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T. T. Wang^a; L. H. Sharpe^a

^a Bell Telephone Laboratories, Incorporated Murray Hill, New Jersey

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The Mechanical Properties of Rubber Particles in Rubber-Reinforced Glassy Polymers

T. T. WANG AND L. H. SHARPE

*Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey 07974*

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ABSTRACT

The effect of thermal stresses on mechanical properties of the rubber particle in rubber-reinforced glassy polymers is studied. It is found that the rubber particle in the glassy polymer tends to be softer than the one in its stress-free state because of thermally induced hydrostatic tension which lowers the glass temperature of the rubber particle. The analysis is applied to the case of ABS, and the results show that the shift of glass temperature is significant near the T_g of the rubber particle in its free state. The change in the mechanical properties of the rubber particle in ABS due to the shift is also analyzed.

INTRODUCTION

THE PRESENT paper is concerned with the actual temperature dependent mechanical properties of rubber particles in a glassy matrix, the knowledge of which is important in understanding the effective mechanical properties of rubber-reinforced glassy polymers.

When a rubber-filled glassy polymer is subjected to temperature changes, a state of hydrostatic tension is developed within the rubber particle due to the difference in the thermal expansion coefficients of the rubber particle and the glassy matrix. Since the mechanical properties of the rubber are pressure sensitive a rubber particle in the glassy matrix may have different properties from one in the stress-free state.

To investigate the effect of pressure on the mechanical properties of the rubber particle an idealized model is conceived in which a spherical rubber particle is embedded in an infinite body of glassy material. The result of the stress analysis is then coupled with an experimental relation which describes the shift of the glass temperature with respect to pressure.

The analytical expression is subsequently applied to the case of ABS (Acrylonitrile-Butadiene-Styrene) and the results indicate that the lowering of the glass temperature is rather pronounced near the glass temperature of

the unrestrained rubber. As a result, the rubber particle in ABS remains in the rubbery state over a wider temperature range and is softer than the one in the stress-free state.

ANALYSIS

We consider a rubber-reinforced glassy polymer and focus our attention on a given rubber particle in the composite. The rubber particle is properly bonded to the matrix to form a mechanically strong interface.

Suppose that at the manufacturing temperature, T_0 , the composite is everywhere free from stresses and let \hat{T}_g be the glass temperature of the rubber particle in this stress-free state. As the temperature of the composite is lowered, a state of hydrostatic tension is developed in the rubber due to the difference in the thermal expansion coefficients of the inclusion and the matrix. Consequently, the actual T_g of the rubber is lowered somewhat, say to T_g^1 ($T_g^1 < \hat{T}_g$) which results in softening of the rubber. The softened rubber in turn alters the stress distribution in itself and lessens the amount of hydrostatic tension. Thus the actual T_g of the rubber is shifted higher, say from T_g^1 to T_g^2 ($T_g^1 < T_g^2 < \hat{T}_g$), resulting in slight stiffening of the rubber. As the process keeps repeating itself, an equilibrium state is finally reached in which the actual T_g of the rubber in the composite is no longer the same as \hat{T}_g . The mechanical properties of the restrained rubber (in glassy

polymer) are therefore different from the unrestrained one at a given temperature. It may be noted that this effect has so far escaped attention in studies of the mechanical properties of rubber-reinforced glassy polymers [1, 2]*.

To evaluate the shift of T_g for the rubber particle we consider a model composed of a spherical rubber particle of radius R which is surrounded by an infinite glassy matrix (Fig. 1). Because of the local nature of the stress

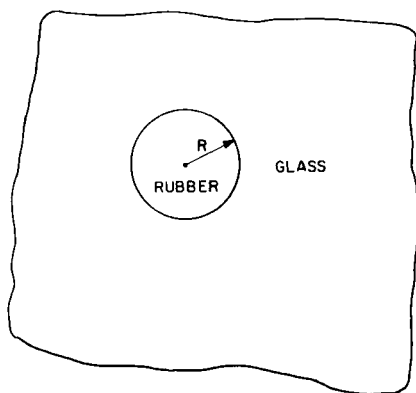


Figure 1.
Model of a rubber particle in a glassy matrix.

