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Relationship between molecular structure and deformation–fracture mechanism of amorphous polymers: 1. Shear yield stress

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The shear yield stress and its temperature dependence of various glassy polymers were measured by tensile and/or compression testing. It was found that the relationship between reduced yield stress by an interchain effect and the characteristic ratio proposed by Wu could not explain our results, especially the temperature dependence of shear yield stress. With two modifications, however – expression of temperature dependence, and size of the effective moving unit – a new relationship was developed that showed good correspondence to experimental data. Shear yield stress and its temperature dependence should be represented by the characteristic ratio, cohesive energy density, glass transition temperature and size of the effective moving unit, $(V_w/n_v)^{1/3}$, where V_w and n_v are the van der Waals volume of a repeat unit and the number of statistical skeletal units in a repeat unit, respectively.

(Keywords: shear yield stress; molecular structure; amorphous polymer)

INTRODUCTION

It is very important to know how materials are deformed and fractured. Glassy polymers show shear yielding and/or crazing before failure. Generally, the polymers that tend to yield show ductile fracture, while those that tend to craze show brittle fracture. Therefore both shear yield stress and crazing stesss must control deformation and fracture behaviour of glassy polymers. In this work, we studied the relationship between shear yield stress and molecular parameters.

It is well known that the shear yielding of crystalline material, such as metal, is explained by a dislocation model on the basis of local motion of atoms. Although shear yielding of glassy amorphous polymers is also caused by local motion of molecules, the yield criterion of a polymer, which is the maximum resistance for this local motion, must be more complex than that of a metal, because of the long molecules. The most accurate model of shear yielding of polymers previously presented is Argon's double kink model[1,2]. It is, however, difficult to estimate the parameters used in this model – related chain flexibility and size of the molecule – from the molecular structure of the polymer. Therefore this model is of limited use for examining the relationship between molecular structure and shear yield stress. On the other hand, Wu[3] proposed a semi-empirical relationship between shear yield stress and molecular parameters that are well studied in relation to molecular structure: glass transition temperature, cohesive energy density and characteristic ratio. However, it has been found that shear yield stress and its temperature dependence were not always correctly represented as functions of molecular parameters on the basis of Wu's relation.

In this work, we developed a new relationship between shear yield stress and polymer structure by examining experimental data of shear yield stress of various amorphous glassy polymers and their temperature dependence.

EXPERIMENTAL

The amorphous polymers used in this work and their characteristics are listed in *Table 1*. Sheets with thicknesses of 2 mm and 6 mm were compression moulded at a temperature about 100 K higher than each glass transition temperature. Specimens for tensile and compression tests were prepared by a cut-routing machine. The shape and size of each specimen are shown in *Figure 1*. Stress–strain curves were measured at crosshead speeds of 5 mm min^{-1} in the tensile test and 0.5 mm min^{-1} in the compression test. The uniaxial yield stress was calculated from the maximum of the stress–strain curve. Shear yield stress was defined by von Mises's yield criterion:

$$(\sigma_1-\sigma_2)^2+(\sigma_2-\sigma_3)^2+(\sigma_3-\sigma_1)^2=6\tau_Y^2 \qquad (1)$$

where σ_1, σ_2 and σ_3 are principal stresses, and τ_Y is the critical shear yield stress. In this case, uniaxial tension or compression, σ_1 is the maximum stress and σ_2 and σ_3 are equal to zero. Therefore shear yield stress is the product of $1/\sqrt{3}$ and the uniaxial yield stress obtained by tensile and/or compression testing. Relatively brittle polymers failed before yielding in the tensile test, so their yield stresses were only measured by compression testing.

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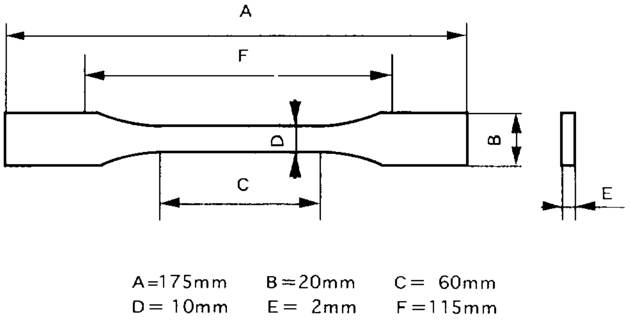
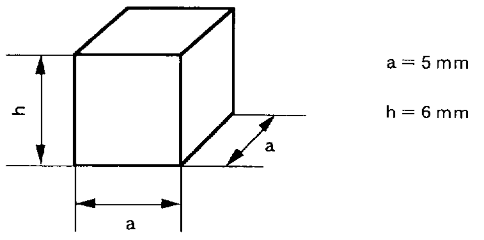
Table 1 Polymer specimens

