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The effect of Freon vapour on fracture behaviour of styrene-acrylonitrile copolymer — I. Craze initiation behaviour

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Environmental stress cracking behaviour of polystyrene and styrene-acrylonitrile copolymer (SAN) has been studied in Freon vapour in view of molecular weight and acrylonitrile content. The critical stress for craze or crack initiation was measured using three-point bending test and the surface damage was examined by scanning electron microscopy. The critical stress increased with an increase of acrylonitrile content in SAN copolymer, which suggests that the craze initiation stress has a good correlation with the solubility parameter difference between the polymer and crazing agent. However, molecular weight did not have any significant effects on the critical stress for craze initiation. For homopolystyrene, relatively large-sized craze was developed in Freon vapour due to the increase of softened layer thickness in the developed craze wall. As acrylonitrile content increases the development of craze is suppressed. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The mechanical failure of polymers is induced more easily in some active environmental agent than in the air under the stressed condition. As a result, polymer fracture at stresses considerably below the normal yield stress, which reduces the service time of polymers. This phenomenon is broadly termed environmental stress crazing or cracking (ESC) behaviour, and it has been a topic of many studies[1–5]. The decrease of fracture resistance by the environment is attributed to the plasticization of polymers[1,6–8], i.e. diffusion of small environmental molecules decreases the glass transition temperature of polymers and reduces the yield stress for cracking or crazing. The stabilization of solid surface by environments also assists the development of crack or craze by reducing surface energy[9–11].

High impact polystyrene (HIPS) and acrylonitrile butadiene styrene copolymer (ABS) resins are widely used in inner liners of refrigerators. However, there exist the serious problem of these polymers cracking owing to the Freon vapour which is used as a foaming agent for polyurethane insulation between the inner liner and the outshell of the refrigerator. Knowledge of failure behaviour in this environment is desirable. However, little work has been reported on the environmental effect of Freon vapour on styrenic polymers[12–15].

In this paper, the environmental stress crazing behaviour of neat polystyrene (PS) and styrene acrylonitrile copolymer (SAN) by Freon vapour has been investigated as a part of the systematic model study to understand the ESC behaviour of HIPS and ABS in Freon vapour. The critical stress for craze or crack initiation is determined as a quantitative evaluation of environmental effect. In addition, the microstructure of developed craze is examined as a

function of acrylonitrile content and molecular weight. Freon 11 ($CFCl_3$) vapour was selected as an environment since Freon 11 has been still widely used as a foaming agent in industries and is known to be a very aggressive environmental cracking agent with respect to styrenic polymers.

EXPERIMENTAL

Materials and specimen preparation

The materials used are illustrated in *Table 1*. They were supplied by Cheil Industry except SAN-5.7 and SAN-11.3 which are laboratory products. The resins were compression molded into sheets at 170°C and cooled very slowly without applied pressure in order to minimize the residual stress. The molded sheets were machined into the desired size of

Table 1 Characteristics of styrenic polymers used

Polymer	$\overline{M_w}$ (10^3g mol^{-1})	$\overline{M_w}/\overline{M_n}$	Acrylonitrile content (wt%)
PS	220	2.2	0
	260	2.2	0
	330	2.3	0
SAN	259	2.2	5.7
	328	2.3	11.3
	96	1.8	24
	180	2.1	24
	150	2.0	24.5
	90	2.1	28
	113	1.8	28
	172	1.9	28
	150	2.0	28.5
	145	2.0	33

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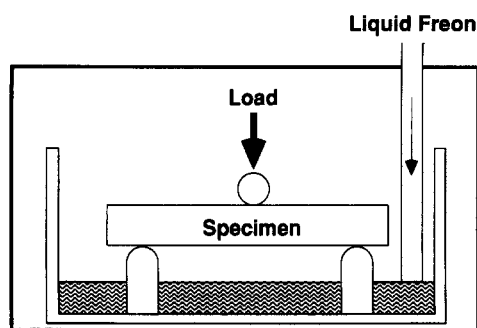
Figure 1 Schematic diagram of test device for craze or crack formation in Freon vapour.

the three-point bending specimen. Freon 11 (CFCl$_3$) were purchased from Ulsan Petrochemical Company (b.p 23.7°C).

