"Molecular Velcro": Dynamics of a Constrained Chain into an Elastomer Network

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ABSTRACT: We discuss the dynamics of the healing process when contact is made between a cross-linked elastomer network and polymers that are end-tethered onto a solid surface. We find that there are generally three stages to the approach to the equilibrium, "mushroom" conformation. Entanglements in the network have a major affect on the time scale of the healing process. Our findings share similar trends with adhesion experiments on PI/PS interfaces conducted by Reichert and Brown; their data show and our model predicts a rapid partial recovery of toughness, followed by a very slow (days) route to equilibrium.

Introduction

In recent years there has been much activity, both theoretically and experimentally, in the study of polymer interfaces. In particular, a chief concern is maximizing interface adhesion, due to the importance in coating and reinforcement applications.

Theoretically, the polymer-polymer interface is especially rich in problems, involving both polymer statics and dynamics. The static properties influence the depth and strength of the interface, and knowledge of polymer dynamics tells us how quickly the interface forms. It is often found that the entangled nature of long polymers has a significant influence on both the interface toughness and formation time. There are a number of practical systems that have physical similarities including a polymer-polymer weld,[1,2] a diblock polymer at the boundary between incompatible homopolymers,[3-5] and solid-polymer interfaces where the solid has polymer chains chemically tethered.[6-9]

In this note we focus on the interface formed between a cross-linked elastomer matrix and N-mer chains (N is the number of Kuhn segments in a grafted chain) that are end-tethered onto a solid surface. We allow for a slight chemical disparity that, for instance, is known to arise in certain systems containing deuterated homopolymers.[17] The nature of the interface depends strongly on the tethered-chain coverage, σ: the bare grafted chains are squashed normal to the surface if $\sigma \ll 1/b^2N^{1/2}$, while if $\sigma \gg 1/b^2N^{1/2}$, they are stretched normal to the surface (the brush regime),[11] where b is the Kuhn length (the Kuhn length refers to the length of the smallest group of connected monomers that have Gaussian end-to-end vector statistics).

Our study has been partially motivated by some experiments of Reichert and Brown (R&B)[3] and more recently by Tirrell *et al.*[9] R&B investigated the adhesion between surfaces of PS and cross-linked PI after a layer of PS-*b*-PI block copolymer had been interdiffused into the PS homopolymer and then quenched. They discovered that the interface had the interesting property of recovering its original toughness, on healing at room temperature, after complete physical failure—hence the term "molecular Velcro". In their experiments they considered the intermediate coverage regime where the PI chains were well overlapped but were not brushlike.

Our aim is to gain insight into the dynamics of this healing process at the molecular level, which in some cases could take many days to complete.

Model

We consider here, for simplicity, the low coverage regime, $\sigma < 1/b^2N$. This enables us to make the assumptions that there is no swelling of the cross-linked network and that the structure local to the surface is not affected by the tethered chains and remains unchanged during healing. On initial formation of the interface, we assume the grafted chains reside in an unentangled layer of network material of width $d \approx a/2$, where a is the characteristic distance between network topological constraints in the *bulk*. In this respect we are saying that the surface is more effective than the network entanglements at confining the surface chain. Unless the cross-link density is very high, the value of a is approximately that for the entangled elastomer melt.

We neglect chain end effects in the network and thus temporary constraints; this is realistic for the case of very long elastomers with a moderate cross-link density.

Paramount to the issue of healing is the extent of penetration, and the dynamic route of the anchored chain into the network. We approach the problem by considering a grafted chain that has partially entered the network at a distance R from the anchor site, via the motion of its free end. The section of the chain that penetrates the network is confined to a tube of diameter a, and consists of N_t monomers, while the remaining, $N_s = N - N_t$, monomers are topologically confined to a *slab* of thickness d. The curvilinear distance from the tube entrance to the chain free end (the N_tth tube monomer) defines the tube length, L (Figure 1).

We calculate the entropic part of the confined chains' free energy using the Green function method. The original calculation using this method for just the tube free energy is detailed in appendix 6.I, ref 10. We calculate the entropic contribution to the free energy, F, by neglecting logarithmic terms and this is strictly valid when the confining dimensions are a lot smaller than the chain-part Gaussian dimension: $bN_s^{1/2} \gg d$ and $bN_t^{1/2} \gg a$. The total free energy is given in eq 1 and includes a "weak" interaction contribution such that it does not significantly affect the local structure of the tethered chain. The first two free

