Effects of Strain Rate and Comonomer on the Brittle–Ductile Transition of Polymers

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Synopsis

The effect of rate on the brittle–ductile transition of polymers can be given by an Arrhenius-type equation with activation energy between those of α and β transitions and given by

$$E_b = \{1/(T_g - T_\beta)\}\{(T_b - T_\beta)E_\alpha + (T_g - T_b)E_\beta\}$$

where E_b is the activation energy for brittle–ductile transition, E_α is that for α transition, E_β is that for β transition, T_g is the glass transition temperature, T_b is the brittle–ductile transition temperature at 0.1 min.$^{-1}$, T_α is the α transition temperature at 1 cps, and T_β is the β transition temperature at 1 cps. The plots of T_b versus the weight fraction (w) of comonomer are sigmoidal, with an inflection point at $w = 0.5$.

INTRODUCTION

Previously we found that plastics can be deep drawn and ironed at temperatures above their brittle–ductile transition temperature T_b.[1] Usually, T_b is conveniently measured at about 0.1 min^{-1} tensile strain rates,[2] whereas the deep-drawing and ironing speeds are about 100 ft/min,[3] or about 10^3 min^{-1}. Thus, it is desirable to know the rate effect on T_b. On the other hand, knowledge of the effect of comonomer on the T_b of copolymers is desirable for designing ductile polymers.

Our results show that the rate effect on T_b can be given by an Arrhenius-type equation with activation energy between those for α and β transitions, and the plot of T_b versus the weight fraction (w) of comonomer is sigmoidal with an inflection point at $w = 0.5$.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) used is Du Pont's Elvacite 2041, $\bar{M}_w = 480{,}000$. Poly(ethyl methacrylate) used is Du Pont's Elvacite 2042, $\bar{M}_w = 170{,}000$, $\bar{M}_n = 75{,}000$. Poly(n-butyl methacrylate) used is Du Pont's Elvacite 2044, $\bar{M}_w = 269{,}000$. Poly(cyclohexyl methacrylate) used is prepared by solution poly-

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merization in toluene with azobisisobutyronitrile, $\bar{M}_w$ = 150,000. Polysty-
rene used is prepared by solution polymerization in toluene with azobisisobu-
tyronitrile, $\bar{M}_w$ = 630,000, $\bar{M}_n$ = 380,000. Poly(vinyl chloride) used is Airco's
480, containing about 97% vinyl chloride and 3% propylene as comonomer,
$\bar{M}_w$ = 57,000, $\bar{M}_n$ = 38,000. Phenoxy resin used is Union Carbide's PKHH,
MW = 30,000. All copolymers of methyl methacrylate/n-butyl methacrylate
and styrene/n-butyl methacrylate are prepared by solution polymerization in
toluene with azobisisobutyronitrile, $\bar{M}_w \simeq$ 480,000; $\bar{M}_n \simeq$ 192,000.
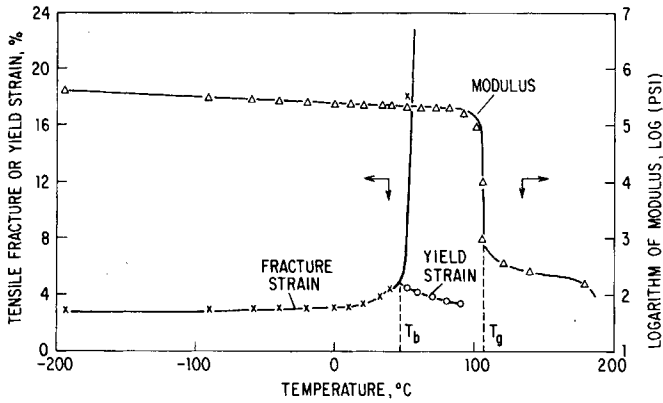

Fig. 1. Tensile strain and modulus behavior of poly(methyl methacrylate) at 0.1 min^{-1} strain
rate.

