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Molecular basis of fracture of latex blends of polystyrene and poly(methyl methacrylate)

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The molecular basis of fracture of polystyrene and poly(methyl methacrylate) homopolymers and their latex blends was investigated with a custom-built dental burr grinding instrument (DBGI). About a third of the chains were cut several times, the remainder not at all. The number of chain scissions in polystyrene and poly(methyl methacrylate) was quantitatively interpreted by the microscopic parameters of craze fibrils and the energy balance between chain scission and chain disentanglement (chain pullout). The probability that a polymer strand in the craze fibrils is scissioned or disentangled was calculated from the fracture energy balance. In addition, the fracture energy of the latex blends of polystyrene and poly(methyl methacrylate) was studied. The large interface between the polystyrene and the poly(methyl methacrylate) did not lead to a small fracture energy, as initially expected. Rather, the latex blend of the two immiscible polymers primarily absorbs the fracture stress by strong co-continuous bulk phases. © *2001 Kluwer Academic Publishers*

1. Introduction

When glassy polymers are stressed to near the breaking point, they tend to craze, forming microscopic fissures with fibrillar material stretching from the floor to the ceiling of the openings. The crazes are often visible to the eye; sometimes the effect is called stress-whitening.

Recent experiments [1] and theories [2] examined the microscopic parameters of craze fibrils in glassy polymers, such as fibril diameter, spacing, and draw ratio. In the crazing process, polymers in the craze zone are drawn into fine fibrils, and voids are introduced between the craze fibrils. A direct measurement of the size of craze fibrils by low-angle electron diffraction methods [3] led to better theoretical approaches to the fracture behavior on a microscopic scale. For example, the craze fibrils of polystyrene and poly(methyl methacrylate) were measured to be about 10 nm with a spacing of about 20 nm.

During crazing, the polymer chain conformation deforms to fit the narrower craze fibrils, since mechanically strong polymer chains have a larger R_g than the craze fibril diameters. The polymer chains are thought to be scissioned, disentangled, or oriented during fibril formation. The critical parameter for determining the fracture mechanism on a molecular scale may be the molecular weight reduction during craze fibril formation and ultimate fracture. However, conventional fracture tests hardly provide quantitative data of the molecular weight reduction since the fractured volume is tiny compared to the whole sample size.

Mohammadi [4] *et al.* developed a dental burr grinding instrument to study the fracture mechanism of polymers on a molecular scale. The glassy polymers are finely fractured by dental burr grinding instrumentation and the torque recorded, providing a measure of the energy necessary to create fracture surfaces [5]. Particle size measurement provides an estimate of the new surface area created. Alternately, the particle volume alone can be used. Dental burr grinding instrumentation combined with gel permeation chromatography, GPC, produces critical information concerning the fracture mechanism, such as fracture energy and molecular weight reduction during fracture. However, no microscopic parameters were considered during the analysis of the fracture data from the dental burr grinding experiments.

The present approach provides a new interpretation of data from the dental burr experiment, trying to combine microscopic phenomenon with changes on the molecular scale during the crazing process of glassy polymers.

As an extension of polystyrene and poly(methyl methacrylate) homopolymer studies, blends of polystyrene and poly(methyl methacrylate) latexes were studied by the same method. These polymers are immiscible, but exhibit a large interphase thickness [6].

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The mechanical strength and fracture behavior of the immiscible interfaces are critical factors governing the mechanical properties of blends. The interface thickness was measured and calculated to be between 2 nm to 5 nm [7–12]. The fracture strength of the interface is about 1/20th of that of the virgin polystyrene[13]. Scanning electron microscopy and XPS revealed that the crack growth at polystyrene/poly(methyl methacrylate) interfaces is both cohesive and adhesive in nature [13]. However, the fracture behavior of immiscible blends on a molecular scale, especially at the interfaces, is not well understood.

A poly(methyl methacrylate)/polystyrene latex blend was used as a model system to investigate the molecular basis of fracture at immiscible interfaces. The poly(methyl methacrylate) latex was made by conventional emulsion polymerization, while the polystyrene latex was made by artificial miniemulsification from narrow molecular weight distribution (anionically synthesized) polymer, thus providing more precise data on the molecular weight reduction after fracture. An ultraviolet detector on the GPC measures only polystyrene molecular weights without interference by poly(methyl methacrylate), while a refractive index detector measures both polymers according to their differential refractive index difference with the solvent.