	C_∞	$\delta^2 \times 10^{-8}$ (J m^{-3})	T_g (°C)	$V_w/n_v \times 10^{29}$ (m^3)	M_w[d] (g mol^{-1})
Polystyrene (PSt)	10.8	3.53	100	5.50	220 000
Poly(methyl methacrylate-*co*-styrene)(3/7)[a]	10.0	3.57	100	5.29	138 000
Poly(methyl methacrylate-*co*-styrene)(6/4)[b]	9.3	3.61	100	5.09	185 000
Poly(methyl maleimide-*co*-isobutene)(5/5)[c]	8.4	3.13	160	7.86	136 000
Poly(methyl methacrylate)	8.2	3.69	100	4.83	99 000
Poly(vinyl chloride) (PVC)	7.6	3.80	80	2.45	156 000
Phenoxy resin	3.7	4.20	97	4.65	57 000
Polyarylate	3.0	4.12	190	6.05	45 000
Polycarbonate of bisphenol-A (PC)	2.4	3.84	150	11.94	56 000
Poly(ether sulfone)	2.4	5.24	225	9.42	57 000
Polysulfone	2.2	4.75	190	9.98	51 000

[a] Molar fraction of methyl methacrylate is 30%
[b] Molar fraction of methyl methacrylate is 60%
[c] Molar fraction of methyl maleimide is 50%
[d] From g.p.c.



tensile specimen



compression specimen

Figure 1 Dimensions of test specimens

For ductile polymers, both tensile and compression tests were used.

Almost all of the characteristic ratios used were from the literature[4]. For poly(methyl methacrylate-*co*-styrene), poly(ether sulfone) and poly(methyl maleimide-*co*-isobutene), characteristic ratios were determined by the following relationship[3]:

$$C_\infty = (\rho n_v RT/3M_r G_N^0)^{1/2} \qquad (2)$$

where ρ is the density, n_v is the number of statistical skeletal units in a repeat unit, R is the gas constant, T is the temperature, M_r is the molecular weight of a repeat unit and G_N^0 is the plateau modulus, which was measured by dynamic oscillation in the melt state.

Cohesive energy densities were calculated by the group contribution method of Askadskii[5].

Glass transition temperatures were measured by d.s.c. at a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

At the yield point, a polymer molecule begins to change from *cis* to *trans* conformation[6,7]. According to the relationship between conformational change and macroscopic deformation recently proposed by Wu[3], shear yield stress is given by:

$$\log[\tau_Y/\delta^2(T_g - T)] = -3.60 + \log C_\infty \qquad (3)$$

or

$$\tau_Y/\delta^2(T_g - T) = 2.51 \times 10^{-4} \times C_\infty \qquad (3a)$$

where τ_Y is the shear yield stress, δ^2 is the cohesive energy density, T_g and T are the glass transition temperature and the testing temperature, respectively, and C_∞ is the characteristic ratio; all variables are in SI units. In this relationship, shear yield stress consists of intermolecular and intramolecular effects. The former are represented by cohesive energy density and the difference between glass transition temperature and testing temperature, while the latter are represented by the characteristic ratio. The characteristic ratio, as a measure of intrinsic molecular rigidity, has been thought to be related to conformational changeability.

The shear yield stresses measured at room temperature are plotted according to equation (3) in *Figure 2*. As reported by Wu, equation (3) could explain the experimental data of shear yield stress to some extent, but it was found that this equation was not adequate over a wide range of testing temperatures, as mentioned in the following discussion.