Determination of critical stress for craze or crack initiation

The critical flexural strain at which craze or crack initiates on the specimen surface was determined by the three-point bending (TPB) test (width 6 mm, thickness 4 mm, span 48 mm). The schematic diagram of the test device is illustrated in *Figure 1*. The specimen was bent using a TPB jig with a universal testing machine (Instron 4206) in an environmental chamber. After 1 min, which is enough time to stabilize the loading condition, liquid Freon was rapidly introduced under the stressed specimen into the chamber. The chamber was maintained at 30°C which is significantly above the boiling point of Freon 11. The introduced liquid Freon vapourized rapidly under the stressed specimen in a chamber and the vapour generated crazes or cracks on the surface of the stressed specimen. The maximum tensile stress, σ_{max} on the bottom surface of the specimen was determined by bending equation (1)[16]:

$$\sigma_{max} = \frac{3PL}{2bd^2} \qquad (1)$$

where P is the bending load, L is the span length, b is the width and d is the thickness of the specimen. After 1 min exposure to the Freon vapour, the specimen was taken out and the surface of the specimen was examined by a low magnification optical microscope. If crazes or cracks were not present on the surface of the specimen, the exposed specimen was discarded and slightly higher stresses was applied to the new specimen. After exposing the Freon vapour the surface of the new specimen was examined again. Through the repeated procedure of this test, the values of critical stress below which neither crazing nor cracking occurs were determined, i.e. only one or two lines of crazes or cracks initiates at that stress.

Microscopy and DSC test

For scanning electron microscopy (SEM) observation, compression molded 0.2 mm thick sheet was bent on a small scale and it was fixed with a metal plate to keep the stressed state. Then the specimen was exposed to Freon vapour in the environmental chamber undergoing critical stress measurements. The specimens were dried in vacuum and crazes or cracks developed by the Freon vapour were examined using SEM (Hitachi S-570) under the stressed state.

Glass transition temperatures (T_g) of Freon diffused region were measured using a differential scanning calorimeter (Perkin-Elmer DSC 7) with a scanning rate of 20°C min^{-1}. A bulk specimen was exposed to Freon vapour for 1 day at room temperature to reach the equilibrium state, then the swelled part on the surface was used for the determination of T_g.

RESULTS AND DISCUSSION

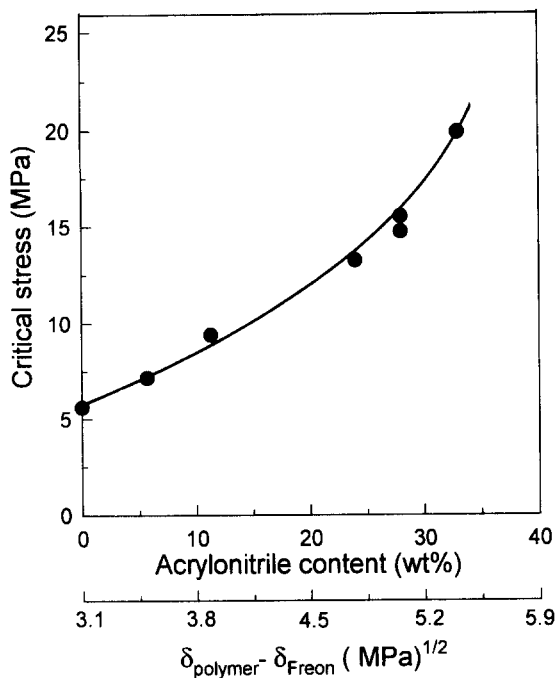*Critical stress for craze and crack initiation*

It is known that the craze or crack development by organic medium requires some induction time in the case of mild condition[3,17,18]. However, in this experiment, above the critical stress the development of damage lines on the surface of PS occurred almost simultaneously with exposure of Freon vapour, because Freon 11 is very aggressive agent to PS. This can be demonstrated clearly by the abrupt decrease of stress of the specimen right after Freon exposure (*Figure 2*). On the other hand, below the critical stress it did not occur for our experimental time, but only swelling occurred in PS. Therefore, at the time of Freon exposure or immediately after Freon exposure the specimen was assumed to exhibit elastic behaviour even though several polymer molecules on the exposed specimen surface might be plasticized by Freon vapour. Thus, at the time of craze initiation, the critical stress can be determined by equation (1) which was derived from the elasticity.

