The Pressure and Temperature Effects on Brittle-to-Ductile Transition in PS and PMMA

K. MATSUSHIGE,* S. V. RADCLIFFE, and E. BAER, *Department of Macromolecular Science and Department of Metallurgy and Material Science, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

Tensile experiments in polystyrene (PS) and poly(methyl methacrylate) (PMMA) conducted at constant strain rate over a wide range of pressure and temperature have shown that a brittle-to-ductile transition is induced in these amorphous polymers by the superposition of hydrostatic pressure as well as by the raise of the experimental temperature. A detailed stress–strain analysis permits explanation of the mechanism for the brittle-to-ductile transition in terms of interaction between two competing processes of plastic yielding—crazing and shear banding phenomena. The crazing and shear banding processes respond quite differently to changes of pressure or temperature, causing shifting of the brittle-to-ductile transition point to where the craze initiation stress and shear band initiation stress again become equal. The evidence that the brittle-to-ductile transition pressure becomes lower with increasing temperature refutes a previously suggested concept that the transition relates primarily to mechanical relaxation phenomena.

INTRODUCTION

The mechanical behaviors of polymers as well as other materials are well known to be affected with a great degree by the changes of experimental conditions and sample preparations. An alternation in fracture modes from brittle to ductile with increasing temperature is one of the most significant cases and many aspects on the brittle-to-ductile transition in polymers have been studied extensively from its practical importance. Vincent[1,2] made considerable efforts to examine the effects of strain rate and basic material variables such as molecular weight, crystallinity, additives, crosslinking, side groups, and molecular orientation on the brittle-to-ductile transition temperature.

In spite of abundant information on factors which influence the brittle-to-ductile transition, the mechanism of the transition itself has been understood only fragmentarily. In the most cases,[1–3] the brittle-to-ductile transition phenomenon in polymers has been explained phenomenologically on the basis of the Ludwick[4]-Davidenkov and Wittman[5] hypothesis, which was originally suggested from the study of the same transition in metals and which assumes that the brittle fracture and plastic flow are independent processes and the brittle fracture stress and the yield stress become equal at the transi-

---

* Present address: Department of Applied Science, Kyushu University, Fukuoka, Japan.

tion temperature. Therefore, in this concept no microstructural features such as the crazing[6,7] and shear banding phenomena,[8] which have been recently recognized to be most responsible for the fracture process in glassy polymers, have been considered at all. Another disputant point in the polymer transition phenomenon is on the relationship between the brittle-to-ductile transition and the mechanical relaxation phenomena. Several authors[9-11] have suggested that the brittle-to-ductile transition always occurs near a glass transition temperature or a lower temperature-relaxation temperature if the polymer exhibits more than one mechanical relaxation. These relationships, however, have been proved not to have a general validity since some polymers are observed to be ductile at the temperature even lower than the lowest temperature-relaxation temperature.[1] In addition to this temperature-induced transition, it has been demonstrated for several polymers that an increased pressure at constant temperature can likewise induce a transition from brittle to ductile.[12-16]

In recent publications,[17,18] we have reported quantitative studies of the way in which superposition of hydrostatic pressure induces the brittle-to-ductile transition in amorphous polymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) at room temperature. Based on the detailed stress–strain analysis in this work, it was suggested that the interaction of the plastic deformation processes of crazing and shear bands appears to be the essential mechanism of the brittle-to-ductile transition phenomenon. Thus, clarification of the pressure dependence of these processes is likely to lead to greater understanding of the transition than it is from the mechanistic viewpoint of the Ludwick-Davidenkov and Wittman hypothesis. The main objectives of the present study are to present more extensive data on the effects of experimental pressure and temperature on the brittle-to-ductile transition point in PS and PMMA and to investigate further the general mechanism and/or factors governing the transition phenomenon. The relationship between the brittle-to-ductile transition and mechanical relaxation phenomena will also be discussed.

EXPERIMENTAL

As detailed explanation of the high-pressure tensile apparatus, specimen geometry, and the procedure to obtain true stress–strain curves has already been done in previous publications,[17-19] only the essentials and some modifications will be described here.