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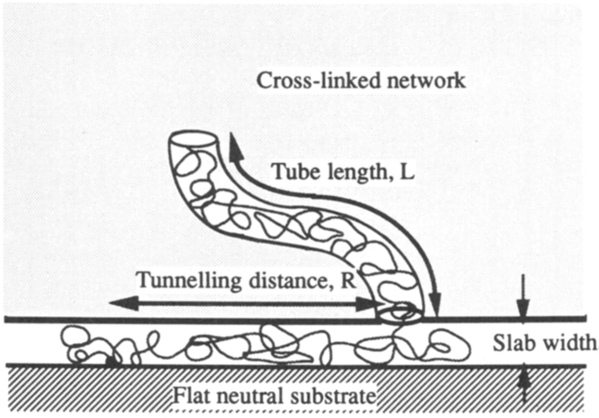

Figure 1. Tethered chain that has partially entered the network.

$$\frac{F}{k_{\mathrm{B}}T} \approx \frac{\pi^2 b^2}{6}\left[\frac{N_{\mathrm{s}}}{d^2} + \frac{2N_{\mathrm{t}}}{a^2}\right] - \frac{\alpha L}{a} + \frac{3}{2b^2}\left[\frac{R^2}{N_{\mathrm{s}}} + \frac{L^2}{N_{\mathrm{t}}}\right] + \Delta\bar{\Sigma}\mu N_{\mathrm{s}} - \Delta\bar{\phi}\chi N_{\mathrm{s}} \quad (1)$$

energy terms are confinement energies for the slab and tube chain segments respectively, whilst, in the same order, terms four and five are the "elastic" energies. The third term accounts for the multiplicity of the state specified by L, the dimensionless constant α (of order unity) is network-model dependent.[10] The last two terms in the free energy account for cases where there are small "chemical" interactions: in the first case tethered chain–surface interactions, and in the second case, tethered chain–network interactions. The chain–network interactions are characterized by the Flory parameter χ whilst μ quantifies the difference between the energies of a tethered chain–surface contact and network–surface contact. $\Delta\bar{\phi}$ and $\Delta\bar{\Sigma}$ are, respectively, the difference in the average tethered-chain volume fraction and surface fraction between the slab and tube chain parts. They account for the change in chain–network and chain–surface contacts as the polymer tunnels into the network. The tethered-chain volume fractions are calculated in terms of the slab volume, $R_g^2 d = b^2 d N_{\mathrm{s}}$, and the network volume (the tube volume is not used in this case as the network constraints do not affect the average chain conformation and thus chain–network interactions), $R_g^3 = b^3 N_{\mathrm{t}}^{3/2}$, and the surface volume is characterized by R_g^2 and the depth, b (R_g is the Gaussian radius of gyration for the chain part). Using these values, the volume fraction differences are crudely estimated:

$$\Delta\bar{\phi},\Delta\bar{\Sigma} \approx \frac{b}{d} - \frac{1}{N_{\mathrm{t}}^{1/2}} \quad (2)$$

The dependence on N_{t} may be neglected for substantial network incursions by long chains. We include these energy terms because it is known that surface excesses of chains can be ascribed to very slight chemical differences. Surface excesses of d-PS were observed at a silicon surface, in a d-PS/h-PS blend.[17]

We have neglected the energy associated with entanglement stretching in the network (swelling) and can justify this, for low coverage, with the following argument. The network region, swollen an amount $\Delta V \sim N_{\mathrm{t}} b^3$, by a single tethered chain is $R_g^3 = b^3 N_{\mathrm{t}}^{3/2}$. Using a value for the network modulus, $B \sim kT/a^3$, the swelling energy is

$$F_{\mathrm{swell}} \approx N_{\mathrm{t}}^{1/2}\left(\frac{b}{a}\right)^3 kT \quad (3)$$

This is negligible in comparison to the terms in eq 1. However, it would become significant for a higher coverage.

Stable and Metastable States—"Mushrooms and Runners". By independently minimizing the free energy with respect to the dynamic variables, N_{t} and L, for a fixed value of R, we find the free energy has the potential minima,

$$N_{\mathrm{t}}^{\mathrm{min}} = N - \frac{3}{\pi b^2}\frac{R}{\gamma} \qquad L^{\mathrm{min}} = \frac{\alpha b^2 N_{\mathrm{t}}^{\mathrm{min}}}{3a} \quad (4)$$

where

$$\gamma = \left[\frac{1}{d^2} - \frac{(2 - \alpha^2/\pi^2)}{a^2} + \frac{6}{\pi^2 b^2}(\Delta\bar{\phi}\chi - \Delta\bar{\Sigma}\mu)\right]^{1/2}$$

The existence of a minimum confirms our guess that under certain conditions a grafted chain may enter the network, at a distance from its grafting point to find a metastable equilibrium. The equilibrium must be metastable because over long time scales the classical "mushroom" configuration[11] of unentangled end-grafted chains has be achieved, with $R = 0$. The metastable states with R temporarily fixed we call "runners" in analogy with plants having trailing surface roots. The trailing sections of chain are stretched in the sense that

$$R \sim (N - N_{\mathrm{t}}) \quad (5)$$

It is interesting to note that if $d > d^*$, where

$$d^* \approx \left[\frac{2}{a^2} - \frac{6}{\pi^2 b^2}(\Delta\bar{\phi}\chi - \Delta\bar{\Sigma}\mu)\right]^{-1/2} \quad (6)$$

network incursions of the free end are exponentially suppressed. There is also a corresponding inequality for R such that if $R > R^*$, where

$$R^* = \pi b^2 \gamma N/3 \quad (7)$$

the chain end stays in the surface layer.

