

FRACTURE MECHANICAL STUDIES OF THE STRENGTH
RESULTING FROM POLYMER INTERDIFFUSION

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ABSTRACT

Diffusion coefficients of molecular chains in amorphous polymers at the glass transition temperature T_g can be determined from mechanical studies at interpenetrated interfaces of compatible polymers. From these studies the role that entanglements play in the transfer of forces within polymers in the amorphous solid state may be deduced. Vitreous poly(methylmethacrylate) (PMMA), styrene acrylonitrile copolymer (SAN) and SAN with a small degree of crosslinking have been used to investigate these phenomena.

Diffusion experiments at $T_g < T < T_g + 15$ K in compact tension specimens (CT) were carried out by placing either fracture surfaces or polished surfaces in contact with each other. A diffusion theory was found to predict the relationship between the penetration time and the fracture toughness (K_{Ii}) at the interface: $K_{Ii} \approx t^{1/4}$. This theory was experimentally verified in all the investigated systems. The coefficient of self-diffusion was found to be of the order of $10^{-21} \text{ m}^2 \text{ s}^{-1}$ with an activation energy of 275 kJ mol^{-1} .

Restoration of full material resistance is obtained if the average interpenetration depth $\langle \Delta x^2 \rangle^{1/2}$ amounts to 2 to 3 nm. Such a depth was found for two different molecular weights. It corresponds approximately to the radius of gyration $R_g = 4.8 \text{ nm}$ of a PMMA molecule having the critical molecular weight $M_c = 30'000$. The humidity of the polymer and the polishing of the interfaces were found to have a considerable influence on the diffusion coefficient.

KEYWORDS

Activation energy; adhesion; chain interpenetration; crack healing; diffusion coefficient; fracture toughness; polymer glasses; polymethylmethacrylate, styrene-acrylonitrile; welding.

INTRODUCTION

Different methods of measuring the coefficient of self-diffusion of thermoplastic polymers at temperatures well above the glass transition temperature have been described by several investigators (Büche, 1968; Gilmore, 1979; Klein, 1979; Koch, 1979; Sillescu, 1979; and their collaborators). The manner in which diffusion occurs in polymers has been considered theoretically by De Gennes (1971), Doi and Edwards (1978) and, recently, Graessley (to be published) whose theories are based on the reptation mode of chain diffusion. However, no work has been carried out on chain diffusion in the transition region of thermoplastic polymers, although chain motion heavily influences polymer welding, deformation, and fracture. For example, it is of considerable interest to know which magnitude of chain interdiffusion is necessary to permit that load transfer at a weld line which is achieved in the bulk polymer. Fracture mechanics studies provide the means by which load transfer can be measured quantitatively. This standard technique, used to determine the energy release rate G_I or the stress intensity factor $K_{Ii} = f(\sigma, a)$ is a quite sensitive method to investigate the extremely small diffusion constants of molecules at the glass transition temperature.

The experimental method and the basic considerations how fracture toughness K_{Ii} and interfacial bond strength are correlated, are reported by Jud and Kausch (1979). The method is based on the fact that the material resistance R encountered by a crack travelling in an interfacial region can be taken as a quantitative measure of the strength of the bond between those contacting surfaces forming the interface. Any increase of that strength with contact time (t_p) or temperature (T_p) can be related to an increase in contact area and/or depth of interpenetration of chain molecules by diffusion.

A series of experiments has been performed in order to study the influence of humidity, surface state, chemical cross-linking, molecular weight, and presence of different chemical species on the diffusion behavior. Compact tension specimens were used in all these investigations. In order to demonstrate the validity of the method, a limited number of other specimens were prepared such as single edge notch (SEN) and double torsion (DT). In the basic series, two halves of a CT specimen were held in contact at a temperature T_p above the glass transition temperature. The contact time will be referred to as the penetration time t_p . The stress intensity factor at crack initiation, K_{Ii} , was measured at the interface as has been described previously (Jud, 1979). As shown by Figs. 1 and 2, K_{Ii} increases with