The materials studied in this study, PS (from the Dow Chemical Co.) and PMMA (from Cadillac Plastic and Chemical Co.), were obtained commercially in the form of extruded rods. All the tensile specimens were machined directly from the as-received rods, and the surfaces were carefully polished along the gauge length to minimize possible surface effects in mechanical behaviors. The overall specimen length was 2.40 in., and the reduced gauge section with 1.50-in. R groove was 0.12 in. in diameter.[17] After polishing, the PS specimens were annealed following the method of Bailey.[20] Finally, surface of the gauge section was sealed with Teflon tape and covered with a transparent silicon rubber in order to prevent possible environmental effects due to the surrounding pressure-transmitting fluid or temperature-controlling medium.
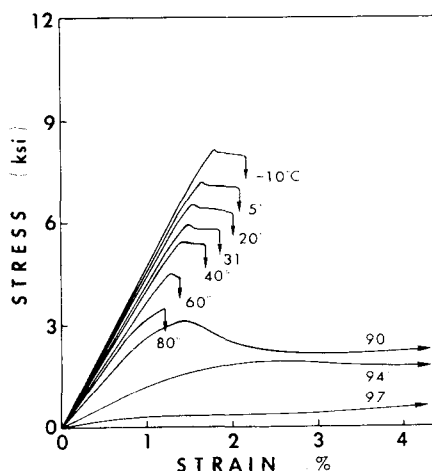
Fig. 1. Effect of temperature on stress–strain behavior of PS at atmospheric pressure.

The apparatus used for the tensile experiments at atmospheric pressure was an Instron machine furnished with a temperature-control chamber which was filled with silicon oil as a medium. To perform the high-pressure measurements at different temperatures, the high-pressure tensile apparatus was equipped with a temperature-control jacket. The test temperature in the both cases was measured with a thermocouple positioned less than 0.3 in. from the tensile specimens and was controlled within ±1.5°C fluctuation during the experiments. All the tensile tests were conducted at a constant crosshead rate of about 0.03 in./min.

RESULTS AND ANALYSIS

Brittle-to-Ductile Transition at Atmospheric Pressure

The tensile experiments on PS and PMMA were carried out over the temperature range from −10°C to 105°C at atmospheric pressure. The temperature effects observed on the stress–strain behavior are shown in Figure 1 for PS and in Figure 2 for PMMA, respectively. In the case of PS, a drastic change in the stress–strain curve appears about 90°C. The stress–strain curves of the specimens tested below 80°C are characteristic of the development of the process of craze yielding.[21] In this process, an extensive growth of crazes across the gauge length of specimen occurs beyond a critical level of stress (the break in the curve) and the specimens fracture at very low strain and perpendicular to the tensile direction. In PS, it is noticeable that the fracture strains and stresses decrease with increasing temperature. In the optical microscope, the well-developed crazes could be observed on the fracture surface and the adjacent side surfaces. In contrast, the stress–strain curve at 90°C shows a distinct yield point, and the specimen exhibits a necking and further cold drawing. At 97°C, the specimen deforms uniformly without the neck formation similar to rubber-like materials. For all the specimens deformed at or above 90°C, no craze formation could be observed on their side surfaces.

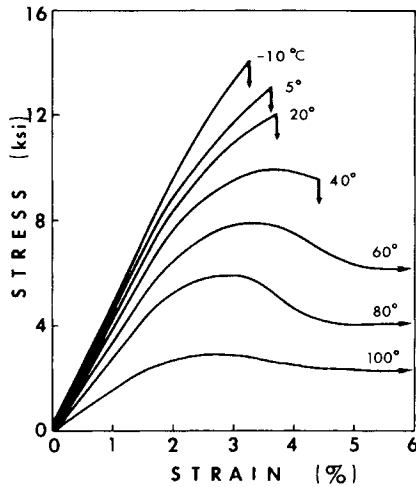In the case of PMMA, the change of fracture mode from brittle to ductile

Fig. 2. Effect of temperature on stress–strain behavior of PMMA at atmospheric pressure.

occurs much less discontinuously in the vicinity of 50°C, as shown in Figure 2. Differing from the case of PS, the fracture strain of PMMA in the brittle fracture region increases gradually with temperature. Further, the stress–strain curves do not exhibit craze yielding, coinciding with the optical observation that only a few and undeveloped crazes could be detected on the side surface of the fractured specimens.

To elucidate the mechanism of the brittle-to-ductile transition, the observed stress–strain curves have been further analyzed in the following manner. Figure 3 shows schematically typical stress–strain curves for brittle and ductile fractures. In general, brittle fracture is considered to occur when a specimen fails at its maximum load (at strains less than, say, 20%, in order to exclude rubbers),[1] but we expand this definition so as to include the case of craze yielding in PS, since there the fracture is caused by the propagation or development of existing crazes, not shear bands, and its fracture strain is less than 3%. For both brittle and ductile fractures, the stress–strain curves show a departure from linearity as indicated by arrows in the figure. From the simultaneous observations of the stress–strain and optical behaviors, we and other research groups have reported that the onset of nonlinearity on the stress–strain curve is accompanied by the initiation of crazes in the brittle fracture region[18,21,22] or by the initiation of shear bands in the ductile fracture region.[6,18,23] Therefore, we define the corresponding stresses as the craze initiation and shear band initiation stresses, respectively.

