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Healing of fractured polymers by interdiffusion

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The healing process of fractured polymers is analysed on the basis of the minor chain model. The healing at the interface by interdiffusion is described in terms of the concentration of minor chains. Chain scission would occur at the surfaces of fractured polymers and the resulting minor chains play an important role in the healing process. The localized minor chains at the interface dominate over the flat distribution of the chains in the bulk of the polymer. The molecular quantities derivable from the concentration profile in the fracture case show drastically different behaviour compared with two pieces of a polymer that are put in contact for interdiffusion, the latter corresponding to the flat chain distribution. The result suggests an alternative to the usual correlation for the time dependence of the fracture toughness. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Interdiffusion at a polymer–polymer interface plays a key role in welding, blends and polymer processing. One way of describing the motion at the interface is the reptation model that was developed by de Gennes[1], and later by Doi and Edwards[2]. Although several investigators[3–5] have studied the motion of polymer chains in the interface region based on the reptation model, including the minor chain reptation model of Kim and Wool[6], their studies are for simple cases such as homogeneous, monodispersed pair of polymers.

We consider here the healing process of fractured polymers. Of interest is the concentration of minor chains that results from interdiffusion when two pieces from a fractured polymer are put in contact above the glass transition temperature (T_g) and the molecular quantities derivable from the concentration profile. Only the case of a symmetrical interface and one-dimensional movement of minor chains is treated.

CONCENTRATION PROFILE

Consider a polymer fractured at a distance from the fractured line z. Because of the nature of the scission, there is a peak created in the chain-end distribution at the interface that is formed by the scission. Therefore, the initial chain-end distribution can be taken as a Gaussian distribution:

$$F(z,m) = \frac{1}{\sqrt{2\pi m)}} \exp\left(-\frac{z^2}{2m}\right) \qquad (1)$$

where $F(z,m)$ is the probability that the chain end consisting of m monomers is at a distance z from the fractured line.

Without loss of generality, one may assume that the chain-end distribution consists of two parts: a flat distribution and a non-flat Gaussian distribution, since the addition of the flat distribution simply shifts the Gaussian distribution upward. This approach has the added advantage of yielding the result obtained, for instance, for a flat distribution at large times by Zhang and Wool[7].

Consider a minor chain of length $l(t)$ that emerges from its tube end at $x = -x_0$ (e.g. Zhang and Wool[7]). The coordinate system is chosen in such a way that the interface plane is at $x = 0$. Assuming random conformation of the minor chain, the probability $p(x, s| - x_0)$ that the sth monomer, which is a terminal segment in the minor chain, is located at x from the interface is given by

$$p(x,s| - x_0) = \frac{1}{\sqrt{2\pi s a^2}} \exp\left(-\frac{(x+x_0)^2}{2sa^2}\right) \qquad (2)$$

where a is the length of the monomer. Therefore, the total number of monomers in minor chains $f(x,t)$ is given by

$$f(x,t) = f_f(x,t) + \int_{s=0}^{s=n'} \int_{z=0}^{z=\infty} \int_{m=0}^{m=N} F(z,m) p(x,s/z) \frac{2\Phi N_a S}{M} dz dm ds \qquad (3)$$

where f_f is for the flat distribution given by

$$f_f(x,t) = \int_{s=0}^{s=n} \int_{x_0=0}^{x_0=\infty} p(x,s| - x_0) \frac{2\Phi N_a S}{M} dx_0 ds \qquad (4)$$

Here $(2\Phi N_a S dx_0/M)$ is the number of minor chain ends

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in the volume element Sdx_0 between the interval distance $(-x_0, -x_0 - dx_0)$, where S is the interfacial cross-sectional area, N_a is Avogadro's number, Φ is the uniform mass density of a bulk polymer in the melt state, and M is the molecular weight of the bulk chains. The number of monomers in a minor chain is denoted by s, n' is the number of monomers in the minor chain for the fractured case and n is the same for the bulk that is to be defined in equation (7), and the number of monomers in the bulk chains is given by N.

