Polymer chain entanglements and brittle fracture: 2. Autohesion of linear polymers

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The influence of chain entanglements on the autohesion of linear polymers was investigated using a stochastic model. The fracture energy of a polymer interface was expressed in terms of the total number of effective crossings, which was in turn related to the molecular-weight distribution and the contact time. Experimental studies of autohesion of dried and polished poly(methyl methacrylate) surfaces at 117°C validated the theoretical predictions.

INTRODUCTION

Polymer–polymer surface interactions are encountered in a number of areas including polymer welding[1] and bioadhesion of polymeric materials on biological tissues[2]. The interpenetration of macromolecular chains at the polymer–polymer interface at a temperature higher than the glass transition temperature is the basis of the diffusion theory of polymer adhesion proposed by Voyutskii[3]. Molecular bridges formed due to polymer self-diffusion are responsible for the adhesive strength. In the cases of polymer autohesion and crack healing, the measured brittle fracture energy increases with the contact time above the glass transition temperature. Eventually it reaches a plateau value equal to the fracture energy of the neat polymer[4–6].

Many theoretical models have been proposed to describe the time dependence of the fracture energy in polymer autohesion. De Gennes[7], Prager and Tirrell[8], Jud et al.[5] and Adolf et al.[9] assumed a chain scission mechanism, whereas Wool[10] invoked a chain pull-out fracture criterion for the polymer chains crossing the junction plane. Kim and Wool[11] also postulated that the fracture strength is proportional to the chain interpenetration thickness. Although these models predict the variation of the fracture energy with the contact time, they do not show the molecular-weight dependence of the fracture energy of neat polymers[5,7,8,10,11]. The analysis of Adolf et al.[9] can establish this dependence but requires the definition of an additional physical parameter.

We have proposed[12] a new molecular theory for the molecular-weight dependence of the polymer fracture properties using structural and entanglement characteristics of the chain macromolecules. A chain scission criterion was invoked for the polymer chain segments being entangled about the fracture plane and theoretical predictions agreed well with experimental data for the fracture energy and strength of polystyrene and poly(methyl methacrylate)

A stochastic model is presented here to examine the effect of chain entanglements on the autohesion of linear polymers and to investigate the dependence of the interfacial fracture energy on the polymer molecular weight and the contact time. The predictions of the model are compared with experimental measurements of the fracture energy of poly(methyl methacrylate) samples.

CHAIN DISENGAGEMENT FROM A TUBE

Polymer chains with molecular weight M much larger than the threshold value corresponding to the onset of chain entanglements, $2M_e$, diffuse by reptation[13–16] in a polymer melt. The reptation theory of polymer diffusion is used here to describe the interpenetration phenomenon of the polymer chains across the junction plane during the autohesion process.

In the stochastic modelling, the equivalent random walk of the actual chain is considered. The equivalent Gaussian chain of a macromolecule is defined so that the mean-square end-to-end distance and the fully extended length of the random chain be the same as the corresponding values of the actual chain[17]. The degree of polymerization N and the statistical link length b of a random chain are related to the degree of polymerization N_0, the bond length l and the characteristic ratio C_∞ of a polycarbon chain by the following expressions.

$$N = 2N_0/3C_\infty \qquad (1)$$

$$b = \sqrt{(3/2)}C_\infty l \qquad (2)$$

A polymer chain is confined in a tube, which is formed by the topological constraints of neighbouring macromolecules. The tube diameter and length are stochastic variables themselves. Nevertheless, they are assumed constant and equal to the corresponding mean values. The tube diameter is equal to the correlation length ξ, which is related to the degree of polymerization between two consecutive entanglements, N_e by:

$$\xi = N_e^{1/2}b \qquad (3)$$

The polymer chain is partitioned into n segments with

$$n = N/N_e \qquad (4)$$

and the confining tube has length $L_t = n\xi$.

The diffusion of a polymer chain along its tube is characterized by a tube diffusion coefficient D_t:
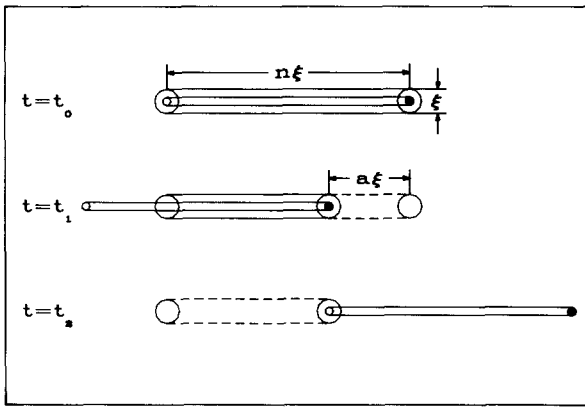
$$D_t = T\mu_1/N \qquad (5)$$

Figure 1 The disengagement of a polymer chain from its tube of length $n\xi$ and diameter ξ at time t_0 is caused by chain reptation and is accomplished in two steps. First, one chain end (filled circle) reaches its maximum excursion $a\xi$ to the left at time t_1 without moving to the right farther than $(n-a)\xi$. Afterwards the same chain end advances a distance $n\xi$ to the right for the first time at time t_2 without moving to the left any farther than its position at time t_1. The broken lines designate the lost portions of the original tube. The location of the left boundary of the remainder of the original tube at time t_1 is immaterial

Here T is the absolute temperature and μ_1 is a constant independent of N. The motion of a chain end is Brownian and is described by the one-dimensional Fokker–Planck equation[18]:

$$\frac{\partial}{\partial t} p(0,0;x,t) = D \frac{\partial^2}{\partial x^2} p(0,0;x,t) \qquad (6)$$

where $p(0,0;x,t)\,\mathrm{d}x$ stands for the probability that a chain end located at $x=0$ at $t=0$ is found between x and $x+\mathrm{d}x$ after time t $(t \geqslant 0)$. The curvilinear coordinate x has been normalized with respect to the correlation length and the diffusion coefficient D is equal to D_1/ξ^2.