2. Experimental

2.1. Latex film preparation

Polystyrene with narrow molecular weight distribution (Pressure Chemical Co.) was used to prepare latex particles by direct miniemulsification [14]. Poly(methyl methacrylate) latex was prepared by a conventional emulsion polymerization with the following recipe: 0.18×10^{-6} m^3 distilled water, 60 g analytical grade methyl methacrylate, 0.25 g NaHCO$_3$, 0.25 g K$_2$S$_2$O$_8$, and 0.90 g sodium lauryl sulfate. The polymerization was carried out at 70 °C under a nitrogen atmosphere. Latexes or latex blends were dried and surfactant and co-surfactant were removed by water and methanol extraction. The cleaned latex powder was pressed at 10 MPa at 110 °C to 125 °C for 30 min to 1 h to prepare latex films. Then, the latex films were annealed at 150 °C for 3 days in a vacuum oven. This latter results in substantially equilibrium conditions.

2.2. Fracture experiments

A custom-built dental-burr grinding instrument, DBGI [5], was used for the study of the fracture mechanism of fully annealed latex films (Fig. 1). The instrument contains three basic parts. (a) a clock motor to rotate the head of a micrometer with a block of sample (0.8 mm in thickness, 10 mm in width) glued to its spindle tip, causing the sample to be moved down with a velocity of 127 nm/s. (b) a viscometer motor which rotates the dental burr at 1000 revolutions per minute (RPM) and measures the torque to grind the sample. Twelve sharp edges of the burr impact the polymer sample, breaking off small pieces. (c) a motor that moves the dental burr back and forth past the sample with a period of 4 s per pass, together with a vial to collect the ground powder. The burr is cooled with dropping water, also aiding in collecting the ground power. As a result of all motions of the DBGI, the polymer sample is theoretically broken into small particles with an average thickness of 500 nm and an average width of 50 μm.

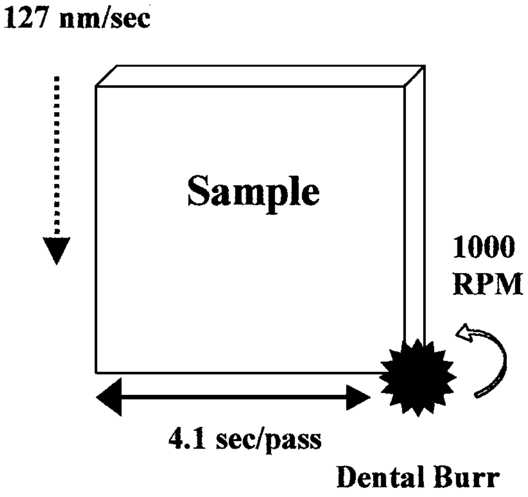


Figure 1 Schematic diagram of dental burr grinding instrumentation. Polymer films (typically 10 mm in width and 0.8 mm in thickness) move down while a rotating dental burr moves horizontally back and forth to grind the sample.

2.3. Molecular weight

The molecular weight and molecular weight distribution of the samples were measured by gel permeation chromatography (Waters Co.) equipped with refractive index and UV detectors, the latter with a cutoff wavelength of 250 nm. Since poly(methyl methacrylate) does not have a chromophore absorbing UV light longer than 250 nm, only polystyrene molecular weights were measured by the UV detector without any interference of poly(methyl methacrylate). Poly(methyl methacrylate) was observed only via the refractive index detector. The molecular weights of polystyrene and poly(methyl methacrylate) were calculated by using polystyrene standards (Pressure Chemical Co.) without any further correction.

