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Relationship between molecular structure and deformation–fracture mechanism of amorphous polymers: 2. Crazing stress

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The crazing stress and its temperature dependence of various amorphous glassy polymers were measured by three-point bending of round-notched bars, and the correlation with molecular parameters was studied. Only the factor of void formation by scission of entangled molecular chains did not correctly describe the temperature dependence of crazing stress. It was possible to describe crazing stress and its temperature dependence when the factors of both void and fibril formation were taken into consideration. Crazing stress and its temperature dependence can be represented by surface free energy, entanglement density, entanglement mesh size, bond energy and shear yield stress.

(Keywords: crazing stress; molecular structure; amorphous polymer)

INTRODUCTION

How a material deforms before it breaks is one of its most important characteristics. Shear yield stress and crazing stress are the factors determining the deformation and fracture mechanisms. We previously reported the relationship between molecular parameters and shear yield stress and its temperature dependence of amorphous glassy polymers[1]. Shear yield stress is represented by the characteristic ratio, cohesive energy density, glass transition temperature and size of the effective moving unit. In this work, we studied the relationship between crazing stress and molecular parameters.

The relationships between crazing stress and structure of the polymer chain have been reported by Kramer and Berger[2] and Wu[3]. Kramer and Berger reported that the deformation mode of crosslinked polystyrene changed from crazing to shear plastic deformation with an increase of crosslink points and entanglement points[2]. Based on this theory, Wu further reported a correlation between crazing stress and entanglement density in various types of polymers[3]. Kramer and Berger obtained crazing stress using a tensile test, while Wu obtained it by first determining crazing strain using Bergen's elliptical jigs[4], then multiplying by Young's modulus. However, these methods are not suitable for obtaining the crazing stress of a tough polymer such as polycarbonate of bisphenol-A (PC), because crazing cannot be created by methods that control mechanical conditions alone[5].

To obtain mechanical conditions where crazing occurs, a method has been proposed in which an experimental piece with a round notch is bent to create an internal craze[6–9]. This method allows the generation of an internal craze, even for tough polymers such as PC, in order to find mechanical conditions where crazing occurs.

In this work, we obtained crazing stresses of various amorphous glassy polymers by three-point bending of round-notched bars and studied the relationship between crazing stress and structure of the polymer.

EXPERIMENTAL

The amorphous polymers used in this work and their characteristics are listed in *Table 1*. Sheets with a thickness of 6 mm were compression moulded at temperatures about 100 K higher than each glass transition temperature. Specimens for three-point bending were prepared by machining. The shape and size of a specimen are shown in *Figure 1*. We used this specimen for a three-point bending test at a crosshead speed of 2 mm min^{-1} to generate an internal craze. A thin section was sliced from the test piece with craze using a microtome, and the distance between the notch tip and the nucleation point of the craze was measured. The stress distribution around a notch, shown in *Figure 2*, was obtained using slip-line field theory, and crazing stress was calculated from the equation:

$$\sigma_c = \tau_Y[1 + 2\ln(1 + x/r)] \qquad (1)$$

where τ_Y is shear yield stress, x is the distance between the notch tip and the nucleation point of the craze, and r is the notch radius. Shear yield stress was determined from a tensile and/or compression test using von Mises yield criterion[1].

Entanglement density ν_e is described by the equation:

$$\nu_e = \rho/M_e \qquad (2)$$

where ρ and M_e are density and entanglement molecular weight, respectively. Entanglement molecular weight is acquired from the equation:

$$M_e = \rho_T RT/G_N^0 \qquad (3)$$

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where ρ_T is the melt density at temperature T, R is the gas constant and G_N^0 is the plateau modulus. The plateau modulus was measured by dynamic oscillation in the melt state. The plateau modulus was regarded as the storage shear modulus at a frequency where $\tan\delta$ is a minimum[10-12].

RESULTS AND DISCUSSION

Wu reported that crazing stress σ_c is proportional to the square root of entanglement density ν_e because the craze was initiated by scission of the entangled polymer chains[3]:

$$\log\sigma_c = 0.5\log\nu_e - 6.56 \qquad (4)$$

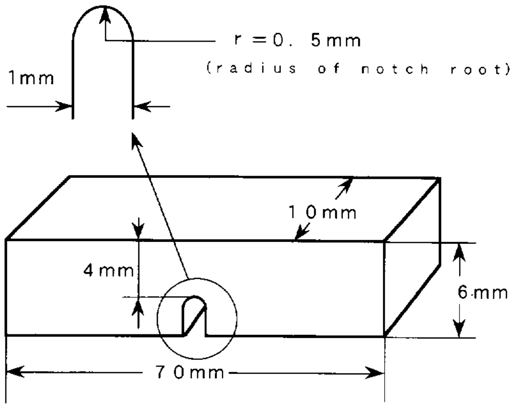

Figure 1 Dimensions of test specimen

where σ_c is in units of Pa and ν_e is in m^{-3}. *Figure 3* shows a bilogarithmic plot of the crazing stress, measured at room temperature by three-point bending of a round-notched bar, against entanglement density, according to equation (4). The data have some deviation at large entanglement density. A correction for this deviation is described later in the present paper.