As the polymer chain diffuses along the tube, the tube is gradually destroyed and replaced by newly formed portions. Nevertheless, the tube length is always constant. A polymer chain escapes from its original tube once the maximum separation of two positions of a chain end about its starting position is equal to the tube length. The process of chain disengagement from its tube is depicted in *Figure 1*.

The fraction of n-segment polymer chains that have not been disengaged from their original tubes at time t is calculated[8] as:

$$P(t,n) = D \int_0^t \mathrm{d}t_1 \int_0^n \mathrm{d}a \frac{\partial}{\partial x} p(x,t_1,a,n)\Big|_{x=-a}$$

$$\times \int_0^n \mathrm{d}x \frac{\partial}{\partial a} p(x,t-t_1,a,n)\Big|_{a=0} \qquad (7)$$

where $p(x,t,a,n)$ is the solution of equation (6) subject to absorbing boundary conditions at $x=-a$ and $x=n-a$:

$$p(x,t,a,n) = \frac{2}{n} \sum_{i=1}^{\infty} \sin\left(\frac{i\pi a}{n}\right) \sin\left(\frac{i\pi(x+a)}{n}\right)$$

$$\times \exp\left(-\frac{i^2 \pi^2 D t}{n^2}\right) \qquad (8)$$

The term

$$D \frac{\partial}{\partial x} p(x,t,a,n)\Big|_{x=-a}$$

in equation (7) is equal to the probability that a chain end initially located at $x=0$ reaches the point $x=-a$ for the first time at times between t and $t+\mathrm{d}t$ without ever crossing the point $x=n-a$. Also, the term

$$\frac{\partial}{\partial a}(x,t,a,n)\,\mathrm{d}a$$

is equal to the probability that a chain end starting from $x=-a$ at $t=0$ is found between x and $x+\mathrm{d}x$ at time t without moving farther than $x=-a-\mathrm{d}a$ to the left and $x=n-a$ to the right. From equations (7) and (8) the function $P(t,n)$ is described as:

$$P(t,n) = \frac{16}{\pi^2} \sum_{i=1,j}^{\infty}{}' \sum_{j=1}^{\infty}{}' \frac{1}{i^2-j^2}$$

$$\times \left[\exp\left(-\frac{j^2\pi^2 Dt}{n^2}\right) - \exp\left(-\frac{i^2\pi^2 Dt}{n^2}\right) \right]$$

$$+ \frac{16Dt}{n^2} \sum_{j=1}^{\infty}{}' \exp\left(-\frac{j^2\pi^2 Dt}{n^2}\right) \qquad (9)$$

The prime in the summation symbol designates summation over all odd integers.

The time and segment-number dependences of the function $P(t,n)$ can be lumped into that of the dimensionless time τ defined as:

$$\tau = t/\tau_r \qquad (10)$$

with

$$\tau_r = n^2/2D \qquad (11)$$

The parameter τ_r is the reptation time, i.e. the time required for a polymer chain to diffuse along its tube. Then, equation (9) is modified to give the fraction of polymer chains $P(\tau)$ that have not been disengaged from their original tube at time τ as:

$$P(\tau) = \frac{16}{\pi^2} \sum_{i=1,j}^{\infty}{}' \sum_{j=1}^{\infty}{}' \frac{1}{i^2-j^2}$$

$$\times \left[\exp\left(-\frac{j^2\pi^2\tau}{2}\right) - exp\left(-\frac{i^2\pi^2\tau}{2}\right) \right]$$

$$+ 8\tau \sum_{j=1}^{\infty}{}' \exp\left(-\frac{j^2\pi^2\tau}{2}\right) \qquad (12)$$

Also, the fraction of polymer chains $Q(\tau)$ that have been disengaged from their original tubes and, therefore, have completely relaxed at time τ is obtained as:

$$Q(\tau) = 1 - P(\tau) \qquad (13)$$

DYNAMICS OF CROSSING DENSITY

Problem definition

The polymer chains that can interpenetrate at the polymer–polymer interface at contact time τ are those that have been disengaged from their original tubes, as well as the escaped chain portions (referred to as minor chains[11]) of the macromolecules still confined in part of their original tubes as shown in *Figure 2*. Each partially relaxed polymer chain is responsible for two minor chains of segment numbers n_1 and n_2 such that $0 < n_1 + n_2 < n$.

Let $P(n_1, n_2\tau, n)\,\mathrm{d}n_1\,\mathrm{d}n_2$ be the fraction of n-segment partially relaxed polymer chains at time τ associated with two minor chains with segment numbers between n_1 and
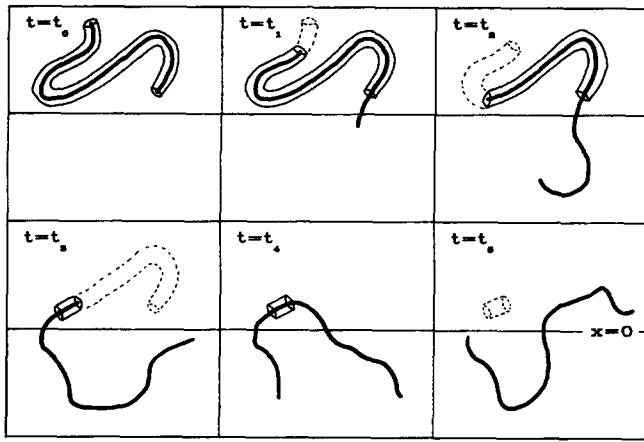
Figure 2 The chain interpenetration across the junction plane $x = 0$ is accomplished through the gradual destruction of the confining tube at the time t_0 at which the polymer–polymer interface was formed. The polymer chains that can cross the interface are the relaxed chains and the minor chains of partially relaxed chains