3. Results

3.1. Fracture energy

The fracture energies of latex films of pure polystyrene, pure poly(methyl methacrylate), and their latex blends were obtained by DBGI. Fig. 2 illustrates that the

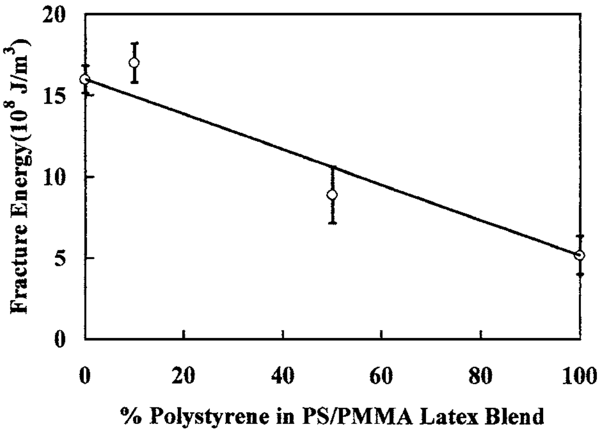


Figure 2 The fracture energy of latex blends of polystyrene and poly(methyl methacrylate) as measured by DBGI. Error bars express the standard deviation of measurements.

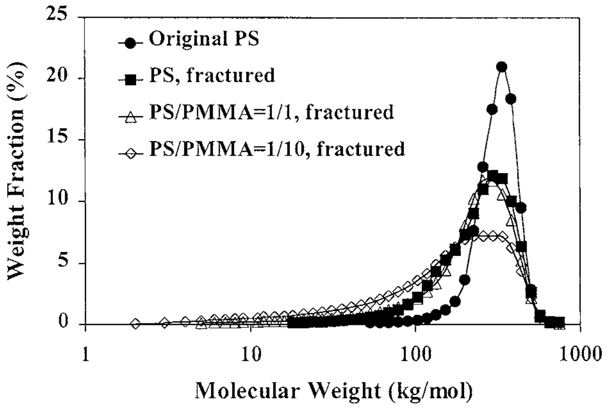


Figure 3 Molecular weight of polystyrenes measured by GPC with UV detector. Circles represent molecular weights before scission by dental burr instrument and others are molecular weight after fracture.

fracture energy of poly(methyl methacrylate) is three times higher than that of polystyrene. A straight line or possibly a sigmoidal curve describes the fracture energy of the latex blends as a function of composition, but the best model cannot be chosen due to the small number of data points. However, a sharp minimum in the mid-range compositions was not observed.

3.2. Molecular weight

The GPC chromatograms of original polystyrene and ground polystyrene were first normalized to have the same area under the chromatogram. Fig. 3 shows the GPC results of molecular weights of polystyrene before and the after the fracture experiments. With decreasing fractions of polystyrene in the latex blends, the number-average molecular weight of polystyrene after fracture experiments became lower, concomitant with a broader molecular weight distribution.

The GPC chromatogram of the ground polystyrene, and polystyrene after the fracture experiments, was separated mathematically into two parts: original polystyrene and scissioned polystyrene. The normalized chromatogram of the ground polystyrene was subtracted from that of the original polystyrene, see Fig. 4. The positive peak of the subtraction result represents the lower molecular weight fragments produced by the grinding experiments. In addition, the area under the positive peak represents the percent of the scissioned polystyrene. (Negative areas, not shown, indicate removal of original chains via scission. Of course, this area is equal but opposite to the area of scissioned chains.) Based on the normalized subtraction method, the molecular weight of the scissioned polystyrene portion can be obtained.

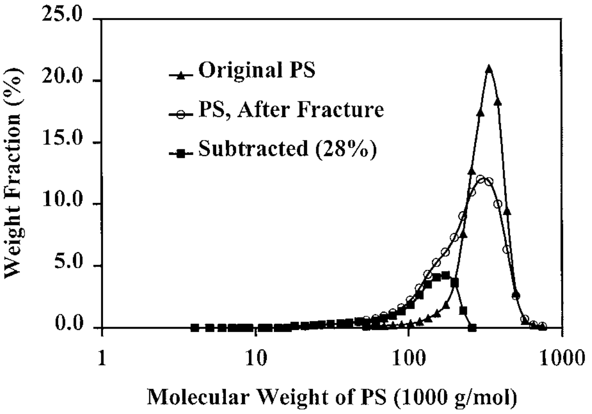


Figure 4 Molecular weight of a polystyrene fully annealed sample before and after fracture. The GPC chromatogram was separated into two peaks by a subtraction method: original polystyrene and the rest is that of the scissioned polymers. The percentage of each peak was obtained by integrating the area under the curves.

