

The Molecular Basis of Fracture in Polystyrene Films: Role of Molecular Weight

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SYNOPSIS

The molecular basis for fracture was examined using a custom-built Dental Burr Grinding Instrument, which cuts at a depth of 500 nm per pass. A direct miniemulsification method was used to form uniform-sized latex particles from narrow molecular weight distribution, anionically synthesized polystyrenes. Several polystyrenes were examined as a function of molecular weight, and blends were made of high and low molecular weight polystyrenes. In addition, a broad molecular weight polystyrene was included for comparison. These latexes were dried and cleaned, and molded under mild conditions, followed by annealing for various lengths of time at 144°C. The Dental Burr Grinding Instrument measures the total energy required to fracture the sample. The total number of chains undergoing scission per unit volume was determined via GPC before and after the fracture process. Using an energy balance approach, the total number of chains undergoing pullout (from either side of the fracture surfaces) was estimated. In order to obtain a broader picture of the process, data collected by Mohammadi et al., and by Sambasivam et al., were integrated into the analysis. Basically, at very low molecular weights, ca. 32,000 g/mol, substantially 100% pullout occurs. At the midmolecular weight range, about 150,000 to 180,000 g/mol, chain scission and chain pullout contributions to the total energy are approximately equal. For very high molecular weights, the chain scission contribution is about 90%. A scaling relationship is proposed between the molecular weight of the polymer and the fraction of chains undergoing scission. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Strength development at polymer-polymer interfaces has been a key issue because it bears on adhesion, coating, and welding.^{1,2} For polymer-polymer interfaces, adhesion is achieved by diffusion of polymeric chains across the interface. The concept of healing of a polymer-polymer interface has been addressed by several workers.³⁻⁹ Adolf et al.⁷ compared theoretical results of healing and fracture behavior with experimental data for glassy polymers [polystyrene and poly(methyl methacrylate)] using a model based on chain entanglements. They found that molecular weight and molecular weight distri-

bution are important in determining the plateau fracture stress. In polydisperse samples, the healing occurred faster due to the diffusion of the short chains; however, the bulk strength was achieved at a much later time. The fracture stress increases with molecular weight and reaches a plateau value for high molecular weights, which was explained in terms of the effective crossings across the fracture plane.

Latex films provide an excellent model system to study both the healing and the re-creation of the interface by fracture. Healing studies on latex films have been extensively studied using direct energy transfer methods, DET,¹⁰⁻¹² and small-angle neutron scattering, SANS.¹³⁻¹⁷ Hahn et al.¹³ studied the effect of molecular weight, crosslinking, and immiscibility of the matrix polymer during the interdiffusion of deuterated poly(*n*-butyl methacrylate) in a matrix

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of the protonated species and found that the short chains diffused faster on annealing, leading to a "smearing effect," similar to the results obtained by Adolf et al.⁷ Yoo et al.¹⁵ investigated the latex film formation process in broad molecular weight distribution polystyrene ($M_w = 250,000$ and $2,000,000$ g/mol) using SANS. The interrelationship between the depth of interdiffusion and tensile strength buildup was studied. For the lower molecular weight film, full tensile strength was achieved at a depth of interdiffusion corresponding to about one radius of gyration. However, for the higher molecular weight, full strength was achieved at a depth smaller than the radius of gyration of the chains. This was attributed to the location of chain ends at the particle surface, leading to faster interdiffusion. Mohammadi et al.¹⁸ studied the fracture behavior of emulsion polymerized polystyrene latex films using a fine dental burr hand grinder. Molecular weight reduction on grinding was measured as a function of annealing time. The number of chain scissions per unit area vs. annealing time showed four distinct regions: induction, mixed, peak, and recovery. A similar trend was observed in tensile strength measurements. In the induction region, the number of chain scissions per unit area did not change appreciably with annealing time due to the lack of effective physical entanglements at low interpenetration depth; in the mixed regime, due to the formation of entanglements, the number of chain scissions increased; a drop in the chain scissions in the peak region was attributed to the change in the crack path from the interface to through the particles; the recovery region was caused by the randomization of the chains.