$n_1 + dn_1$, and n_2 and $n_2 + dn_2$, respectively. The sequence of events for the formation of two minor chains is presented in *Figure 3*. The double density function $P(n_1, n_2, \tau, n)$ is calculated by solving a first-passage problem[18] twice:

$$P(n_1, n_2, \tau, n) = -\frac{n^4}{4} \int_0^\tau d\tau_1 \int_0^{n_t} da \frac{\partial}{\partial x}$$

$$\times p(x, \tau_1, a, n_t)|_{x = -a} \int_0^{\tau - \tau_1} d\tau_2$$

$$\frac{\partial}{\partial x} \left(\frac{\partial}{\partial a} p(x, \tau_2, a, n_t)|_{a = 0} \right)\bigg|_{x = n_t}$$

$$\times \frac{\partial}{\partial a} p(n_1, \tau - \tau_1 - \tau_2, a, n_t)|_{a = 0}$$

$$+ \frac{n^4}{4} \int_0^\tau d\tau_1 \int_0^{n_t} da$$

$$\frac{\partial}{\partial x} p(x, \tau_1, a, n_t)|_{x = n_t - a} \int_0^{\tau - \tau_1} d\tau_2$$

$$\frac{\partial}{\partial x} \left(\frac{\partial}{\partial a} p(x, \tau_2, a, n_t)|_{a = 0} \right)\bigg|_{x = n_t}$$

$$\frac{\partial}{\partial a} p(n_2, \tau - \tau_1 - \tau_2, a, n_t)|_{a = 0} \quad (14)$$

with

$$n_t = n_1 + n_2 \quad (15)$$

The polymer chains crossing the junction plane are able to support stresses only if they are entangled about the interface. These chain crossings are referred to as effective crossings. Chain entanglements are assumed to occur at the end of each segment, excluding the final one. (The number of segments n is assumed integer.) The minor chains that can form effective crossings are those with degrees of polymerization larger than N_e. The total number of entanglements in an n_1-segment minor chain is $[n_1]$. (The symbol $[n_1]$ represents the integer part of n_1.) The first entanglement along a minor chain is located after $n_1 - [n_1]$ segments or $(n_1 - [n_1])N_e$ statistical links from its starting point. The chain segment from the

starting point of the minor chain to the first entanglement may be part of an effective crossing.

The number of effective crossings of a minor chain depends on the length of the remaining portion of the original tube as well as the configuration of the other minor chain. A minor chain of n_1 segments can form at most $[n_1]$ effective crossings if there exists an entanglement along the chain confined in the remaining portion of the original tube as shown in *Figure 4a*. Then, its starting point can be considered anchored in space and the number of effective crossings of the minor chain does not depend on the interpenetration of the other minor chain. Nevertheless, if there is no entanglement located along the chain confined in the remainder of the original tube, the calculation of the number of effective crossings of one minor chain is coupled to that of the other minor chain as shown in *Figures 4b* and *4c*.

Consequently, the total number of effective crossings $N_{eff}(\tau, n)$ per unit area of the $x = 0$ plane, assumed to be the junction or refracture plane, by n-segment linear polymer chains at time τ is calculated as follows:

$$N_{eff}(\tau, n) = Q(\tau) N_{eff}(\infty, n) + 2 \int_1^{n-1} dn_1 \, A_{m_1}(n_1, n)$$

$$\times \int_0^{n - [n_1] - 1} dn_2 \, (n_1, n_2, \tau, n)$$

$$+ 2 \int_1^n dn_1 \, A_{m_2}(n_1, n)$$

$$\times \int_{n - [n_1] - 1}^{n - n_1} dn_2 \, P(n_1, n_2, \tau, n)$$

$$+ 4 \int_1^{n-1} dn_1 \int_{n - [n_1] - 1}^{n - n_1} dn_2 \, P(n_1, n_2, \tau, n)$$

$$\times \int_0^\infty dx_0 \, r(x_0, n) \int_0^\infty dx_1 \, p_{n_1 - [n_1]}(x_0; x_1)$$

$$\times \int_0^\infty dx_2 \, \pi_{n - n_1 - n_2}(x_1; x_2)$$

$$\times \int_{-\infty}^0 dx_3 \, p_{n_2 - [n_2]}(x_2; x_3) \quad (16)$$

The first term of the right-hand side of equation (16) results from the polymer chains that have been completely disengaged from their original tubes. Here $N_{eff}(\infty, n)$ is the effective crossing density of n-segment linear polymer chains at infinite time, which is equal to the corresponding value of the neat polymer[12]:

$$N_{eff}(\infty, n) = N_{eff}(\infty, \infty)(n - 2)/n \quad (17)$$

with

$$N_{eff}(\infty, \infty) = \frac{\sqrt{2/3\pi} \, \rho b N_A}{M_s N_e^{1/2}} \quad (18)$$

where ρ is the polymer density, N_A is the Avogadro number and M_s is the molecular weight of the statistical link.

If the chain portion confined in the remainder of the original tube includes at least one entanglement the effective crossings of the minor chains are described in the second term. The coefficient 2 is related to the presence of two minor chains per polymer chain. The function
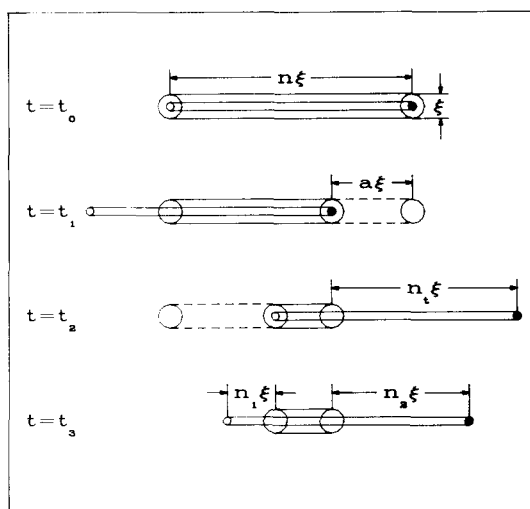
Figure 3 The partial relaxation of an n-segment polymer chain results in the formation of two minor chains with n_1 and n_2 segment numbers $(n_1 + n_2 = n_t < n)$. Here one chain end (filled circle) advances to its farthest position to the left, $a\xi$, and to the right, $(n_t - a)\xi$, for the first time at times t_1 and t_2, respectively. The same result can also be achieved if the particular chain end reaches its extreme point to the right before that to the left

