Analysis of Ultraviolet Radiation Effects on Yield Stress of Polymethyl Methacrylate

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The combined effects of ultraviolet radiation and vacuum on the mechanical properties of a typical rigid plastic have been investigated as a function of strain rate, tensile test temperature, and irradiation dose. It has been shown that the yield stress can be expressed as a simple function of strain rate and test temperature for nonirradiated polymethyl methacrylate. For this polymer, whose primary degradation process under irradiation consists of scissioning with consequent production of monomer at the irradiation temperature, it is also possible to predict the yield stress in terms of the radiation dose. This has been accomplished by including a term describing the plasticizing effect of the residual monomer in the yield stress expression.

Introduction

In space flight, plastics will be subjected to environmental factors that can substantially change their properties. To predict these changes we must understand the mechanisms which cause them.

NASA Ames Research Center is developing empirical expressions to describe the changes in mechanical behavior of rigid plastics subjected to ultraviolet radiation in vacuum. In the present part of this study, polymethyl methacrylate below its glass transition temperature has been used. Based on work by various experimenters[1] in the temperature range of interest, this material was believed to undergo scission to form monomer when subjected to ultraviolet radiation at frequencies below about 2700 Å. The questions pertinent to the current study were: 1) what changes in yield stress occur when the material is exposed to the test environment; 2) can these changes be related to changes in test temperature, strain rate, and monomer concentration; 3) can the degradation process be related to the rate of impingement of incident photons; and 4) finally, and most important, can these changes be expressed analytically with a reasonable scientific foundation?

Some preliminary results from this study have been reported.[2] The present paper significantly extends the development of the equation relating yield stress to changes induced by exposure to the vacuum and ultraviolet radiation environment.

Experiment

American Society for Testing and Materials Standard D-638 tensile specimens were cut from polymethyl methacrylate (Plexiglass UVA II) $\frac{1}{32}$-in. sheet stock. Tensile tests were performed at various constant strain rates from 0.0029 to 2.9 in./in./min. The tensile specimens were tested over a temperature range from −50° to +90°C and temperature control was maintained within ±1°C for each test. For specimens modified by monomer absorption or irradiation as described below, tensile tests were run after the completion of the absorption or irradiation.

To induce absorption of methyl methacrylate monomer, the samples were first heated in a closed container for one hour at 76°C; then, monomer was placed in the bottom of the container, which was again covered, and the 76°C temperature was maintained. Different exposure times produced different monomer concentrations. After exposure, the specimens were placed for 24 hr in a heated vacuum desiccator and were maintained at approximately 70°C. The weight fraction of residual monomer was then determined gravimetrically.

The polymethyl methacrylate sheet stock was irradiated at a pressure of 10^{-6} torr for various times with the unfiltered output of the General Electric UA-2 mercury vapor lamp. The lamp was positioned so as to give one solar constant of ultraviolet radiation in the wavelength region from 2000 to 2700 Å. The surface temperature of the samples was independently maintained at 100°C within ±2°C.

Films approximately 1 mil thick were solvent cast from Plexiglass sheet stock dissolved in benzene. Absorption of methyl methacrylate monomer was induced in these 1-mil thick specimens in the same manner as already described for the $\frac{1}{32}$-in. sheet stock. The 6.125-μ infrared absorption peak in the films containing various quantities of monomer was calibrated against monomer content determined gravimetrically. The infrared absorption spectra were then compared to those of the irradiated 1-mil films to determine the amount of monomer in the irradiated polymer.

Analysis

As reported in an earlier paper,[2] it has been found that the yield stress for unmodified polymethyl methacrylate depended on the strain rate and tensile test temperature. [Similar behavior has also been noted for polyethylene terephthalate (Mylar), polyvinyl chloride, and polystyrene.[3]] A plot of yield stress vs the logarithm of the strain rate at various temperatures gave a family of parallel lines. These were shifted laterally to form one master curve as shown in Fig. 1.