As shown in Figure 4, PS exhibits the essentially same temperature dependences for both the craze initiation and fracture stress curves in the brittle fracture region. A similar correlation can be seen for the set of shear band initiation and yield stresses in the ductile fracture region. However, these two sets of curves show quite different temperature dependences, and, furthermore, they intersect in the temperature region where the brittle-to-ductile transition was observed. Another characteristic point in Figure 4 is that the craze initiation stress shows a substantial lowering around 35°C and the temperature dependence becomes much higher above that temperature. Haward et al.[24] observed similarly the irregular temperature dependence of the
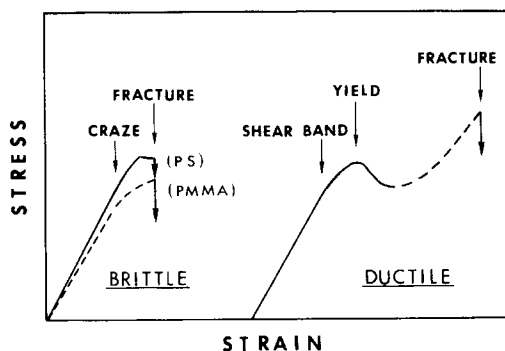
Fig. 3. Typical stress–strain curves for brittle fracture without (PMMA) and with craze yielding (PS) and ductile fracture. An inflection point on the stress–strain curve for the brittle fracture corresponds to the craze initiation point; that for the ductile fracture corresponds to the shear band initiation point.
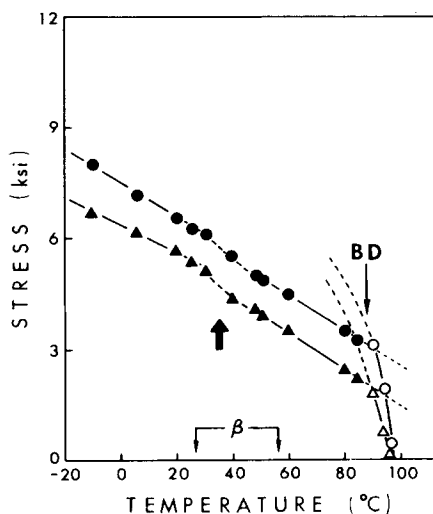

Fig. 4. Temperature dependences of (▲) craze initiation, (△) shear band initiation, (●) fracture, and (○) yield stresses in PS. Arrow BD indicates brittle-to-ductile transition point.

craze initiation stress in PS at the same temperature range (see Fig. 3 in ref. 24), although they did not notice this phenomenon. The possibility that this irregular behavior might relate to the β-relaxation in PS will be discussed later.

For PMMA, the temperature dependences of these various stresses are shown in Figure 5. Similar to the case of PS, the curve of craze initiation stress intersects with that of shear band initiation stress at the brittle-to-ductile transition temperature. However, the temperature dependences of these stresses above and below the transition do not show much difference and the shear band initiation stress in the brittle fracture region estimated by the extrapolation of the curve seems to be only 10% to 20% higher than the observed craze initiation stress. From the combination of this estimation and the reported fact[6,7] that the crazes produce highly stress-concentrated portions at the craze tips, it is reasonable to deduce that the shear band initiates just
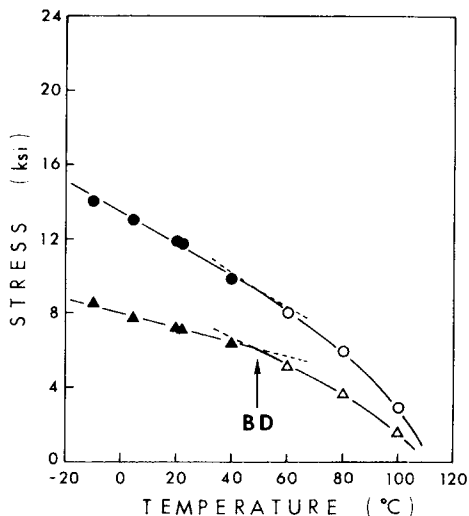
Fig. 5. Temperature dependences of (▲) craze initiation, (△) shear band initiation, (●) fracture, and (○) yield stresses in PMMA. Arrow BD indicates brittle-to-ductile transition point.

after the occurrence of craze formation in this temperature region of 40° to −10°C and thus supresses the further development of crazes. This phenomenon might be the reason why PMMA shows only a few crazes and does not exhibit the craze yielding on the stress–strain curves typical of PS.

