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A model for the different crazing behaviour of amorphous polymer glasses

By G. A. KARDOMATEAS and I. V. YANNAS

Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, U.S.A.

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ABSTRACT

A molecular-level analysis that explains the differences in crazing behaviour encountered in polymeric glasses is presented. Considering the separation of molecules or segments of them as the controlling mechanism for crazing (at the initiation stage), it is found that in vinyl polymers such as polystyrene and polymethyl methacrylate, which craze at all temperatures below the glass transition, separation is opposed by much smaller intermolecular barriers than in non-vinyl polymers such as polycarbonate and polyphenylene oxide which show mostly shear yielding and craze only in a narrow temperature regime immediately below the glass transition. For the latter polymers a relevant molecular yield mechanism can be described. The analysis also explains the higher tendency to crazing as temperature increases, as well as the suppression of crazing with pressure.

§ 1. INTRODUCTION

Two kinds of crazing behaviour have been observed in glassy amorphous polymers. Type I polymers such as polystyrene (PST) and polymethyl methacrylate (PMMA) craze at all temperatures below the glass transition temperature (T_g). Type II polymers such as polycarbonate (PC) and polyphenylene oxide (PPO) craze only just below T_g, but show shear yielding at lower temperatures (Wellinghoff and Baer 1978).

Crazing in polymeric glasses is generally thought to be preceded by a dilatational stress field. Sternstein and Ongchin (1969) experimented with PMMA and formulated a craze initiation criterion based on the first stress invariant I_1 and a normal yielding factor (or stress bias. σ_b) defined as the difference in principal stress, $\sigma_b=\sigma_1$-σ_2. The underlying explanation is that the dilatational component of the applied stress field increases the molecular mobility, and at a sufficient local mobility the stress bias operates to elongate the molecules in the direction of the greatest principal stress. The requirement that the stress field be dilatational ($I_1>0$) is in keeping with the absence of crazing in compression. According to Argon, Hannoosh and Salama (1977), the localized dilatational field that is required for the nucleation of crazes depends upon the presence of packing heterogeneities in the glass where the microvoiding necessary for craze nucleation could be produced by the stress concentration.

Fellers and Kee (1974) concluded that craze nucleation is independent of molecular weight in polystyrene, but makes a very important contribution to the final craze morphology, whereas Pitman, Ward and Duckett (1978) found that the molecular weight affects the crazing stress in polycarbonate. Fellers and Huang (1979) suggested that crazes initiate most easily in volumes with relatively low density and with few molecular entanglements. The role of molecular entanglements on crazing has been investigated in detail by Donald and Kramer (1982 a, b) and it was concluded that the competition between shearing and crazing was dependent on the entanglement density; the highest entanglement density polymer forms shear bands and rarely crazes. Steger and Nielsen (1978) proposed a qualitative model whereby the statistical heterogeneity of the glass structure leads to weak regions within the polymer which serve as nucleation sites. The connection between the molecular structure of the glassy polymers and their mechanical behaviour had been also recognized and investigated by Argon and Bessonov (1977). In their study of the plastic deformation of a series of aromatic polyimides it was shown that as the spacing between natural hinges on polymer molecules (which is analogous to the quantity referred later as the moment arm length l) increases with increasing chemical complexity, the plastic deformation becomes less local.

Polymers were classified according to their structural parameters by Yannas and Luise (1982) in two types according to the relative contribution of inter- and intramolecular energy barriers to their stiffness. The strophon theory was proposed according to which deformation is accompanied by rotation around backbone bonds and the irreducible backbone segment which can undergo such rotation is made up, to a first approximation, of 3 virtual bonds (and named 'strophon'). A molecular mechanism of yielding based on the strophon theory has also been proposed by Yannas (1974).