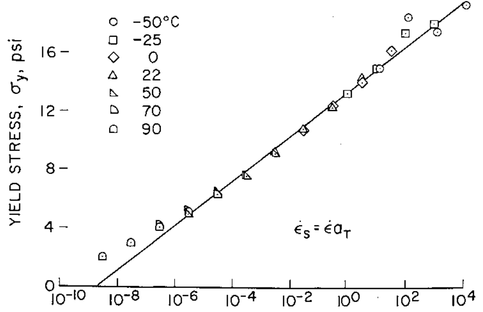

Fig. 1 Yield stress of polymethyl methacrylate as a function of shifted strain rate (referenced at 22°C).

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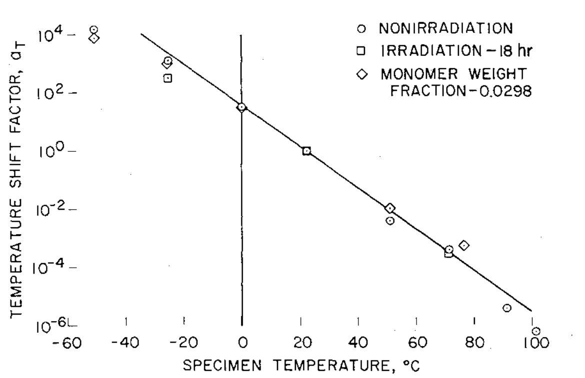

Fig. 2 The temperature shift factor for polymethyl methacrylate as a function of temperature (referenced at 22°C).

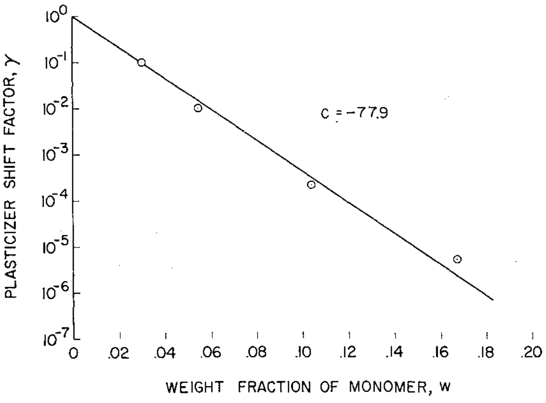

Fig. 3 The plasticizer shift factor for monomer in polymethyl methacrylate as a function of weight fraction of monomer.

The engineering portion of this curve, from a yield stress of about 2000 to 20,000 psi, was approximated by a straight line and represented by

$$\sigma_y = K \ln[(\dot{\epsilon}/\dot{\epsilon}_0)a_T] \tag{1}$$

where

σ_y = yield stress, psi
$\dot{\epsilon}$ = strain rate, in./in./min
a_T = temperature shift factor
K, $\dot{\epsilon}_0$ = const

From Eq. (1) and the data of Fig. 1, $K = 668$ psi and $\dot{\epsilon}_0 = 1.6 \times 10^{-9}$ in./in./min for these particular test samples.

The temperature shift factor a_T is shown in Fig. 2 and may be represented by

$$a_T = \exp(3.69 - 0.1676T) \tag{2}$$

(referenced at 22°C) and applicable from −50° to +70°C.

The implication of Eq. (1) is that the slope of the yield stress master curve is independent of temperature over the range of applicability of Eq. (2). A change in test temperature then becomes effectively equal to a change in strain rate. This equivalence is apparent in Eq. (1) since the variable is the product of $\dot{\epsilon}$ and a_T. In a similar manner, it was found that adding monomer, a plasticizer, has the same effect as increasing the test temperature or decreasing the strain rate. Thus, a plasticizer shift factor γ was defined by an expression

$$\gamma = e^{cw} \tag{3}$$

where

γ = plasticizer shift factor
w = weight fraction of plasticizer
c = −77.9 for methyl methacrylate

The variation of the plasticizer shift factor γ as a function of weight fraction of methyl methacrylate in polymethyl methacrylate is shown in Fig. 3. The value of the constant c will, in general, be dependent upon the kind of plasticizer molecule considered. Some additional values for c are given in Ref. 2.