It is noticeable that the brittle-to-ductile transition temperatures observed in this study, which agree well with the reported transition temperatures of 90°C for PS[25] and 40–45°C for PMMA[3,26] are located very closely to the α-relaxation temperature of PS and β-relaxation temperature of PMMA, respectively. As a consequence, it has been suggested[9–11] that these two polymers are good examples of a clear correlation between the brittle-to-ductile transition and these mechanical relaxation phenomena. However, it will be proved in the next section that this good correlation does not exist for either polymer when they are tested under a hydrostatic pressure environment.

Pressure and Temperature Dependences on the Brittle-to-Ductile Transition

As has been reported,[17,18] the superposition of hydrostatic pressure on the tensile specimen can induce a brittle-to-ductile transition *at room temperature*. Figure 6 shows the pressure effects on the stress–strain curves of PS tested at constant temperature of 31°C.[17] The fracture mode of PS changes from brittle to ductile between 0.3 kb and 0.4 kb, while Young's modulus increases almost continuously with pressure. The stress–strain curves were analyzed in the manner described in the preceding section, and the obtained pressure dependences of characteristic stresses are shown in Figure 7. Although at atmospheric pressure the craze initiation stress is much lower than the shear band initiation stress, the superposition of hydrostatic pressure raises the stress necessary for the onset of crazing more rapidly than that for the onset of shear band formation, and these two stresses become equal at the brittle-to-ductile transition pressure. Quite similarly, PMMA has been
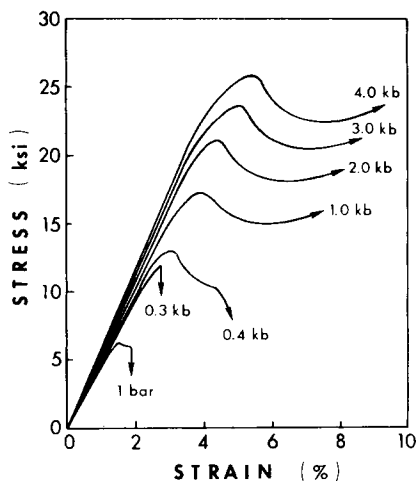
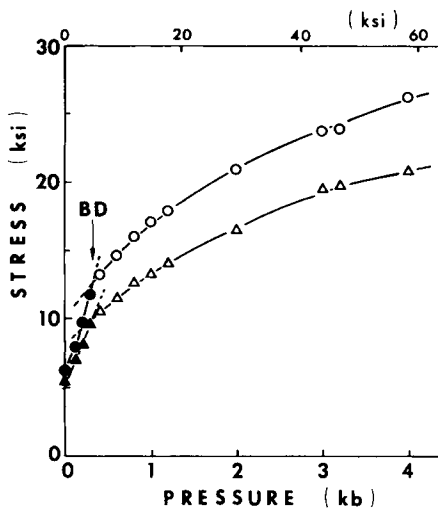Fig. 6. Effect of pressure on stress–strain behavior of PS at 31°C.

Fig. 7. Pressure dependences of (▲) craze initiation, (△) shear band initiation, (●) fracture, and (○) yield stresses in PS at 31°C.   Arrow BD indicates brittle-to-ductile transition point.

proved to exhibit its brittle-to-ductile transition between 0.2 kb and 0.3 kb at 23°C.[18]

The above observations demonstrate that the brittle-to-ductile transition in amorphous polymers can be induced either by the raising of experimental temperature or by the superposition of hydrostatic pressure.   However, a deeper knowledge of how these two individual phenomena are connected to each other is not immediately apparent.   In this regard, to investigate how the experimental temperature affects the brittle-to-ductile transition pressure offers a possible approach to understand the fundamental mechanism controlling the brittle-to-ductile transition phenomenon in amorphous polymers.   To study the temperature effects on the mechanical behaviors in PS and PMMA under pressure, the tensile experiments have been carried out
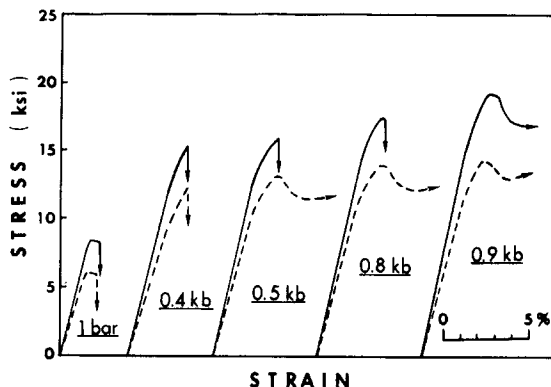
Fig. 8. Effect of pressure on stress–strain behavior of PS at different temperatures of (——) 5°C and (– – –) 40°C.
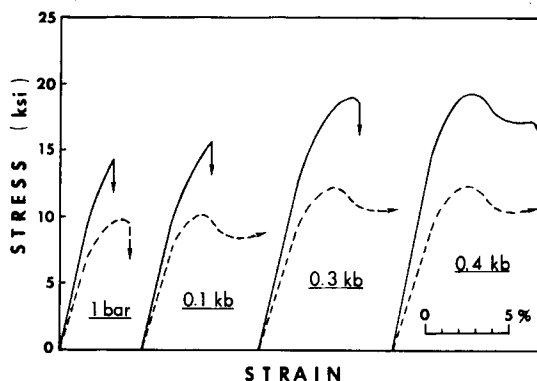