It should be noted that the damage lines such as craze lines were developed around the mid-point of the outer side of the bent specimen at which the tensile stress shows a maximum. Thus, the measured critical stress is the tensile stress.

The critical stress for craze initiation of pure PS in Freon vapour was about 6 MPa, which is much lower than that in the air, about 20 MPa[19]. As acrylonitrile content of SAN copolymer increases the critical stress increased remarkably, which implies that the SAN copolymer with high acrylonitrile content is less susceptible to Freon vapour (*Figure 3*). The crazing resistance is closely related to the compatibility between polymer and ESC agent[8,9]. In the case of stress crazing/cracking of polymers in liquid environment, excellent correlation exists between solubility parameter of the crazing/cracking agent and critical stress for craze or crack formation, i.e. the critical stress decreases as the solubility parameter of the crazing agent approaches that of the polymer[7,9,20]. In this experiment, as the acrylonitrile content of SAN copolymer increases the
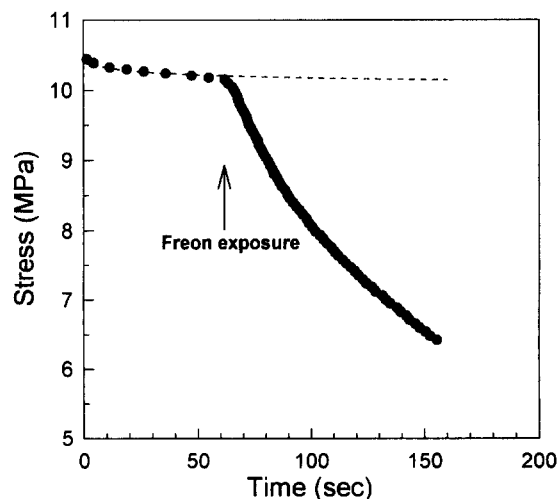
Figure 2 Relaxation behaviour of polystyrene in Freon vapour. Dotted line represents relaxation curve in the air.

Figure 3 Effect of acrylonitrile content on critical stress for craze initiation of SAN copolymers.

Figure 4 Effect of molecular weight of styrenic polymers on critical stress for craze initiation.
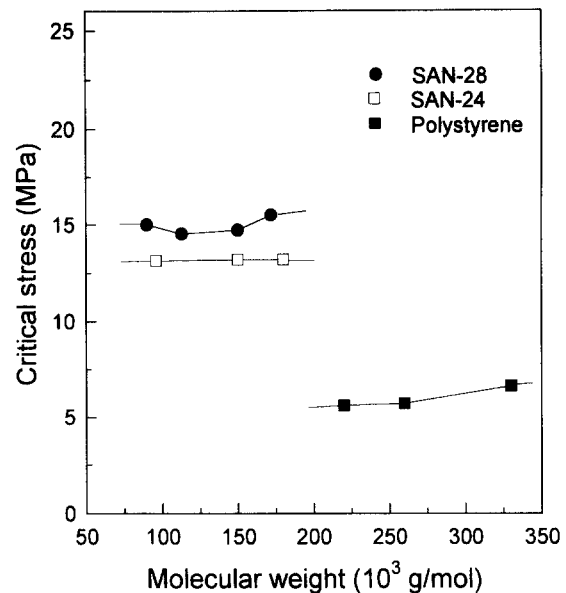
solubility parameter difference between Freon and SAN copolymer increases, since the solubility parameter of PS, poly(acrylonitrile) and Freon 11 are 18.6, 25.6 and 15.5 MPa$^{1/2}$, respectively[21]. As a result, good correlation was also found between craze initiation stress and solubility parameter difference, i.e. craze initiation stress increases as solubility parameter difference increases (*Figure 3*).

The increase of critical stress with acrylonitrile content can be interpreted as plasticization of the polymers. If the small Freon molecule diffuses into the surface of the specimen (which is highly strained), the polymer chain can start to flow due to plasticization. The diffused Freon molecules near the surface appear to trigger the chain flow. For pure PS the plasticization occurs relatively easy, which results in quite low craze initiation stress. However, as the acrylonitrile content in SAN copolymer increases, the progress of plasticization on the specimen surface becomes more difficult. As a result the critical stress for the initiation of chain flow such as crazing becomes high.