By using a direct miniemulsification technique,¹⁹ Mohammadi et al.²⁰ studied the contribution of various fracture micromechanisms in narrow molecular weight distribution, anionically synthesized polystyrene latex films of $420,000$ g/mol. In these latex films the size distribution of the latex particles was also narrow (about 1.02). By connecting the dental burr to a rheometer, which measured the torque, the energy required to fracture was obtained. This was the basis for the new Dental Burr Grinding Instrument.²¹ The fracture energy per unit area and the number of chain scissions per unit area were obtained as a function of annealing time. Three different regions were obtained in both cases: mixed, peak, and recovery. This was different from the broad molecular weight distribution latex films, which had an induction period before the chain scissions started to increase. This difference was attributed to the absence of sodium sulfate end groups in the miniemulsified latex films, which probably

caused a hindrance to interdiffusion arising from electrostatic attraction between the sodium sulfate end groups.

Recently, Zosel et al.²² studied strength development in crosslinked and uncrosslinked poly(butyl methacrylate) latex films. For the uncrosslinked latex films, fracture energy obtained from tensile experiments increased with annealing time, and then reached a plateau after an interpenetration depth corresponding to the radius of gyration of the polymer chains was reached. In the crosslinked latex films, no improvement in energy was observed on annealing due to the absence of physical entanglements at the interface.

The main objective of this work is twofold: (1) to understand the role of molecular weight and molecular weight distribution on the mechanical properties of latex films, a series of model narrow molecular weight distribution, anionically synthesized polystyrenes and their blends were studied; (2) to study the effect of processing on the fracture behavior, compression molded, solvent cast, and latex films were made by using a commercial free radically synthesized polystyrene. The fracture experiments were carried out using the Dental Burr Grinding Instrument.²¹ This work continues an earlier study²³ involving low ($32,000$ g/mol) and medium ($151,000$ g/mol) narrow molecular weight distribution polystyrenes. Thus, this article will report on how the ratio of chain scission to chain pullout changes with annealing time and molecular weight.

THEORY

Crack healing in polymers involves the diffusion of polymer chains across the initial interface, and subsequent formation of physical entanglements by individual chains on both sides of the initial crack. The theory has been developed by de Gennes,³ Kim and Wool,⁸ and Prager and Tirrell.⁶ Molecular weight, temperature, and time elapsed are the most important variables. The de Gennes reptation model⁴ forms the basis for understanding polymer chain diffusion today. Wool et al.⁹ reported that after the reptation time, the molecular properties of the interface should approach that of the virgin state.

The number of bridges crossing the interface, $N(t)$, which is considered to be held on both sides of the crack plane by entanglements, is given by⁶

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

This leads to a buildup of the fracture energy, G_{IC} , which scales with time as³

$$G_{IC} \sim t^{1/2} \quad (2)$$

for times less than the reptation time, τ , which is given by⁹

$$\tau = r^2/3\pi^2 D \quad (3)$$

where r is the polymer chain end-to-end distance, and D is the self-diffusion coefficient (obtained from ref. 16 and corrected for molecular weight). For molecular weights not higher than eight times M_c , G_{IC} depends on the first power of the molecular weight.⁹ For the present experiments, G_{IC} will be approximated by the fracture energy as determined through the torque on the dental burr, converted to energy units.

The total energy to fracture, as described above, is determined through the torque on the dental burr. The number of scissions per unit volume, as determined from the reduction in the molecular weight (as discussed below) yields the total energy required for scission. The remainder is considered in two categories: the energy to straighten the chains, related to rubber elasticity, and the energy for chain pullout, a viscoelastic phenomenon. The former will be shown to be small, but the latter is comparable to that of chain scission for medium molecular weights. The subject of healing, interdiffusion, and refracture was recently reviewed².

The number of chain scissions per unit volume, N_a , was calculated using the following equation:

$$N_a = N_A \cdot \rho \cdot (1/M_n - 1/M_n^0) \quad (4)$$

where N_A , ρ , M_n^0 , and M_n are Avogadro's number, density of polystyrene (1.05 g/cm³), the initial and the final number-average molecular weights, respectively.