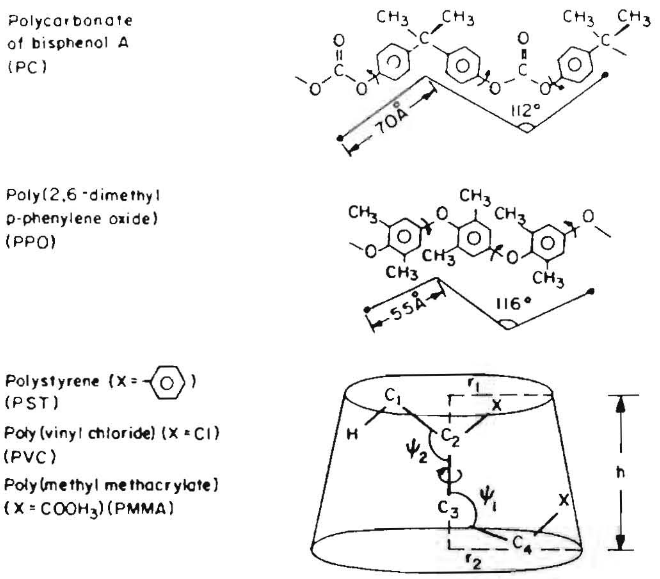
In the following, evidence will be presented that the magnitude of the repulsive term of the intermolecular energy barrier may be able to account for the difference in crazing behaviour, namely, the appearance or not of crazes. Craze growth and the craze tip advance mechanisms are not considered in this analysis.

§2. ANALYSIS

On a molecular level, any explanation of crazing must provide for void formation in an initially continuous polymer. This suggests that separation of molecules or segments thereof to form voids is the controlling mode of deformation in craze initiation. Chain scission, an alternate conceivable mechanism at the molecular level, has been shown to be possible in polystyrene crazes at room temperature; but it cannot be generalized to all polymers. In fact it is not expected for low molecular weight polymers or at elevated temperatures (when stresses are relatively low), not even for polystyrene (Kramer 1983). In addition, this mechanism is more representative of post-initiation phenomena, when (at somewhat higher stresses) a sufficient level of orientation and drawing has taken place to allow the scission mechanism to operate (Donald and Kramer 1982 b). Chain scission is not included in the present analysis (which means that our results for polystyrene are more conservative in the sense that the contribution of chain scission would further promote crazing).

Thus we assume in the following that the appearance of crazing depends on how easy it is for the forces between the molecules to be overcome. We refer to both the attractive and repulsive forces, since separation on one side necessarily brings a molecule closer to its neighbour on the other. The energy barriers which impede such a segment translation are primarily those which result from the interaction of spatially neighbouring groups on polymer chains, namely, the intermolecular energy barriers. Among these are barriers resulting from Van der Waals forces, polar interactions and hydrogen bonds.

Fig. 1



Structural parameters of polymers (not to scale) adapted from Yannas and Luise (1982).

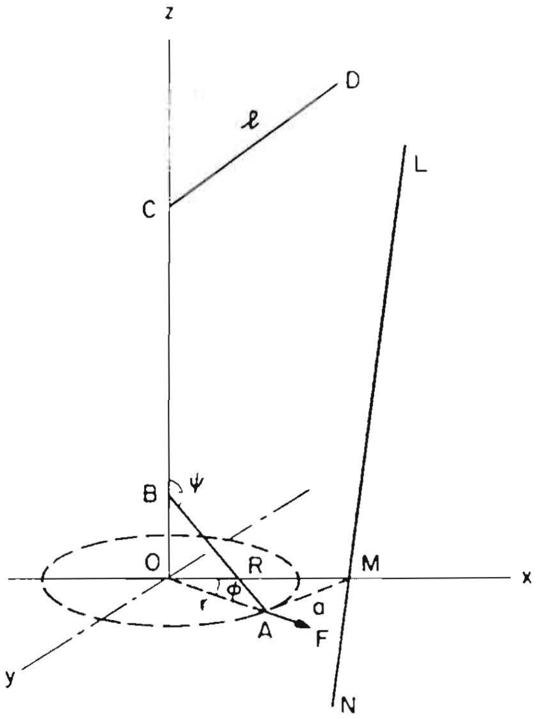
The fundamental physical model is shown in fig. 1 and is defined in terms of the known geometry of the polymer repeat unit, representing the macromolecule as a sequence of three rigid segments (strophon) (Yannas 1974). Tabulated values of the structural parameters (bond lengths, bond angles, etc.) can be obtained from various sources (e.g. Tonelli 1972, Wilkes Folt and Krimm 1973) and are given in table 1. For the interaction between chains, the intermolecular potential is taken here as the Lennard-Jones 6–12 potential (Lennard-Jones 1924). Geometrical parameters of major importance are the distance between two chains R and the quantity r, referred as the 'sweep radius' or mechanical moment arm (fig. 2). The sweep radius r is a function of the virtual bond length l, the virtual bond angle ψ and also of the size of the side group which may be attached to A. In the glassy state the chain–chain distance R is not a fixed quantity (as in a crystal) but varies over a range. However, the average value of R, as