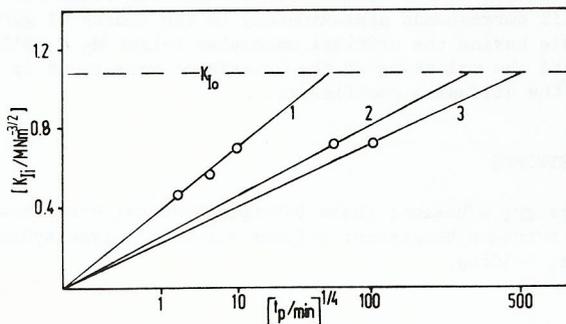


Fig. 1. Fracture toughness vs. penetration time to the power $\frac{1}{4}$ for dried PMMA 7H, 1. $T_p = 390$ K, 2. $T_p = 385$ K, 3. $T_p = 382$ K.

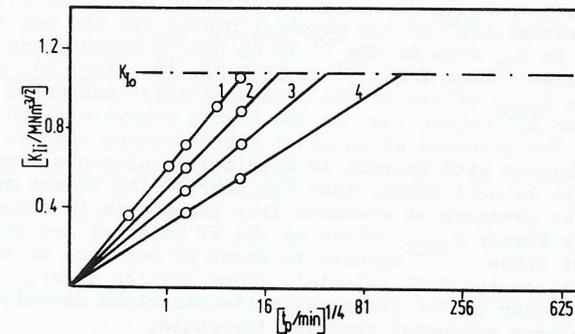


Fig. 2. Fracture toughness vs. penetration time to the power $\frac{1}{4}$ for undried PMMA 7H, 1. $T_p = 390$ K, 2. $T_p = 385$ K, 3. $T_p = 382$ K, 4. $T_p = 378$ K.

penetration time from very small values up to the full strength K_{I0} of the bulk polymer. The kinetics of the build-up of bond strength can be studied by varying the temperature. It is shown by Jud, Kausch and Williams (to be published) that material transport by diffusion must occur before the joint strength reaches the bulk strength (K_{I0}).

DIFFUSION MODEL

A diffusion process is possible between identical or compatible polymers which derives from the random molecular motion at $T > T_g$. The coefficient of self-diffusion D characterizes the displacement of the center of gravity of a chain by all possible chain movements, namely the longitudinal, transversal and rotational movement. At an interface chain diffusion will lead to the interpenetration of molecules from either side of the interface and to the formation of physical cross-links. We assume that the energy G_{Ic} required for separation of the contacting surfaces is proportional to the number N of cross-links and to the contact area ratio (A/A_0). If N_0 is that number of links which gives rise to the full fracture energy G_{I0} , we may write:

$$\frac{G_{Ic}}{G_{I0}} = \left(\frac{A}{A_0}\right) \left(\frac{N}{N_0}\right). \quad (1)$$

The achievement of complete contact ($A/A_0 = 1$) for a surface with some initial roughness requires the distortion of that roughness under the action of interfacial pressure, both external and from surface work. In polymers, the time dependence of this process will arise from viscoelasticity, and the duration will be governed by the current material stiffness. Clearly for high temperatures ($T > T_g$) the modulus is low, and even under surface forces alone, total contact will be achieved rapidly.

Diffusion is, therefore, the governing process, and the most simple concept seems to be the inverse proportionality between the rate of link formation and the number already formed. We may write, therefore:

$$\frac{dN}{dt} = \left(\frac{2N_0}{\tau_0}\right) \frac{N_0}{N} \quad (2)$$

where τ_0 is the time necessary to establish N_0 links per unit fracture area. Thus

$$N = N_0 \left(\frac{t}{\tau_0} \right)^{\frac{1}{2}}. \quad (3)$$

In Eq. (1), we may write $A/A_0 = 1$ for the assumed complete contact so that

$$\frac{G_{Ic}}{G_{Io}} = \left(\frac{t}{\tau_0} \right)^{\frac{1}{2}} \quad (4)$$

and in terms of stress intensity factor, we have:

$$\frac{K_{Ii}}{K_{Io}} = \left(\frac{G_{Ic}}{G_{Io}} \right)^{\frac{1}{2}} = \left(\frac{t}{\tau_0} \right)^{\frac{1}{4}}. \quad (5)$$

The parameter τ_0 used here may be related to a conventional diffusion coefficient D via the Einstein relation:

$$\langle \Delta x^2 \rangle = 2D\tau_0 \quad (6)$$

where $\langle \Delta x^2 \rangle^{\frac{1}{2}}$ is the mean penetration depth corresponding to the establishment of N_0 cross-links.

