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Energy-Consuming Micromechanisms in the Fracture of Glassy Polymers. 2. Effect of Molecular Weight on the Fracture of Polystyrene

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ABSTRACT: Narrow molecular weight distribution polystyrene latex films of low molecular weight (M_n = 32 000; PDI = 1.04) and medium molecular weight (M_n = 151 000; PDI = 1.02) were made by using a direct miniemulsification technique. Compression molding of the cleaned and dried latex powder was carried out at 110 °C and 10 MPa for 20 min, followed by annealing at 144 °C for various times. Fracture of the latex films was carried out using a custom-built dental burr grinding instrument from which the total fracture energy was determined. Molecular weights before and after fracture were determined using gel permeation chromatography (GPC). From the number of chain scissions, the chain scission energy and the uncoiling energy (due to rubber elasticity) were calculated. Then, by using an energy balance approach, the viscoelastic energy for pullout was calculated. Total fracture energies of 174×10^6 J/m^3 (or 17 J/m^2) and 460×10^6 J/m^3 (or 230 J/m^2) were obtained for fully annealed, low and medium molecular weight latex films, respectively. About 1×10^{24} scissions/m^3 (or 7×10^{17}/m^2) were obtained for the fully annealed, medium molecular weight sample via GPC, while the low molecular weight latex films did not show any apparent change in the molecular weight on grinding. Under fully annealed conditions, the contribution to the total energy from chain scission was about 40% for the medium molecular weight and about 0% for the low molecular weight film. Present data are compared with high molecular weight polystyrene (M_n = 420 000; PDI = 1.19), where about 90% chain scission and 10% pullout were reported at long annealing times. In all cases, the contribution from the uncoiling energy was negligible. Molecular frictional coefficient values obtained using Prentice's model indicate that the temperature for the chain pullout process is about 150–250 °C.

I. Introduction

Interfaces play a key role in determining the mechanical properties of polymer latex films, blends, composites, etc.[1–3] While the process of healing the interface is a critical issue, the reverse process of recreating the interface in order to understand the molecular basis of failure[2] also provides insight. In this regard, films formed from latex serve as an example model system, since they provide large interfacial area between neighboring particles. The interdiffusion kinetics and strength development in latex films have been extensively studied by small-angle neutron scattering (SANS)[4–8] and DET.[9–12] Recreating the interface or crack formation in a material first involves the uncoiling of chain segments spanning the crack path caused by rubber elasticity effects (Figure 1), followed by either chain pullout, which is a viscoelastic dissipation of the fracture energy, or chain scission, which involves the stretching of all the bonds between two entanglements to the point of rupture.[13,14] For chain scission to occur, the chain segment involved has to be held firmly, by either entanglements or cross-links.[13]

When interdiffusion across the interface occurs, full strength in the system is achieved when the entanglement density at the interface reaches the bulk value.

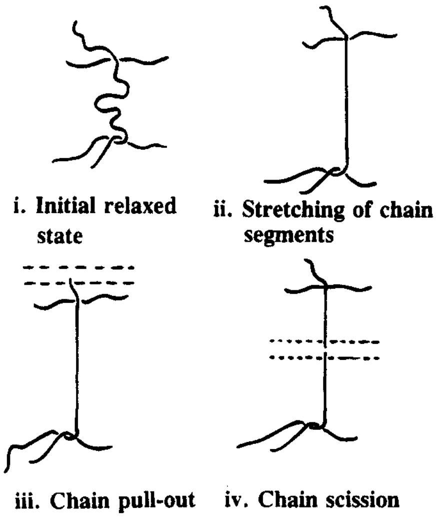
i. Initial relaxed state
ii. Stretching of chain segments
iii. Chain pull-out
iv. Chain scission

Figure 1. Micromechanisms involved during crack propagation in glassy polymers.[2]

In the case of immiscible polymers, where thermodynamic forces prevent the healing process, block copolymers have been used to reinforce the interface.[15–21] Creton et al.[18] measured the fracture toughness of a polystyrene (PS)–poly(2-vinyl pyridine) (PVP) interface, reinforced with PS–PVP diblock copolymers. The degree of polymerization and the areal density of the block copolymers determined the fracture toughness of the interface. For good toughness, at least one effective entanglement of the diblock copolymer with its respective homopolymers was required. Three different molecular mechanisms[17] were found responsible for failure at the interface, namely, chain scission at a low chain

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Table 1. Literature Survey of Fracture Studies on Polystyrene

name	method	mol wt	result
Popli and Roylance[a]	flexing (room temp)	$(4-7) \times 10^3$ (broad)	no scission
Sambasivam et al.[b]	grinding (room temp)	32 000 (narrow)	no scission; 100% pullout
Yang et al.[c]	impact (room temp)	133 000 (broad)	10^{24} scissions/m^3; scission
Sambasivam et al.[b]	grinding (room temp)	151 000 (narrow)	10^{24} scissions/m^3; scission (40%), pullout (60%)
Mohammadi et al.[d]	grinding (room temp)	420 000 (narrow)	10^{24} scissions/m^3; scission (90%), pullout (10%)
Willett et al.[e]	microtoming (room temp)	$(5-130) \times 10^4$ (narrow)	$10^{23}-10^{24}$ scissions/m^3; mainly pullout
Fordyce et al.[f]	grinding (cryo. temp)	$(2-10) \times 10^5$ (narrow)	10^{23} scissions/m^3; mainly scission
Wool and Rockhill[g]	microtoming (room temp)	$(1-20) \times 10^5$ (broad)	10^{23} scissions/m^3; mainly scission