Table 1. Structural parameters for type I (vinyl) and type II (non-vinyl) polymers.

Type I polymer	ψ_1 (degrees)	ψ_2 (degrees)	l (Å)	r_1 (Å)	r_2 (Å)
PST	114	112	1·53	4·0	4·5
PVC	112	112	1·53	2·15	2·7
PMMA	122	110	1·53	2·9	3·6

Type II polymer	ψ (degrees)	l (Å)	r (Å)
PC	112	7·0	6·5
PPO	116	5·5	4·9

Fig. 2



Geometrical relation between a strophon ABCD and the local axis LMN of the neighbouring chain.

well as its distribution, can be estimated by analysis of radical distribution functions obtained by X-ray diffraction and other methods (Wignall and Longman 1973).

The interaction between the rotating strophon ABCD and neighbouring chain LMN is schematically represented in a simplified model in fig. 2. Any arbitrary force, when applied to the strophon, will have a component in the ABC plane and directed along line OA. This force is the only one capable of producing a translation of the reference segment ABC relative to the neighbouring molecule LMN. Such a translation will be opposed by the intermolecular barriers that arise from the interaction with segments of adjacent chains: such interaction can be primarily repulsive (at close distances) or attractive (at moderate distances). The repulsive interaction turns out to be far larger and increases rapidly in magnitude as the two chains come closer. Thus the biggest resistance is encountered by the molecule lying closer. As the strophon rotates, the distance of the point A from the molecule closest to it is $R-r$, and this will be selected as a reference distance for the repulsive barrier. Therefore calculation of the force necessary to overcome the intermolecular barrier to translation of the strophon can be made by assuming that the points A and M in fig. 2 interact with a Lennard-Jones potential arising from a reference intermolecular distance $a=R-r$. The Lennard-Jones potential is given by

$$E(a)=E_0[(a_0/a)^{12}-2(a_0/a)^6], \quad (1)$$

where a_0 is the equilibrium length of bond AM and E_0 is the equilibrium energy of the secondary bond AM. Values of E_0 for interactions between pairs of like but relatively complex small molecules in a condensed system range from about 0·5–5 kcal mol^{-1} (Moelwyn-Hughes 1965). This quantity was estimated from the zero-point enthalpy (H_0^0) data of Bondi, compiled by Van Krevelen (1976), taking into account only the one rigid segment of the strophon which is assumed to participate in the intermolecular interaction, as modeled by segment AB in fig. 2. Estimation of the zero-point enthalpy of the rigid segment is based on the molecular structure of strophons in table 1 by assuming hexagonal packing of nearest-neighbour quasi-lattice sites. The parameter a_0 varies from about 3–6 Å and can be calculated from the Van der Waals volume V_w of one rigid segment of the strophon which participates in the chain-chain interaction, depicted as segment AB in fig. 2. The quantity V_w has been tabulated by Van Krevelen (1976) for a large variety of groups. In calculating a_0 it is assumed that the chain–chain interaction is spherically symmetrical.