The molecular weights of ground polystyrene and scissioned polystyrene are listed in Table I. The molecular weights of samples PS, PS/PMMA = 1/1, and PS/PMMA = 1/9 were measured by GPC with UV detector. Hence those molecular weights only represent polystyrene. By contrast, the molecular weight of the PMMA sample was measured by refractive index detector.

While only about a third of the chains were scissioned, those cut were scissioned multiple times. The data indicate that the polystyrene molecular weight was reduced further with decreased polystyrene composition in the latex blend. In addition, a calculation of the average number of chain scissions per scissioned polystyrene chain shows considerable difference with different polystyrene compositions in the latexes. The scissioned polystyrene in the 10% polystyrene blend had 6.4 scissions per chain on average, while the fractured polystyrene in 100% polystyrene had only 2.0 scissions per chain, on average.

Table I further shows that 31% of poly(methyl methacrylate) chains in the sample were scissioned, and the number-average molecular weight of the scissioned poly(methyl methacrylate) was 16,000 g/mol. With a similar volume fraction of scissioned polymer, poly(methyl methacrylate) has many more scissions per chain than polystyrene.

TABLE I GPC results of $M_n = 290$ and $M_w = 322$ kg/mol polystyrene and poly(methyl methacrylate), $M_n = 401$ and $M_w = 901$ kg/mol, in latex blends after fracture experiments

	Ground polymer*			Scissioned polymer**		
Sample	M_n	M_w	% of chains scissioned	M_n	M_w	No. Scissions/ Scissioned polymer***
PS	186	262	28%	102	136	1.8
PS/PMMA = 1/1	121	245	32%#	56	124	4.2
PS/PMMA = 1/9	64	200	48%#	39	95	6.4
PMMA	47	610	31%	16	110	24

*Ground polystyrene is the GPC result of the fractured sample which includes scissioned polystyrene and intact polystyrene.

**Scissioned polystyrene was obtained by the subtraction method described in the text.

***No. Scission/ scissioned polystyrene = (M_n of original polystyrene)/(M_n of scissioned polystyrene) − 1

#Polystyrene chains only.

4. Discussion

4.1. Fracture energy per volume vs. per surface

Since the fracture surface area after the dental burr grinding experiment was difficult to determine due to the combination of latex blending and cracks propagating into the bulk of the sample [15], the fracture energy per unit volume was preferred to fracture energy per unit surface area. However, the fracture energy per unit surface can be estimated using the experimental conditions. Since the dental burr slices the samples into 500 nm thickness, the minimum total surface area per slice can be expressed by the sample cross section. Since the sample is actually powdered by the dental burr, the total surface area created is significantly larger. Thus the general relationship,

$$G_{\mathrm{v}} \times A \times th = G_{1\mathrm{c}} \times A \qquad (1)$$

where G_{v}, $G_{1\mathrm{c}}$, A, and th represent fracture energy per volume, fracture energy per area, sample cross section, and slicing thickness, respectively.

Of course, the dental burr experiment results in mixed modes of fracture energy and failure. The value calculated as $G_{1\mathrm{c}}$ of polystyrene, 230 J/m^2, falls into the range of the reported values from 200 to 1000 J/m^2 [16, 17]. The calculated $G_{1\mathrm{c}}$ of poly(methyl methacrylate), 880 J/m^2, is higher than the typical fracture energy [18], 500 J/m^2, but comparable. This agreement shows that the present fracture test method produces data similar to conventional fracture tests. Conventional fracture tests produce cracks not only at the surface but also into the bulk, as does the dental burr experiment. Hence, both conventional and dental burr experiments have some degree of uncertainty in the measurement of fracture surface area.

4.2. Crack tip density

The large damage zone per unit volume produced by the dental burr grinding instrument provides detailed information of damage zones on a molecular scale. By contrast, since most conventional fracture experiments are performed on specimens much larger than the size of the damage zones, molecular information of the damage zone can not be easily obtained.