If it is assumed that the monomer concentration in the polymer increases as a linear function of time of irradiation, then Eq. (3) will take the form

$$\gamma = e^{\beta t} \tag{4}$$

where

t = time at constant dose rate
β = const for a particular environment and dose rate

Thus, Eq. (1) can be generalized to include the effect of plasticizer as follows:

$$\sigma_y = K \ln[(\dot{\epsilon}/\dot{\epsilon}_0)a_T\gamma] \tag{5}$$

where γ may be given by either Eq. (3) or (4).

Results and Discussion

The variation of yield stress of polymethyl methacrylate as a function of fraction of absorbed monomer for various strain rates is shown in Fig. 4. It will be noted that the yield stress decreases substantially and linearly as the monomer content increases to about 10%. Incidentally, the dependence of yield stress on strain rate is to be expected since it is characteristic of many polymeric materials.

Results of the variation in yield stress due to time of irradiation are given in Fig. 5 along with comparable results, from Fig. 4, which will be discussed later. Initially, the yield stress decreases rapidly as the time of irradiation is increased. Thereafter, the decrease is essentially linear with further irradiation. Again, the expected variation due to strain rate is evident. The initial decrease has been attributed to the observed formation of surface defects which cannot be satisfactorily explained at present, but reached a maximum depth of about 0.004 in. within 6 hr. The reduction in yield stress in this time period is consistent with results obtained by Berry[4] on the effect of crack depth on yield stress of polymethyl methacrylate. The linear decrease in yield stress with further irradiation is, as previously mentioned, attributed to the gradual increase in concentration of

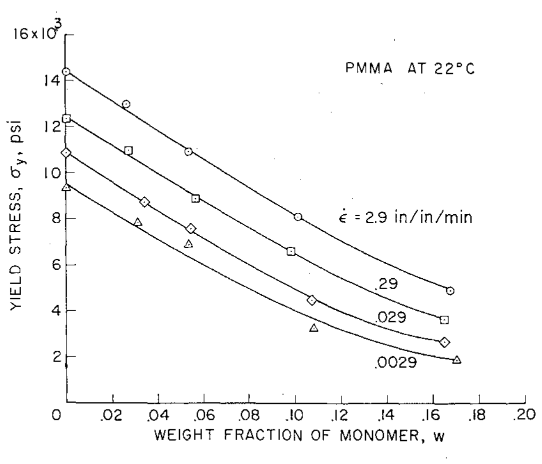

Fig. 4 The effect of strain rate and weight fraction of monomer on yield stress of polymethyl methacrylate at 22°C.

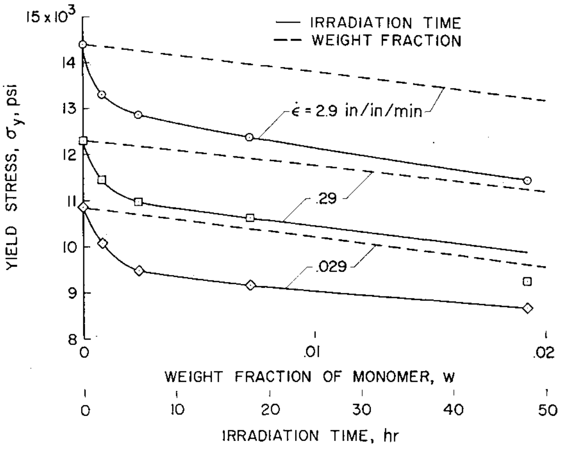

Fig. 5 Comparison of yield stresses of irradiated and absorbed monomer specimens of polymethyl methacrylate; ultraviolet flux equals one solar constant.

monomer due to scission of polymer caused by ultraviolet radiation. When the effects of surface defects are excluded linear dashed lines can be drawn which parallel the average of the three sets of irradiation data. On the assumption that this variation in yield stress is due to monomer, these dashed lines should correspond to the comparable data in Fig. 4. Therefore, a second scale on the abscissa of Fig. 5 indicates the corresponding amount of monomer which should be present in the specimens after a given time of irradiation. For example, after 50 hr of irradiation,t here should be about 2% residual monomer in the specimen to produce the observed yield stress decrease.