Assuming absence of thermal activation, we require a force $\mathrm{d}E/\mathrm{d}a$ (in the direction of a) to overcome the intermolecular energy barrier. This force F_{inter} is given by

$$F_{\text{inter}} = \frac{\mathrm{d}E}{\mathrm{d}a} = 12E_0(a_0/a)^6[1-(a_0/a)^6]/a. \tag{2}$$

Let us now compare the value given by eqn. (2) at the chain–chain clearance (reference separation distance) $a = R - r$ for the various polymers. In table 2 we have tabulated the Lennard-Jones parameters and also the mean interchain distance R, estimated at 0 K (Yannas and Luise 1982) along with the calculated values of F_{inter} for the various polymers. Clearly, F_{inter} is much smaller (by orders of magnitude) for type I (vinyl) polymers which means that the resistance to translation of the strophon is much smaller in these polymers. Type II (non-vinyl) polymers cannot craze because they are opposed by very large intermolecular barriers. Figure 3(*b*) gives a semi-logarithmic plot of the repulsive F_{inter} versus a, the separation distance, while fig. 3(*a*) shows that the attractive force (from the chains that lie further) is smaller by many orders of magnitude, and thus insignificant. Let us now examine the temperature and pressure effects which are important in suppressing or promoting crazing.

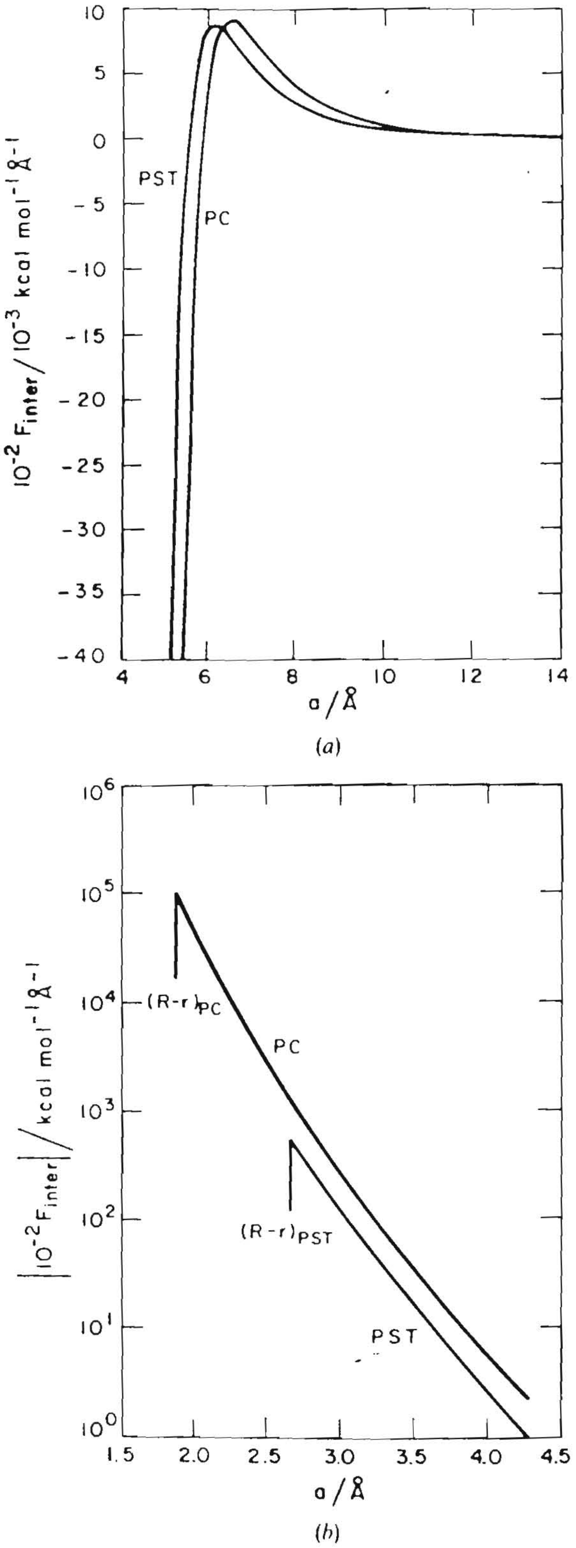
§3. TEMPERATURE AND PRESSURE EFFECTS

An increase in temperature causes, by thermal expansion, an increase in the molar volume and, consequently, an increase in R. Bond lengths between atoms are virtually independent of temperature, and this holds for bond lengths between segments of a polymer chain (Van Krevelen 1976). The mean interchain distance at any temperature,

Table 2. Repulsive intermolecular force at 0 K. We have used the smaller radius (based on C_2–X projection for PST, PMMA and on C_2–C_1–H projection for PVC, fig. 1) since separation of segments only may be the case.