[a] Popli, R.; Roylance, D. *Polym. Eng. Sci.* **1982**, *22*, 1046. [b] Present work. [c] Yang, A. C.-M.; Lee, C. K.; Ferline, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 1123. [d] Mohammadi, N.; Klein, A.; Sperling, L. H. *Macromolecules* **1993**, *26*, 1019. [e] Willett, J. L.; O'Connor, K. M.; Wool, R. P. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2583. [f] Fordyce, P.; Fanconi, B. M.; Devries, K. L. *Polym. Eng. Sci.* **1984**, *24*, 421. [g] Wool, R. P.; Rockhill, A. T. *J. Macromol. Sci., Phys.* **1981**, *B20*, 85.

density of the copolymer, chain pullout for a low molecular weight of the diblock, and crazing ahead of the crack tip for a high chain density and a high molecular weight of the copolymer. This last mechanism is the preferred mechanism for tough polymers. Washiyama et al.[19] also measured the fracture toughness and investigated the failure mechanisms of the PS−PVP planar interfaces reinforced with deuterated PS−PVP diblock copolymers as a function of the areal chain density. In the case where the molecular weights of both blocks were above the critical limit for entanglements, a critical interface chain density was observed, at which a transition in the failure mechanism from chain pullout to crazing occurred.

In homopolymer systems, molecular fracture studies in the past have always focused on either chain scission or chain pullout as the dominant energy-consuming mechanism. Table 1 provides a summary of the literature on molecular fracture studies of polystyrene. Present data are also included for comparison. It is evident that the major energy-consuming mechanism is dependent on molecular weight. Also, experimental parameters such as temperature affect the failure mechanism.[22] From Table 1, it is seen that the extent of chain scission is about $10^{23}-10^{24}$ scissions/m^3 for molecular weights above M_c (which is about 30 000 for polystyrene). However, this observation is based on equilibrated systems.

In nonequilibrated systems, such as in incompletely annealed latex films,[14] for a given molecular weight, the extent of chain scission depends on annealing time, in addition to other parameters, as mentioned above. Mohammadi et al.[14] studied the fracture behavior of polystyrene latex films of high molecular weight (M_n = 420 000; PDI = 1.19), annealed at 144 °C, as a function of annealing time using a custom-built dental burr grinding instrument. The number of chain scissions and the fracture energy per unit area increased with annealing time in significant agreement with theories of Wool, de Gennes, Prager, and Tirrell. Under fully annealed conditions, about 90% of the total energy was from chain scission and the remainder (10%) was from chain pullout. A mechanism involving the scissor-action opening of the bond angle between carbon−carbon bonds and concomitant stretching of all the 300 bonds trapped between the entanglements was found to be responsible for most of the energy consumption. Using the same grinding instrument, the changes in the controlling molecular mechanism for low (M = 32 000) and medium (M = 151 000) molecular weight polystyrene (PS) latex films, fractured at a constant burr rotational frequency of 16 Hz, are reported in this paper.

The main objective of this work is to investigate how the failure micromechanisms vary with molecular weight and annealing time. In the fracture experiments, the mechanical energy required to grind the sample is assumed to arise from various molecular processes such as chain uncoiling due to rubber elasticity, chain scission, and chain pullout.[14] It should be noted that the fracture energies obtained from the grinding experiment are essentially G_{IC} values measured by standard fracture mechanics tests, as shown in the Discussion section.

II. Theory

Healing and Fracture of Polymer Interfaces. The theory of healing a polymer−polymer interface system has been addressed by de Gennes,[23,24] Prager and Tirrell,[25] Jud et al.,[26] and Kim and Wool.[27] Two important variables that control the interdiffusion of polymer chains at a given temperature are time and molecular weight. The interdiffusion process results in the chains moving back and forth across the interface forming bridges, termed "stitching". The number of bridges crossing the interface, $N(t)$, is given by Prager and Tirrell[25] as

$$N(t) \sim t^{1/2}M^{-3/4} \qquad (1)$$

According to de Gennes,[24] the fracture energy, G_{IC}, is given by

$$G_{IC} \sim t^{1/2} (t<\tau) \qquad (2)$$

where τ is the reptation time (see Discussion). For $t > \tau$, the virgin state conditions are achieved. In the present case, the number of chain scissions (N_a) is approximated to be equal to the number of bridges across the interface, and the fracture energy measured from the grinding instrument provides a measure of G_{IC}.

Frictional Coefficient. When a crack propagates through a polymer, depending on the crack velocity and/or the proximity of the chain end, chain pullout from the crack path or scission of the main-chain bond can be expected. Prentice[28] showed that, under chain pullout conditions, the fracture energy, γ, is related to the molecular friction coefficient, μ_0, as

$$\mu_0 = 2\gamma/vnL^2 \qquad (3)$$

For numerical calculations (below), γ was taken as E_P, the energy for chain pullout (see below), v is the velocity of the burr, 8.3×10^{-3} m/s, $n = N_0 - N_a$, where N_0 is the total number of chains/m^3, and N_a is the number of chain scissions/m^3. The quantity L is 75-mers × 2.534 Å/mer = 190 Å.