$A_{m_1}(n_1, n)$ stands for the effective crossing density of n-segment polymer chains due to the n_1-segment minor chains assumed to have their starting point anchored. It is derived in the Appendix as:

$$A_{m_1}(n_1, n) = N_{eff}(\infty, \infty)\{[n_1] - 1 + (n_1 - [n_1])^{1/2}\}/n \tag{19}$$

The last two terms refer to the minor chains of partially relaxed chains that do not include an entanglement in the portion confined in the remainder of the original tube. The third term is due to the chain segments between two consecutive entanglements along the minor chains. The function $A_{m_2}(n_1, n)$ represents the effective crossing density of n-segment polymer chains caused by the n_1-segment minor chains assumed to have their starting point dangled. It is also derived in the Appendix as:

$$A_{m_2}(n_1, n) = N_{eff}(\infty, \infty)([n_1] - 1)/n \tag{20}$$

The contribution of the chain segments whose portion is confined in the remainder of the original tube is described in the fourth term of equation (16). The coefficient 4 accounts for the two minor chains and the two half-spaces they originate from. The density function $r(x_0, n)$ is given[12] by:

$$r(x_0, n) = \rho N_A / M_s n N_e \tag{21}$$

where $r(x_0, n) dx_0$ is the number of n-segment chains starting between x_0 and $x_0 + dx_0$ per unit area. Also, $p_k(x_0; x_k) dx_k$ is the probability that the end of the kth segment of a polymer chain starting from x_0 is found between x_k and $x_k + dx_k$, and $\pi_k(x_0; x_k) dx_k$ is the probability that the end of the kth segment of a polymer chain starting from x_0 and not crossing the $x = 0$ plane is found between x_k and $x_k + dx_k$ (x_0 and x_k have the same sign). The function $p_k(x_0; x_k)$ is Gaussian:

$$p_k(x_0; x_k) = \frac{\beta_k}{\pi^{1/2}} \exp[-\beta_k^2 (x_k - x_0)^2] \tag{22}$$

with

$$\beta_k = \sqrt{(3/2)}/k^{1/2}\xi \tag{23}$$

The density function $\pi_k(x_0; x_k)$ is derived in the Appendix as:

$$\pi_k(x_0; x_k)$$
$$= \frac{\beta_k\{\exp[-\beta_k^2(x_k - x_0)^2] - \exp[-\beta_k^2(x_k + x_0)^2]\}}{\pi^{1/2} \text{erf}(\beta_k x_0)} \tag{24}$$

An approximate solution

The exact solution of the problem as stated in the previous section, though feasible, is very cumbersome. Most of the difficulty arises from the coupling of the interpenetration processes of the two minor chains. An approximate solution is presented here to overcome this difficulty. The value of $N_{eff}(\tau, n)$ may be calculated as follows:

$$N_{eff}(\tau, n) = Q(\tau)N_{eff}(\infty, n) + 2 \int_1^n dn_1 \, A_m(n_1, n)$$
$$\times \int_0^{n - n_1} dn_2 \, P(n_1, n_2 \tau, n) \tag{25}$$

The function $A_m(n_1, n)$ is the effective crossing density of the n_1-segment minor chains out of n-segment polymer chains. The functions $A_{m_1}(n_1, n)$ and $A_{m_2}(n_1, n)$ are limiting values of that of $A_m(n_1, n)$:

$$A_{m_1}(n_1, n) \geqslant A_m(n_1, n) \geqslant A_{m_2}(n_1, n) \tag{26}$$

Recognizing that $[n_1] + (n_1 - [n_1])^{1/2} \geqslant n_1 \geqslant [n_1]$ we assume that:

$$A_m(n_1, n) \simeq N_{eff}(\infty, \infty)(n_1 - 1)/n \tag{27}$$

From equations (25) and (27) the total number of effective crossings at contact time τ is derived as:

$$N_{eff}(\tau, n)/N_{eff}(\infty, \infty)$$
$$= Q(\tau)(n-2)/n + \frac{16}{\pi^2} \sum_{i=1, j}^{\infty}{}' \sum_{j=1}^{\infty} \frac{c_j(n)}{i^2 - j^2}$$
$$\times \left[\exp\left(-\frac{j^2\pi^2\tau}{2}\right) - \exp\left(-\frac{i^2\pi^2\tau}{2}\right)\right]$$
$$+ 8\tau \sum_{j=1}^{\infty}{}' c_j(n)\exp\left(-\frac{j^2\pi^2\tau}{2}\right) \tag{28}$$

with

$$c_j(n) = (-1)^{j+1} \frac{(n-1)}{n} - \frac{\sin(j\pi/n)}{j\pi} \tag{29}$$
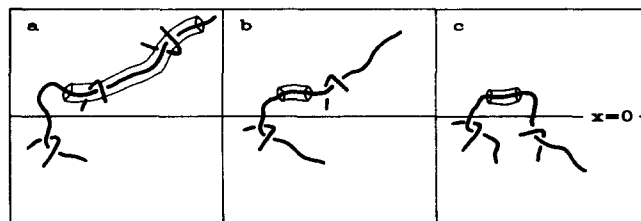