In the previous paper[1], we studied the temperature dependence of shear yield stress, because it is well known that both deformation and fracture behaviour of polymers are affected by the testing temperature. Therefore we also studied the temperature dependence of crazing stress. It has been previously reported that crazing stress generally has less temperature dependence compared to shear yield stress[7]. We measured the crazing stress of polystyrene (PSt), poly(vinyl chloride) (PVC) and polycarbonate of bisphenol-A (PC) at various temperatures. The results are plotted against the difference between glass transition temperature and testing temperature, $T_g - T$, in *Figure 4*. It is clear that crazing stress is temperature dependent to some extent, and it cannot be ignored. Equation (4) does not contain a term for temperature dependence. Thus, we attempted to express temperature dependence by the following method. Entanglement density can be obtained from equation (2), where density varies depending on the temperature. Assuming that the entanglement molecular weight is constant, independent of temperature, the change of entanglement density was calculated from the temperature dependence of density. We then determined

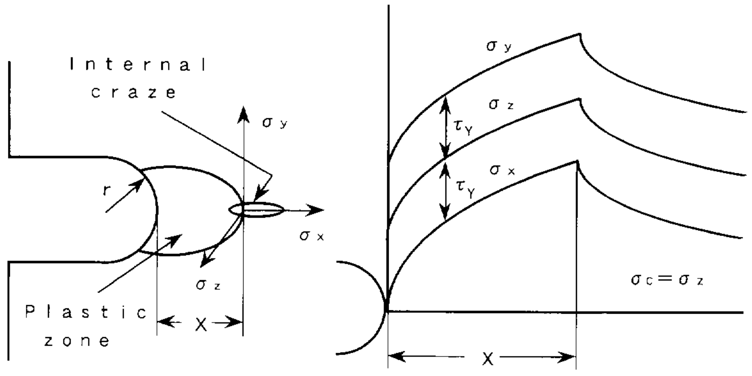

Figure 2 Definition of the stress components and stress distribution

Table 1 Polymer specimens

	C_∞	$\nu_e \times 10^{25}$ (m^{-3})	T_g (°C)	M_w[d] ($g\ mol^{-1}$)
Polystyrene	10.8	2.47	100	220 000
Poly(methyl methacrylate-*co*-styrene) (3/7)[a]	10.0	4.58	100	138 000
Poly(methyl methacrylate-*co*-styrene) (6/4)[b]	9.3	6.02	100	185 000
Poly(methyl maleimide-*co*-isobutene) (5/5)[c]	8.4	3.55	160	136 000
Poly(methyl methacrylate)	8.2	7.83	100	99 000
Poly(vinyl chloride)	7.6	18.7	80	156 000
Phenoxy resin	3.7	30.7	97	57 000
Polyarylate	3.0	28.9	190	45 000
Polycarbonate of bisphenol-A	2.4	34.3	150	56 000
Poly(ether sulfone)	2.4	25.3	225	57 000
Polysulfone	2.2	28.9	190	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.

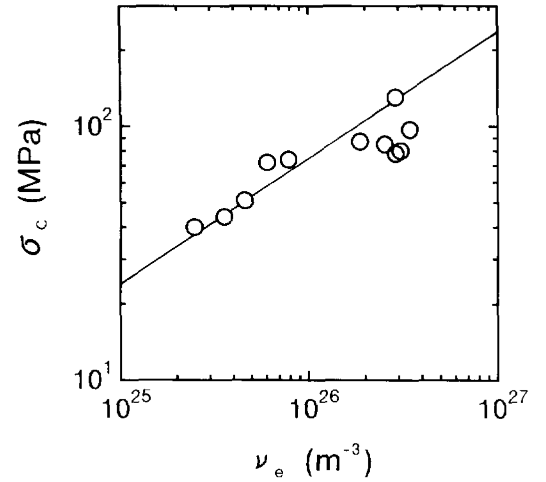

Figure 3 Crazing stress *versus* entanglement density according to equation (4). Crazing stresses were measured at room temperature