III. Experimental Section

Latexes were prepared from narrow molecular weight polystyrene using a direct miniemulsification technique (see

Table 2. Recipe for Direct Miniemulsification[29]

ingredient	weight (g)	ingredient	weight (g)
	Aqueous Phase		
DDI water	100.0	cetyl alcohol	0.255
sodium lauryl sulfate	0.435	stearyl alcohol	0.109
	Oil Phase		
polystyrene	2.0	cetyl alcohol	0.255
cyclohexane	20.0	stearyl alcohol	0.1095

Table 2 for recipe).[29] The aqueous and oil phases were mixed in a water bath at 50 °C. Further homogenization of the latex was carried out by sonification using an ultrasonifier. The homogenized latex was then filtered through a 0.4-μm polycarbonate membrane. Solvent was removed from the latex by vacuum distillation. Stable latex with an average diameter of 0.2 μm and a particle size distribution of 1.4 (D_w/D_n), measured by transmission electron microscopy (TEM), was produced. Surfactant and cosurfactants were removed by repeated extraction with hot DDI water and methanol, respectively. Cleaned latex was then dried in the vacuum oven at 50 °C for a week. Glass transition temperatures were measured to be 104 and 103 °C for the completely dry latex powder of low and medium molecular weight latex samples, respectively, using a Mettler DSC at a heating rate of 10 °C/min. Films were made from the dry latex powder by compression molding at 110 °C and 10 MPa for 20 min in a tetrahedron press. Annealing of the latex films was carried at 144 °C for various times.

Fracture Experiments. A custom-built dental burr grinding instrument[30] was used to fracture the latex films annealed for different times. Grinding was carried out at room temperature with water cooling, at a burr rotation frequency of 16 Hz. Molecular weight measurements were made before and after grinding by using gel permeation chromatography (GPC). The total fracture energy was obtained from the torque on the burr, as measured by a rheometer.

Scanning Electron Microscopy of Ground Polystyrene Surface. Ground surfaces of the low and medium molecular weight samples were studied in the JEOL scanning electron microscope. A compression-molded film of narrow high molecular weight polystyrene (M_n = 450 000; PDI = 1.06) was also studied for comparison. The ground surfaces were initially sputter-coated with Au/Pd to prevent radiation damage and charging.

Calculations. The number of chain scissions per unit volume was calculated using the following equation:

$$N_a = N_A \varrho (1/M_n - 1/M_n^0) \qquad (4)$$

where N_A, ϱ, M_n^0, and M_n are Avogadro's number, the density of polystyrene (1.05 g/cm^3), and the initial and final number-average molecular weights, respectively. To express the quantities in eq 4 in terms of per unit area, N_a', the right-hand side of eq 4 is multiplied by $D_{av}/6$, where D_{av} is the average clump diameter measured using photon correlation spectroscopy (N4 MD Coulter analyzer). For the energy contributions, an energy balance equation was used to calculate the viscoelastic contribution:

$$E_T = E_U + E_S + E_P \qquad (5)$$

where E_T = total fracture energy/m^3 (experimental) (also denoted as G_I when the fracture energy is expressed per unit area); E_U = uncoiling energy (from rubber elasticity theory); E_S = stretching and subsequent covalent bond breakage energy (109° bond deformation); and E_P = chain pullout energy (viscoelastic contribution).

IV. Results

Figures 2 and 3 show a Wool plot of fracture energy and number of chain scissions/m^3 versus annealing time to the power of 0.5 for the 151 000 latex films. It is evident that the fracture energy and the number of chain scissions increase initially up to about 60 min, beyond which a plateau is reached. At annealing time t = 0, the rather high fracture energy is probably due to some interdiffusion during the molding process. The initial increase in the energy can be explained by the increase in the number of chains crossing the interface and forming effective entanglements. Similarly, for the same reason, the number of chain scissions increase. After the film is completely annealed, further annealing does not alter the number of bridges across the interface. Hence, a constant value in the energy and number of chain scissions per unit volume is attained. Values in Figures 2 and 3, while showing slight possible maxima, were plotted as straight lines, which will be discussed below. Table 3 shows the contributions from various molecular mechanisms. The pullout energy (E_P) dominates at all annealing times, and the uncoiling energy is negligible.

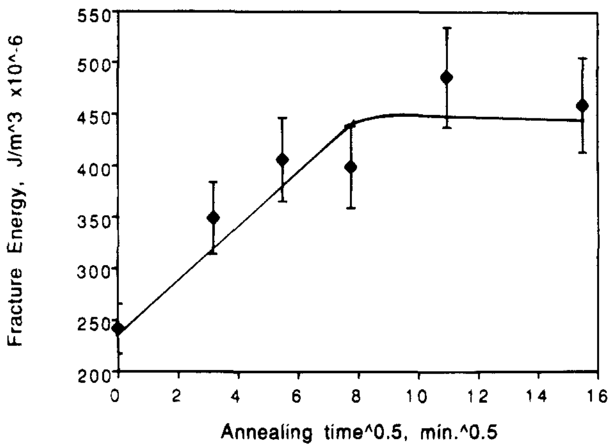

Figure 2. Plot of fracture energy per unit volume versus annealing time to the power of 0.5 for medium molecular weight (M_n = 151 000; PDI = 1.02) polystyrene latex films.