The monomer concentration profile for the minor chains, $C_A(x, t)$, occurring at x from the interface at time t is given by

$$C_A(x,t) = \frac{1}{N_a S} f(x,t) \tag{5}$$

An approximation is made in carrying out the integration for $f(x,t)$. When a polymer is fractured, most of the chain ends formed by the scission would be at the edge so that the Gaussian distribution can be thought of as a delta function, i.e. $F(z,m) \simeq F(z,m)\delta(z)$.

With this approximation, substitution of equation (3) into equation (5) and carrying out of the indicated integration yields

$$\begin{aligned} C_A = \frac{\Phi}{M}\Bigg[& n\,\mathrm{erfc}\left(\frac{x}{a\sqrt{2n}}\right) - \sqrt{\frac{2n}{\pi}}\frac{x}{\mathrm{a}}\exp\left(-\frac{x^2}{2na^2}\right) \\ & + \frac{x^2}{a^2}\mathrm{erfc}\left(\frac{x}{a\sqrt{2n}}\right)\Bigg] \\ & + \frac{2\Phi}{M}\sqrt{\frac{2N}{\pi}}\Bigg[\sqrt{\frac{2n'}{\pi}}\frac{1}{a}\exp\left(-\frac{x^2}{2n'a^2}\right) \\ & - \frac{x}{a^2}\mathrm{erfc}\left(\frac{x}{a\sqrt{2n'}}\right)\Bigg] \end{aligned} \tag{6}$$

where

$$\begin{aligned} n &= \frac{N}{L} l(t) = \frac{N}{L}(16Dt/\pi)^{1/2} = \frac{1}{a}(16Dt/\pi)^{1/2} \\ n' &= \frac{N'}{L'} l'(t) = \frac{N'}{L'}(16D't/\pi)^{1/2} = \frac{1}{a}(16D't/\pi)^{1/2} \\ N' &= (\pi N/2)^{1/2} \\ L' &= N' \cdot \mathrm{a} \\ M' &= (\pi/2N)^{1/2} M \\ D &\propto M^{-1} \\ D' &\propto (M')^{-1} \sim M^{-1/2} \end{aligned} \tag{7}$$

Here l is the average minor chain length[7], D is the one-dimensional curvilinear diffusion coefficient and L is the contour length of the chain of N monomers. The primed quantities of l', N', D' and L' are the counterparts of l, N, D, and L for the fractured case.

After the reptation time of the bulk chains, T_r, has elapsed, i.e. when $t = T_r$, $l = L/2$ and $n = N/2$, and noting that $M = M_0 \cdot N$, equation (6) reduces to

$$C_A(x, T_r)/(\Phi/M) = \left(0.5 + \frac{x^2}{d^2}\right)\mathrm{erfc}\left(\frac{x}{d}\right)$$

$$\begin{aligned} & - \sqrt{\frac{1}{\pi}}\frac{x}{d}\exp\left(-\frac{x^2}{d^2}\right) \\ & - 2\sqrt{\frac{2}{\pi}}\Bigg[\frac{x}{ad}\mathrm{erfc}\left(\frac{x}{\sqrt{ad(\pi/2)^{1/2}}}\right) \\ & - \frac{1}{\sqrt{ad\sqrt{2\pi}}}\exp\left(-\frac{x^2}{ad\sqrt{\pi/2}}\right)\Bigg] \end{aligned} \tag{8}$$

where $d \equiv \langle r^2\rangle^{1/2} = (Na^2)^{1/2}$, i.e. d is the square root of the mean square end-to-end distance (r) of the Gaussian chains. Calculated concentration profiles are shown in *Figure 1*. This shows normalized concentration profiles as a function of the distance from the interface at various times. Because of the abundance of minor chains at the interface, the profiles approach the profile at the reptation time ($t/T_r = 1$) very rapidly, as opposed to the gradual approach for the flat distribution[7].