The decrease of T_g in Freon diffused specimen was identified by DSC measurement. The PS specimen showed noticeable swelling phenomena in Freon vapour and the T_g of Freon diffused PS was near -30°C. As acrylonitrile content increases the degree of swelling becomes reduced. The SAN-24 did not show any swelling phenomena compare to SAN-5.7. Thus it is concluded that acrylonitrile groups in the SAN polymers suppress the diffusion of Freon molecules and then the plasticization by Freon vapour is reduced, which results in an increase of critical stress.

The effect of molecular weight on critical stress is shown in *Figure 4*. Over this range of molecular weight, no marked difference in critical stresses was observed for PS and SAN copolymer with molecular weight. This result is similar to those reported by Henry[7] and Bergen[22] for the stress cracking of SAN copolymers by several liquid agents. This result may be due to the fact that the solubility of polymer is mainly controlled by chemical structure of repeating group rather than the number of repeating units[23].

However, a somewhat different result is reported[3]. The critical stress of PS increases with increasing chain length of ESC agents such as alcohols and hydrocarbons, although they have similar solubility parameters. These results imply that the activity of the solvent depends on its molecular motion, since large molecules diffuse in polymers more slowly than small molecules. Therefore, the length of polymer may possibly affect the critical stress, because the low molar mass chain has less entanglements. So the low molar mass polymer has less restriction for chain flow and craze formation[24]. Furthermore, a low molar mass polymer chain has many imperfections in the structure due to end groups, which enables many defects for craze initiation points. In our experiment, however, the molecular weight of the specimen is much greater than the critical molecular weight above which the fracture energy has equilibrium value[19]. Therefore, the effect of molecular weight on critical stress may not be apparent. From the results of *Figures 3 and 4* it is certain that the main factor for determining critical stress for craze initiation is the chemical structure of polymer such as acrylonitrile content rather than molecular weight.

Surface damages of PS and SAN

Figure 5 shows the top view of the damage zone of homo PS and SAN copolymers which were exposed to Freon vapour under the stressed state using a bending jig. On the surface of PS specimen, well-developed craze fibrils can be seen. As acrylonitrile content increases the shape of craze became more narrow and the craze structure was less developed, and eventually it changed to a narrow yield band for SAN-33. The microscopic observation is consistent with the results of the critical stress, i.e. the SAN copolymer with higher acrylonitrile content requires a higher critical stress for the initiation of damage and it is less susceptible to crazing in Freon vapour.

The craze fibril diameter of PS formed in Freon was around 100–300 nm which is much larger than that of dry craze, generally 4–10 nm in the PS film[25]. The thickness of PS craze by Freon vapour was above 10 μm in maximum size which is also much larger than that of dry craze. The development of a huge craze structure can be explained using a meniscus instability mechanism[26]. The perturbation
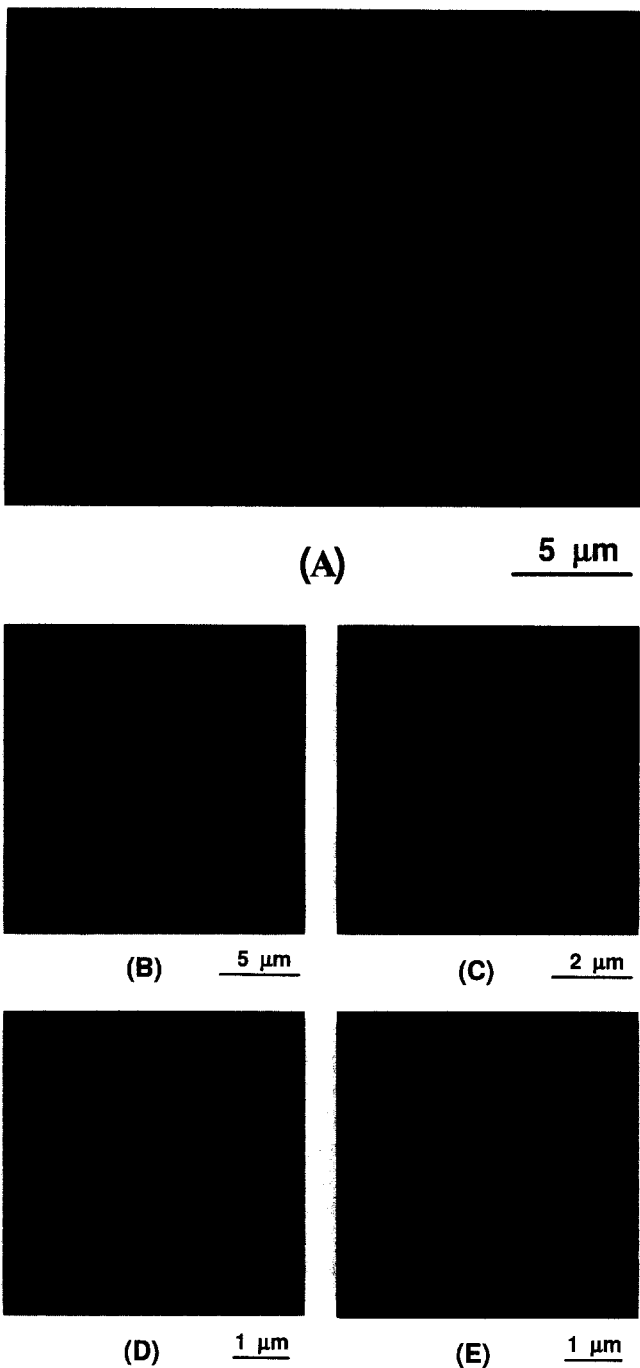
(A) 5 μm