To verify the assumption that monomer was produced by irradiation of polymethyl methacrylate, two tests were made. First, the evolved vapors were collected and analyzed in a mass spectrometer. These vapors were found to be essentially all methyl methacrylate. Second, as described in the section on experiment, some of the same polymer was recast into specimens 1 mil thick. From the analysis of the infrared absorption peak of irradiated films and films with absorbed monomer, it was concluded that residual monomer was present in the irradiated films. The quantitative amount of monomer found in the irradiated films is indicated in Fig. 6.

There is, at present, no assured technique for measuring directly the quantity of monomer in the relatively thick irradiated sheet stock, which, of necessity, was used in the tensile tests. Since monomer is formed near the polymer surface during irradiation, the diffusion of monomer into the bulk of the material becomes an important parameter that is dependent on thickness. Thus, the thin-film data in Fig. 6 cannot justifiably be used quantitatively at present in the estimation of monomer content in the thick specimens.

Therefore, based on the data available, the assumptions on monomer content indicated in Fig. 5 appear valid and the results will be used as a quantitative measure of the increase of monomer concentration as a function of time of irradiation. Thus, a value of $\beta = -0.0312$/hr can be calculated by use of Eqs. (3) and (4).

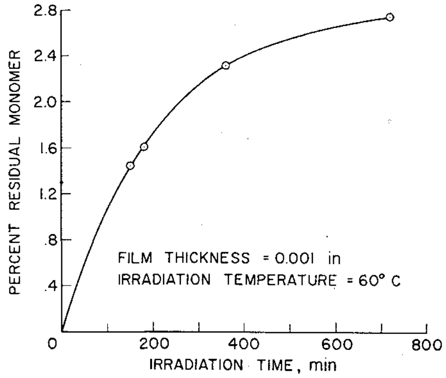

Fig. 6 The variation of residual monomer content in thin films of polymethyl methacrylate as a function of irradiation time; ultraviolet flux equals one solar constant.

The value of yield stress after a given time of irradiation and at any given value of strain rate and temperature within the limits previously indicated can, therefore, be predicted from Eq. (5) when a correction is made for surface defects; that is,

$$\sigma_y(t, T, \dot{\epsilon}) = K \ln[(\dot{\epsilon}/\dot{\epsilon}_0)a_T\gamma] - \sigma_c \qquad (6)$$

where $\sigma_c \cong 0.1(\sigma_y)_{t=0}$ based on the data of Fig. 5. This value is in reasonable agreement with those obtained by Berry.[4]

Concluding Remarks

Based on the results of this preliminary investigation, a semiempirical expression has been developed which can be used for evaluating the effects of radiation on the mechanical properties of polymethyl methacrylate. Although of limited scope to date, this is the first step of an investigation from which it is hoped that a more general prediction of the behavior of rigid polymers in the environment of space can be made.

One important outgrowth of this investigation has been the development of an equation which predicts the yield stress behavior of polymethyl methacrylate under a wide combination of temperatures, strain rates, and monomer concentrations. It is reasonable to expect that this equation can be generalized to include many of the rigid polymers.

References

[1] Cowley, P. R. E. J. and Melville, H. W., "The photo degradation of polymethyl methacrylate. Part I, The mechanism of degradation," Proc. Roy. Soc. (London) **A210,** 461–481 (1952).

[2] Lohr, J. J. and Parker, J. A., "The combined effects of ultraviolet radiation and vacuum on the tensile yield properties of polymethyl methacrylate," *American Chemical Society Polymer Preprints* (John S. Swift Co., New York, 1963), Vol. 4, no. 2, pp. 368–377.

[3] Lohr, J. J., "Yield stress master curves for various polymers below their glass transition temperatures," Trans. Soc. Rheol. (to be published).

[4] Berry, J. F., "Fracture processes in polymeric materials. 1. The surface energy of polymethyl methacrylate," J. Polymer Sci. **50,** 107–114 (1961).