* A somewhat related problem—effects of differential thermal expansion of rubber particle and glassy matrix on mechanical behavior of the matrix in the vicinity of the rubber particle—has recently been discussed. See Beck, R. H., et al., *J. Poly. Sci., Part B, Poly. Letters* 6, 707 (1968).

distributions one expects that such a model would provide a good approximation to the actual picture of a rubber particle in the rubber-reinforced glassy polymer if the volume fraction of the rubber in the glassy polymer is sufficiently small.

We assume, for the sake of simplicity, that the mechanical properties of the glassy polymer remain unchanged at temperatures below T_o and that when T_g of the rubber is shifted by a certain amount, the temperature dependent Young's modulus and shear modulus are also shifted by the same amount at all temperatures.

The thermoelasticity solutions* to the present problem are readily available elsewhere [3]. Applying the proper boundary conditions, namely, the radial displacement at the center of the rubber is zero, the radial stresses and radial displacements at the interface are equal for the glassy matrix and the rubber, and the radial stress of the glassy matrix at infinity vanishes, we obtain the expressions for the hydrostatic pressures on the rubber P^r and the glassy matrix P^g at a given temperature T as follows:

$$P^r = \frac{1}{3} \frac{(T - T_o)(\alpha^r - \alpha^g)E^g}{\frac{1 - 2\nu^r}{\lambda} + \frac{1 + \nu^g}{2}} \quad (1)$$

$$P^g = 0 \quad (2)$$

where, with the superscripts r and g representing respectively the rubber and the glassy polymer, α is the volume thermal expansion coefficient, ν the Poisson's ratio, E the Young's modulus and $\lambda = E^r/E^g$. For convenience, α 's are assumed to be constant in the above analysis.

Before we relate the pressure change in the rubber to the shift in glass temperature it is recalled that the existing thermodynamic relation between pressure and glass temperature [4, 5] does not correlate satisfactorily with experimental observations for many substances [6-8]. A brief survey of test data [6, 9, 10, 11] shows that under hydrostatic pressure ($P > 0$) the value of $\frac{dT_g}{dP}$ is approximately constant and ranges between 0.004 and 0.044

$^{\circ}\text{C}/\text{bar}$ for a variety of polymers. In particular, the coefficient $\frac{dT_g}{dP}$ of natural rubber was found to be 0.024 $^{\circ}\text{C}/\text{bar}$ and we will use this value later for

* Here it is tacitly assumed that the rubber behaves elastically. Because of the viscoelastic effect of the rubber the present analysis provides the severest situation that could happen to the rubber. A better analysis can be had if one takes into account the viscoelastic effect.

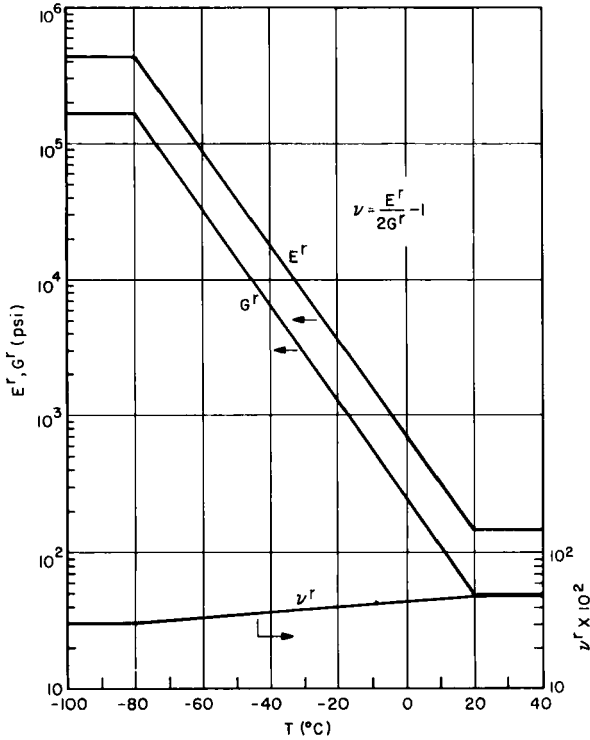


Figure 2. Temperature-dependent mechanical properties of rubber particles.

polybutadiene in our illustrative calculation. If one assumes that these data are also valid when the materials are under hydrostatic tension ($P < 0$) then it may be safe to adopt the following form for the pressure dependent glass temperature,

$$\frac{dT_g}{dP} = a \tag{3}$$

where a is a constant which ranges between 0 and 0.05 °C/bar.