It is well known that both deformation and fracture behaviour of polymers are affected by testing temperature. By decreasing the testing temperature, for example, a polymer becomes more brittle. Since equation (3) involves the temperature term $T_g - T$, it is interesting to see whether equation (3) accurately explains the experimental data. Typical results for the temperature dependence of shear yield stress τ_Y are shown in *Figure 3*. The observed τ_Y increased as the difference between

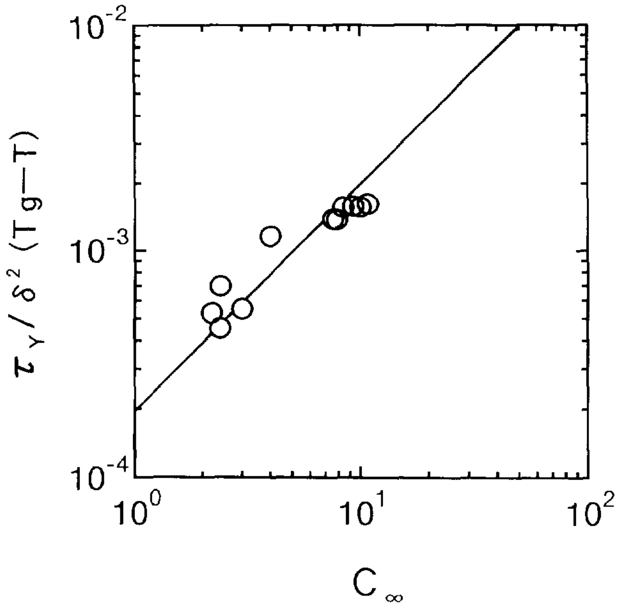


Figure 2 Reduced shear yield stress *versus* characteristic ratio according to equation (3)

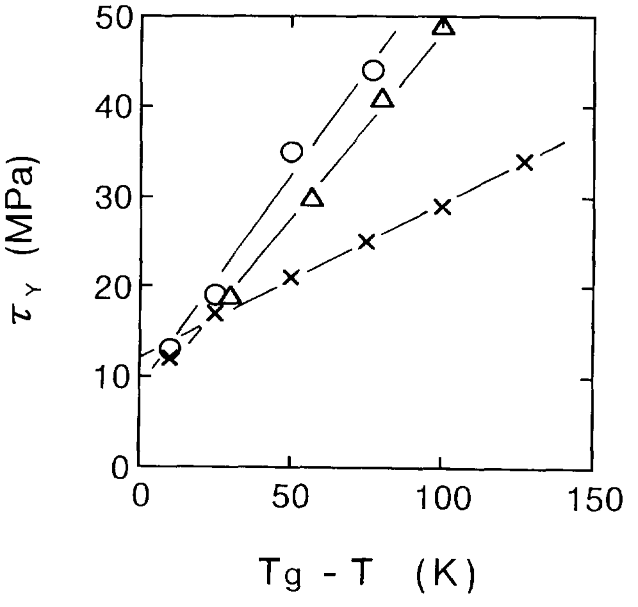


Figure 3 Typical results for the temperature dependence of shear yield stress: ○, polystyrene; △, poly(vinyl chloride); ×, polycarbonate of bisphenol-A

glass transition temperature and testing temperature ($T_g - T$) increased, as expected. It should be noted, however, that τ_Y was not zero but had finite values, of around 10 MPa, for each polymer measured near to the glass transition temperature (see Appendix). These results indicate that equation (3) is not correct in expressing the temperature dependence of shear yield stress, because the left side of equations (3) and (3a) will be divergent at $T = T_g$. The reduced shear yield stresses measured at various temperatures for PC, PVC and PSt, as well as those obtained at room temperature for other polymers, were plotted as a function of the characteristic ratio C_∞ according to equation (3) in *Figure 4*. It is obvious that equation (3) does not have universality, especially for PC. After much trial and error, we found that the following expression could explain the experimental data better than equation (3), as shown in *Figure 5*:

$$\tau_Y = A_1 C_\infty \delta^2 (T_g - T) + A_2 \tag{4}$$

A_1 and A_2 were determined as 1.28×10^{-4} and 1.21×10^7, respectively, by best-fitting using the above equation, when all variables are in SI units.