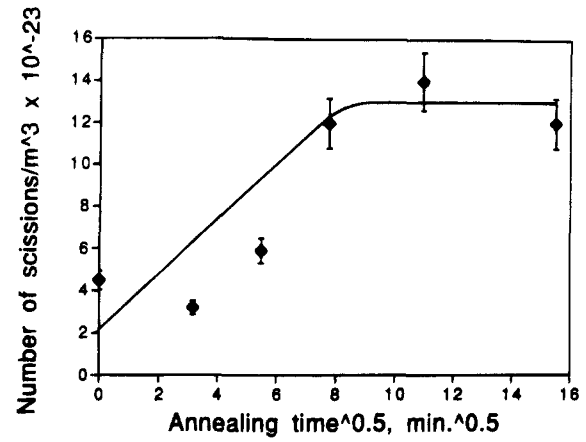

Figure 3. Plot of number of chain scissions per unit volume versus annealing time to the power of 0.5 for medium molecular weight (M_n = 151 000; PDI = 1.02) polystyrene latex films.

Table 4 shows the results from the fracture experiments and the various energy contributions for the low molecular weight latex films. Since there was no apparent change in the molecular weight on grinding, it was assumed that there is no chain scission. Also, the fracture energy does not change significantly on annealing. This sample is right at the critical molecular weight required for entanglements to occur, which indicates that the chains on interdiffusion probably fail to form effective entanglements. Later, in the presence of a crack, these chains are able to disentangle or pull out from the crack path. Since, pullout is the only

Table 3.[a] **Energy Contributions for Narrow Molecular Weight Polystyrene Latex Films (Shell Development Co.) (Latex Molecular Weight = 151 000,**[b] **PDI = 1.02)**

annealing time, min	N_a/m^3 × 10^{-23}	N_a'/m^2 × 10^{17}	clump diameter, μm	E_S, × 10^{-6} J/m^3	E_U, × 10^{-6} J/m^3	E_P, × 10^{-6} J/m^3	E_T,[c] × 10^{-6} J/m^3	G_I, J/m^2
0	4.5	1.0	1.4	67	0.5	174	242	55
10	3.2			48	0.4	301	349	
30	5.9			87	0.7	318	406	
60	12			176	1.4	221	399	
120	14			206	1.7	278	486	
240	12	7.0	3.0	176	1.4	282	459	230

[a] E_S = stretching and subsequent covalent bond breakage energy (109° bond angle opening); E_U = uncoiling energy (rubber elasticity); E_P = pullout energy; E_T = total fracture energy/m^3; G_I = total fracture energy/m^2; N_a = no. of scissions/m^3; N_a' = no. of scissions/m^2. [b] Initial molecular weight. [c] Error: ±10%.

Table 4.[a] **Energy Contributions for Low Narrow Molecular Weight Polystyrene Latex Films (Pressure Chemical Co.) (Latex Molecular Weight = 32,000;**[b] **PDI = 1.02)**

annealing time, min	N_a/m^3	N_a'/m^2	clump diameter, μm	E_S, × 10^{-6} J/m^3	E_U, × 10^{-6} J/m^3	E_P, × 10^{-6} J/m^3	E_T,[c] × 10^{-6} J/m^3	G_I, J/m^2
0			0.6			154	154	15
120			0.6			174	174	17

[a] E_S = stretching and subsequent covalent bond breakage energy (109° bond angle opening); E_U = uncoiling energy (rubber elasticity); E_P = pullout energy; E_T = total fracture energy/m^3; G_I = total fracture energy/m^2 N_a = number of scissions/m^3; N_a' = number of scissions/m^2. [b] Initial molecular weight. [c] Error: ±10%.

energy-consuming process in these films, the total fracture energy is low compared to the medium molecular weight films, shown above.

SEM Analysis of Ground Polystyrene Surfaces. Figure 4 shows the SEM micrographs of the ground PS surface for three different molecular weights: M_n = 32 000, 151 000, and 450 000. The first two latex films were annealed at 144 °C for 120 min before grinding, and the third compression-molded high molecular weight film was annealed at 144 °C for 10 h. It is evident from the micrographs that there is a distinct fernlike pattern in the high molecular weight film. This pattern is not observed in the low molecular weight film. It should be noted that the spacing between the branches of the fernlike pattern are much smaller than the spacing between the teeth of the dental burr, which is about 100 μm. Qualitatively, it can be seen that the ground surface of the medium molecular weight film is a combination of a fernlike pattern (50%) and a smoother topography, which is extensively found on the surface of the low molecular weight film. It is possible that the ground surface morphologies reveal information about the micromechanisms of failure.

V. Discussion

According to the reptation theory, it is assumed that the strength of the interface reaches a maximum value when the chains have traveled a distance of about one R_g. The time required for the chains to travel through this distance is termed as the reptation time, τ, which for the present systems were calculated from the center of mass diffusion coefficient, D, using the following relationship:[3]

$$\tau = R^2/(3\pi^2 D) \qquad (6)$$

where R is the end-to-end distance. The quantity τ for the medium molecular weight is calculated to be about 6 min at 144 °C by using eq 6. Similarly, τ for the low molecular weight sample is calculated to be about 6 s. Since most of the data in Figures 2 and 3 correspond to annealing times much longer than the reptation time, classically, the films should be completely annealed with little further property changes. However, property changes continue for several times the reptation time. At long annealing times, there are considerable contributions from both chain scission and chain pullout to the total fracture energy for the medium molecular weight films (see Table 3). Under fully annealed conditions, the chain scission energy contribution is about 40% and the chain pullout energy contribution is about 60%. This contrasts the results from the 420 000 polystyrene latex films,[14] where the chain scission energy contribution was 90% and the chain pullout contribution was about 10%.