Dynamics

We will now consider the dynamics of the healing process. In general there are three stages to the approach to the equilibrium mushroom configuration.

(i) Rapid Network Penetration. The conformational relaxation of a Gaussian chain, from a perturbed state to its equilibrium state, is well described by the Rouse model.[10] In this model, the "end-to-end" relaxation of a n Kuhn-unit segment (the conformational change between the mth and $m + n$th units) is dominated by chain motion on time scales of the order $\tau_n \approx \tau_1 n^2$. The Kuhn unit has a characteristic relaxation time, τ_1.

The first dynamic occurrence on making the interface is the diffusion of the grafted chain (initially completely flattened) into the unentangled surface layer of the cross-linked network. For this process, the relevant chain segment size is that of a Gaussian "blob" of diameter d, $N_d = (d/b)^2$. This has a characteristic time

$$\tau_d \approx \tau_1 (d/b)^4 \quad (8)$$

We reiterate that d is the special value of a at the surface due to the enhanced confinement from the surface.

Once embedded in this layer the chain free end will do one of two things. If there is a tunneling solution at the chain end-to-end distance R, the chain will bury itself into the network to the extent dictated by the minima eq 2. Otherwise, the chain free end diffuses in the slab only when it reaches $R < R^*$. As both processes involve the motion of the chain free end, the appropriate Rouse relaxation time is of the order, $\tau_{\mathrm{N}} \sim \tau_1 N^2$. If the surface topology and chemistry are such that $d > d^*$, the chain

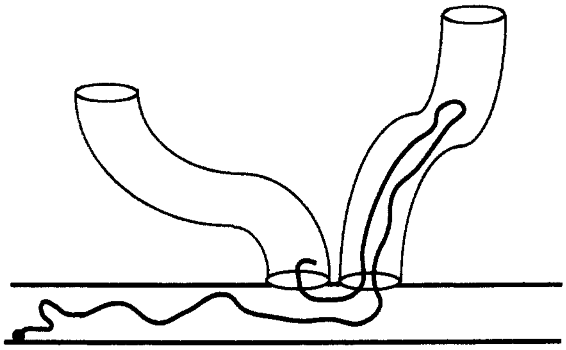

Figure 2. Chain free end moving into an adjacent tube by tunneling back to the tube entrance.

cannot tunnel into the network until the free end reaches the grafting point, $R = 0$. In this case the chains reach the final "mushroom" state much faster than when having to pass through metastable "runner" states.

(ii) "Breathing" Mode Relaxation. Once buried in the network, the chain may renew its conformation by back-tracking down its current tube and tunneling out into a new tube. This process is completed when the chain free end has found its way back to the tube entrance and is similar to the "breathing" mode relaxation of star polymers (Figure 2).

To calculate the characteristic occupation time of a particular tube, τ_T, we use the simple theory of the activated process, following the treatment of entangled star polymers.[12] It yields the result

$$\tau_T \propto \exp[(F[L=0;R] - F[L^{\min};R])/kT] \tag{9}$$

This expression can be evaluated, neglecting logarithmic terms (and thus fluctuations), by substituting the minima eq 2 back into the free energy expression. The result is

$$\tau_T \propto \exp\left[\frac{\alpha^2 b^2 N}{6a^2} - \pi(\gamma - \gamma_0)R\right] \qquad \gamma_0 = \left(\gamma^2 - \frac{\alpha^2}{\pi^2 a^2}\right)^{1/2} \tag{10}$$

where we find γ_0 by minimizing F with $L = 0$. The first term in the exponential gives the longest tube occupation time (when $R = 0$). This is when the grafted chain becomes essentially a star arm in a fixed network.[10,12] It is known that these time scales can be very long (a few days for well entangled PI chains at room temperature). The value of τ_T is less than that for a star arm with $N = N_t^{\min}$ due to the absence of a fixed monomer at the entrance of the tube.