NUMBER OF MONOMERS CROSSING THE INTERFACE

The number of monomers $N(t)$ crossing the interface by time t is obtained as follows:

$$\begin{aligned} N(t) &= \int_0^{\infty} C_A/(\Phi/M_0)dx \\ &= \frac{1}{N\sqrt{\pi}}\left(\frac{2}{3}na\sqrt{2n} + \sqrt{2N}n'\right) \end{aligned} \tag{9}$$

Substitution of equation (6) for n, n', D and D' into

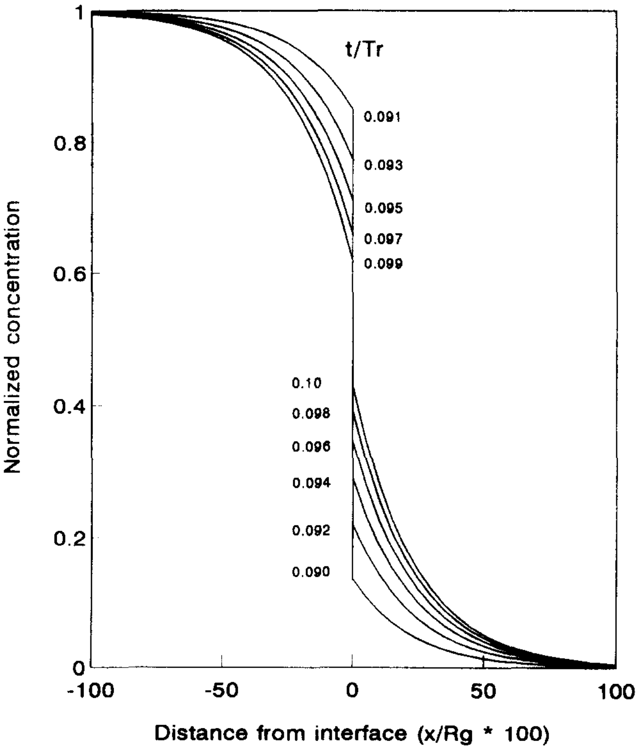

Figure 1 Normalized concentration profile at the interface R_g is the radius of gyration and T_r is the reptation time

equation (9) yields

$$N(t) = \frac{4}{aN\pi} D_0^{3/4} M^{-3/4} t^{1/2} \left(\frac{4}{3} \sqrt{\frac{2a}{\sqrt{\pi}}}\, t^{1/4} + \sqrt{2N} D_0^{-1/4} M^{1/2} \right) \qquad (10)$$

where D has been used as $D = D_0 M^{q}$ ($q = -1$, for D and $q = -1/2$ for D').

The first term in the parentheses of equation (10) is that corresponding to the flat distribution that was obtained by Zhang and Wool[7]. The second term is the contribution due to the minor chains formed by scission. It is of interest to find the time it takes for the first time, t_e, to be of the same order of magnitude as that for the second term. This time follows from equation (10) and is

$$t_e = \left(\frac{\sqrt{2N} D_0^{-1/4} M^{1/2}}{\frac{4}{3}\sqrt{\frac{2a}{\sqrt{\pi}}}} \right)^4 \qquad (11)$$

The first term in the parenthesis of equation (10) is set equal to the second term for t_e. Using the values in *Table 1* for polystyrene, for example, the time becomes

$$t_e \sim (3 \times 10^{11})^4 \mathrm{s}$$

This time can be compared with the reptation time T_r, which is

$$T_r \simeq \frac{L^2}{D\pi^2} = 10^5 \mathrm{s}$$

It is seen that it takes a much longer time than the reptation time for the effect of the scission to die out to approach the flat distribution case. Thus, the scission effect is dominant over a long period of time. It follows then, that

$$N(t) \sim t^{1/2} M^{-5/4} \qquad (12)$$

This compares with the flat distribution result[7], given by $t^{3/4} M^{-7/4}$. Our result here for the scission happens to coincide with the widely used model that $N(t) \sim t^{1/2}$ for $t > T_r^7$.