In the previous papers from this laboratory,[6,7,14] a slight maximum in both mechanical properties and energy consumed was noted at the annealing time comparable to the reptation time. However, in the present system, most of the data are obtained from the postreptation time regime, where no maximum is expected. Even though the data in Figures 2 and 3 show a maximum value at 120 min, it is considered to be a statistical variation in the data. Hence, a straight line is drawn instead of a maximum at 120 min. Recent fracture studies on latex film blends containing high and low molecular weight polystyrene show a similar behavior.[31]

Fracture Area versus Fracture Volume. The present study expresses the fracture energy in terms of per unit volume rather than per unit area. Primarily, this is because the SEM analysis of the fracture surface showed that the interior of the sample is also involved in the fracture process.[2] Second, the fracture surface generated is fractal in nature.[3] In such cases, the use of Euclidean models to describe a non-Euclidean surface may create substantial error in the calculations. Thus, the per unit volume basis gives a more conservative result. For comparison with the present results, Mohammadi et al.'s data[14] were converted to a per unit volume basis. However, by measuring the average diameter of the clumps generated using photon correlation spectroscopy (Coulter N4 MD analyzer), the surface area generated was calculated for selected samples; see Tables 3 and 4.

Figure 5 shows the comparison of the fracture energies for three different molecular weights (M = 32 000, 151 000, and 420 000[14]) of polystyrene latex films as a function of annealing time. At t = 0, the medium and high molecular weight latex films have comparable

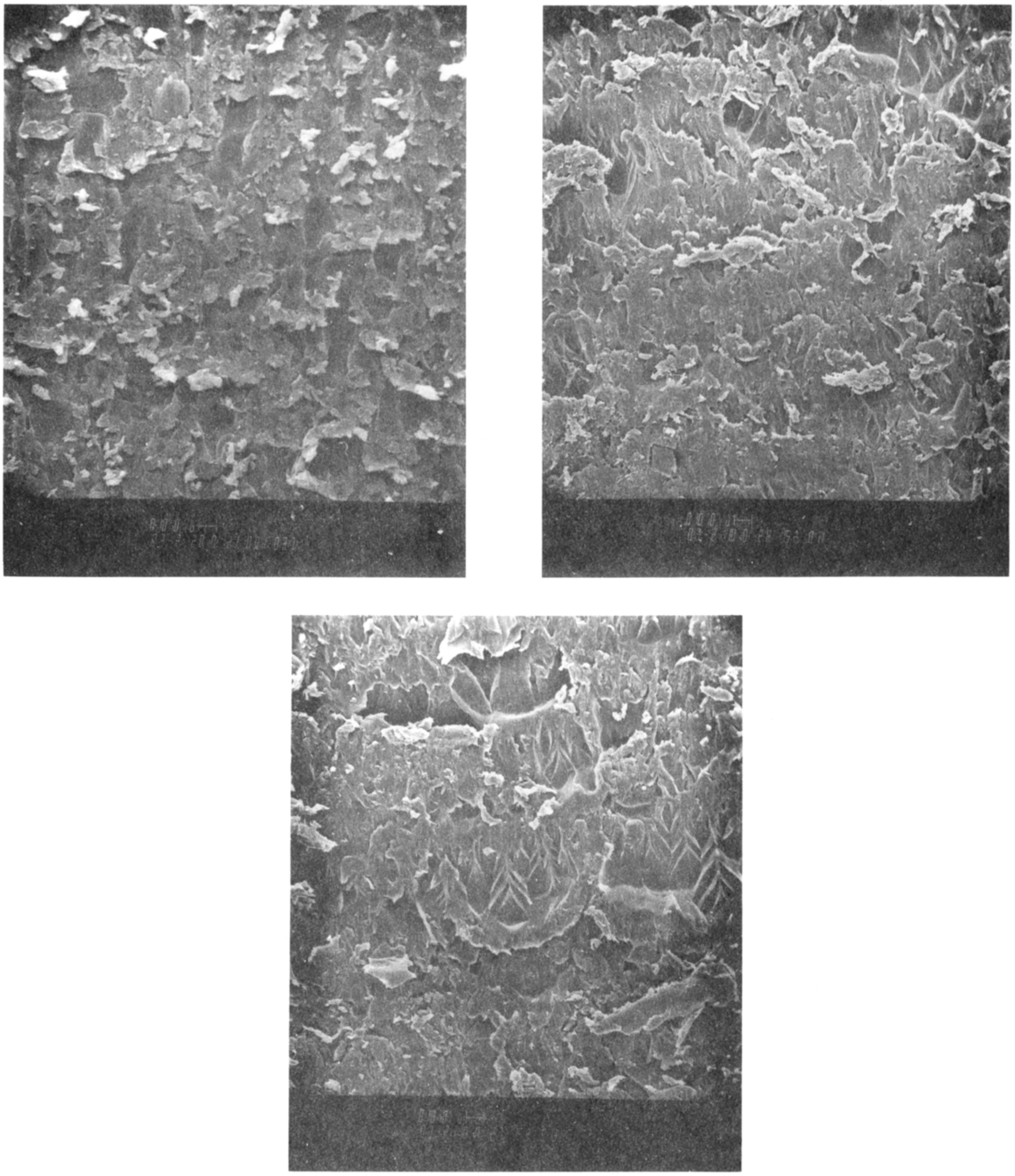

Figure 4. SEM micrographs of the ground surface of polystyrene films. Upper left: MW = 32 000. Upper right: MW = 151 000. Bottom: MW = 450 000.