EXPERIMENTAL

Material: poly(methylmethacrylate) (PMMA 7H, $M_w = 120'000$; $M_w/M_n = 1.6$) from Röhm GmbH., and styrene acrylonitrile (SAN) Luran 368R copolymer (25 mol % AN, $M_w = 120'000$) from BASF, have been investigated. Both have the same glass transition temperature, $T_g = 102 - 104^\circ\text{C}$, and are completely compatible, as shown for instance by Jelinek (1972) and Krause (1978). Compact tension (CT) specimens were compression moulded from granules and vacuum dried during 50 - 100 h at $T = 100^\circ\text{C}$. A geometry $L \times W \times D = 25 \text{ mm} \times 26 \text{ mm} \times 3 \text{ mm}$ was employed, and cracks were introduced by milling and subsequently sharpened by a razor blade. The specimens were fractured in tension and gave smooth fracture surfaces. For one series of specimens, these surfaces were brought in contact again and very lightly pressed together by an elastic band. This sandwich-like preparation was then placed in a pre-heated hot press, and a slight pressure of about 1 bar was applied normal to the major specimen surface. The specimen temperature T_p was set to $\approx 1 \text{ K}$ to 15 K above the glass transition temperature. The pressure was needed to establish full contact between the fracture surfaces, but it was so small that the specimen geometries were not changed. A second series of experiments were executed with undried samples. For the third series of experiments, flat surfaces were made by polishing the fracture surfaces and arbitrarily selected surfaces were then welded together as described above.

A further series of experiments was carried out using a PMMA of $M_w = 2 \cdot 10^6$. $M_w/M_n = 4$, (PMMA 233 supplied by Röhm GmbH.). The same procedure was followed as described above. A final series of experiments was done in the same manner using γ -irradiated SAN samples. Different and small degrees of chemical cross-linking were achieved by applying various doses of irradiation.

RESULTS AND INTERPRETATION

The fracture toughness at crack initiation $K_{Ii} = p\sqrt{af(a)}/DB$ was determined as a function of contact time and temperature. The rather large scatter in these measurements required a large number of specimens per experiment. In Figs. 1 and 2 the results of series 1 and 2 for dried and rehealed specimens at different T_p have been plotted. The excellent representation of the experimental data by straight lines in a $t_p^{\frac{1}{4}}$ plot should be noted. Such a time dependence had been predicted by the diffusion model discussed above. For comparison, in Fig. 3 the results from series 1, 2 and 3 for one value of T_p (390 K) are plotted in a $\log K_{Ii}$ vs. $\log t_p$ diagram. The effect of drying and polishing is clearly visible. Fig. 4 shows the results for a high molecular PMMA (series 4), and Fig. 5 summarizes the data obtained for cross-linked SAN material (series 5).

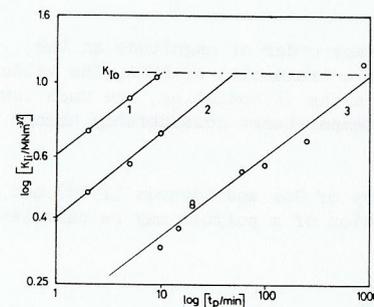


Fig. 3. Fracture toughness vs. penetration time in a double logarithmic scale for

1. undried PMMA 7H
 2. dried PMMA 7H
 3. polished dried PMMA 7H
-) at $T_p = 390 \text{ K}$

Fig. 4. Fracture toughness vs. penetration time to the power $\frac{1}{4}$ for dried PMMA 233, 1. $T_p = 395 \text{ K}$, 2. $T_p = 378 \text{ K}$.