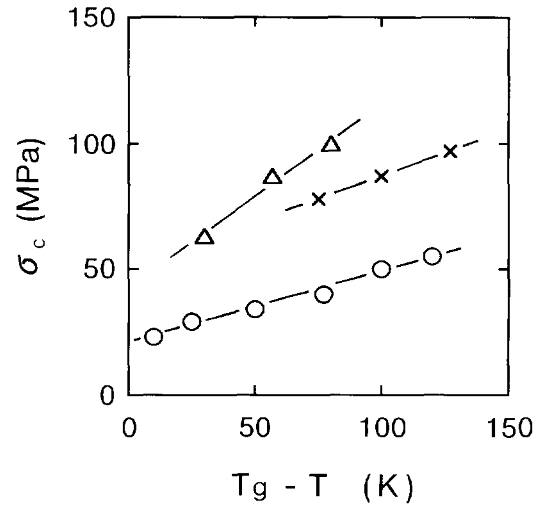

Figure 4 Typical results for the temperature dependence of crazing stress: ○, polystyrene; △, poly(vinyl chloride); ×, polycarbonate of bisphenol-A

Table 2 Experimental and predicted values of crazing stress at various temperatures

	$T_g - T$ (K)	Crazing stress, σ_c (MPa)	
		Experiment	Prediction
Polystyrene	77	40	40.0
	100	50	40.1
	120	55	40.2
Poly(vinyl chloride)	30	63	86.8
	57	87	87.0
	80	100	87.2
Polycarbonate of bisphenol-A	75	78	96.6
	100	87	96.8
	127	97	97.0

the change of crazing stress from equation (4) and the results are shown in *Table 2*. Measured crazing stresses at various temperatures are plotted in *Figure 5* according to equation (4). Because changes of entanglement density with temperature are extremely small, the temperature dependence of crazing stress cannot be represented by this method.

As described before, the relationship between crazing stress and entanglement density presented by Wu has some deviation at high entanglement density and cannot represent the temperature dependence of crazing stress. So our work aimed to obtain the relationship with more correspondence to experimental data. The mechanism of crazing can be explained as follows. Expansion stress acts around the notch tip due to the constraint of strain. When expansion stress reaches a critical value, voids form close to the tip of the plastic zone. Then, deformation is concentrated between voids due to plastic instability, causing this area to be stretched to become a fibril, then form a craze. For amorphous polymers, the critical stress of void formation is large because it has a small structural fluctuation. Hence, as soon as voids are generated, the conditions for plastic instability are satisfied, forming a craze. In this mechanism, crazing stress is influenced by the processes of both void formation and fibrillation of a non-deformed molecular chain. Wu considered void formation without any stress needed for fibrillation. According to Kramer and Berger's theory[2], crazing stress should be represented by the following equation, with consideration of both void and fibril formation:

$$\log \sigma_c = A_1 \log[(\gamma + \nu_e dU/4)\sigma_f] + A_2 \qquad (5)$$

where γ, U and σ_f are surface free energy, bond energy and fibrillation stress, respectively. The term d is entanglement mesh size and was acquired from the equation:

$$d = C_\infty N_v \langle 1v^2 \rangle \qquad (6)$$

where C_∞, N_v and $\langle 1v^2 \rangle$ are the characteristic ratio, the number of statistical skeletal units between entanglement points, and the mean square length of a statistical skeletal unit, respectively. A statistical skeletal unit is the minimum movable unit by free rotation around its backbone axis[3]. Surface free energy (4×10^{-2} N m^{-1}) and bond energy (6×10^{-19} J) are assumed to be constant, regardless of the type of polymer.

The deviation at high entanglement density in Wu's

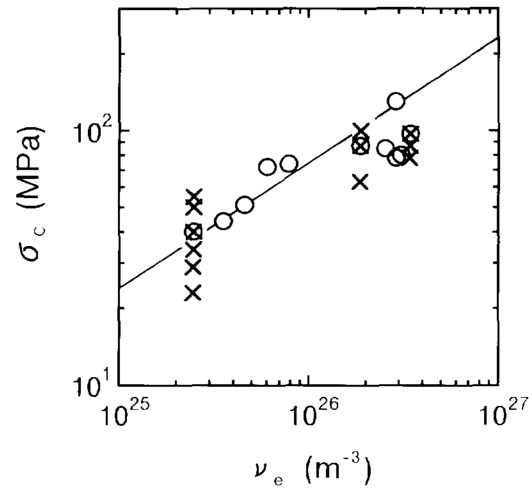

Figure 5 Crazing stress *versus* entanglement density according to equation (4). Crazing stresses and entanglement densities were measured at various temperatures for PC, PVC and PSt (×) and at room temperature for other polymers (○)