As noted above, the DBGI slices the latex film by a thickness of 500 nm per pass. Since polystyrene with molecular weight of 290,000 g/mol has an end-to-end distance of 36 nm, the thickness of the slice is much larger than the size of the polymer chain. If fracture occurred only between slices, 30% of polymer chains could not have chain scissions. The mechanical stress on a polymer sample, produced by the impact of the rotating dental burr, likely introduces multiple craze paths into the polystyrene bulk where the distances between craze paths must be comparable to the size of a polystyrene chain.

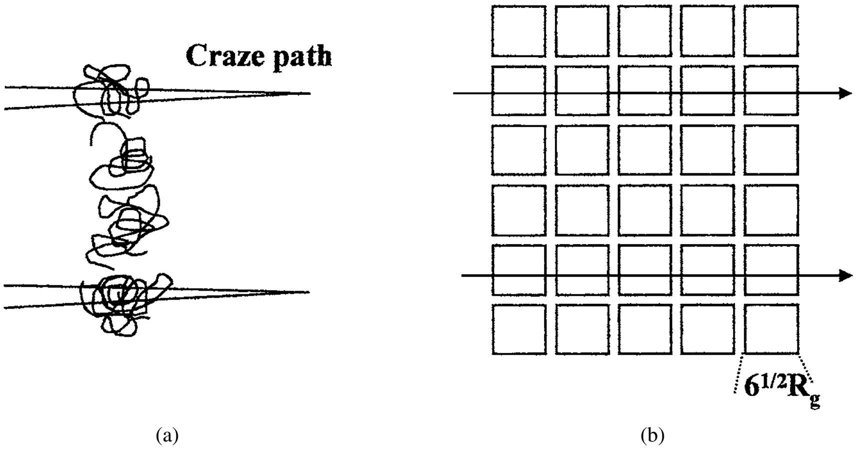
4.3. Volume fraction of craze zone

In Table I, the scissioned polystyrene and poly(methyl methacrylate) comprises 28 and 31% of the total polymer, respectively. Since both polystyrene and poly (methyl methacrylate) have a much higher molecular weight than their respective entanglement molecular weights ($M_{\mathrm{e}} = 19{,}100$, $M_{\mathrm{e}} = 8{,}800$ g/mol, respectively), the molecular weight of polymer chains in the craze zone should be reduced under fracture stress. The present experimental conditions were calculated to produce about 30 percent of craze zone and 70% of intact zone for homopolymers of polystyrene and poly(methyl methacrylate).

4.4. The distance between crazes

Chains in the path of a growing craze are likely to be cut several times, this being a function of R_{g}, M, and M_{e}. Chains in between crazes will be relatively unaffected, Fig. 5a.

An over-simplified model places chains in cubical boxes, length of side $6^{1/2}R_{\mathrm{g}}$, Fig. 5b. The end-to-end distance of a polymer chain is used as a length of the box. Each box holds several chains to normal density. The data in Table I show that about a third of the chains are subject to multiple scissions. Then the distance between crazes is $3 \times 6^{1/2}R_{\mathrm{g}}$. This provides an over-simplified phenomenological approach to understanding the behavior of chains being cut several times or not at all.



(a) (b)

Figure 5 Schematic diagrams of polymer chains in and between craze paths. (a) Polymer chains in a craze path have multiple scissions but polymer chains between craze paths do not have scissions. (b) The cubical boxes represent the size of a polymer chain. The cubical boxes on craze paths (arrows in (b)) have polymer chains scissioned.

This model suggests that the material making up the fibrils consist largely of broken chains, mostly with multiple scissions. The polymer in between the fibril-containing openings is relatively undamaged, with few scissions.

4.5. Energy contributions for polystyrene and poly(methyl methacrylate)

The total fracture energy, E_t, mainly consists of carbon-carbon bond breakage energy, E_s, and viscoelastic energy (chain pullout), E_p. Other contributions such as uncoiling energy and surface tension to form the craze fibril are relatively small under the present experimental conditions (high molecular weight and low temperature).

$$E_t = E_s + E_p \tag{2}$$

To break a carbon-carbon bond in linear polymer chains, all the carbon-carbon bonds between physical entanglements are assumed to be activated [4, 19, 20, 28]. The quantity E_s under the present experiments can be expressed;

$$E_s = E_{c-c} \times N_{c-c} \times N_s \tag{3}$$

where E_{c-c}, N_{c-c}, and N_s represent the activation energy of a carbon-carbon bond, the number of carbon-carbon bonds between entanglements, and total number of chain scissions per unit volume, respectively. The quantity of 340 kJ/mol was used as E_{c-c} and N_s of polystyrene and poly(methyl methacrylate) [6] equal to 370 and 180, respectively.