EXPERIMENTAL

Latexes were made by a direct miniemulsification technique.¹⁹ The oil phase contained about 10% polystyrene in cyclohexane, and cosurfactants, cetyl alcohol and stearyl alcohol, while the aqueous phase contained deionized distilled (DDI) water, sodium lauryl sulfate, and the cosurfactants, cetyl alcohol and stearyl alcohol. The two phases were mixed by mechanical stirring followed by sonification to yield a homogenized latex. In brief, solvent (cyclohexane)

was removed by vacuum distillation. Surfactant and cosurfactants were removed by repeated hot DDI water and methanol extraction, respectively. The latex was then dried at 60°C for 7 days under vacuum. This recipe yields particles with an average size of about 200 nm. Glass transition temperature measurements were made before and after latex formation using Mettler DSC at a heating rate of 10°C/min. Latex films were made by molding the dry latex powder at 110°C for 20 min under a pressure of 10 MPa. Annealing of the films was carried out at 144°C for various times. Fracture studies were made using the Dental Burr Grinding Instrument²⁰ at a burr rotational frequency of 16.6 Hz. The dental burr was obtained from SS White Burs Inc. (FG 7572). The burr is connected to a rheometer,²¹ so that the cutting torque, and, hence, the cutting energy, are measured. The average height of cut per pass is about 500 nm, which shaves off up to several particle diameters per pass. Molecular weight measurements were made before and after grinding using GPC (Waters Associates) with THF as the mobile phase at a flow rate of 1 mL/min.

Blends of High and Low Molecular Weight Polystyrenes

Films were made from anionically polymerized polystyrenes containing blends of high and low molecular weight polystyrene latexes. Two types of polystyrene latex blends were made: (1) Blend I—separate direct miniemulsified latexes of high ($M_n = 600,000$ g/mol; PDI = 1.02; $T_g = 107^\circ\text{C}$) and low ($M_n = 34,000$ g/mol; PDI = 1.04; $T_g = 102^\circ\text{C}$) molecular weight polystyrene were prepared, where PDI represents the polydispersity index. After solvent removal, equal volume of the two latexes were mixed by mechanical stirring for 24 h to obtain a blend of high and low molecular weight latex particles. (2) Blend II—the high and low molecular weight polystyrene samples were dissolved together in the oil phase before direct miniemulsification. The glass transition temperature, T_g , of both blends was about 106°C. For completeness, values are also reported from anionically polymerized polystyrenes of narrow molecular weight distribution of $M = 32,000$ and 151,000 g/mol²³ and 420,000 g/mol.²⁰

Styron (Broad Molecular Weight) Polystyrene

To study the effect of processing on the fracture behavior, latex films, compression-molded films, and solvent cast films were made from Styron 6069 polystyrene ($M_n = 180,000$ g/mol, PDI = 1.8), sup-

plied by Dow Chemical Company. Latex films of Styron were made by the direct minemulsification procedure used for the blend latex films, described above. Compression-molded films were made by molding Styron at 204°C for 20 min at 7 MPa. Solvent cast films were made by drying a 25% (w/w) Styron solution in tetrahydrofuran (THF). The solution was mechanically stirred for 30 min before casting on a Petri dish. After drying the cast film at room temperature under the fume hood for a week, it was transferred to a vacuum oven for further drying. The temperature was gradually increased from 30 at 5°C/day. A portion of the sample was removed after drying at 60°C for 2 weeks. The remainder portion was further dried until the temperature reached 100°C, and it was maintained at that temperature for two weeks.

RESULTS AND DISCUSSION

Summary of Previous Work

Figure 1 summarizes the fracture energy for polystyrene latex films of different molecular weights [$M_n = 420,000$ (PDI = 1.19);²⁰ 151,000 g/mol (PDI = 1.02);²³ and 32,000 g/mol (PDI = 1.04)].²³ The data from latex films of Styron 6069 are also included for comparison. At time $t = 0$, the medium and high molecular weight films have comparable fracture

energies. This suggests that fracture occurs at the particle–particle interface, which is similar in both cases. As the annealing time increases, the difference between fracture energies of the medium and high molecular weight latex films increases. Interestingly, the fracture energy for the high molecular weight sample undergoes a clear maximum at a fairly short annealing time, related to a change in the fracture mechanism from through the particle–particle interface, to through the particles. Under completely annealed conditions, the fracture energy depends on the molecular weight, which is related to the number of physical entanglements per unit volume. The low molecular weight ($M_n = 32,000$ g/mol) latex films do not show any improvement in the fracture energy on annealing. Because this sample is right at the critical molecular weight for entanglements, it was concluded that the chains on interdiffusion did not form effective entanglements to resist the crack, and failed only by chain pullout.