OTHER QUANTITIES DERIVABLE FROM THE CONCENTRATION PROFILE

The concentration profile given by equation (8) can also be used to derive several molecular quantities of interest. Consider first the average interpenetration depth $X(t)$. This depth can be obtained from

$$X(t) = \int_0^\infty x C_A(x,t)dx \Big/ \int_0^\infty C_A(x,t)dx \qquad (13)$$

Use of equation (6) in equation (13) leads to

$$X(t) = at^{1/4} M^{-1/4} \frac{\left(D_0^{1/4} t^{1/4} + \frac{4}{3}\sqrt{\frac{2N}{\pi}}\sqrt{\frac{2}{a\sqrt{\pi}}} M^{5/8} \right)}{\left(\frac{4}{3}\sqrt{\frac{2a}{\sqrt{\pi}}} t^{1/4} + \sqrt{2N} D_0^{-1/4} M^{1/2} \right)} \qquad (14)$$

Table 1 Values used for polystyrene example

$M_0 = 102\,\mathrm{g\,mol^{-1}}$	$N = 2000$	$a = 10^{-7}\,\mathrm{cm}$
$T_g = 400\,\mathrm{K}$	$\eta = 4 \times 10^5\,\mathrm{Pa\,s}$	
$D = 1.38 \times 10^{-17}\,\mathrm{m^2\,s^{-1}}$ (from $D\,\eta = CkT$, T at T_g)		
$D_0 = 2.8 \times 10^{-15}\,\mathrm{m^2\,s^{-1}}$		

Here again, the first term in the parenthesis of equation (14) is for the flat distribution and the second term corresponds to the effect of the scission. The time t_e can also be calculated using the values in *Table 1* and is

$$t_e \simeq (2 \times 10^{11})^4 \mathrm{s}$$

It is seen that for a long time (much longer than the usual reptation time, but smaller than t_e) the second term in the numerator of equation (14) dominates and therefore the first term can be neglected to give

$$X(t) \sim t^{1/4} M^{-1/8} \qquad (15)$$

For the polymer with no scission, the dependence[7] is $t^{1/4} M^{-1/4}$.

The number of bridges intersecting a unit area of the interface is the same as the number of monomers per unit volume at the interface. Therefore, equation (8) yields

$$p(t) = C_A(0,t) = \frac{\Phi}{M_0} \left(\frac{n}{N} + 2\sqrt{\frac{2N}{\pi}} \frac{1}{aN} \sqrt{\frac{2n'}{\pi}} \right) = C_1 t^{1/2} M^{-3/2} + C_2 t^{1/4} M^{-9/8} \qquad (16)$$

where C_1 and C_2 are constants that are independent of t and M. The second term dominates again and one has

$$p(t) \sim t^{1/4} M^{-9/8} \qquad (17)$$

This compares with the time dependence of $p(t)$ of $t^{1/2}$ for the flat distribution[7]. The value of t_e for the number of bridges for styrene is about $(3 \times 10^{11})^4$ s.

FRACTURE ENERGY

The fracture energy G can be measured by a mechanical test. It is correlated to the fracture toughness K_{Ii} as follows[8–10]:

$$G \sim K_{\mathrm{Ii}} \qquad (18)$$

In crack healing experiments, the fracture energy is considered to be linearly dependent on the number of entanglements at the interface[6,8,9], i.e.

$$K_{\mathrm{Ii}}^2 = a_1 \bar{n} \qquad (19)$$

where a_1 is the proportionality constant. The concentration of entanglements per unit surface area, $\bar{n}$, increases proportionally to the average length of chain interpenetration, $\langle l^2 \rangle^{1/2}$. However, $\langle l^2 \rangle^{1/2}$ is the average length of a broken chain and thus it must be replaced by the interpenetration depth. In general, the relationship between l and X is given[6] by

$$l \sim X^2 \qquad (20)$$

It follows then that

$$\frac{\bar{n}}{\bar{n}_0} = \frac{X^2}{l_0} \qquad (21)$$

where the subscript denotes full healing time. Use of equation (21) in equation (19) yields

$$K_{\mathrm{Ii}} = a_2 X \tag{22}$$

where a_2 is a constant.