fracture energies when considered on a per unit volume basis. This is probably due to the fracture, mainly at the particle–particle interface, which is weak initially in both cases. On further annealing, the high molecular weight latex film shows a maximum close to the reptation time, beyond which time the difference in energies for the high and medium molecular weight latex films becomes smaller. Under fully annealed conditions, the high and medium molecular weight films have similar fracture energies, while the low molecular weight latex films have a much lower fracture energy.

Figure 6 shows a comparison of the number of chain scissions versus annealing time for the medium and high molecular weight polystyrene latex films. At $t = 0$, the higher molecular weight film has a larger number of scissions per unit volume than the medium molecular weight film. A maximum in the number of chain scissions per unit volume was observed for the high molecular weight latex film close to the reptation time, similar to the fracture energy versus time curve (Figure 5). For the medium molecular weight sample, no maximum is observed, and a constant value for the number of chain scissions is reached after about 60 min. Under completely annealed conditions, the high molecular weight film has a higher number of chain scissions than the medium molecular weight film, a

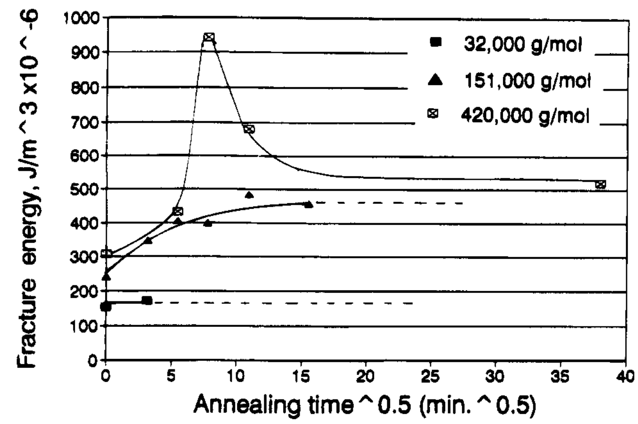

Figure 5. Fracture energy versus annealing time for three different molecular weights of polystyrene latex films (M_n = 32 000, 151 000, and 420 000).

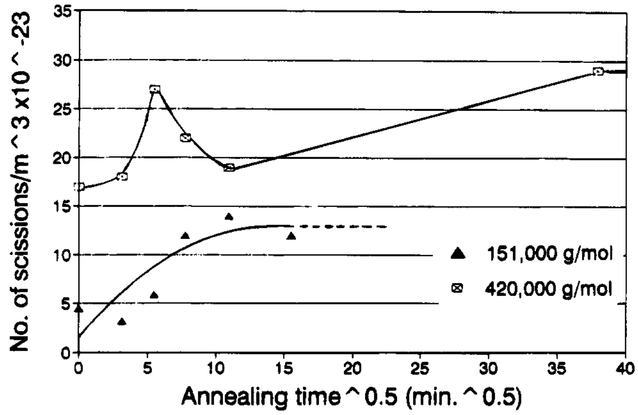

Figure 6. Number of chain scissions versus annealing time for M_n = 151 000 and 420 000 polystyrene latex films.

result of a higher number of physical entanglements per unit volume. The 32 000 sample has a zero number of chain scissions at all times, as shown above.

It is to be emphasized that the fracture energy values obtained from the grinding instrument are essentially G_{IC} values obtained by standard techniques. While G_{IC} ideally involves a simple tensile mode, the dental burr grinding experiment provides a more complex environment. However, the basic idea is the same, and numerical comparisons are important.

Consider the molecular weight dependence of fracture toughness in the virgin state, shown in Table 5. The "∞" molecular weight sample is a network containing 1.2 mol % of divinylbenzene as the cross-linker. While other workers have reported a range of values (Table 5), the present values are comparable. According to Wool et al.,[3] the fracture parameters become independent of molecular weight above a certain limiting molecular weight, M^*, which is 250 000 for polystyrene. The present values increase greatly between 32 000 and 151 000 and then are essentially constant. The theories shown in Table 5 are more or less supported, except that the leveling off of molecular weight seems to be below 250 000. Under pullout conditions, Evans[32] predicts an $M^{2.0}$ dependence, while Wool et al.[3] predict an $M^{1.0}$ dependence for $M < M_c$.

Comparison of Diffusion and Fracture Studies. A comparison of the results from the healing and subsequent fracture experiments of latex films was made. The interdiffusion depth of polymer chains obtained from SANS[8] and the fracture energy, chain scission, and chain pullout results from the grinding experiment were compared for the M = 151 000 sample, in a series of cross plots (Figures 7 and 8). For interdiffusion studies, the annealing temperature for the latex films was 135 °C, and for the fracture studies, the annealing temperature was 144 °C. All data were corrected to 144 °C.