Figure 2 shows the number of chain scissions per unit volume vs. annealing time for the medium and high molecular weight polystyrene latex films. (No apparent change in the molecular weight was observed for the low molecular weight latex films.) At $t = 0$, the high molecular weight sample has a higher number of chain scissions. A peak in the number of scissions was observed at the reptation time for the high molecular weight sample.²⁰ This peak was not

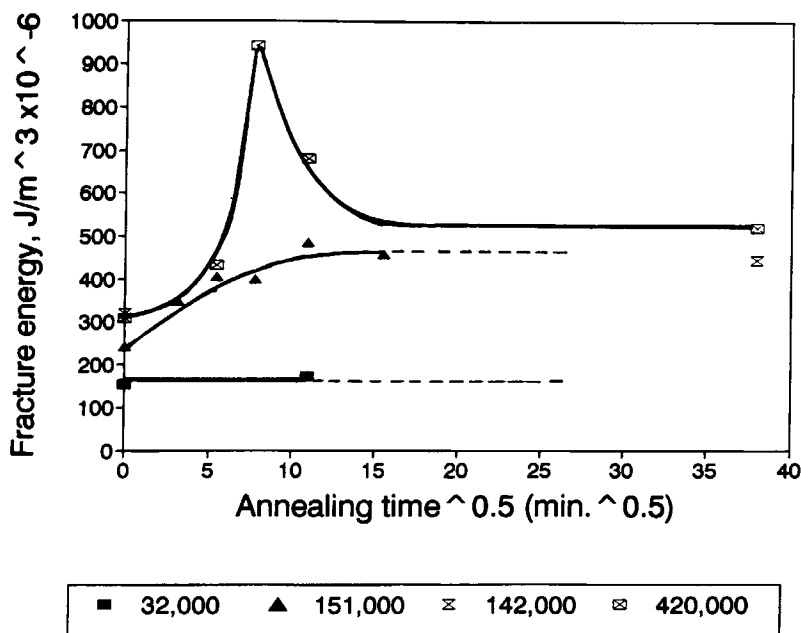


Figure 1 A Wool plot, showing the fracture energy vs. annealing time to the 0.5 power for three narrow molecular weight distribution polystyrene latex films, and Styron 6069 latex films (142,000 g/mol) annealed at 144°C for various times.

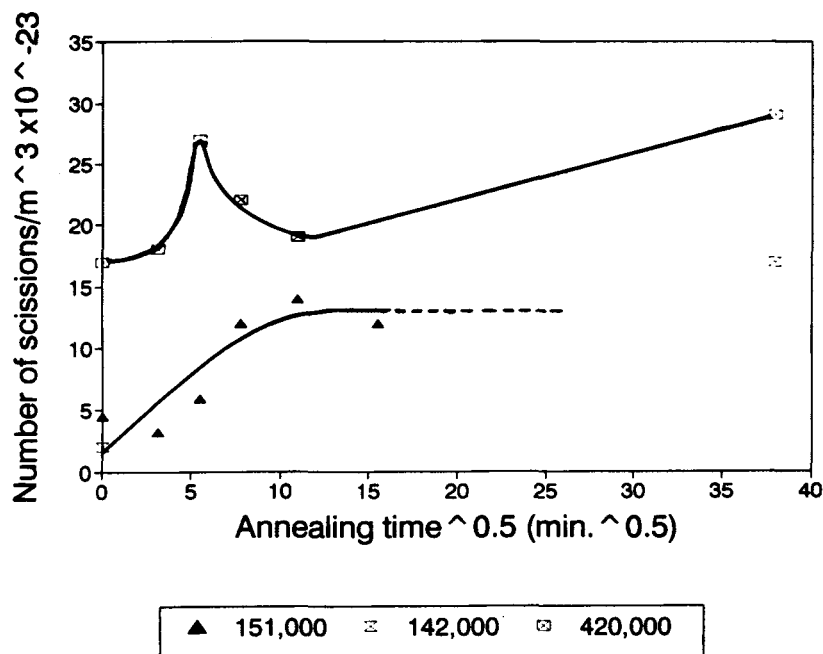


Figure 2 Number of chain scissions vs. annealing time for medium and high molecular weight polystyrene latex films, and Styron 6069 latex films (142,000 g/mol) annealed at 144°C for various times.

observed for the medium molecular weight polystyrene. Under completely annealed conditions, the high molecular weight latex film has a higher number of chain scissions per unit volume than the medium molecular weight film. This is a direct consequence of the higher number of physical entanglements per unit volume, which is related to the molecular weight. Table I summarizes the role of molecular weight on the contributions from the major molecular micromechanisms of fracture. As the molecular weight increases, the tendency for the chains to pull out decreases.