Combining Eqs. (1) and (3) and noting that P^r is actually the difference between the present pressure and the atmospheric pressure we obtain

$$\Delta T_g = \frac{a}{3} \frac{(T - T_0)(\alpha^r - \alpha^g)E^g}{\frac{1 - 2\nu^r}{\lambda} + \frac{1 + \nu^g}{2}} \tag{4}$$

where $\Delta T_g (= T_g - \hat{T}_g)$ is the shift in T_g at a given temperature T , and λ and ν^r are in general transcendental functions of $(T + \Delta T_g)$. Equation (4)

provides us with an analytical expression whereby the amount of shift at a given temperature can be obtained for a particular composite material.

As an example, we consider an ABS material. The physical constants of the styrene matrix are $\alpha^g = 3.3 \times 10^{-4}/^\circ\text{C}$, $E^g = 4.35 \times 10^5 \text{psi}$, $\nu^g = 0.3$.* The temperature dependent mechanical properties of the rubber particles will be somewhat idealized in a piecewise linear manner as shown in Figure 2. Or, expressed mathematically

$$E^r(T) = E^g \left(\frac{1}{3000} \right)^{\frac{T+80}{100}} \text{psi}$$

$$G^r(T) = G^g \left(\frac{1 + \nu^g}{3000 \times (1 + \nu_o^r)} \right)^{\frac{T+80}{100}} \text{psi}$$

where G is the shear modulus and $\nu_o^r (= 0.475)$ is the Poisson's ratio of the rubber at 20°C . In addition, the thermal expansion coefficient of the rubber α^r is $8.1 \times 10^{-4}/^\circ\text{C}$.

If we assume that under dynamic stretching the lateral deformation of the rubber is in phase with the longitudinal deformation [13] then at a given temperature, ν^r is related to E^r and G^r as in linear elasticity

$$\nu^r(T) = \frac{E^r}{2G^r} - 1.$$

The stress free temperature T_o is taken to be 80°C which is the temperature at which the glassy matrix begins to soften in heating. Substituting these values into (4), ΔT_g may be solved for given T and a .

Figure 3 shows the results for some selected values of a . The amount of shift appears to be quite substantial near \hat{T}_g of the rubber.

In Figure 4 we show how the actual E vs T curve will look for the rubber particle in ABS when $a = 0.024 \text{ }^\circ\text{C}/\text{bar}$. The shift widens considerably the temperature range of the rubbery state and renders the rubber particle softer than the one in the stress-free state at a given temperature.

* Here we use the real parts of the complex mechanical constants. The values given are those obtained at high strain rates.

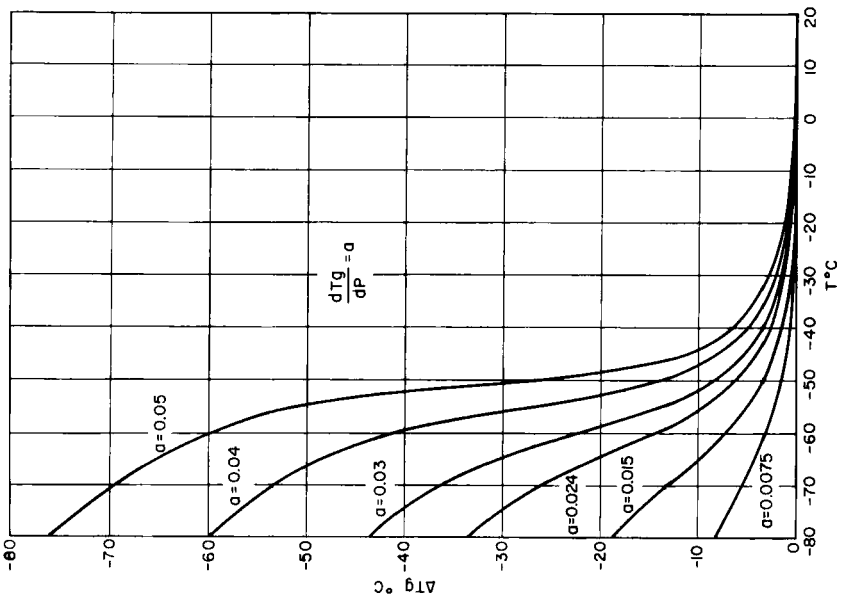


Figure 3. Shift of T_g of the rubber particle in the glassy matrix due to temperature changes.