Fig. 9. Effect of pressure on the stress–strain behavior of PMMA at different temperatures of (— —) 10°C and (- - - -) 40°C.

under pressure and at various temperatures of 5°, 20°, 31°, 40°, and 50°C for PS and −10°, 5°, 23°, 30°, and 40°C for PMMA.

The resulting pressure effects on the stress–strain curves of PS at 5°C are shown and compared in Figure 8 with those for specimens tested at the higher temperature of 40°C. It is obvious that the increase of the experimental temperature lowers the brittle-to-ductile transition pressure as well as the characteristic stresses, such as fracture stress and yield stress, and also Young's modulus. At 5°C, PS fractures in a brittle manner up to 0.8 kb, but the fracture mode changes to ductile above 0.9 kb. As the temperature is raised, the brittle-to-ductile transition pressure becomes lower and lower, and the transition appears between 0.4 kb and 0.5 kb at 40°C. Similar temperature effects can be also observed in PMMA, as shown in Figure 9. PMMA exhibits the brittle-to-ductile transition between 0.3 kb and 0.4 kb at −10°C, while the transition appears below 0.1 kb when the tensile experiments are performed at higher temperature of 40°C.

The stress–strain curves of the specimens tested under pressure and at different temperatures have been analyzed and the pressure dependences of the craze initiation and shear band initiation stresses at various temperatures are shown in Figure 10 for PS and in Figure 11 for PMMA, respectively. It is
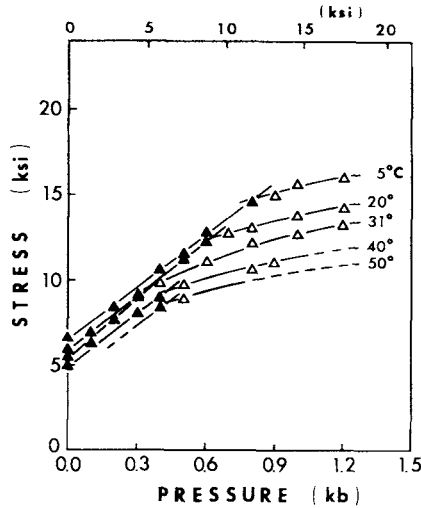
Fig. 10. Pressure dependences of (▲) craze initiation stress and (△) shear band initiation stress in PS at different temperatures of 5°, 20°, 31°, 40°, and 50°C.
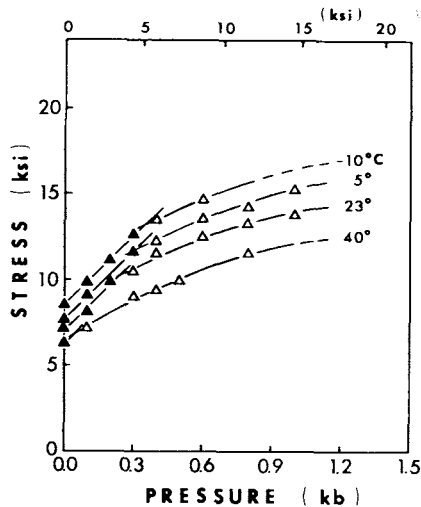

Fig. 11. Pressure dependences of (▲) craze initiation stress and (△) shear band initiation stress in PMMA at different temperatures of −10°, 5°, 23°, and 40°C.

again noticeable that the two curves for the craze initiation and shear band initiation stresses intersect at the brittle-to-ductile transition pressure irrespective of the test temperature for the both cases of PS and PMMA.

Based on the data given in Figures 10 and 11, the pressure and temperature dependences of craze initiation stress ($d\sigma_{ci}/dP$ and $d\sigma_{ci}/dT$) and those of shear band initiation stress ($d\sigma_{sb}/dP$ and $d\sigma_{sb}/dT$) are calculated and the values are listed in Table I. Since these values vary with the temperature and/or pressure, the table lists the values averaged over the examined temperature and/or pressure regions. From the comparisons of the data on the pressure and temperature dependences, it is apparent that craze formation is much more suppressed by the increase of the superposed pressure than is

shear band formation (i.e., $(d\sigma_{ci}/dP)/(d\sigma_{sb}/dP) > 1$). In contrast, increased temperature affects shear band initiation process more strongly than crazing (i.e., $(d\sigma_{ci}/dT)/(d\sigma_{sb}/dT) < 1$). These results demonstrate that the crazing and shear banding phenomena have different sensitivities to the changes in environmental pressure and temperature, which is in keeping with the view that very different rather than similar supermolecular processes are involved in these two phenomena. This point is examined further in the next section.