Latex Blends

Figure 3 shows the fracture energy results for blends I and II. Surprisingly, both types of blends show similar energy values as a function of annealing time. At $t = 0$, the fracture energy in both blends (approximately $225 \times 10^6 \text{ J/m}^3$) is close to the value of the pure medium molecular weight film ($\sim 230 \times 10^6 \text{ J/m}^3$). On annealing, the chains interdiffuse across the particle-particle interface, and the fracture energy increases. In this system, the low molecular weight chains interdiffuse into the high molecular weight²⁴ due to their higher mobility, a situation similar to a swelling process. A plateau in the fracture energy is obtained beyond 250 min,

which corresponds to the reptation time, τ , of the high molecular weight chains in blends I and II at the annealing temperature of 144°C, calculated using eq. (3). At this point ($t = \tau$), the low molecular weight chains have long since completely randomized, and the high molecular weight chains have traveled one radius of gyration to overlap with each other forming effective entanglements. Once this conformation is reached, a plateau in the energy values is obtained. The fracture energy at the plateau (about $300 \times 10^6 \text{ J/m}^3$) is much lower than that for the separate medium and high molecular weight latex films, which were $460 \times 10^6 \text{ J/m}^3$ and $520 \times 10^6 \text{ J/m}^3$, respectively. As one would expect, the addition of low molecular weight chains reduces the mechanical properties.

Figure 4 shows the corresponding number of chain scissions as a function of annealing time for blends I and II. As the chains interdiffuse, the number of chain scissions increase. Under completely annealed conditions, a constant value of chain scission is reached (about 5×10^{23} scissions/ m^3). Figure 5 shows the contributions of chain pullout and chain scission as function of annealing time. The chain scission contribution reaches a plateau value (about 25%). This contrasts with previous results for the high molecular weight films,²⁰ where the chain scission contribution reached 90% under completely

Table I Comparison of Results from Fracture of Various Fully Annealed Polystyrene Latex Films

Sample	Result ^a	Reptation time, τ^b
$M_n = 420,000 \text{ g/mol}^{19}$ (PDI = 1.19)	Chain scission energy: 90% Chain pullout energy: 10%	96 min
$M_n = 151,000 \text{ g/mol}^{23}$ (PDI = 1.02)	Chain scission energy: 40% Chain pullout energy: 60%	6 min
$M_n = 32,000 \text{ g/mol}^{23}$ (PDI = 1.04)	Chain scission energy: 0% Chain pullout energy: 100%	6 s

^a At 25°C; ^b144°C.

annealed conditions. It is clear that the low molecular weight component has significantly reduced the scission process and favored pullout. Even though the blends contain equal weight fractions of high and low molecular weight, the low molecular weight chains constitute about 93% by number, which is responsible for the extensive pullout process. The rather large error bar range in Figures 3 and 4 are thought to arise because of slight differences in mixing statistics.

Broad Molecular Weight Distribution Polystyrenes

Results for Styron 6069 polystyrene are shown in Table II. The fracture energies are the same for the compression-mold, fully dried solvent-cast film, and the fully annealed latex film. For the solvent-cast film, at an incomplete stage of drying ($T_g = 66^\circ\text{C}$),

the energy to fracture is low due to the plasticization effect of the residual solvent (about 9% of THF). A slight degradation was observed in the solvent-cast films, perhaps due to the drying process. In the Styron 6069 latex films, the fracture energy is lower at zero annealing time. On annealing the film for 1 day, the interface heals sufficiently that the fracture energy is restored to near equilibrium. The results of the latex films are included in Figures 1 and 2 for comparative purposes.