It is obvious, however, that the result seems to have some deviation from a linear relationship according to equation (4); we therefore considered the effective moving

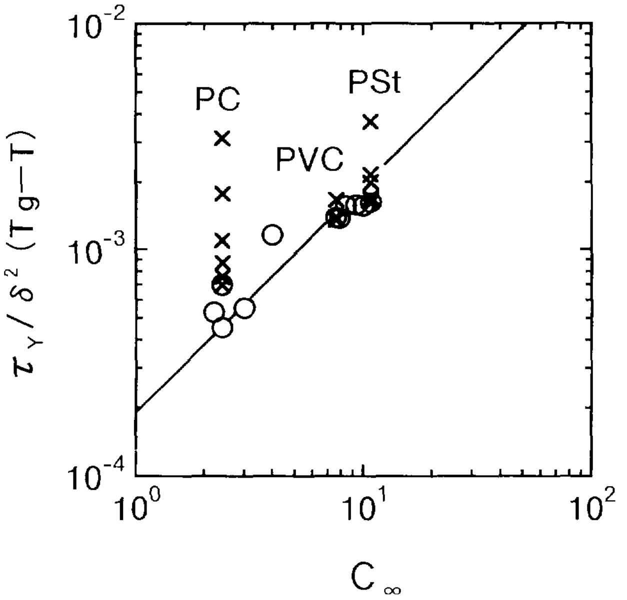


Figure 4 Reduced shear yield stress *versus* characteristic ratio according to equation (3). Shear yield stresses were measured at various temperatures for PC, PVC and PSt (×) and at room temperature for other polymers (○)

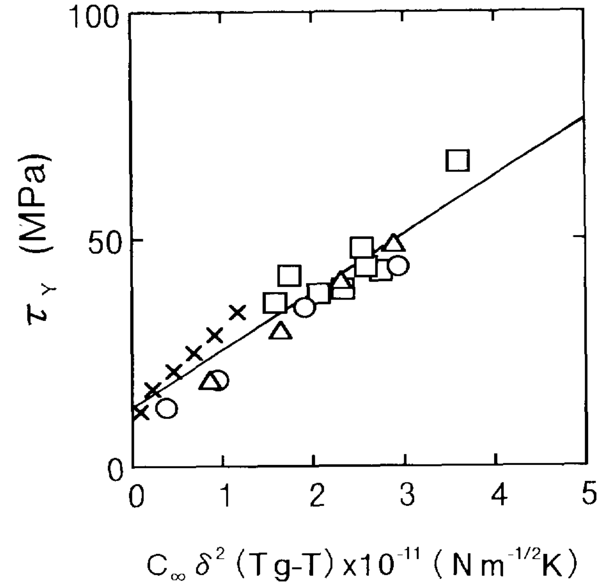


Figure 5 Correlation of shear yield stress with molecular parameters, C_∞, δ^2 and $T_g - T$. Shear yield stresses were measured at various temperatures for PSt (○), PVC (△) and PC (×) and at room temperature for other polymers (□). The solid line is the best fit of equation (4) with $A_1 = 1.28 \times 10^{-4}$ and $A_2 = 1.21 \times 10^7$, and the correlation coefficient $\gamma = 0.948$

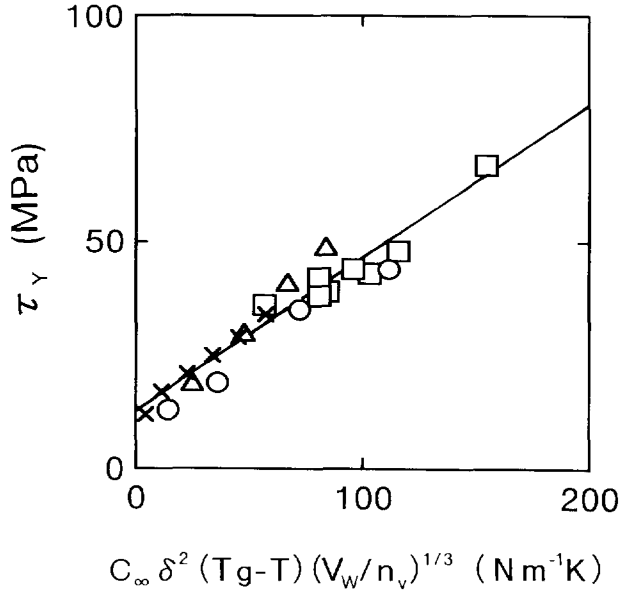


Figure 6 Correlation of shear yield stress with molecular parameters. C_∞, δ^2 and $T_g - T$, $(V_w/n_v)^{1/3}$. The symbols are the same as in *Figure 5*. The solid line is the best fit of equation (5) with $A_1 = 3.40 \times 10^5$ and $A_2 = 1.21 \times 10^7$, and the correlation coefficient $\gamma = 0.963$