Table 5. Fracture Energies for Polystyrene

mol wt	G_{IC}, J/m^2	ref
Present Work (for Fully Annealed Latex Films)		
32 000	17	
151 000	230	
420 000	230	*a*
∞	265	*b*
Others		
100 000	200	*c*
250 000	1000	*c*
100 000	1000	*d*
111 000	98	*e*

Theories for $G_{IC}(t=\infty)$ (for M in the Range 30 000 < M < 250 000)

author	mol wt dependence	ref
de Gennes	$\sim M^0$	*f*
Prager and Tirrell	$\sim M^0$	*g*
Jud et al.	$\sim M^{1/2}$	*h*
Kim and Wool	$\sim M^{1.0}$	*i*

[a] Mohammadi, N.; Klein, A.; Sperling, L. H. *Macromolecules* **1993**, *26*, 1019. [b] Present work on cross-linked polystyrene (cross-linker: 1.2 mol % divinylbenzene). [c] Wool, R. P.; Yuan, B.-L.; McGarel, O. J. *Polym. Sci. Eng.* **1989**, *29*, 1340. [d] Greco, R.; Ragosta, G. *Plast. Rubber Process. Appl.* **1987**, *7*, 163. [e] Robertson, R. E. *Toughness and Brittleness of Plastics*; Deanin, R. D., Crugnola, A. M., Eds.; Advances in Chemistry Series 154; American Chemical Society: Washington, DC, 1976. [f] de Gennes, P.-G. *Hebd. Seances Acad. Sci., Ser. B* **1980**, *291*, 219. [g] Prager, S.; Tirrell, M. *J. Chem. Phys.* **1981**, *75*, 5194. [h] Jud, K.; Kausch, H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204. [i] Kim, Y. H.; Wool, R. P. *Macromolecules* **1983**, *16*, 1115.

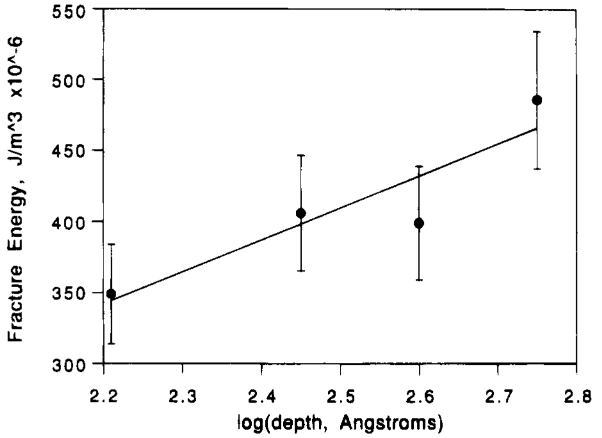

Figure 7. Plot of fracture energy versus interdiffusion depth for medium molecular weight (M_n = 151 000; PDI = 1.02) polystyrene latex films.

Figure 7 shows a plot of fracture energy versus log interdiffusion depth. It can be seen that there is a slight increase in energy with increasing interdiffusion. As mentioned earlier, most of the data are in the postreptation time regime, where minimal changes in properties are expected. Figure 8 shows a log–log plot of the number of chain scissions and chain pullouts versus interdiffusion depth. While the number of chain scissions increase with depth, the number of chain pullouts decrease. As expected, the increase in the interdiffusion depth with time leads to a decreasing probability of chain pullout. However, the pullout at all times is

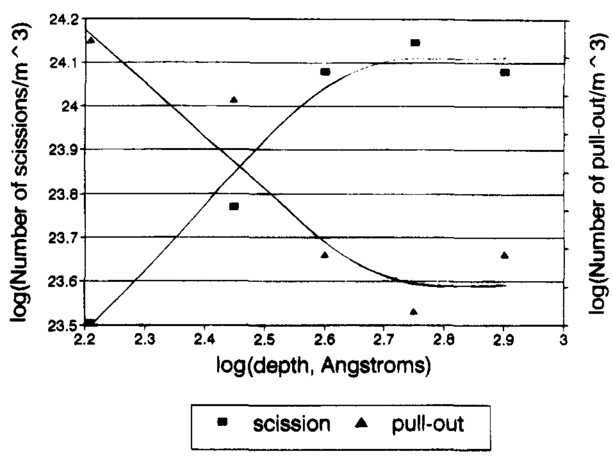

Figure 8. Plot of number of chain scissions and chain pullout per unit volume versus interdiffusion depth for medium molecular weight (M_n = 151 000; PDI = 1.02) polystyrene latex films.

Table 6. Viscoelastic Energy for Chain Pullout: A Comparison of Theoretical and Experimental Values

pullout energy, J/m^3	basis
311 × 10^6	H. Mark approach to pull out 150 mers
49 × 10^6	using Evan's eq 7 for 150 mers between entanglements
260 × 10^6	expl for latex samples (M_n = 151 000)

assumed to be limited to chain ends (Figure 1). Thus, there is a competition between chain pullout and chain scission at the interface, which seems to reach a constant value at long annealing times, close to the virgin state.