(B) 5 μm

(C) 2 μm

(D) 1 μm

(E) 1 μm

Figure 5 Structure of crazes formed in Freon vapour at bended state: (A) homo PS; (B) SAN-5.7; (C) SAN-11; (D) SAN-24; and (E) SAN-33

Figure 6 Craze interfibril spacing of SAN copolymers by Freon vapour

wave length (λ), which is fibril spacing, has the following relation[27]:

$$\lambda_{max} \sim 12\Gamma/bS \qquad (2)$$

where Γ is the surface tension, b is a constant of order 1, and S is the average stress on the craze–matrix interface. When the Γ of pure PS and SAN copolymers, which is approximately 40 mN m^{-1} at 20°C in air[28] and the critical stress of the polymers are applied to the equation, the value of λ_{max} is an order of 10^{-7}–10^{-8} m. This value decreases much more if the decrease of surface tension by Freon environment is considered. However, the observed interfibril spacing from *Figure 5*(A), which is an order of 10^{-6} m, is much larger than the calculated value from equation (2) (*Figure 6*). Furthermore, as acrylonitrile content decreases, the observed interfibril spacing increased rapidly and the
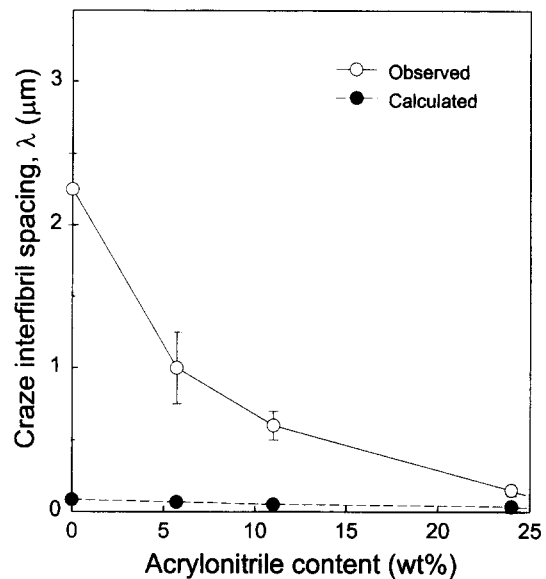
observed values deviate much from the estimated value from equation (2).

This discrepancy is conceived as a result of the increase of softened layer at the craze wall. It is known that the interfibril spacing becomes independent of both craze stress and surface energy as the thickness h of flow-active layer at craze wall increases[25]. The interfibril spacing is given by $\lambda_{max} \sim \pi h$ in that case. Considering the degree of swelling and T_g depression in the polymers, this case is the most likely to be found in the PS and SAN copolymer containing a low acrylonitrile content. Thus, it is believed that the enlargement of PS craze structure by Freon vapour results from the decrease of stress on the craze–matrix interface and the increase of the softened layer at craze wall. The behaviour as seen in *Figure 6* reveals that the environmental stress crazing is closely related with the plasticization of specimen surface and the plasticization becomes more favourable as acrylonitrile content decreases. On the other hand, the reduction of surface tension by the Freon environment seems to have little effect in the formation of craze structure since it leads decrease of the fibril spacing as seen in the equation, $\lambda_{max} \sim 12\Gamma/bS$.