Table II shows that E_s of polystyrene and poly(methyl methacrylate) consist of 48% and 69% of the total fracture energies, respectively. Earlier data are provided for comparison. The reminder of the energy consumed is assumed to be related to chain pull-out.

4.6. Molecular basis of fracture mechanism of homopolymers

Polystyrene and poly(methyl methacrylate) showed very different fracture behavior on the molecular scale. The number-average molecular weight of the fractured poly(methyl methacrylate) was only 16,000 g/mol while that of polystyrene was 102,000 g/mol (Table I).

Recent research [1, 2] revealed that molecular entanglements of the polymer chains play a critical role in the craze process of glassy polymers. The number of entanglements or equivalently, the number of the strands in the polymer network determines the craze stress and mechanism of plastic deformation. In the crazing process, voids are introduced and polymer chains become fibrils by a surface drawing process. In the course of this process, a certain fraction, p, of the strands in the crazing zone must be disentangled (pull-out) or scissioned in order to form the void in the polymer bulk. Kuo *et al.* [21] calculated the probability p that an entangled strand must either be disentangled or broken to form the fibril surface. The ratio of the average craze fibril spacing, D_o, to the root-mean-square end-to-end distance of a strand (the root-mean-square end-to-end distance of M_e), d, was used to determine the probability p. Berger [3] experimentally measured the D_o and calculated the probability p for polystyrene and poly(methyl methacrylate) to be 0.368 and 0. 402, respectively.

TABLE II Comparison of fracture data per unit volume

Polymer	M_n (kg/mol)	No. of scissions (10^{24}/ m^3)	Fracture energy (10^6 J/m^3)	%E_s	Reference
PS	151	1.2	459	54	Ref. (26)
PS	290	1.2	520	48	Present work
PMMA	485	7.1	880	80	Ref. (27)
PMMA	401	11	1600	69	Present work

The probability p implies critical information about the molecular weight of polymers in craze fibrils. Berger [22] calculated the number-average molecular weight of polymer chains in the craze fibril, assuming that chain scission is the only fracture energy absorbing process,

$$\frac{1}{M'} = \frac{1}{M_n} + \frac{p}{M_e} \tag{4}$$

where M'_n, M_n, and M_e represent the number-average molecular weight of polymer chains in the craze fibril, the number-average molecular weight of original polymer, and entanglement molecular weight.

However, chain pullout (disentanglement) and other processes as well as chain scission absorb fracture energy. Therefore the Equation 4 should be modified as follows,

$$\frac{1}{M'} = \frac{1}{M_n} + \frac{p}{M_e}\frac{E_s}{E_t} \tag{5}$$

where E_s/E_t represents the ratio of scissioned chains to (scissioned + disentangled chains) in the craze fibrils.

The calculation results indicate that the molecular weights of polystyrene and poly(methyl methacrylate) in the craze fibrils are 74,000 g/mol and 32,000 g/mol, respectively. The difference between this calculated molecular weight in the craze fibril and the original molecular weight of polystyrene and poly(methyl methacrylate) explains why a polymer chain, especially poly(methyl methacrylate), had many chain scissions.

The experimental data in Table I show that the number-average molecular weight of scissioned polystyrene and poly(methyl methacrylate) were 102,000 and 16,000 g/mol, respectively. The origin of the difference between the calculated and experimental molecular weight of scissioned polymers is not immediately clear, but may be partly experimental errors as well as possible unknown factors. Chain orientation in the craze fibrils was ignored, for example. Also, much recent data suggest that the actual craze tip is above the glass transition temperature of the polymers; i.e., the action actually takes place in the melt [6, 26, 28].