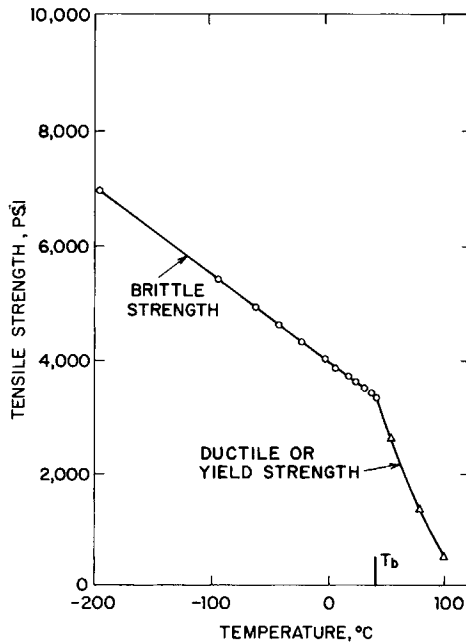Fig. 2. Tensile strength of poly(methyl methacrylate) at 0.1 min^{-1} strain rate.

TABLE I

Glass, α, β, and Brittle-Ductile Transition Temperatures for Some Homopolymers[a]

	T_g, °C	T_α, °C	T_β, °C	T_b, °C	$q = (T_g - T_b)/T_g$ using °K
Poly(methyl methacrylate)	105	120	25[b]	45	0.159
Poly(ethyl methacrylate)	65	78	20[b]	23	0.124
Poly(n-butyl methacrylate)	20	60	20[b]	−25	0.154
Poly(cyclohexyl methacrylate)	90	133	−80[b]	68	0.061
Polystyrene	100	90	50[c]	90	0.027
Poly(vinyl chloride)	80	85	−40[d]	10	0.198
Polycarbonate of bisphenol A	150	150	−100[e,f]	−200[g]	0.835
Phenoxy (reaction product of epichlorohydrin/bisphenol A, MW ~30,000) resin	88	—	—	−60	0.401

[a] T_g = Glass transition temperature; T_α = α transition temperature; T_β = β transition temperature, T_b = brittle–ductile transition temperature at 0.1 min⁻¹. All T_α and T_β are from dynamic mechanical measurements at 1 cps, except for (f), which is by dielectric measurements.

[b] J. Heijboer, in *Physics of Non-crystalline Solids*, North Holland Publishing Co., 1965, pp. 231 ff.

[c] S. G. Turley and H. Keskkula, *J. Polym. Sci. C*, 14, 69 (1966).

[d] W. Sommers, *Kolloid Z.*, 167, 97 (1959); K. Schimieder and K. Wolf, *ibid.*, 134, 149 (1953); G. W. Becker, *ibid.*, 140, 1 (1955).

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[f] S. Matsuoka and Y. Ishida, *J. Polym. Sci. C*, 14, 247 (1966).

[g] R. A. Ekvall and J. R. Low, Jr., *J. Appl. Polym. Sci.*, 8, 1677 (1964).

Tensile Measurements

Specimens of $\frac{1}{4}$ in. × 2 in. × 0.004 in. are prepared by casting from polymer solutions in toluene (for acrylics and styrene), methylethyl ketone (phenoxy), or cyclohexanone [poly(vinyl chloride)]; baked at 120°C for 24 hr under vacuum to remove the solvents; and then annealed at progressively lower temperatures for 48 hr.

Tensile stress–strain curves are obtained by using an Instron tester at various strain rates and temperatures.

RESULTS

The T_b can be determined either from the fracture strain-versus-temperature plots, or from the tensile strength-versus-temperature plots. The two methods give exactly the same results. As an example, Figure 1 shows the fracture strain-versus-temperature plot at 0.1 min⁻¹ strain rate for poly-(methyl methacrylate). At low temperatures, the fracture strains are less than 5%, but increase rapidly at about 45°C, which is the T_b. Figure 2 shows the tensile strength-versus-temperature plot at 0.1 min⁻¹ strain rate for poly-(methyl methacrylate). The break point at 45°C is the T_b. The upper curve is the brittle strength and the lower curve is the ductile (yield) strength.