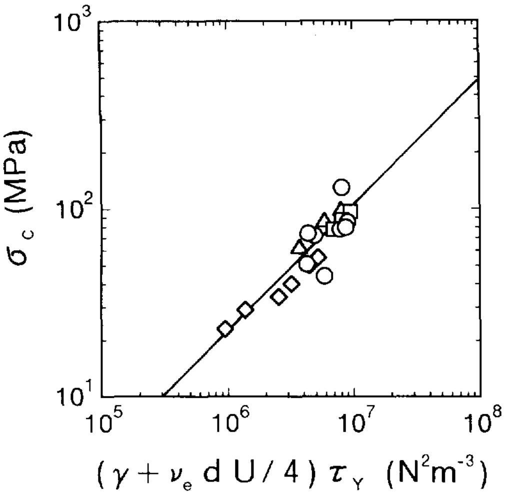

Figure 6 Correlation of crazing stress with molecular parameters, γ, ν_e, d, U and τ_Y. Crazing stresses were measured at various temperatures for PSt (◇), PVC (△) and PC (□) and at room temperature for other polymers (○). The solid line is the best fit of equation (5) with $A_1 = 0.679$ and $A_2 = 3.26$

relation was corrected in equation (5) as follows. Wu represented the contribution of the molecular chain scission to void formation by the number of entanglement points per unit volume. However, a void is formed by the separation of bulk material into two parts and a new fibril surface is formed. When a fibril surface is formed, the entangled molecular chains which originally cross the surface of a fibril might be broken. Therefore it is thought that the contribution of molecular chain scission should be represented by the number of entangled molecular chains that cross the unit area. The number of entangled molecular chains crossing the unit area is represented by $\nu_e d$. Therefore the term for the contribution of the molecular chain scission is represented by $\nu_e d$ in equation (5).

On the other hand, the temperature dependence of crazing stress was represented in the following way in equation (5). Although the contribution of void formation hardly changes with temperature, fibril formation, which is a kind of plastic deformation, should exhibit temperature dependence. However, stress in fibrillation is unknown. Fibrillation occurs when deformation is concentrated among voids due to plastic instability. Conformational change of the molecular chain and intermolecular slippage occur; the molecular chains become oriented and orientational hardening occurs. It is thought that fibrillation stress is the stress required for conformational change and intermolecular slippage to occur. Although it is not known that the mechanisms of craze fibrillation and shear yielding are the same, we assumed that fibrillation stress is proportional to shear yield stress, because conformational change and intermolecular slippage also occur in shear yielding. We previously reported that the relationship between molecular structure and shear yield stress and its temperature dependence can be represented by the equation[1]:

$$\tau_Y = A_3 C_\infty \delta^2 (T_g - T)(V_w/n_v)^{1/3} + A_4 \tag{7}$$

where δ^2 is the cohesive energy density, V_w is the van der Waals volume of a repeat unit, and n_v is the number of statistical skeletal units in a repeat unit. Constants A_3 and A_4 are 3.4×10^5 and 1.21×10^7, respectively, when all variables are in SI units. We used this relationship to express the temperature dependence of crazing stress.

Figure 6 shows measured values of the crazing stress plotted according to equation (5). It is clear that equation (5) is a good expression of the relationship between polymer structure and crazing stress and its temperature dependence. Constants A_1 and A_2 in equation (5) were determined as 0.679 and 3.26, respectively, by best-fitting, when all variables are in SI units.

CONCLUSION

We studied the relationship between molecular parameters and the crazing stress measured by three-point bending of round-notched bars for various types of amorphous glassy polymers. We tried to utilize equation (5), in which both void and fibril formation are taken into consideration. Crazing stress and its temperature dependence could be expressed by using shear yield stress as fibrillation stress.

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REFERENCES

1 Yamamoto, T. and Furukawa, H. *Polymer* 1995, **36**, 2389
2 Kramer, E. J. and Berger, L. L. *Adv. Polym. Sci.* 1990, **91/92**, 1
3 Wu, S. *Polym. Eng. Sci.* 1990, **30**, 753
4 Kamber, R. P. *Polym. Commun.* 1983, **24**, 292
5 Narisawa, I., Ishikawa, M., Murayama, T. and Ogawa, H. *Kobunshi Ronbunshu* 1979, **36**, 543
6 Ishikawa, M., Narisawa, I. and Ogawa, H. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 1791
7 Ishikawa, M., Ogawa, H. and Narisawa, I. *J. Macromol. Sci. Phys. Edn* 1981, **B19**, 421
8 Ishikawa, M. and Narisawa, I. *J. Mater. Sci.* 1983, **18**, 1974
9 Ishikawa, M. and Narisawa, I. *J. Mater. Sci.* 1983, **18**, 2826
10 Wu, S. *J. Polym. Sci. Part B, Polym. Phys. Edn.* 1987, **25**, 557
11 Wu, S. *J. Polym. Sci. Part B, Polym. Phys. Edn.* 1987, **25**, 2511
12 Wu, S. *J. Polym. Sci. Part B, Polym. Phys. Edn.* 1989, **27**, 723