Figure 12 shows the temperature dependences of the brittle-to-ductile transition pressure obtained from the stress–strain measurements. Both polymers—PS and PMMA—show a similar general trend in that the brittle-to-ductile transition pressure becomes higher with decreasing temperature. This temperature dependence of the transition pressure, however, is the inverse of that expected from the concept that the brittle-to-ductile transition relates to mechanical relaxation phenomena, because the temperatures of both the mechanical α- and β-relaxations are known to become higher with increasing pressure. The reasons for this discrepancy, and for the irregular temperature dependence of the transition pressure observed in PS around 40°C, will be discussed in detail in the next section.

DISCUSSION

From the tensile experiments of PS and PMMA under the wide range of pressure and temperature performed in this study, the following general features may be attributed to the brittle-to-ductile transition phenomenon in amorphous polymers: (1) The pressure dependence of the craze initiation stress is considerably higher than that of the shear band initiation stress. (2) The temperature dependence of the craze initiation stress is considerably lower than that of the shear band initiation stress. (3) The two curves of the craze initiation stress and the shear band initiation stress intersect at the point where the brittle-to-ductile transition (whether pressure or temperature) is observed, and the craze initiation stress always becomes higher than the shear band initiation stress above this transition point. (4) The brittle-to-ductile transition pressure becomes higher with decreasing temperature, and, conversely, the transition temperature becomes lower with increasing pressure.

While items (1) and (2) suggest that the crazing and shear banding phenomena have quite different formation mechanisms, Brady and Yeh[27] have reported that there exist several similarities between the craze morphology and shear band morphology in PS. However, the fact that the superposition

TABLE I
Comparison of Pressure and Temperature Dependences of Craze Initiation Stress
(σ_{ci}) and Shear Band Initiation Stress (σ_{sb}) in PS and PMMA

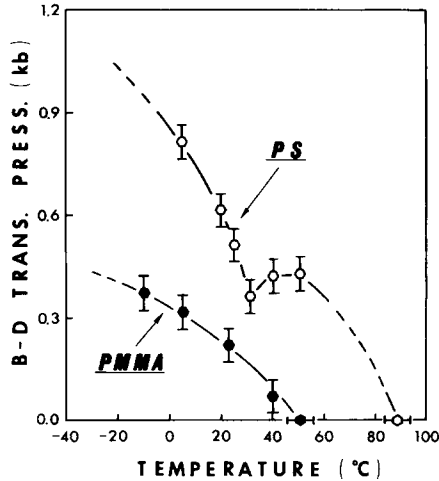|	$\dfrac{d\sigma_{ci}}{dP}$, ksi/kb	$\dfrac{d\sigma_{sb}}{dP}$, ksi/kb	$\dfrac{d\sigma_{ci}}{dP}\Big/\dfrac{d\sigma_{sb}}{dP}$	$\dfrac{d\sigma_{ci}}{dT}$, ksi/°C	$\dfrac{d\sigma_{sb}}{dT}$, ksi/°C	$\dfrac{d\sigma_{ci}}{dT}\Big/\dfrac{d\sigma_{sb}}{dT}$
PS	11	4	2.7	−0.2	−1.1	0.18
PMMA	13	6	2.2	−0.5	−0.8	0.63

Fig. 12. Temperature dependences of brittle-to-ductile transition pressure in PS and PMMA.

of hydrostatic pressure affects the crazing more than the shear banding is in accord with the well-established difference in their formation mechanisms whereby the crazing involves void formation but shear banding essentially does not. Moreover, the larger temperature dependence of the shear banding over the crazing implies that the molecular motions associated with the banding, such as molecular sliding,[23] can be enhanced by the increase in temperature much more than the molecular motions for craze formation.

From item (3), a satisfactory explanation can be deduced for the general mechanism of the brittle-to-ductile transition phenomenon, whether the transition is induced either by the increase of temperature or by the superposition of pressure. The explanation is simply that the material fractures in a brittle manner if the crazes can initiate at lower stress level than the shear bands at the test conditions of temperature and pressure. If they cannot, the fracture mode will be ductile because the shear bands that form before the initiation of the craze function so as to suppress the initiation of new crazes or propagation of existing crazes[28-30] which normally lead the specimen to brittle fracture. Thus, the competition of and interaction between the crazing and shear banding play a particularly important part in the brittle-to-ductile transition phenomenon in amorphous polymers.