Type	Polymer	E_0 (kcal mol^{-1})	a_0 (Å)	R (Å)	$R-r$ (Å)	$F_{\text{inter}} \times 10^{-2}$ (kcal mol^{-1} Å^{-1})
II	PC	2·0	5·9	8·4	1·9	101427
II	PPO	2·4	5·9	6·9	2·0	62455
I	PST	1·8	5·6	6·7	2·7	500·6
I	PVC	0·6	4·2	5·1	2·95	1·49
I	PMMA	1·7	5·4	6·3	3·4	14·5

Fig. 3



(*a*)

(*b*)

(*a*) The attractive intermolecular barrier to chain translation versus separation distance *a*, and (*b*) the repulsive intermolecular barrier to translation versus separation distance on a semilogarithmic plot.

$R(T)$ can be found from the molar volume $V_g(T)$, if we assume that the repeat unit is spherically symmetrical (Yannas and Luise 1982) ·

$$R(T)=2[(3/4\pi N)V_g(T)]^{1/3}, \tag{3}$$

$$V_g(T)=V_g^{298\,\mathrm{K}}+a_g(T-298), \tag{4}$$

where N is Avogadro's number, and a_g is the thermal expansion coefficient of the glassy polymer. In the above equations $V_g(T)$ is the molar volume of the polymer repeat unit, rather than that of the segment or of the strophon, since the mean interchain distance is related most closely to the repeat unit. The quantity $V_g(298\ \mathrm{K})$ has been tabulated by Van Krevelen (1972) for some polymers and may also be calculated, using the group contribution method, from the constituent chemical groups. We give in table 3 the resulting intermolecular force at room temperature (298 K). A more interesting temperature level is, however, at the glass transition, since non-vinyl (type II) polymers craze at temperatures near T_g. Thus let us consider the effect of such a temperature change. For the non-vinyl polymers considered here, PC and PPO, at the shear-to-craze transition (Wellinghoff and Baeer 1978), eqns. (3) and (4) give for PC, $T_g=423$ K, $R(410\ \mathrm{K})=8{\cdot}84$ Å and $F_{\mathrm{inter}}\times 10^{-2}=6259\ \mathrm{kcal\ mol^{-1}\ Å^{-1}}$, and for PPO, $T_g=484$ K, $R(450\ \mathrm{K})=7{\cdot}27$ Å and $F_{\mathrm{inter}}\times 10^{-2}=6855\ \mathrm{kcal\ mol^{-1}\ Å^{-1}}$. These values of F_{inter} are substantially smaller than the values given in table 2. Such a decrease in intermolecular barriers with increase in temperature could explain the prospensity to crazing observed in type II polymers near T_g, and also the decrease in the threshold stress required for craze formation with increasing temperature observed in type I polymers. Notice that the 'threshold' F_{inter} is almost the same for the two polymers considered here. Figure 4 gives a plot of the absolute value of the (repulsive) intermolecular force versus temperature for polycarbonate, starting from room temperature.