CONCLUSION

For the initiation of crazes in the Freon environment, the acrylonitrile content in SAN copolymer has a significant effect on the critical stress in initiating crazes. However, the molecular weight does not influence the critical stress. The compatibility between polymers and Freon vapour is found to be important in critical stress.

In a Freon vapour environment a large-sized craze developed. Furthermore the development of a large-sized craze was suppressed as increase of acrylonitrile content. This enlargement of the craze structure is attributed to an increase in the flow active layer in the craze wall, which results from the high plasticization of polymer.

ACKNOWLEDGEMENTS

REFERENCES

1. Kramer, E. J., in *Developments in Polymer Fracture*, ed. E. H. Andrew. Applied Science, London, 1979, p. 55.
2. Kambour, R. P. J., *Polymer Science and Macromolecular Review*, 1973, **7**, 1.
3. Narisawa, I., *Journal of Polymer Science, A2* , 1972, **10**, 1789.
4. Amold, J. C., *Journal of Material Science*, 1994, **29**, 3095.
5. Kramer, E. J. and Bubeck, R. A., *Journal of Polymer Science: Polymer Physics Edition*, 1978, **16**, 1195.
6. Kefalas, V. A. and Argon, A. S., *Journal of Material Science*, 1988, **23**, 253.
7. Henry, L. F., *Polymer Engineering and Science*, 1974, **14**, 167.
8. Kambour, R. P., Gruner, C. L. and Romagosa, E. E., *Journal of Polymer Science: Polymer Physics Edition*, 1973, **11**, 1879.
9. Bernier, G. A. and Kambour, R. P., *Macromolecules*, 1968, **1**, 393.
10. Brown, H. R. and Kramer, E. J., *Polymer*, 1981, **22**, 687.
11. Andrews, E. H. and Bevan, L., *Polymer*, 1972, **13**, 337.
12. Miller, P. and Kramer, E. J., *Journal of Material Science*, 1990, **25**, 1751.
13. Savadori, A., Bacci, D. and Marega, C., *Polymer Testing*, 1987, **7**, 59.
14. Cho, K., Lee, M.S. and Park, C.E., *Polymer*, 1997, **0**, 0. (in press).
15. Cho, K., Lee, M.S. and Park, C.E., *Polymer*, 1997, **38**, 4641–4650.
16. Williams, J. G., *Stress Analysis of Polymers*, 2nd ed. Wiley, New York, 1980, p. 134.
17. Gent, A. N. and Hirakawa, H., *Journal of Polymer Science A2*, 1968, **6**, 1481.
18. Hoa, S. V., *Polymer Engineering and Science*, 1980, **20**, 1157.
19. Kinloch, A. J. and Young, R. J., *Fracture Behavior of Polymers*. Applied Science, London, 1983, p. 238.
20. Mai, Y. W., *Journal of Material Science*, 1976, **11**, 303.
21. Brandrup, J and Immergut, E. H., ed., *Polymer Handbook*, 3rd edn. Wiley-InterScience, New York, 1989, p. VII.
22. Bergen, R. L. Jr, *SPE Journal*, 1968, **24**, 77.
23. Paul, D. R., and Newman, S., *Polymer Blends*. Academic, New York, 1978, Vol. 1, p. 46.
24. Martin, J. R., Johnson, J. F. and Cooper, A. R., *Journal of Macromolecular Science—Reviews of Macromolecular Chemistry*, 1972, **C8**, 57.
25. Donald, A. M. and Kramer, E. J., *Philosophy Magazine*, 1981, **A43**, 857.
26. Kramer, E. J., in *Crazing in Polymers*, ed. H. H. Kausch. Springer, Berlin, 1983, p. 10.
27. Brown, H. R., *Journal of Polymer Science: Polymer Physics*, 1989, **27**, 1273.
28. Brandrup, J. and Immergut, E. H., ed., *Polymer Handbook*, 3rd edn. Wiley-InterScience, New York, 1989, pp, VI–415.