Table I summarizes the T_b at 0.1 min⁻¹ strain rate thus obtained for a number of homopolymers. Those for the copolymers are shown in Figures 3

and 4. The Arrhenius plot of the rate effects on T_b are given in Figure 5. The activation energies thus obtained are listed in Table II.
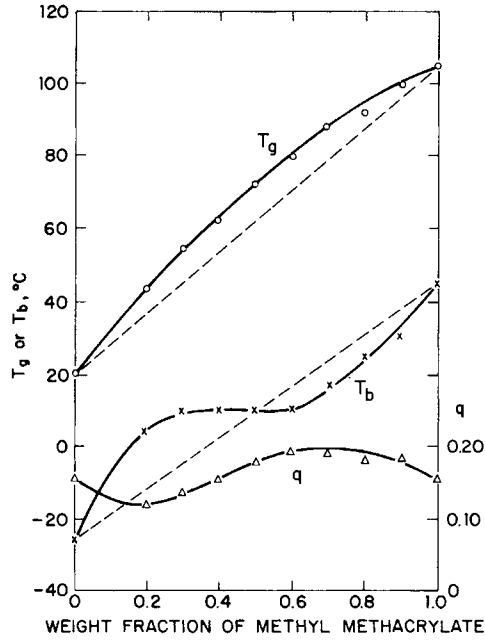

Fig. 3. Glass transition, brittle–ductile transition temperatures, and q values for copolymers of methyl methacrylate and n-butyl methacrylate.
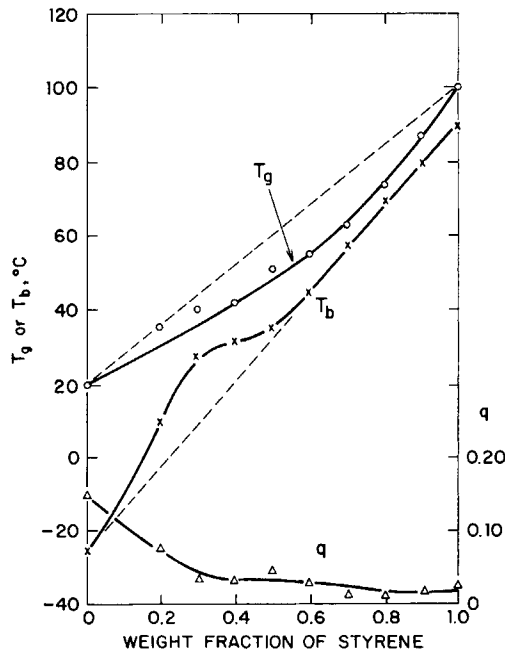

Fig. 4. Glass transition, brittle–ductile transition temperatures, and q values for copolymers of styrene and n-butyl methacrylate.

Our T_b value of 90°C for polystyrene is identical to the one quoted by Andrews.[4] Our T_b value of 45°C for poly(methyl methacrylate) agrees reasonably with a value of 55°C reported by Vincent.[2] On the other hand, our value of 10°C for poly(vinyl chloride) is very different from the value of −75°C reported by Vincent.[2] The cause of this disparity is unknown.

DISCUSSION

Ductility Versus Stiffness

Figure 1 shows that modulus undergoes a transition over several decades at the glass transition temperature (T_g), but the fracture strain undergoes a transition at T_b. The T_g is related to the stiffness, T_b to the ductility.

A polymer is sticky and rubbery above T_g; brittle below T_b; hard and ductile between T_g and T_b. Thus, the wider the breadth between T_g and T_b, the more useful a polymer will be as hard and ductile plastics and coatings. We may thus define a ductility parameter, q, based on the ratio of $T_g - T_b$ to T_g.

Table I shows that q values $[= 1 - (T_b/T_g)]$ are not constant, ranging from a high value of 0.853 for polycarbonate to a low value of 0.061 for poly(cyclohexyl methacrylate). The q value may be regarded as a ductility parameter. The higher the value, the greater the ductility.

Effect of Rate

Figure 5 shows that the rate effect on T_b can be given by an Arrhenius-type equation:

$$\Delta \left(\frac{1}{T_b} \right) = - \frac{2.303R}{E_b} \Delta (\log v) \tag{1}$$

where T_b is the brittle–ductile transition temperature, v is the strain rate, R is the gas constant, and E_b is the activation energy. Plots of $\log v$ versus $1/T_b$ give straight lines. The activation energies found are 44 kcal/mole for poly(methyl methacrylate), 77 kcal/mole for polystyrene, and 54 kcal/mole for poly(vinyl chloride). These are between the activation energies for α and β transitions, as shown in Table II.

It is interesting to note that Sherby and Dorn[5] reported a value of 48 kcal/mole for the activation energy of creep below 47°C for poly(methyl methacrylate). This value is in good agreement with our value of 44 kcal/mole for the brittle–ductile transition.