Figure 4 The chain segment from the starting point of a minor chain to the first entanglement located across the junction plane is part of an effective crossing, if there is at least one entanglement located along the chain portion confined in the remainder of the original tube (a). If the confined chain portion forms no entanglements, this first segment may (b) or may not (c) be part of an effective crossing depending on the interpenetration of the other minor chain
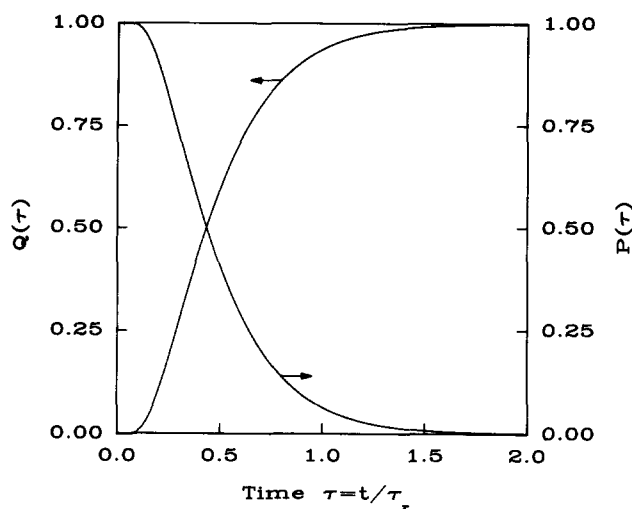
Figure 5 Variation of the fraction of polymer chains that have been disengaged from their original tube, $Q(\tau)$, as well as that of the fraction of partially relaxed polymer chains, $P(\tau)$, with the normalized time τ

Asymptotic solution

The variation of the crossing density $N_{eff}(\tau, n)$ with the number of chain segments n is due to the inability of the terminal segment to form an effective crossing. For high values of n the effect of the dangling ends is diminished and the total number of effective crossings per unit area is obtained as:

$$N_{eff}(\tau, \infty) = Q(\tau)N_{eff}(\infty, \infty) + 2 \int_0^n dn_1 \, A_m(n_1, n)$$

$$\times \int_0^{n-n_1} dn_2 \, P(n_1, n_2, \tau, n) \qquad (30)$$

with

$$A_m(n_1, n) = N_{eff}(\infty, \infty)n_1/n \qquad (31)$$

The solution of equation (30) is given by

$$N_{eff}(\tau, \infty)/N_{eff}(\infty, \infty)$$

$$= Q(\tau) + \frac{16}{\pi^2} \sum_{i=1,j}^{\infty} \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{i^2 - j^2}$$

$$\times [\exp(-j^2\pi^2\tau/2) - \exp(-i^2\pi^2\tau/2)]$$

$$+ 8\tau \sum_{j=1}^{\infty} {}' \exp(-j^2\pi^2\tau/2) \qquad (32)$$

Effect of molecular-weight distribution

Though the crossing density $N_{eff}(\tau, n)$ has been calculated for integer values of n, the validity of equation (28) can be extended to any value of n greater than 2. For polydisperse polymeric materials equation (21) is modified as:

$$r(x_0, \bar{n}) = \rho N_A/M_s \bar{n} N_e \qquad (33)$$

where $\bar{n}$ is defined in terms of the number-average degree of polymerization $\bar{N}_n$ as:

$$\bar{n} = \bar{N}_n/N_e \qquad (34)$$

If $F(n, m)$ is the chain segment distribution with the vector m standing for the distribution parameters, the effective chain crossing density for a polydisperse polymer is given by:

$$N_{eff}(t, m) = (1/\bar{n}) \int_2^{\infty} nN_{eff}(t, n)F(n, m) \, dn \qquad (35)$$

The lower integration limit in the integral is 2 instead of 0 as polymer chains with degrees of polymerization smaller than $2N_e$ cannot be entangled about the junction plane. The chain segment distribution $F(n, m)$ is expressed in terms of the molecular-weight distribution $F(M, m)$ as follows:

$$F(n, m) = M_e F(M, m) \qquad (36)$$

FRACTURE ENERGY AND TOUGHNESS

The fracture energy $G_F(\tau, n)$ of a polymer interface between two n-segment polymers at normalized contact time τ is related[12] to the total number of effective chain crossings $N_{eff}(\tau, n)$ of the junction plane through the equation:

$$G_F(\tau, n) = N_{eff}(\tau, n)N_e \varepsilon_s \qquad (37)$$

The parameter ε_s is the energy required to break a statistical link. Therefore, for a monodisperse polymer we obtain that:

$$\frac{G_F(\tau, n)}{G_F(\infty, n)} = \frac{N_{eff}(\tau, n)}{N_{eff}(\infty, n)} \qquad (38)$$

The fracture toughness K_F is defined for a plane stress condition[1] as:

$$K_F = (EG_F)^{1/2} \qquad (39)$$

where E is the tensile modulus of elasticity. The value of E is independent of the contact time t and remains constant during the autohesion process[10]. Thus, the normalized fracture toughness at contact time t is calculated as:

$$\frac{K_F(t, m)}{K_F(\infty, m)} = \left(\frac{N_{eff}(t, m)}{N_{eff}(\infty, m)} \right)^{1/2} \qquad (40)$$

for a polydisperse polymer.

RESULTS AND DISCUSSION

The fraction of polymer chains $Q(\tau)$ that have been disengaged from their original tube at normalized time τ has been calculated from equations (12) and (13). Its variation with the time τ, as well as that of the complementary fraction $P(\tau)$, is shown in *Figure 5*. At a time equal to twice the reptation time 99.9 % of the chains have relaxed from their original configuration. The average tube disengagement (or escape) time $\tau_e(n)$ of an n-segment chain is defined as:

$$\tau_e(n) = \int_0^{\infty} t \, dQ(t, n) \qquad (41)$$

and is calculated as

$$\tau_e = \tau_r/2 \qquad (42)$$

The reptation time of a polymer chain of molecular weight M scales to M^3 as deduced from equation (11):