Further, this concept of the transition mechanism provides the answer as to why the temperature dependences of the brittle-to-ductile pressure in PS and PMMA differ from that expected from the idea that the transition relates to the mechanical relaxation phenomena. As described above, the brittle-to-ductile transition phenomenon is caused by the interaction between two independent *plastic deformations* of crazing and shear banding and is not due to a direct effect of the mechanical relaxation motions. Therefore, the brittle-to-ductile transition point depends upon how the changes of pressure and/or temperature affect the craze initiation and shear band initiation processes and hence shift the intersection point of the initiation stresses for these two processes. In this regard, there exists no reason to expect the brittle-to-ductile transition to shift with changes in pressure and/or temperature in the same manner as do the mechanical relaxation processes.

Despite this absence of a direct effect of relaxations on the brittle-to-ductile transition, there are some secondary or indirect effects in the case of the β-relaxation in PS. As shown in Figure 12 and more clearly in Figure 13, the brittle-to-ductile transition pressures in PS change irregularly with decreasing temperature around 40°C. At atmospheric pressure, the craze initiation stress curve of PS showed the irregular lowering around 35°C (Fig. 4), which is very close to the reported β-relaxation temperature range of 25–60°C.[31] Further, Boyer[32] found from the analysis of Maxwell and Rahm's data[33] on crazing that the apparent activation energy of the β-relaxation in PS agrees with the activation energy for the crazing. Therefore, above the β-relaxation temperature, if this β-relaxation really enhances the formation of crazes in PS, it could be expected that the stress necessary to initiate crazes will become substantially lower, and hence brittle fracture will be more favored. Naturally, the brittle-to-ductile transition phenomenon under pressure will be also influenced indirectly by the existence of such β-relaxation, and the pressure necessary to induce the transition will become discontinuously higher in order to compensate for the substantial lowering in the craze initiation stress. As demonstrated in Figure 13, where the pressure dependence of the β-relaxation temperature is assumed to be about 4°C/kb (by analogy with PMMA[34]), the discontinuous increase in the brittle-to-ductile transition pressure is actually observed at the region where the transition curve meets with the β-relaxation curve. Thus, the hypothesis that the β-relaxation in PS lowers the craze initiation stress and indirectly affects the brittle-to-ductile transition process can explain simultaneously the both experimental facts of the irregular lowering of craze initiation stress observed at atmospheric pressure and the irregular region of the temperature dependence of the transition pressure.

In contrast to PS, the pressure–temperature characteristics for PMMA do not show irregularities, despite Boyer's[32] interpretation that the β-relaxation in PMMA is also associated with the crazing phenomenon. The experimental results, however, do not give any distinct evidence for a relationship between the β-relaxation and the craze initiation stress curve and/or the brittle-to-ductile transition curve in this polymer. Rather, PMMA exhibits at atmospheric pressure its brittle-to-ductile transition at about 45°C near to the reported β-relaxation temperatures.[35,36] It is possible that this near coincidence of the latter with the transition temperature at atmospheric pressure is preventing experimental observation of its effect.

.

CONCLUSIONS

Tensile experiments on PS and PMMA conducted over a wide range of pressure and temperature have shown that the brittle-to-ductile transition in these amorphous polymers is strongly affected by both the pressure and by the temperature. By using detailed stress–strain analyses, the pressure and temperature dependences of the craze initiation and the shear band initiation processes were elucidated as the fundamental processes controlling the mechanism of the brittle-to-ductile transition. The major conclusions of this study may be summarized as follows:

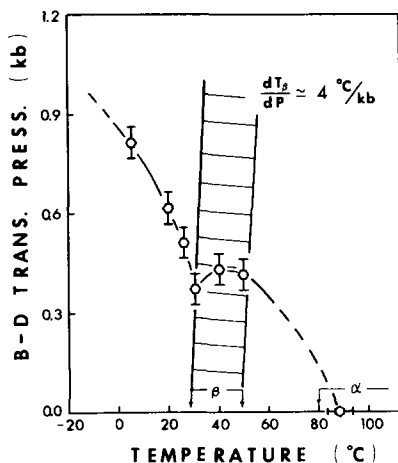1. Pressure affects the craze initiation stress considerably more than the

Fig. 13. Influence of β-relaxation on temperature dependence of brittle-to-ductile transition pressure in PS.

shear band initiation stress. However, temperature acts in exactly the opposite manner.