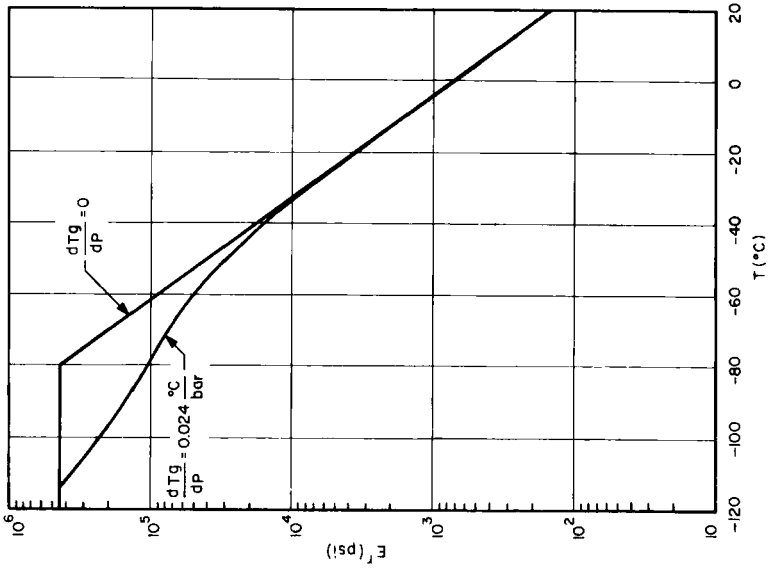


Figure 4. Comparison between the temperature-dependent Young's moduli of a free rubber particle and a rubber particle in the glassy matrix.

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REFERENCES

1. E. H. Merz, G. C. Claver, and M. J. Baer, "Studies on Heterogeneous Polymeric Systems," *J. Polymer Sci.*, **22**, (1956), p. 325.
2. S. Newman, and S. Stella, "Stress-Strain Behavior of Rubber-Reinforced Glassy Polymers," *J. Appl. Polymer Sci.*, **9**, (1965), pp. 2297-2310.
3. S. Timoshenko, and J. N. Goodier, *Theory of Elasticity*, McGraw-Hill Book Co., New York, (1951).
4. P. Ehrenfest, Commun. Kammerlingh Onnes Lab. University Leiden, Suppl. (Leiden, 1933), p. 75b.
5. R. O. Davies, and G. O. Jones, "The Irreversible Approach to Equilibrium in Glass," *Proc. Roy. Soc. (London)* **A217**, (1953), p. 26.
6. J.-M. O'Reilly, "The Effect of Pressure on Glass Temperature and Dielectric Relaxation Time of Polyvinyl Acetate," *J. Polymer Sci.*, **57**, (1962), p. 429.
7. M. Goldstein, "Some Thermodynamic Aspects of the Glass Transition: Free Volume, Entropy, and Enthalpy Theories," *J. Chem. Phys.* **39**, (1963), p. 3369.
8. G. Gee, "The Thermodynamic Analysis of the Effect of Pressure on the Glass Temperature of Polystyrene," *Polymer*, **7**, (1966), p. 177.
9. K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z.*, **183**, (1962), p. 110.
10. S. Matsuoka, and B. Maxwell, "Response of Linear High Polymers to Hydrostatic Pressure," *J. Polymer Sci.*, **32**, (1958), p. 131.
11. J. E. Anderson, D. D. Davis, W. P. Slichter, "Pressure Dependence of Molecular Motion in Some Polymers," To be published in *Macromolecules*.
12. N. Hirai, and H. Eyring, "Bulk Viscosity of Polymeric Systems," *J. Polymer Sci.* **37**, (1959), p. 51.
13. Z. Rigbi, "Phase Shifts in Stress-Strain Relationships of Viscoelastic Materials," *Rheologica Acta.*, **5**, No. 1, (1966), p. 28.