Table III shows the breakdown of the energies to fracture for the samples in Table II. Except for the nonannealed latex film, the energy for chain scission is significantly larger than that of chain pullout. Under molded conditions, of course, in the latex films, there are few physical entanglements. At 180,000 g/mol, the contribution of chain scission is between a half and three-quarters of the total energy to fracture. This sample differs from the $M = 151,000$

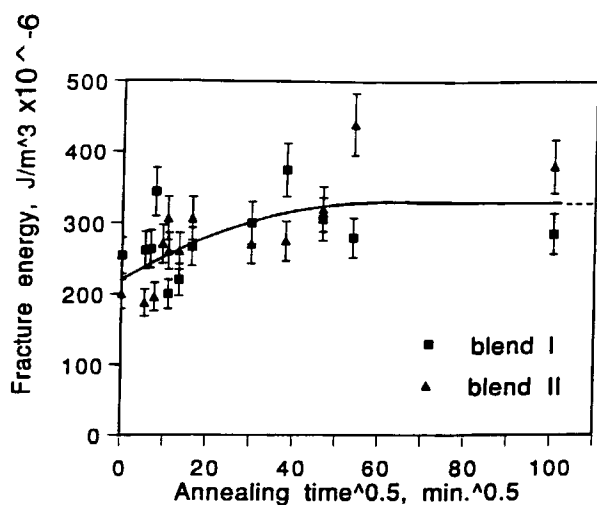


Figure 3 Plot of fracture energy vs. annealing time for polystyrene latex blends I and II annealed at 144°C for various times.

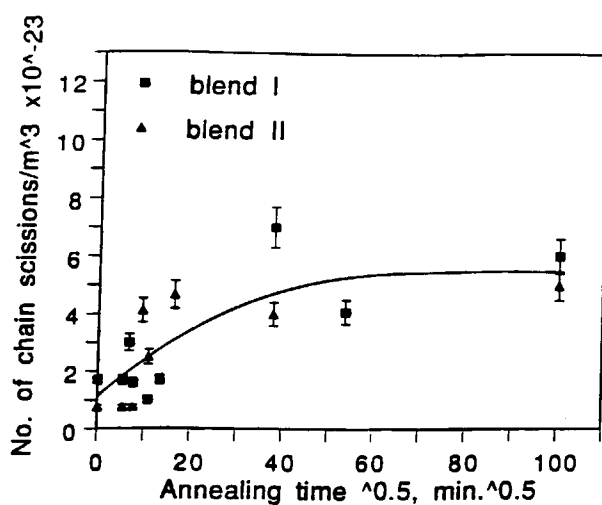


Figure 4 Plot of number of chain scissions vs. annealing time for polystyrene latex blends I and II annealed at 144°C for various times.

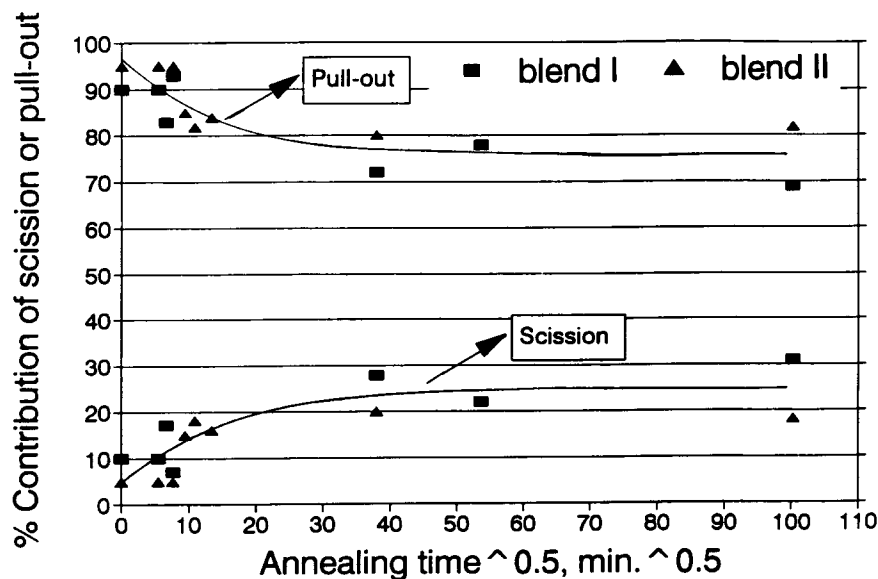


Figure 5 Contribution of chain scission and chain pullout to the total fracture energy for blends I and II.

g/mol²³ sample in two ways: it is both slightly higher in average molecular weight, and much broader in distribution.