2. These two initiation stresses become equal at the brittle-to-ductile transition pressure and/or temperature, suggesting that the transition is induced by the interaction between competing microplastic deformation processes—crazing and shear banding.

3. The brittle-to-ductile transition pressure decreases with increasing temperature due to the quite different pressure and temperature dependences of the craze initiation and the shear band initiation stresses.

4. This transition is not primarily dependent on mechanical relaxation phenomena.

References

1. P. I. Vincent, *Polymer*, 1, 425 (1960).
2. P. I. Vincent, *Plastics* (Lond.), 27, 115 (1962).
3. P. Beadmore, *Phil. Mag.*, 19, 389 (1969).
4. P. Ludwik, *Z. Ver. Deut. Ing.*, 71, 1532 (1927).
5. N. N. Davidenkov and F. Wittman, *Phys. Tech. Inst. (USSR)*, 4, 300 (1937).
6. R. P. Kambour, *J. Polym. Sci. Macromol. Rev.*, 7, 1 (1973).
7. S. Rabinowitz and P. Beadmore, *Crit. Rev. Macromol. Sci.*, March (1972).
8. E. J. Kramer, *J. Macromol. Sci. Phys.*, B10(1), 191 (1974).
9. A. J. Staveman and F. Schwarzl, in *Die Physik der Hochpolymeren*, Vol. 4, H. A. Stuart, Ed., Springer, Berlin, 1956.
10. B. Maxwell, J. P. Harrington, and R. E. Monica, Princeton University Plastics Laboratory, Technical Reports 24A, Princeton, N.J., 1952.
11. E. A. W. Hoff and S. Turner, *Bull. Amer. Soc. Test. Mat.*, 225, TP208 (1957).
12. L. Holliday, J. Mann, G. A. Pogany, H. Pugh, and D. A. Gunn, *Nature*, 202, 381 (1964).
13. G. Biglione, E. Baer, and S. V. Radcliffe, Proceeding of the Second International Conference, Brighton, 1969, P. L. Pratt, Ed., Chapman and Hall, London, 1969.
14. H. Pugh, E. F. Chandler, L. Holliday, and J. Mann, *Polym. Eng. Sci.*, 11, 463 (1971).
15. S. K. Bhateja and K. D. Pae, *Polym. Lett.*, 10, 531 (1972).

16. J. A. Sauer, S. K. Bhateja, and K. D. Pae, Third Inter-American Conference on Materials Technology, Rio de Janeiro, Brazil, 1972.

17. K. Matsushige, S. V. Radcliffe, and E. Baer, *J. Mater. Sci.*, **10,** 833 (1975).

18. K. Matsushige, S. V. Radcliffe, and E. Baer, Report from Department of Macromolecular Science, Case Western Reserve University, TR No. 270, Feb. 1975, to be published.

19. G. Das and S. V. Radcliffe, *J. Jap. Inst. Metals,* **9,** 334 (1968).

20. J. Bailey, Mod. Plast., 24 127 (1946).

21. J. Hoare and D. Hull, *Phil. Mag.,* **26,** 443 (1972).

22. I. Narisawa, *J. Polym. Sci. A-2,* **10,** 1789 (1972).

23. A. S. Argon, R. D. Andrews, J. A. Godrick, and W. Whitney, *J. Appl. Phys.,* **39,** 1899 (1968).

24. R. N. Haward, B. M. Murphy, and E. F. T. White, *J. Polym. Sci. A-2,* **9,** 811 (1971).

25. E. H. Andrews, *Fracture in Polymers,* Oliver and Boyd, 1968, p. 53.

26. E. A. W. Hoff, *J. Appl. Chem.,* **2,** 441 (1952).

27. T. E. Brady and G. S. Y. Yeh, *J. Mater. Sci.,* **8,** 1083 (1973).

28. C. B. Bucknell, D. Clayton, and W. E. Keast, *J. Mater. Sci.,* **7,** 1443 (1972).

29. M. Higuchi and H. Ishi, *Rept. Res. Inst. Appl. Mech., Kyushu University,* **16,** 69 (1968).

30. S. Wellinghoff and E. Baer, *J. Macromol. Sci.-Phys.,* in press.

31. K-H. Illers, *Zeit. Electrochemie,* **65,** 679 (1961).

32. R. F. Boyer, *Polym. Eng. Sci.,* **8,** 161 (1968).

33. B. Maxwell and L. F. Rahm, *Ind. Eng. Chem.,* **41,** 1990 (1949).

34. E. J. Parry and D. Tabor, *Polymer,* **14,** 628 (1973).

35. K. Wolf, Physikertagung, München, 1956, p. 153.

36. R. Haldon and R. Simha, *J. Appl. Phys.,* **39,** 1890 (1968).