Energy for Chain Pullout. In the grinding experiments, the pullout energy was obtained as a remainder portion of the total fracture energy. However, two separate calculations can be made using theoretical models. The first is based on the Evans model[32] to obtain the energy for partial chain pullout, E_P:

$$E_P = kTN_e^2/2 \tag{7}$$

where k is the Boltzmann constant, T is temperature, and N_e is the number of mers between entanglements, which is about 150 for polystyrene. The second calculation was based on the Mark[33] approach. According to this approach, the carbon–carbon bond energy well is assumedto be in its ground state at a distance of 1.54 Å and is assumed to be broken if it is stretched to 2.534 Å, an energy of 380 kJ/mol being required. Results of these two calculations are compared with the experimental value from the latex samples in Table 6. Surprisingly, both completely independent calculations yielded values of the same order of magnitude as the experimental value.

The pullout energies per unit area calculated from the grinding experiments are about 40 and 122 J/m^2 for the 151 000 latex films at t = 0 and 120 min, respectively, which is much higher than the pullout energy obtained by Creton et al.[18] and Washiyama et al.[19] for PS–PVP block copolymers with N = 800 (where N is the degree of polymerization), which is about 1–5 J/m^2, and by Creton et al.[21] for PS–PI block copolymers, which is about 3 J/m^2. The rather high values obtained for the homopolymer system are probably due to higher number of chains crossing a unit area of interface (see Table 7) compared to the block copolymer reinforced interface.

Table 7. Molecular Basis of Fracture at Block Copolymer and Homopolymer Interfaces

property	block copolymer	homopolymer
i. force to break a single chain	2 × 10^{-9} N/bond[a]	5.7 × 10^{-9} N/bond[b]
ii. static friction coefficient/mer	6.3 × 10^{-12} N/mer[c]	1.2 × 10^{-10} N/mer[b]
iii. fracture toughness, G_{IC}	15 J/m^2 [c]	2.3 × 10^2 J/m^2 [b]
iv. areal chain density at saturation	0.11 chains/nm^2 [c]	1.93 chains/nm^2 [b]
v. energy per chain[d]	1.4 × 10^{-16} J/chain	1.2 × 10^{-16} J/chain
vi. interfacial tension	3.2 ergs/cm^2 [c]	0

[a] Creton, C.; Kramer, E. J.; Hui, C. Y.; Brown, H. R. *Macromolecules* **2992**, *25*, 3075. [b] Present work (for M = 151 000). [c] Washiyama, J.; Kramer, E. J.; Hui, C. Y. *Macromolecules* **1993**, *26*, 2928. [d] Obtained by the ratio of fracture toughness and the areal chain density at saturation.

A comparison of the two systems, as shown in Table 7, indicates that the toughness of the copolymer-reinforced interface is lower than that of the homopolymer system. However, dividing G_{IC} by the actual areal chain density gives essentially a constant result, so the number of chains crossing the interface per unit area (and anchored on both sides) represents the important quantity.

Frictional Coefficient. Using Prentice's eq 3,[28] the molecular friction coefficient, μ_0, was calculated. The energy for chain pullout, E_P, was used as the fracture energy, γ; the velocity of the burr (8.3 × 10^{-3} m/s) was assumed to be the velocity of chain pullout, which yields the lower bound value. The impact velocity of crack propagation in a glassy polymer (620 m/s) was used as the upper bound velocity of chain pullout. Solving for μ_0, the frictional coefficient per unit length of mer, a value of 6.0 × 10^2 dyn·s/cm^2 was obtained using the lower bound velocity and a value of 8.0 × 10^{-3} dyn·s/cm^2 was obtained for the upper bound velocity.

The mer frictional coefficient, ζ_0, was calculated by multiplying μ_0 by 2.534 Å/mer. The mer frictional coefficient is indicative of the resistance experienced by the mer while moving through its surroundings. The quantity, ζ_0, was calculated to be 1.5 × 10^{-5} and 2.0 × 10^{-10} dyn·s/cm for the lower and upper bound velocities of pullout assumed, respectively. Comparison of the mer frictional coefficient data with literature values[34] gave an estimate of the temperature of chain pullout to be between 150 and 250 °C for the lower and upper bound burr velocities, respectively. This agrees well with the general notion that the temperature of the actual chain pullout in fracture processes has to be above the glass transition temperature. It must be emphasized that the temperature of the water cooling the burr actually rose only 2–3 °C, which corresponds to about 10^4 J/m^3. However, the temperature of the chain experiencing the pullout apparently is raised very signficantly. Washiyama et al.[19] calculated the static friction coefficient per monomer, which is similar to the mer friction coefficient, ζ_0, to be about 6.3 × 10^{-12} N/bond, which is about 2 orders of magnitude smaller than the present value of 1.0 × 10^{-10} N/bond. This is probably due to a higher strain rate in the present experiment, which is 8.3 × 10^{-3} m/s compared to a speed of 3 × 10^{-6} m/s used in their experiments.

VI. Conclusions

Whether a chain "pulls out" of one surface or "scissions" during fracture depends on the number of chain entanglements formed during interdiffusion. At low molecular weights, chain pullout is the dominating molecular mechanism of failure. For the medium molecular weight, 151 000, the contributions to the total energy from chain scission and chain pullout mechanisms are roughly equally divided. The medium molecular weight film is near the midpoint of the crossover in the failure mechanism. Above 400 000, the values are 90% scission and 10% pullout. The chain pullout energy was theoretically calculated to be between 50 and 300 × 10^6 J/m^3, with the experimental value being 260 × 10^6 J/m^3 in good agreement. For fully equilibrated systems, the chain pullout energy remains constant. Evaluation of frictional coefficients indicates that the actual temperature of chain pullout is in the range of 150−250 °C.

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