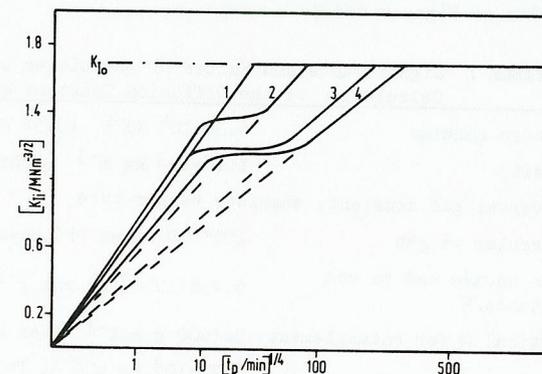
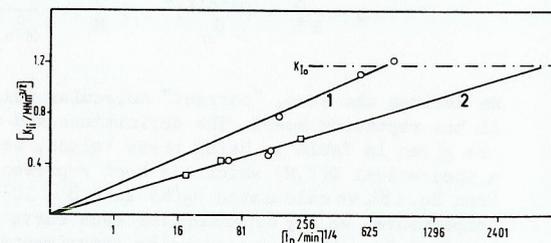


Fig. 5. Fracture toughness vs. penetration time to the power $\frac{1}{4}$ for SAN Luran 368R, 1. dried, 2. dried and γ -irradiated (35 Mrad), 3. dried and γ -irradiated (100 Mrad), 4. dried and γ -irradiated (200 Mrad).

All these graphs reveal a diffusional behavior although there are some anomalies in Fig. 5. In every case, t_p ($N = N_0$) can be determined and thus $\tau_0(T) = t_p(N_0, T)$. If one assumes that the critical number N_0 of links and their volume density do not depend on temperature, then from Eq. 6 it follows that:

$$\frac{D(T)}{D_0} = \frac{\tau_0(T_0)}{\tau_0(T)} \quad (7)$$

The experimental values from Figs. 1-5 are well represented by an Arrhenius law of D:

$$D(T) = D_0 \cdot \exp(-E_a/RT) \quad (8)$$

with $E_a = 275$ kJ mol⁻¹. This value is of the same order of magnitude as the 400 kJ mol⁻¹ reported by McCrum (1976) for the α -transition of PMMA. The values found in the literature which has been cited in the introduction, are much lower. They refer, however, to main chain motion at temperatures considerably higher than T_g .

Graessley (to be published) analyzes the theory of Doi and Edwards (1978) and points out that the coefficient of self-diffusion of a polymer may be calculated from measurable viscoelastic quantities:

$$D = \frac{G_0}{135} \cdot \left(\frac{\rho \cdot R \cdot T}{G_0}\right)^2 \cdot \left(\frac{R_e^2}{M}\right) \cdot \frac{M_c}{M^2 \eta_0(M_c)} \quad (9)$$

He derives the same, "correct" molecular weight-dependence of D as De Gennes (1971) in his reptation model. The definitions and values of the quantities used in Eq. (9) are given in Table 1. Using these values, we obtain for dry PMMA 7H of $M = 120'000$ a theoretical $D(T, M)$ which has been represented as solid line 1 in Figs. 6 and 7. From Eq. (8), we calculated $D_0(M)$ as $4.8 \cdot 10^{15}$ m²/s. Taking $T_0 = 382$ K as reference temperature, we may determine for each curve in Figs. 1 and 2 the ratio $\tau_0(T)/\tau_0(T_0)$ and from Eq. (7) the corresponding experimental value of $D(T)$. These values are indicated as circles in Figs. 6 and 7.