The activation energy for brittle–ductile transition E_b can be estimated from the activation energies for α and β transitions, E_α and E_β, by the empirical relation

$$E_b = \left(\frac{T_b - T_\beta}{T_g - T_\beta} \right) E_\alpha + \left(\frac{T_g - T_b}{T_g - T_\beta} \right) E_\beta \tag{2}$$

where T_b is at 0.1 min⁻¹ and T_β at 1 cps. The agreement between the calculated and the experimental values of E_b is quite good for poly(methyl methacrylate) and polystyrene, but less satisfactory for poly(vinyl chloride), as shown in Table II. Additional data are needed to test the universality of eq. (2).

	E_b, kcal/mole	E_α, kcal/mole	E_β, kcal/mole	E_b calculated by eq. (2), kcal/mole
Poly(methyl methacrylate)	44	100	24	43
Polystyrene	77	84	35	74
Poly(vinyl chloride)	54	131	16	64

[a] The subscripts b, α, and β refer to brittle—ductile transition, α transition, and β transition, respectively. E_α and E_β are obtained from Arrhenius plots of the data collected by N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, pp. 257–263, 414, 426.

Equation (2) is consistent with the proposition of Roetling[6] that yielding arises from a combination of α and β relaxation processes, in accordance with the flow theory of Ree and Eyring.[7] Brittle fracture in plastics is usually a consequence of craze formation and propagation so that brittle–ductile transition is a transition from craze growth to shear yielding.[8] It is not known how eq. (2) can be obtained from such fundamental consideration.

Effect of Comonomer

Poly(methyl methacrylate) and polystyrene have very similar T_g (105°C versus 100°C) and monomer molecular weight (100 versus 102), but very dif-
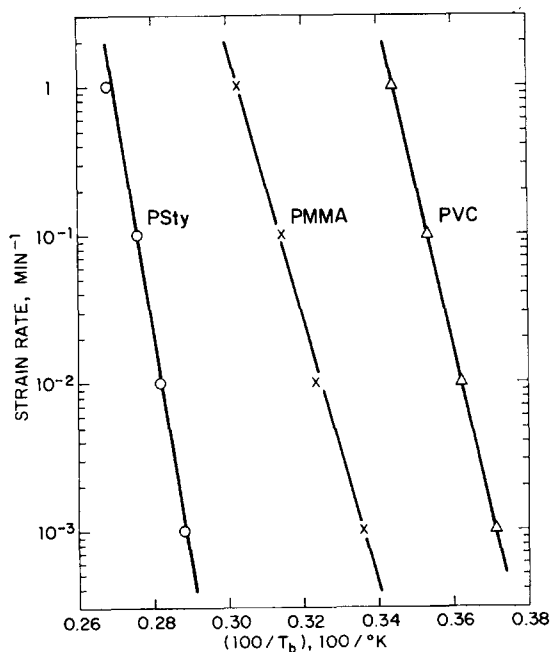

Fig. 5. Arrhenius-type plots of rate vs. brittle–ductile transition temperature for poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and polystyrene (PSty).

ferent T_b (45°C versus 90°C at 0.1 min^{-1}). Poly(methyl methacrylate) is more ductile ($q = 0.159$) than polystyrene ($q = 0.027$). Thus, we expect that copolymers of methyl methacrylate (MMA) and n-butyl methacrylate (nBMA) will be more ductile (having higher q value) than the corresponding copolymers of styrene (Sty) and nBMA. This is, indeed, observed as shown in Figures 3 and 4.

For instance, 50/50 by weight of copolymer of MMA/nBMA has a T_b of 10°C (at 0.1 min^{-1}), a T_g of 72°C, and a q value of 0.180, whereas that of Sty/nBMA has a T_b of 35°C (at 0.1 min^{-1}), a T_g of 51°C, and a q value of 0.049. Thus, MMA/nBMA is more ductile than the corresponding Sty/nBMA.

The plots of T_b versus w are sigmoidal, with an inflection point at $w = 0.5$. For the copolymers of MMA/nBMA, the upper curve shows negative deviations from linearity, whereas the lower curve shows positive deviations. On the other hand, for the copolymers of Sty and nBMA, the upper curve is nearly linear, whereas the lower curve shows positive deviations. It should be noted that T_g-versus-w curves show positive deviations from linearity for the copolymers of MMA/nBMA and negative deviations for those of Sty and nBMA.

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