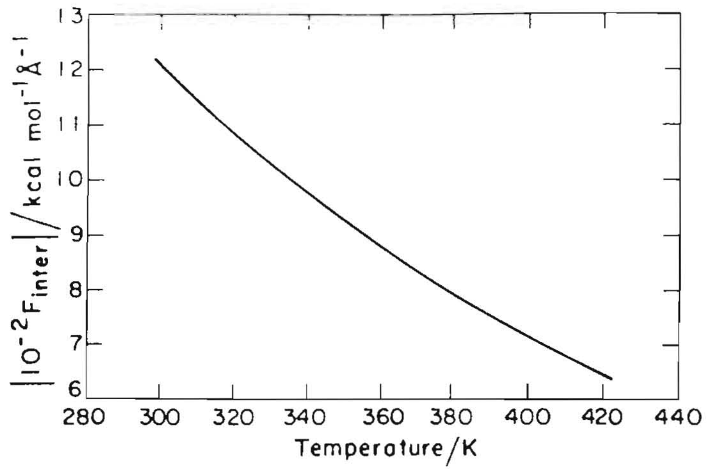
Crazing is suppressed by hydrostatic pressure since, according to the postulated mechanism, separation of molecules cannot occur easily under such conditions. A transition from crazing to yielding is found for polystyrene under a hydrostatic pressure of about 0·7 GPa (or 10^5 psi, (Kambour 1973)). We assume (Yannas and Luise 1982) that a pressure increase from p_0 to p at constant temperature results simply in the compression of the intermolecular distance from $R(p_0)$ to $R(p)$ by an amount ΔR, which is the result from of hydrostatic compression of an elastic sphere of volume $V(p)$ with radius $R(p)$ and compressibility k, so that

$$k=-\frac{1}{\Delta P}\frac{\Delta V}{V(p)}=-\frac{1}{\Delta P}\frac{3\Delta R}{R(p)}. \tag{5}$$

Table 3. Intermolecules force at 298 K. R is calculated from eqn. (3), F_{inter} from eqn. (2).

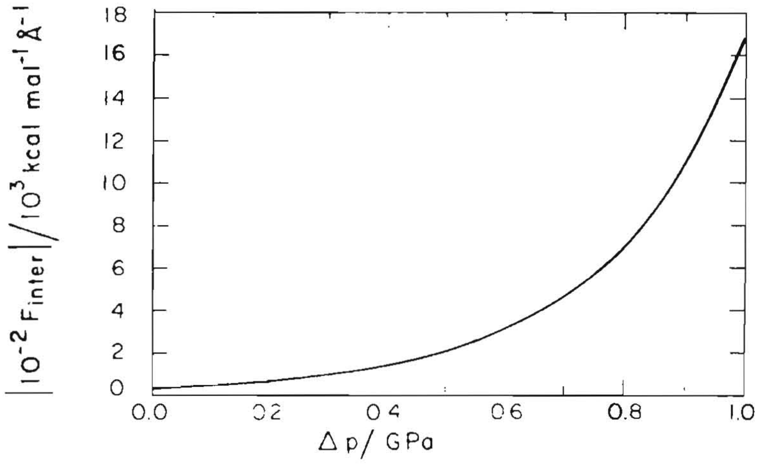
Type	Polymer	$V_g(298\ \mathrm{K})$ ($\mathrm{cm^3\ mol^{-1}}$)	a_g ($\mathrm{cm^3\ mol^{-1}\ K^{-1}}$)	$R(298\ \mathrm{K})$ (Å)	$F_{\mathrm{inter}}\times 10^{-2}$ ($\mathrm{kcal\ mol^{-1}\ Å^{-1}}$)
I	PC	210·35	0·0674	8·73	12624
I	PPO	114·1	0·04564	7·12	15616
II	PST	99	0·0287	6·79	326
II	PVC	95·1	0·0276	5·23	0·82
II	PMMA	85·6	0·0252	6·47	11·5

Fig. 4



Intermolecular barrier versus temperature for PC.