The strain rate used in the grinding experiment is about 5×10^{-2} m/s with the burr rotational frequency of about 16.6 Hz. This is about two orders of magnitude lower than the strain rate used in an Izod impact test, which is about 3.46 m/s.²⁵ In the Izod test, most of the energy is transferred into kinetic energy of the fractured piece of plastic. How-

ever, previous calculations indicate that the kinetic energy of the ground powder is negligible compared to the total fracture energy.²

A Simple Unifying Relationship

Using scaling concepts, de Gennes⁵ derived the algebraic relationships between the maximum relaxation time of the chains in their tubes, τ_{\max} , which is the time required for complete renewal of the tube

Table II Fracture Studies on Styron 6069 Polystyrene (Dow Chemical Co.) ($M_n = 180,000$ g/mol; PDI = 1.8)

Sample	Initial Mol. wt.	Final Mol. wt.	^a N _a	^a Energy $\times 10^{-6}$ J/m ³
Latex films:				
0 min.	142,000	134,000	0.2×10^{24}	320
1 day	142,000	102,000	1.7×10^{24}	445
($T_g = 105^\circ\text{C}$)				
Compression Molded	180,000	113,000	2.2×10^{24}	443
($T_g = 107^\circ\text{C}$)				
Solvent cast:				
Dried at 60°C	147,000	113,000	1.3×10^{24}	242
(2 weeks)				
($T_g = 66^\circ\text{C}$)				
Dried at 100°C	147,000	97,000	2.2×10^{24}	413
(2 weeks)				
($T_g = 102^\circ\text{C}$)				

^a Error: $\pm 10\%$; N_a = Number of chain scissions per m³.

Table III Various Energy Contributions for Styron 6069 Polystyrene (Dow Chemical Co.)
($M_n = 180,000$ g/mol; PDI = 1.8)

Sample	$E_S \times 10^{-6}$ J/m ³	$E_U \times 10^{-6}$ J/m ³	$E_V \times 10^{-6}$ J/m ³	$E_T \times 10^{-6}$ J/m ³	% Contribution of scission
Latex films:					
0 min.	34	0.3	286	320	11
1 day	250	2.0	193	445	56
Compression molded	323	2.6	117	443	73
Solvent cast:					
Dried at 60°C	191	1.6	49	242	79
Dried at 100°C	323	2.6	87	413	78

E_S = Stretching and subsequent covalent bond breakage energy (chain scission); E_U = uncoiling energy (rubber elasticity); E_V = chain pullout energy; E_T = total fracture energy.

that constrains the chain, and its molecular weight, M . In brief,

$$\tau_{\max} = \tau_1 M^3 \quad (5)$$

where τ_1 represents the shortest relaxation time, independent of the molecular weight,

Even though the sample as a whole is not substantially above room temperature during the grinding process, molecular friction analysis suggests that the temperature of actual chain pullout is between 150 and 250°C.^{2,23} For the present purposes, it must be noted that as the molecular weight increases, it becomes more difficult to reform new entanglements, given the time scale of the experiment. This phenomenon depends on the maximum relaxation time, which according to eq. (5) scales with M^3 .

The portion of the chain capable of entanglements is given by $M - 32,000$ (in g/mol) for polystyrene, because the ends of the chain do not form entanglements. The fraction, F , of chain scission energy contribution, F , in fracture scales as the ratio of the τ_{\max} values. Taking the ratio to the total molecular weight removes the constant of proportionality,

$$F = [(M - 32,000)/M]^3 \quad (6)$$

Equation (6) assumes that the chains are in repetitive motion under pullout stresses in the glassy state.

