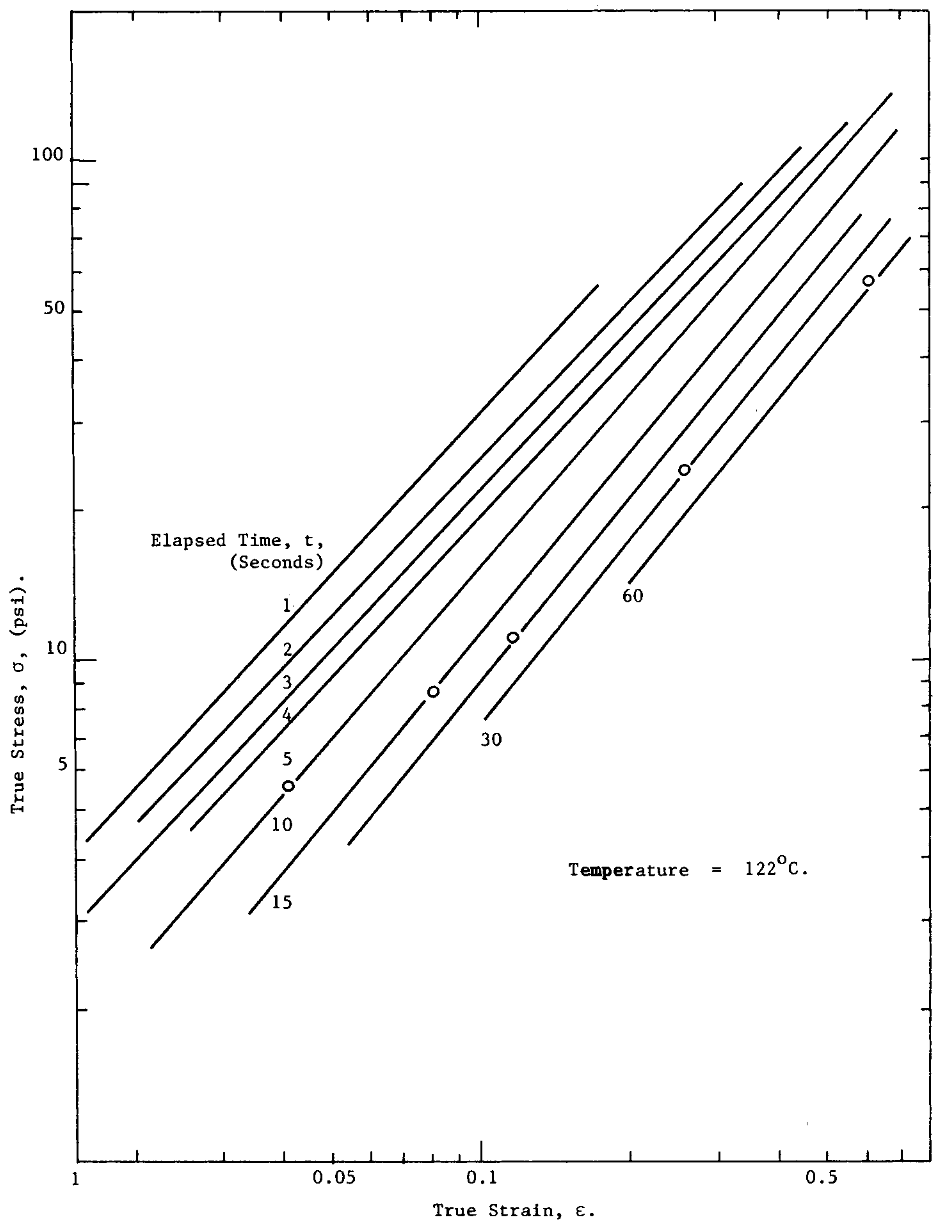

Fig. 11. Data points of true stress σ and true strain ϵ at constant elapsed time t for HIP, from step-speed test. The lines shown are those in Fig. 7.

is plotted against the logarithm of the true strain at constant elapsed time in Figures 6 and 7 for PMMA and HIP, respectively. Data points in all these figures could be fitted by straight lines, except for HIP at small times and strains (Fig. 5). Hence, a constant velocity stress–strain–time relationship of the form $\sigma = Kt^{m'}\epsilon^n$ is obeyed by these two materials. Values of m' and n are given in Table I. This sort of relationship is also followed by the data at constant strain rates of Smith[16] for SBR vulcanizates and polyisobutylene.

To determine whether the relationship $\sigma = Kt^{m'}\epsilon^n$ held for only constant cross-head speed tests or, on the contrary, was valid for more general loading patterns,

TABLE I
Values of m' and n in $\sigma = Kt^{m'}\epsilon^n$ for PMMA and HIP

Material	m'	n
PMMA	−0.052	1.0
HIP	−0.33	1.1

tensile tests were performed on PMMA and HIP at 165°C and 122°C, respectively, in which the cross-head speed was changed in steps during the straining. The resulting engineering stress–engineering strain curves are plotted for PMMA in Figure 8, and for HIP in Figure 9. Engineering stress–engineering strain curves at constant cross-head speeds are included in Figures 8 and 9 for comparison. It can be noted that a step change in cross-head speed does not cause a step change in stress so viscous (strain rate dependent) flow must be negligible in these materials at these temperatures. Stress and strain data at various elapsed times from the step-change tests are compared with the data from constant cross-head speed test in Figures 10 and 11. It can be seen that two sets of data coincide.

The conclusion is that the relation $\sigma = Kt^{m'}\epsilon^n$ is valid for a general loading sequence at these temperatures. It should be noted that a sequence of decreasing cross-head speed was not investigated.

CONCLUSION

At the thermoforming temperatures of 165°C for PMMA and 122°C for HIP, a stress–strain–time relationship of the form $\sigma = Kt^{m'}\epsilon^n$ is found.

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