Fig. 5



Intermolecular barrier versus pressure, Δp, for PST.

where Δp is positive when ΔV is negative. Integrating gives

$$R(p)=R(p_0)\exp(-k/3\Delta p)\approx R(p_0)(1-\tfrac{1}{3}k\Delta p). \tag{6}$$

For PST, the Young's modulus $E=3{\cdot}1$ GPa, the Poisson's ratio $\nu=\frac{1}{3}$ (McClintock and Argon 1966) and the compressibility is

$$k=3(1-2\nu)\ E=0{\cdot}322\ \text{GPa}^{-1}. \tag{7}$$

When the pressure $\Delta p=0{\cdot}7$–$7{\cdot}0$ GPa (corresponding to 10^5–10^6 psi) the second factor in the product in (6) varies between 0·926–0·26 and thus, within this pressure range, the chain–chain distance R and, consequently, the intermolecular barrier, show a sharp increase which inhibits crazing. This is shown by fig. 5, which gives a plot of the intermolecular force versus pressure for polystyrene at room temperature. Again the 'threshold' value of the intermolecular barrier is around

$$F_{\text{inter}} \times 10^{-2} = 7000\,\text{kcal mol}^{-1}.$$

§4. Discussion

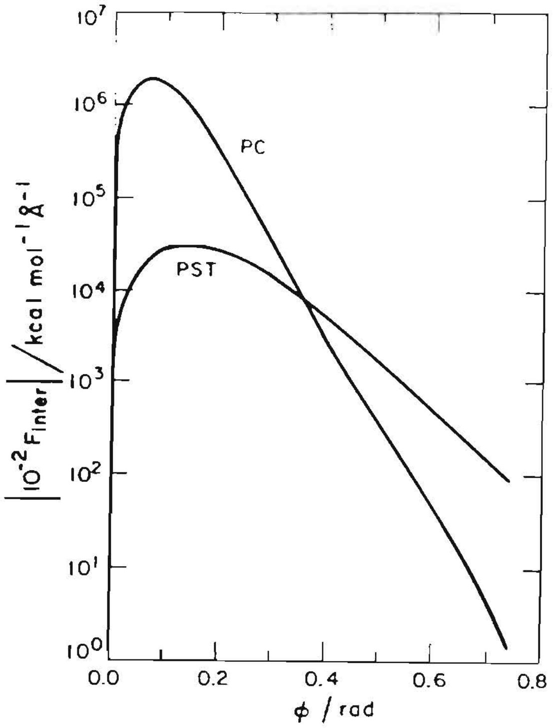
In the study of polymeric glasses, the conditions for craze nucleation (Argon and Hannoosh 1977), the mechanisms of growth and craze tip advance (Donald and Kramer 1981) and the craze fibril breakdown and fracture process (Murray and Hull 1970) are becoming well understood in those polymers that exhibit crazing. However, why certain polymers craze while others do not has yet to be determined. The model presented above relates quantitatively this difference in crazing behaviour to molecular parameters. An important parameter in the preceding calculations is the sweep radius r (or moment arm l). Indeed, the main characteristic of the vinyl polymers is the smaller moment arm l which is also the main reason for the low intermolecular obstacle to chain translation. Type II polymers are instead characterized by the greater lengths of each rigid segment (moment arm). Argon and Bessonov (1977) had connected the spatial extent of the deformation with the molecular parameters, specifically the length of the stiff segments in the polymer chain, which is analogous to the moment arm length l of the strophon model. Their experiments on four oxyaromatic polyimides supported the notion that the deformation becomes highly localized the 'natural hinge spacing' (or length of stiff units) decreases, which is the case for type I polymers, where crazing—a local deformation mode—is dominant. In type II polymers, with small interchain separation distance $R-r$, local high density packing is possible. These are points of 'entanglement' defined as points of very close chain–chain contact (characterized by a high repulsive intermolecular force F_{inter}). Type I (vinyl) polymers, however, have a low 'entanglement' density (due to their relatively large distance R-r from the nearest neighbour chain). In this context, Donald and Kramer (1982 a) concluded that the highest entanglement density polymers form shear bands more easily and Wellinghoff and Baer (1978) have observed bundle-like structures (nodules) in type II polymers which moved as unit when the polymer was stretched. Notice that this would necessarily lead to delocalization of strain since the mean number of neighbouring molecules acting collectively as a microbundle is large. Wellinghoff and Baer (1978) have also reported that the addition of about 30% 2,6-dimethyl polyphenylene oxide (2MPPO) a transition from a type I to a type II glass. In the framework of the present model, the strong polyphenylene ring interaction between 2MPPO and PST results in an increased intermolecular barrier which suppresses crazing.