$$\tau_r = \tau_1 M^3 \qquad (43)$$

where the monomer relaxation time τ_1 is temperature-dependent. Consequently, the time required for the fracture energy of a polymer–polymer interface to attain the value of the neat polymer depends on the polymer molecular weight and the temperature.
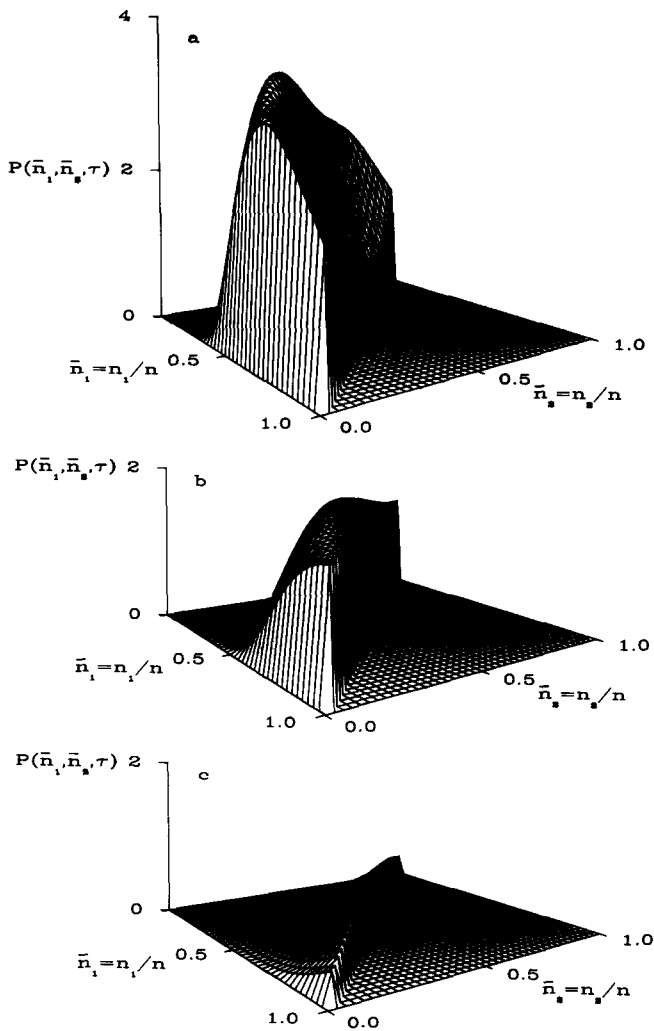
Figure 6 Variation of the probability density function $P(\bar{n}_1, \bar{n}_2, \tau)$ with the normalized minor chain lengths $\bar{n}_1$ and $\bar{n}_2$ at normalized times τ equal to 0.25 (a), 0.50 (b) and 1.00 (c)

The dependence of the probability density function $P(n_1, n_2, \tau, n)$ on the parameters n_1, n_2 and n can be lumped to that of dimensionless segment numbers defined as $\bar{n}_1 = n_1/n$ and $\bar{n}_2 = n_2/n$. Then, equation (14) can be modified to yield the fraction $P(\bar{n}_1, \bar{n}_2, \tau) d\bar{n}_1 d\bar{n}_2$ of partially relaxed chains at time τ associated with two minor chains with segment numbers in the range from $\bar{n}_1$ to $\bar{n}_1 + d\bar{n}_1$, and $\bar{n}_2$ to $\bar{n}_2 + d\bar{n}_2$, respectively. The change of the density function $P(\bar{n}_1, \bar{n}_2, \tau)$ with the values of $\bar{n}_1$ and $\bar{n}_2$ has been calculated numerically for the τ values of 0.25, 0.50 and 1.00, and is shown in *Figure 6*. The fraction of chains with specified minor chain lengths initially increases with time and reaches a maximum value. Thereafter it decreases, reaching a zero value at large times. This dependence results from the gradual disengagement of the polymer chains from their original tubes. The function $P(\bar{n}_1, \bar{n}_2, \tau)$ is symmetric with respect to $\bar{n}_1$ and $\bar{n}_2$ and its abrupt decrease along the line $\bar{n}_1 + \bar{n}_2 = 1$ is due to the chain relaxation. Also, the integral

$$\int_0^1 d\bar{n}_1 \int_0^{1-\bar{n}_1} d\bar{n}_2 \, P(\bar{n}_1, \bar{n}_2, \tau)$$

is equal to $P(\tau)$.

The number of effective crossings per unit interface, $N_{\text{eff}}(\tau, n)$, by n-segment polymer chains at contact time τ is

an invariant quantity, i.e. it is independent of the selection of the equivalent Gaussian chain. The value of $N_{\text{eff}}(\infty, \infty)$ is an invariant quantity[12]. The number of chain segments n is also an invariant equal to M/M_e. The parameter M_e is a material property and its value can be measured by independent experiments[19].

The normalized fracture energy $G_F(\tau, n)/G_F(\infty, n)$ is calculated from equations (28) and (38). Its variation with $\tau^{1/2}$ for the n values of 5, 10,. 20 and 50 is presented in *Figure 7*. The value of $G_F(\tau, n)/G_F(\infty, n)$ increases with the time τ and eventually reaches a plateau value equal to 1. The interfacial fracture energy regains 99.9% of the fracture energy of the neat polymer after a time of $1.4\tau_r$. This time is shorter than that for the tube disengagement as minor chains can also interpenetrate across the junction plane.

The time lag required for the growth of minor chains of molecular weight larger than M_e is responsible for the sigmoidal nature of the curves showing the time dependence of the fracture energy. The average time τ_t required for a polymer chain to diffuse a distance of ζ along its tube is equal to τ_r/n^2. For high values of n the value of τ_t is much smaller than that of τ_r and the sigmoidal nature of the curve diminishes. Thus, the value of $G_F(\tau, n)/G_F(\infty, n)$ increases as the number of chain segments n increases for the same value of τ.

The asymptotic value of the crossing density, $N_{\text{eff}}(\tau, \infty)$, given by equation (32) can be also derived[12] as:

$$N_{\text{eff}}(\tau, \infty) = N_t(\tau) N_e^{-1/2} \tag{44}$$

where $N_t(\tau)$ stands for the total number of chain crossings of the junction plane at contact time τ. The value of $N_t(\tau)$ was calculated by Prager and Tirrell[8] and is only dependent on τ.