The interpenetration depth obtained in the previous section (equation (14)) can now be used in equation (22) to arrive at the following relationship:

$$K_{\mathrm{Ii}} \sim t^{1/4}\left(\alpha + \frac{\gamma}{t^{1/4} + \beta}\right) \tag{23}$$

where the parameters α, β and γ are given by

$$\alpha = \frac{3}{4}\sqrt{\frac{a}{2}}\left(\frac{\pi D_0}{M}\right)^{1/4} \tag{24}$$

$$\beta = \frac{3}{4}\sqrt{\frac{N\sqrt{\pi}}{a}}\left(\frac{M^2}{D_0}\right)^{1/4} \tag{25}$$

$$\gamma = \sqrt{2\pi N}\left(\frac{1}{\pi}M^{1/8} - \frac{9}{32}\right)M^{1/4} \tag{26}$$

The time dependence of the fracture toughness K_{Ii} obtained here, i.e. equation (23), differs from the correlation that has been used in the past, i.e. the simple $t^{1/4}$ dependence[8,9]. In view of the difference, the data reported in the literature are analysed according to equation (23) and the results are shown in *Figures 2* and *3*. Shown in *Figure 2* are the data by Nguyen *et al.*[8] for the crack healing of SAN carried out at various levels of irradiation dose that causes crosslinking. The solid curves in the figure are the ones that are the best fit to the data according to equation (23). The parameters thus chosen are given in *Table 2*. It is seen that the value of α decreases with the dose. The decrease is due to an increase in the molecular weight (see equation (24)). It is also seen that the values of β and γ increase with increasing dose but not at 800 Mrad. An increase in the dose results in more crosslinking and thus a decrease in the chain segment length, leading to an increase in β and γ. At 800 Mrad, the original fracture toughness of the virgin material was not recovered[8] and this fact might be the reason for the abnormal behaviour.

Shown in *Figure 3* are the data by Jud *et al.*[9] for the crack healing of SAN–SAN and PMMA–PMMA polymer pairs [SAN = styrene acrylonitrile, PMMA = poly(methyl methacrylate)] at 390 K. The parameters in *Table 3* are the ones used to draw the solid curves in the figure. The parameters in the table for the SAN pair are similar in their magnitude to those for the PMMA pair, indicating that the segmental length and the molecular weight would be of the same order of magnitude.

The healing of polymer blends is similar to crack healing. Therefore, the data by Kausch *et al.*[10] are analysed for the blend of 5% PPO (M_w = 16 000) and 95% PS (M_w = 240 000). The best fit curve is shown in *Figure 4* along with the data. It is seen that the healing of polymer blends can be well represented by equation (23), particularly when one of the polymers (PPO) is much shorter than the other. The best fit parameters in *Table 4* are of the same order of magnitude as those for crack healing.

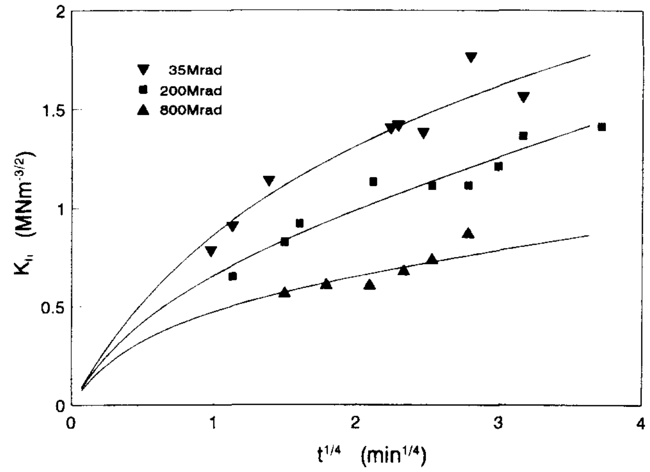

Figure 2 Fracture toughness as a function of $t^{1/4}$ with various irradiation dose in SAN. Data from Nguyen *et al.*[8]