TABLE 1 Significance and Values of Quantities used for Calculation of the Diffusion Constant of PMMA 7H

$G_0(T)$	Plateau modulus	$6.36 \cdot 10^4$ Nm ⁻² (0.52 $\rho RT/M_c$)
$\rho(T_0)$	Density	$1.14 \cdot 10^3$ kg m ⁻³ (Schreyer, 1972)
R, T	Universal gas constant, absolute temperature	
M	Molecular weight	120'000 (own GPC measurements)
R_e^2/M	Mean square end to end distance/M	$0.456 \cdot 10^{-20}$ m ² mol g ⁻¹ (Kirste, 1975)
M_c	Critical M for entanglement	30'000 g mol ⁻¹ (Van Krevelen, 1976, p. 339)
$\eta_0(T, M_c)$	Zero shear viscosity for M_c	$3.78 \cdot 10^8$ Ns m ⁻² at T=387 K (Van Krevelen, 1976, p. 342) $2.14 \cdot 10^7$ Ns m ⁻² at T=390 K

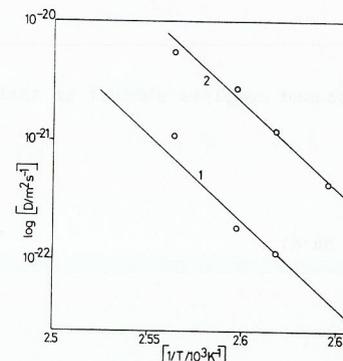


Fig. 6. Logarithm of diffusion coefficient vs. the reciprocal temperature for PMMA 7H, 1. dried, 2. undried.

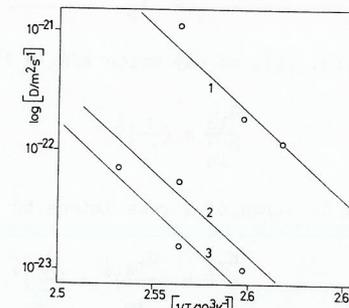


Fig. 7. Logarithm of diffusion coefficient vs. the reciprocal temperature for 1. dried PMMA 7H, 2. polished, dried PMMA 7H, 3. dried PMMA 233.

For humid PMMA, larger diffusion coefficients are obtained as evidenced by the points on line 2 in Fig. 6. Through these points a straight line can be drawn which is parallel to the theoretical line 1. In Fig. 7, the effects of surface polishing (line 2) and molecular weight ($M = 2 \cdot 10^6$, line 3) on D are clearly visible. The diffusion coefficient of the high molecular weight sample is larger than predicted by Eq. (9) which is probably due to the larger polydispersity of that material. This phenomenon needs some further study.

With the thus derived diffusion coefficients one calculates from Eq. (6) average depths of interpenetration of the order of 2.5 nm. This is about one half of the radius of gyration of a PMMA molecule of the critical molecular weight. The fact that only extremely small distances of chain interpenetration are necessary for strength restoration is underlined by results of our irradiation experiments (Fig. 5). The samples represented by curve 4, were irradiated with a dose of 200 Mrad which had led to an average cross-link density of one per (4 nm)³. The average length of a chain segment between cross-link points can then be estimated to be 100 nm. The length of a remaining free chain end will be 50 nm and thus smaller than the 75 nm extended length of a chain having critical molecular weight. The diffusional mobility and the possible penetration depths of the remaining free chain ends and of the network chains are hindered by the presence of chemical cross-links. The curves 1 to 3 in Fig. 5 reveal that during a first phase, intensive contact is established between the two surfaces fairly independently from cross-link density. During this phase, chain ends up to 50 nm length seem to penetrate into the opposite matrix evidently without being able to form any entanglements. In a second phase, longer segments and perhaps parts of the network interpenetrate which leads to an increase in K_{II} by entanglement formation in the third phase. The network mobility seems to be just sufficient to permit restoration of the original strength.

CONCLUSION

Through the use of fracture mechanics specimens, chain interdiffusion at polymer interfaces can be measured in a sensitive but indirect way. The interdiffusion

becomes more difficult in dried PMMA and/or SAN samples, it is further hindered by polishing the fracture surfaces before contacting them and by introducing permanent cross-links through γ -irradiation. The absolute values of chain interpenetration, estimated on the basis of the Graessley theory, amount to 2.5 nm. Such small depths are obviously sufficient to transmit in a short-time experiment the full material strength and to initiate in a repeated fracture experiment the plastic deformation of a zone of up to several μm depths.

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