The variation of the asymptotic value of the normalized fracture energy $G_F(\tau, \infty)/G_F(\infty, \infty)$ with $\tau^{1/2}$ is also shown in *Figure 7*. It is seen that for small times $G_F(\tau, \infty)$ scales to $\tau^{1/2}$. Furthermore, we find that the equation:

$$G_F(\tau, \infty)/G_F(\infty, \infty) \simeq 1.546 \, \tau^{1/2} \tag{45}$$

provides a good estimate of the normalized fracture energy with a second decimal point accuracy for $\tau \leqslant 0.17$.
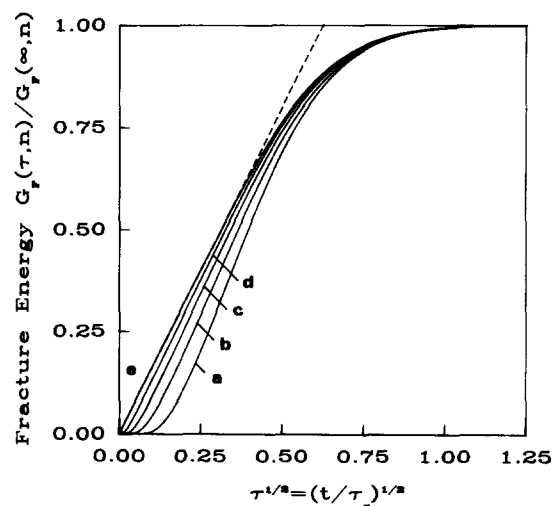

Figure 7 Variation of the normalized fracture energy $G_F(\tau, n)/G_F(\infty, n)$ with the square root of the normalized contact time $\tau^{1/2}$ for monodisperse polymers with number of segments n equal to 5 (curve a), 10 (curve b), 20 (curve c), 50 (curve d) and infinity (curve e). The broken line has a slope of 1.596
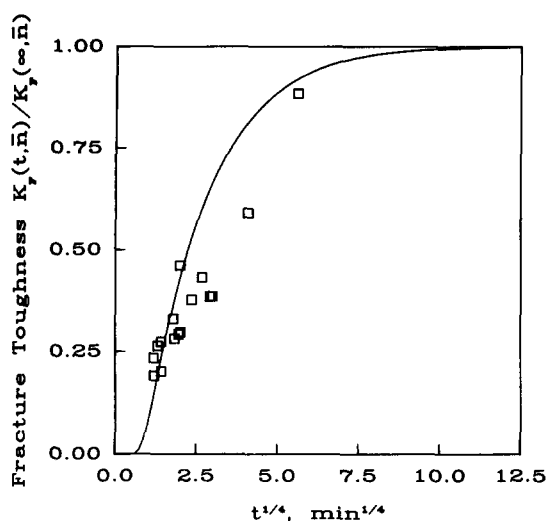
Figure 8 Comparison of theoretical predictions with experimental results[5] of the variation of the normalized fracture toughness $K_F(t,\bar{n})/K_F(\infty,\bar{n})$ of poly(methyl methacrylate) with the fourth root of the contact time $t^{1/4}$ at 390 K for samples obeying the most probable molecular-weight distribution with $\bar{n}=6$

The $t^{1/2}$ dependence of the fracture energy of high-molecular-weight polymers is only valid for monodisperse polymers. In polydisperse polymers there exists a spectrum of relaxation times for different sized chains that causes such a time dependence to decay.

Theoretical predictions of the variation of the normalized fracture toughness $K_F(t,\bar{n})/K_F(\infty,\bar{n})$ with $t^{1/4}$ calculated from equation (40) are compared in *Figure 8* with experimental measurements[5] for polydisperse poly(methyl methacrylate) (PMMA). The polymer samples obeyed the Schultz–Flory most probable molecular-weight distribution[20]:

$$F(M,\bar{M}_n) \simeq (1/\bar{M}_n)\exp(-M/\bar{M}_n) \qquad (46)$$

where the number-average molecular weight $\bar{M}_n$ was 60 000. Dried and polished PMMA surfaces were brought in contact for a time t at the temperature of 390 K. This temperature is higher than the glass transition temperature[21] of PMMA ($T_g = 378$ K) and, therefore, the polymer chains are mobile and can interdiffuse across the junction plane. After time t the polymer interfaces were quenched to 20°C to freeze the chain interpenetration process and the fracture toughness was measured.

It is observed that the predictions of the model are in good agreement with the experimental data. For high-molecular-weight monodisperse polymers the variation of the fracture toughness with $t^{1/4}$ would have been linear for small times. The important feature of the proposed model is that it includes no adjustable parameters. The material properties of PMMA used in the calculations are the molecular weight between entanglements, M_e (equal[19] to 10 000), and the monomer relaxation time, τ_1 (equal to 3.87×10^{-11} s at 390 K).

The preceding analysis is valid for autohesion of fully annealed polymer surfaces. Here there is no dependence of the molecular-weight distribution on the distance from the interface. On the contrary, for crack healing the molecular-weight distribution depends on the position. Owing to chain scission during polymer fracture[12] there are more shorter polymer chains in the vicinity of the crack than in the bulk of the material. Nevertheless, the same fundamental phenomena of chain interpenetration

also govern the crack healing process. The knowledge of the spatial distribution of the chain ends will enable us to predict the fracture strength recovery of a cracked polymer specimen.

CONCLUSIONS

The interpenetration of polymer chains during the polymer autohesion process was investigated. A stochastic model was developed to calculate the number of effective chain crossings $N_{\text{eff}}(t,M)$ per unit junction area by polymer chains of molecular weight M larger than $2M_e$ at contact time t. The model couples the recently proposed polymer fracture theory and the reptation theory of polymer self-diffusion. The fracture energy $G_F(t,M)$ of the polymer–polymer interface is proportional to $N_{\text{eff}}(t,M)M_e$. The value of $G_F(t,M)$ scales to the square root of the contact time for t values smaller than the reptation time and for monodisperse polymers with $M \gg 2M_e$. Theoretical predictions of the change of the normalized fracture toughness with the contact time agreed with experimental results for poly(methyl methacrylate).