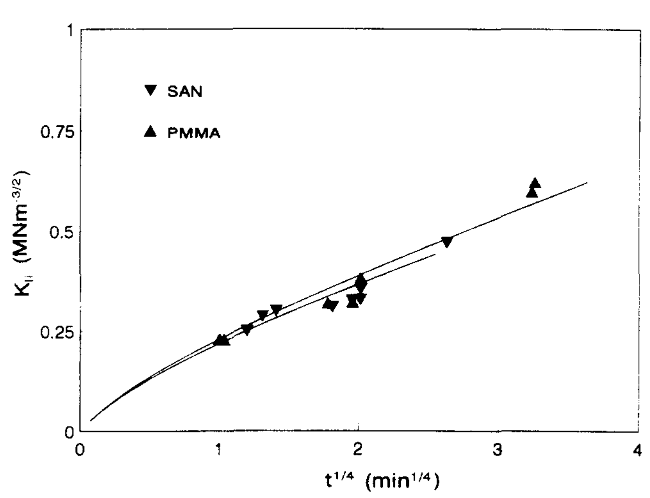

Figure 3 Fracture toughness as a function of $t^{1/4}$ in SAN–SAN and PMMA–PMMA polymer pairs. Data from Jud *et al.*[9]

Table 2 Parameters used to fit the SAN data[8]

Parameter	35 Mrad	200 Mrad	800 Mrad
α	0.296	0.164	0.099
β	1.60	1.74	1.91
γ	1.25	1.26	1.08

Table 3 Parameters used to fit the data[9] of SAN–SAN and PMMA–PMMA polymer pairs

Parameter	SAN	PMMA
α	0.136	0.125
β	1.51	1.50
γ	1.24	1.24

CONCLUSIONS

The healing process of fractured polymer has been treated on the basis of the minor chain model. Because of the concentrated minor chains present at both sides of the fractured line (area) that is formed by the scission, the interdiffusion behaviour is drastically different from the behaviour that results when two pieces of the same amorphous polymer are put into contact above T_g, which corresponds to the flat segmental distribution. The molecular quantities derivable from the concentration

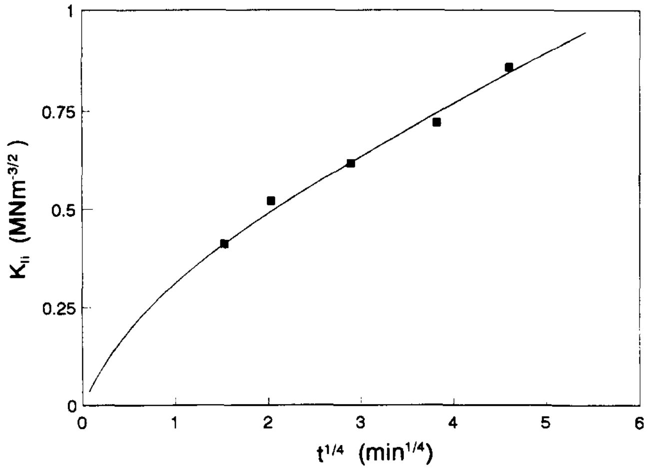

Figure 4 Fracture toughness as a function of $t^{1/4}$ in 5% PPO/95% PS polymer blend. Data from Kausch *et al.*[10]

Table 4 Parameters used to fit the data[10] of the 5% PPO/95% PS (polystyrene) polymer blend

Parameter	5% PPO/95% PS
α	0.121
β	1.75
γ	1.18

profile, such as the average interpenetration depth, are much larger in magnitude for the same time than those for the flat distribution case. It is notable that the time dependence of the number of monomers crossing the interface is $t^{1/2}$, as in the widely used model, unlike that for the flat distribution. The time dependence of all the derivable molecular quantities is weaker by a factor of $t^{1/4}$ compared with the flat distribution case.

One of the molecular quantities derived has been utilized to arrive at an alternative to the usual correlation used for the time dependence of the fracture toughness. Nevertheless, it should be noted that for a complete analysis, consideration should be given to both the concentration of broken chains at the fracture surface and the increased surface roughness due to the formation of crazes during the fracture event.

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