Further evidence for such mobility has been furnished by the results of Oleinik et al.²⁶ They studied the extent of plastic strain in glassy polymers such as polystyrene, poly(methyl methacrylate), epoxies, etc., undergoing compressional deformation at room

temperature in a calorimeter. They determined the work of deformation, and the heat involved in the process. They found that most of the work was stored in the system as internal energy. A typical strain for polystyrene was in the range of 30–40%. The internal energy evaluated by Oleinik et al. is about 8×10^6 J/m³ for polystyrene ($M = 1 \times 10^6$ g/mol,) which is significantly larger than the uncoiling energy due to rubber elasticity effects reported for polystyrene films studied in this work, see E_U , Table III for an example that assumes full extension. Assuming the statistical theory of rubber elasticity with $M_c = 32,000$ g/mol for polystyrene, a 30% compressional strain should require an energy of 1×10^4 J/m³, computed as an entropy change. The important point is that the chains must have rearranged their conformations under compressional stresses in order to exhibit rubber elasticity effects. Because both E_U values and statistical theory of rubber elasticity values are smaller than Oleinik's value, the remainder must be due to internal energy changes, perhaps of the E_V type. Table IV compares the results obtained using eq. (6) with the experi-

Table IV Comparison of Chain Scission Energy Contribution as a Function of Molecular Weight in Polystyrene

M (g/mol)	F^* (theory)	F (expt.)
32,000	0	0
151,000	0.48	0.4
180,000	0.55	0.67
420,000	0.79	0.90
∞	1	Not available
(networks)		

* From eq. (6).

Table V Upper Bound Calculation of the Total Fracture Energy

M (g/mol)	$E_{U,ub}$, J/m ³	$E_{S,ub}$, J/m ³	$E_{P,ub}$, J/m ⁰	$E_{T,ub}$, J/m ³
32,000	—	—	230×10^6	230×10^6
151,000	12×10^6	1440×10^6	118×10^6	1570×10^6
420,000	19×10^6	2300×10^6	48×10^6	2367×10^6
∞	25×10^6	2940×10^6	—	2965×10^6

$E_{U,ub}$ = Upper bound uncoiling energy (rubber elasticity); $E_{S,ub}$ = Upper bound scission energy ($=F \cdot N_e \cdot E_{s,b}$); $E_{P,ub}$ = upper bound energy to pull out 150 mers ($=[1 - F] \cdot N_e \cdot E_p$); $E_{T,ub}$ = upper bound total fracture energy.

mental values for the different narrow molecular weights of polystyrene. Although the correlation is good, yet to be determined are the values for a polymer network, the equivalent of an infinite molecular weight polymer. The correlation between the theoretical and experimental values provides a basis for determining other physical and mechanical quantities, to be explored in future articles.

An upper bound relation for the total energy to fracture per unit volume, using the scaling relationship given by eq. (6) is shown below:

$$E_{T,ub} = F \cdot N_e \cdot E_{s,b} + [1 - F] \cdot N_e \cdot E_p + E_U \quad (7)$$

where, $E_{T,ub}$ is the upper bound total fracture energy, F is the chain scission energy contribution defined by eq. (6), and is also the fraction of possible effective entanglements; N_e is the total number of theoretical entanglements for an infinite molecular weight; E_p is the energy required to pull out one segment;²³ $E_{s,b}$ is the energy to break one —C—C— bond times the 300 bonds between physical entanglements, and E_U is the uncoiling energy arising from rubber elasticity effects. Table V shows the results for the three different narrow molecular weights. As it is evident, eq. (7) yields a higher value for the various energy contributions than the experimental data. This is because eq. (7) assumes that all the entanglements are involved in the scission process. The product of $F \cdot N_e$, which represents the upper bound number of chain scissions per unit volume, is one order of magnitude higher than the experimental value. The value at infinite molecular weight represents the predicted upper bound limit to fracture any crosslinked sample by first stretching, then scissioning, the chain at 32,000 g/mol intervals.

CONCLUSIONS

Chain pullout or chain scission at the particle-particle interface depends on the number of physical

entanglements per unit volume, which in turn, depends on the molecular weight of the polymer chain. At the low end of the molecular weight spectrum, pullout dominates, while at the high end, chain scission dominates. In the midrange of molecular weights, 150,000 to 180,000 g/mol, the energies for chain scission and chain pullout are comparable. Addition of a low molecular weight component (50%) to a high molecular weight polystyrene in blend systems reduces the extent of chain scission and favors chain pullout.

The authors are pleased to thank the National Science Foundation for support through Grant No. ECD-9117064, the companies that make up the Polymer Interfaces Center for their collective support, Shell Development Co. for the medium molecular weight polystyrene, and Dow Chemical Co. for Styron 6069.

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Received June 26, 1994

Accepted November 21, 1994