(iii) *R* Coordinate Hopping. On time scales greater than τ_T, the appropriate free energy is the R parametrized potential of eq 1, given by the substitution of the minimum values of N_t and L:

$$F(R) \approx \frac{\pi^2 b^2 N}{3a^2} + \pi\gamma R \tag{11}$$

As γ cannot be negative, the chain end's equilibrium position is always in the tube above its graft point. In the case where γ is positive the chain end moves there by hopping in and out of tube entrances, for $R < R^*$.

Crudely, the time taken for the chain end to tube-hop from its initial starting position, R_0, to the graft point is calculated by integrating over the intervening tube occupation times,

$$\tau_R \propto \exp\left(\frac{\alpha^2 b^2 N}{6a^2}\right)[1 - \exp(-\pi(\gamma - \gamma_0)R_0)] \tag{12}$$

Interface Toughness

We will now consider how the R distribution relaxes during the healing process and see what bearing this might have on the interface toughness. When the grafted chain is first accommodated in the surface layer, the free end conformation is described by the end-to-end vector of a two dimensional random walk;

$$P_0(R) \sim \exp\left(-\frac{R^2}{b^2 N}\right) \tag{12}$$

At equilibrium, $P(R)$ is given by the Boltzmann distribution of the R parametrized free energy:

$$P_{\text{eq}}(R) \sim \exp(-\pi\gamma R) \tag{13}$$

If we compare the average value of R from the two distributions,

$$\langle R^2\rangle_0^{1/2} \sim bN^{1/2} \qquad \langle|R|\rangle_{\text{eq}} \sim \frac{1}{\pi\gamma} \tag{14}$$

where γ^{-1} is typically of order a, it is clear that for long chains the R distribution is considerably narrowed at equilibrium. This result has implications for the adhesive strength of the interface.

The interface toughness, G, may have several contributing terms, including surface energy, network deformation, and viscous effects from motion of the tethered chain through the network. Experimentally, G also depends on the method of disjoining the interface, which is known to be very sensitive to the rate of deformation. For well entangled chains, the viscous energy dissipated by the "pull-out" of a single tethered chain, can be estimated by tube models.[7,13-16] There are a few differences between the pull-out models, but they generally share the trend that the pull-out energy, G_{po}, increases with N_t. The more simple models predict that the pull-out energy has the relationship

$$G_{\text{po}} \sim N_t^2 \tag{15}$$

although most models predict a positive power of N_t for a lower coverage. The contribution G_{po} to the total toughness will depend on N, σ, the crack velocity, and viscoelastic properties of the network, and it may well dominate in some circumstances.

By substituting the average R values into the expression for $N_t^{\min}$, we can estimate the increase in G_{po} over the healing process, $t > \tau_N$

$$\frac{G_{\text{po}}(t=\infty)}{G_{\text{po}}(t\approx\tau_N)} \approx \left[\frac{1 - 3(\pi^2 b^2 \gamma^2 N)^{-1}}{1 - 3(\pi b \gamma N^{1/2})^{-1}}\right]^2 \tag{16}$$

With the typical parameter values $N = 10^3$, $a = 10b$, and $d = 0.6a$ and no chemical disparities, the pull-out energy ratio is $G_{\text{po}}(t=\infty)/G_{\text{po}}(t\approx\tau_N) \sim 2$. Other pull-out models would predict similar toughening over long time scales for the R-hopping process.

Experimental Comparison

Our work here is strictly applicable to a surface coverage somewhat less than those considered by R&B, as our model of metastable states is only valid when the surface layer is strongly "compressed", and not entangled. However, experimental evidence[3,9] shows that there is a moderate grafted-chain layer thickness (the product of N and σ) which provides the optimum toughness, so our low coverage regime may still be of practical use. Incidentally, the decrease in G for very thick grafted layers is attributed to the suppression of network penetration rather than an inherent affect on the pull-out mechanism.

This aside, the estimates in this short work share similar trends to their data and are not critical on the exact relationship of N to G—only that the toughness increases the length of the chain. On initial formation of the PS/PI interface R&B's data show a rapid partial recovery of the equilibrium toughness: on their plot of G against $t^{1/2}$ (hours) there appears to be an almost instantaneous rise in G, well above the threshold value (the toughness measured without tethered chains). This might correspond to the fast Rouse dynamics in our work that, typically, are measured as $\ll 1$ s (well above the glass transition). The remaining toughness deficit recovered over an exponentially long time (days) as would be expected from the "starlike" relaxation of the R distribution in our work.

Although our model cannot directly account for the two-stage healing process implied in R&B's data, we think it does point to a general dependence, for a wide range of σ, on the presence of an "entangled" metastable state. Indeed, some of our current work suggests that in the case of a higher coverage, trapped entanglements in the grafted layer may provide such a mechanism for retarding the healing process.

In a further paper we will consider the other coverage extreme, that of the melt brush–elastomer interface. In the mean time we await experiments properly applicable to this work.

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