This work provides the mathematical framework for the estimation of the diffusion and relaxation constants of chain macromolecules from autohesion/refracture experiments. Finally, it can be extended to study the adhesion of two different polymers provided that: (i) they are thermodynamically compatible, and (ii) they have similar structural, thermal and diffusional properties.

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APPENDIX

Calculation of the functions $A_{m_1}(n_1,n)$ and $A_{m_2}(n_1,n)$

If we designate by $a_{m_1}(x_0,n_1)$ the average number of effective crossings of the $x=0$ plane by an n_1-segment minor chain starting from and being anchored at x_0 we obtain[12] for $n_1 \leq 1$ that:

$$a_{m_1}(x_0,n_1)=0 \qquad (A.1)$$

and for $n_1 > 1$ that:

$$a_{m_1}(x_0,n_1)= \sum_{k=0}^{[n_1]-1} \Delta a_{k+1}(x_0) \qquad (A.2)$$

The function $\Delta a_{k+1}(x_0)$ stands for the probability that the $(k+1)$th segment of a polymer chain starting from x_0 forms an effective crossing and is calculated for $k=0$ as:

$$\Delta a_1(x_0)= \begin{cases} \displaystyle\int_{-\infty}^{0} \mathrm{d}x_1\, p_{n_1-[n_1]}(x_0;x_1) & (x_0>0) \\ \displaystyle\int_{0}^{\infty} \mathrm{d}x_1\, p_{n_1-[n_1]}(x_0;x_1) & (x_0<0) \end{cases} \qquad (A.3)$$

and for $k \geq 1$:

$$\Delta a_{k+1}(x_o) = \int_{-\infty}^{0} dx_{k+1} \int_{0}^{\infty} dx_k \, p_{n_1-[n_1]+k-1}(x_0; x_k)$$

$$\times p_1(x_k; x_{k+1}) + \int_{0}^{\infty} dx_{k+1} \int_{-\infty}^{0} dx_k$$

$$\times p_{n_1-[n_1]+k-1}(x_0; x_k) p_1(x_k; x_{k+1}) \qquad (A.4)$$

Here $p_k(x_0; x_k) \, dx_k$ is the probability that the end of the kth segment of a polymer chain starting from x_0 is found between x_k and $x_k + dx_k$.

The number of effective crossings per unit area of n-segment polymer chains due to the n_1-segment minor chains assumed to have their starting point anchored, $A_{m_1}(n_1, n)$, is calculated as:

$$A_{m_1}(n_1, n) = \int_{-\infty}^{\infty} dx_0 \, r(x_0, n) a_{m_1}(x_0, n_1) \qquad (A.5)$$

where $r(x_0, n) \, dx_0$ is the number of n-segment chains starting between x_0 and $x_0 + dx_0$. The crossing density $A_{m_1}(n_1, n)$ is eventually derived as:

$$A_{m_1}(n_1, n) = N_{\text{eff}}(\infty, \infty)\{[n_1] - 1 + (n_1 - [n_1])^{1/2}\}/n(A.6)$$

where $N_{\text{eff}}(\infty, \infty)$ stands for the number of effective crossings per unit area of a neat polymer of infinite molecular weight.

If we neglect the effective crossing of the portion of the minor chain from its begining to the first entanglement, the average number of effective crossings of the $x = 0$ plane by an n_1-segment minor chain, $a_{m_2}(x_0, n_1)$, is given for $n_1 < 2$ by:

$$a_{m_2}(x_0, n_1) = 0 \qquad (A.7)$$

and for $n_1 \geqslant 2$ by:

$$a_{m_2}(x_0, n_1) = \sum_{k=1}^{[n_1]-1} \Delta a_{k+1}(x_0) \qquad (A.8)$$

Similarly, the number of effective crossings per unit area of n-segment polymer chains due to the n-segment minor chains assumed to have their starting point dangled, $A_{m_2}(n_1, n)$, is obtained as:

$$A_{m_2}(n_1, n) = \int_{-\infty}^{\infty} dx_0 \, r(x_0, n) a_{m_2}(x_0, n_1) \qquad (A.9)$$

and is derived as:

$$A_{m_2}(n_1, n) = N_{\text{eff}}(\infty, \infty)([n_1] - 1)/n \qquad (A.10)$$

Calculation of the probability density function $\pi_k(x_0; x_k)$

We denote by $\pi_k(x_0; x_k) \, dx_k$ the probability that the end of the kth segment of a polymer chain starting from x_0 and not crossing the $x = 0$ plane is found between x_k and $x_k + dx_k$ (x_0 and x_k have the same sign). The density

function $\pi_k(x_0; x_k)$ is proportional to the solution $p(x_0, 0; x_k, n)$ of the Fokker–Planck equation:

$$\frac{\partial}{\partial n} p(x_0, 0; x_k, n) = \frac{\zeta^2}{6} \frac{\partial^2}{\partial x_k^2} p(x_0, 0; x_k, n) \qquad (A.11)$$

with the absorbing boundary conditions[22]:

$$p(x_0, 0; 0, n) = p(x_0, 0; \infty, n) = 0 \qquad (A.12)$$

where ζ is the mesh size between entanglements.

The density function $\pi_k(x_0; x_k)$ is obtained from the normalization of the solution of equation (A.11):

$$\pi_k(x_0; x_k) = p(x_0, 0; x_k, k) / \int_{0}^{\infty} p(x_0, 0; x_k, k) \, dx_k \qquad (A.13)$$

Hence, we derive that:

$$\pi_k(x_0; x_k)$$
$$= \frac{\beta_k\{\exp[-\beta_k^2(x_k - x_0)^2] - \exp[-\beta_k^2(x_k + x_0)^2]\}}{\pi^{1/2} \text{erf}(\beta_k x_0)}$$
$$\qquad (A.14)$$

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