unit before and after shear yielding in order to refine the relationship. In the glassy state, the effective moving unit could move by overcoming the interaction with neighbouring units. In equations (3) and (4), this interaction is represented by cohesive energy density δ^2 and the difference between glass transition temperature and testing temperature $(T_g - T)$, which is thought to be related to the fraction of free volume[8]. The effect of unit size, however, is not considered in the above equations. It is thought to be reasonable that conformational change needs free volume and it is more difficult as the moving unit becomes larger at the same fraction of free volume. The statistical skeletal unit[3,4], which is a minimum movable unit by free rotation around its backbone axis, is regarded as the effective moving unit. Assuming that the effective volume of a statistical skeletal unit was equal to the van der Waals volume per statistical skeletal unit, V_w/n_v, we refined equation (4) and obtained the following empirical equation with good correspondence to experimental data, as shown in *Figure 6*:

$$\tau_Y = A_1 C_\infty \delta^2 (T_g - T)(V_w/n_v)^{1/3} + A_2 \qquad (5)$$

where V_w and n_v are the van der Waals volume of a repeat unit and the number of statistical skeletal units in a repeat unit, respectively. Constants A_1 and A_2 were also determined as 3.40×10^5 and 1.21×10^7, respectively, by best-fitting using the above equation, when all variables are in SI units. The correlation coefficient was improved from 0.948 for equation (4) to 0.963 for equation (5). The modified parameter $(V_w/n_v)^{1/3}$ is thought to be proportional to the diameter of the effective moving unit, assuming that it is a sphere. This term explains the effect of the moving unit on conformational changeability. Accounting for the effective volume, the experimental results of shear yield stress and its temperature dependence of various polymers are well explained.

CONCLUSION

A new relationship has been derived between the structure of a polymer and shear yield stress containing temperature dependence, which consists of fundamental parameters of the polymer. Shear yield stress and its temperature dependence are represented by the characteristic ratio, cohesive energy density, glass transition temperature, and size of the effective moving unit. This relationship shows good agreement with experimental data.

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REFERENCES

1 Argon, A. S. *Phil. Mag.* 1975, **28**, 839
2 Argon, A. S. and Bessonov, M. I. *Phil. Mag.* 1977, **35**, 917
3 Wu, S. *Polym. Eng. Sci.* 1990, **30**, 753
4 Wu, S. *Polym. Eng. Sci.* 1992, **32**, 823
5 Askadskii, A. A. *Pure Appl. Chem.* 1976, **46**, 19
6 Jansson, J. F. and Yannas, I. V. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2103
7 Ward, I. M. *Polym. Eng. Sci.* 1984, **24**, 724
8 Hasan, O. A., Boyce, M. C., Li, X. S. and Berko, S. *J. Polym. Sci., Part B, Polym. Phys.* 1993, **31**, 185
9 Kramer, E. J. and Berger, L. L. *Adv. Polym. Sci.* 1990, **91/92**, 1

APPENDIX

Wu commented in his paper[3] that the shear yield stress of a polymer whose T_g is a little higher than room temperature has some deviation from his relationship, because chain disentanglement might occur and yielding might occur by the creation of a 'fluid' structure in the region near T_g. In order to confirm the possibility of the 'fluid' structure effect, we carried out tests in the region near T_g using lower molecular weight specimens than in the text, that is, PC having $M_W = 28\,000$ at 130°C. If chain disentanglement occurs at the shear yielding point in this temperature region, the lower molecular weight specimens would exhibit remarkably lower shear yield stress. However, the shear yield stress of 13.7 MPa for PC of lower molecular weight was almost equal to the value of 15.9 MPa obtained for the higher molecular weight PC, within experimental error. So chain disentanglement hardly occurs within the temperature range of our experiment, even near T_g. On the basis of our experimental data of shear yield stress, which showed that chain disentanglement hardly occurs, τ_Y is not extrapolated to zero at $T = T_g$.

In contrast, crazing stress was much affected by the molecular weight, even at room temperature, because its chain disentanglement might be one of the dominant parameters, as previously reported[9].