In addition to translation, large barriers to strophon rotation are also present in type II polymers (Yannas 1974), so that the chains lock tightly against their neighbours. Figure 6 gives a semi-logarithmic plot of the (repulsive) intermolecular force barrier to rotation of the strophon (acting perpendicular to OA in fig. 2), F_{rot}, which can be found from a torque balance on the rotating strophon experiencing an intermolecular moment $\mathrm{d}E/\mathrm{d}\phi$,

$$F_{\text{rot}} = -\frac{12E_0 Rr \sin\phi}{a_0^2 l \sin(\pi-\psi)}[(a_0/a)^{14}-(a_0/a)^{8}], \tag{8}$$

where ψ is the virtual bond angle and ϕ is the rotation angle (see fig. 2). Non-vinyl polymers are also locked against chain translation because of the high intermolecular force barriers F_{inter}. Sequences of locked strophons might be expected to increase in

Fig. 6



Repulsive resistance to rotation versus rotation angle, ϕ, on a semilogarithmic plot.

number with increasing stress; eventually a three-dimensional quasi-random network of intersecting sequences of locked strophons may develop over the entire macroscopic specimen of a type II polymer, the failure of which, by consequent massive rotation and intermolecular slip, is the onset of yielding. Thus, in a type II polymer, the deformation appears in the form of shear bands with overall dimension changes. Type I chains, in contrast, have a greater degree of spatial freedom and can accommodate thus strains locally in the form of voids.

We can outline our model, which essentially relates quantitatively the molecular structure to macroscopic properties as follows. Deformation of glassy polymers to form crazes must be accompanied either by displacements of macromolecules or segments thereof. A tensile force (simulating the negative pressure necessary for crazing) applied to a chain segment lying approximately perpendicularly to it, will tend to displace it. In undergoing such a displacement, the chain pushes up against the neighbouring chains, and, with high intermolecular barriers F_{inter}, the reference chain locks on to its neighbours and stops moving while stress is building up (type II polymers). The strain is delocalized over the scale of the specimen and large-scale deformation (yielding) eventually occurs. If the intermolecular barrier can be overcome (type I polymers), the chain, by pushing against its neighbour, can be displaced transversely, which could increase the intermolecular bond length a to the point where a void forms. In this case the strain can be accommodated locally and crazing occurs. An increase in temperature causes an increase in molar volume due to thermal expansion and consequently a decrease in the intermolecular barriers, thus making crazing more likely to occur.

Inversely, an increase in pressure compresses the intermolecular distance and increases the barrier, thus inhibiting crazing. In this molecule–molecule interaction, the repulsive barrier (from the closest chain) is the largest and thus the most critical; the attractive one (from the distant chains) is of the same order for both type I and II polymers and its absolute value is smaller by many orders of magnitude than that of the repulsive barrier. The length of the rigid chain segment (which acts as a mechanical moment arm) controls mainly the magnitude of the maximum intermolecular barrier.

§ 5. CONCLUSIONS

A molecular model has been presented and used to explain the difference in crazing behaviour observed in the two types of glassy amorphous polymers. Self-consistent calculations show that an interpretation based on the repulsive intermolecular energy barriers to the lateral translation of chain segments is able to account for these differences. A high intermolecular obstacle is present with polymers which do not craze. The length of the rigid chain unit (which is relatively small for vinyl polymers) controls primarily the magnitude of these barriers. Thus type II polymers can be considered as 'more crowded solids' in the sense that there is very little room for either translation or rotation before the repulsive force barrier becomes prohibitively high. The increased tendency to crazing with an increase in temperature as well as the suppression of crazing with hydrostatic pressure are in accordance with the above analysis. In addition, the craze-to-shear transition observed in non-vinyl polymers near the glass transition temperature corresponds to a 'threshold' value for the intermolecular force barrier.

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