4.7. Fracture energy and polystyrene composition in the blends

It is well known that the mechanical strength of the interface in immiscible polymer pairs is weaker than that of homopolymers. Experiments in planar specimens such as lap shear and wedge cleavage were designed to concentrate the mechanical stress at polymer interfaces and measured the fracture behavior. Wedge cleavage fracture experiments [23] showed that the fracture mode in polystyrene/poly(methyl methacrylate) interfaces is mostly adhesive with strength of 1/20th of virgin polystyrene, 20 to 50 J/m^2 [24]. However, the fracture energy in Fig. 2 shows no minimum values of the 50/50 latex blends.

A possible cause is that both the polystyrene and the poly(methyl methacrylate) latex blends form continuous phases at 50/50 composition, and regardless of local composition one polymer or the other always exhibits a continuous phase. Thus, the present results indicate that the interface strength may not play a major role in the overall material strength in these mechanical tests. It is known that in particle mixtures such as a latex blend, a minor component with a very low concentration is isolated and surrounded by other components but starts to be connected to the same component with increasing concentration. According to the scalar percolation theory [6, 25], the critical concentration at which the component becomes infinitely connected to the same component is about 25–30%, assuming a body-centered cubic lattice. Hence the 50/50 latex blend of polystyrene/poly(methyl methacrylate) should be a bi-continuous network. To break the latex blend film, a crack needs to break the continuous bulk phase as well as the weak interfaces. As a result of the bi-continuous phase morphology of the latex blend, the mechanical stress on the latex blend is mainly absorbed by strong bulk continuous phases.

4.8. Number of chain scissions in latex blends

With decreasing composition of polystyrene in the latex blends, the number of chain scissions per scissioned polystyrene chain was increased and the fraction of scissioned polystyrene was increased. While the percent of scissioned polymers was increased 1.7 times, the number of chain scissions per scissioned chain was increased 3.8 times in 10% polystyrene blend compared to 100% polystyrene, indicating that the polymer chains in the interface areas possibly suffer more severe damage than those in the bulk. In addition, Table I shows that poly(methyl methacrylate) [26, 27] has a much higher number of scissions per chain than polystyrene. The number of scissions per polystyrene chain in the latex blend becomes closer to that of poly(methyl methacrylate) with a higher poly(methyl methacrylate) content in the blend. The interface of polystyrene introduced by the neighboring poly(methyl methacrylate) is a possible source of the change in fracture behavior of polystyrene. Researchers [6, 28] assumed that entanglement of polymer mainly causes the chain scissions upon mechanical stress. For example, polystyrene [28] with a molecular weight lower than the critical molecular weight did not show any measurable chain scissions.

A quantitative explanation of why polystyrene chains in the latex blend were so highly damaged is not available. However, there are at least three possible causes of higher numbers of chain scissions with lower polystyrene particle content in a latex blend. First, under the experimental conditions, apparently the poly(methyl methacrylate) undergoes more crazing than the corresponding polystyrene sample. In the blends, the poly(methyl methacrylate) crazes may continue into the polystyrene latex phase [29], causing a greater than expected number of chain scissions in the polystyrene.

Secondly, the crack does not stay at the interfaces. Bernard *et al.* [24] recently found the crack propagation path strongly depends on the thickness of the two polymer layers. Even though the cracks are created at the interface, the crack easily propagates to the weak polymer layer, polystyrene in polystyrene/poly(methyl methacrylate) layers. Larger interface area in polystyrene/poly(methyl methacrylate) latex blends provide for more crack initiation, which might be deviated into the polystyrene phase and in turn produce more cracks in the polystyrene.

Thirdly, the interface properties such as entanglement density depend on the poly(methyl methacrylate) as well as polystyrene. Although polystyrene and poly(methyl methacrylate) are not miscible, the very low interfacial energy [30] of 0.17 J/m^2 at 140 °C indicates that the two polymers are well mixed at least in the interfaces. The polymer mixture in the interface is expected to have certain average properties of polystyrene and poly(methyl methacrylate). For instance, the entanglement molecular weight (M_e) of the mixture probably has a value between 19,100 (M_e of polystyrene) and 8800 g/mol (M_e of poly(methyl methacrylate)). The higher entanglement density presumably leads to higher number of scissions per chain in the polystyrene part of the blends.

The concept of chain scission taking place during fibrillar formation differs from earlier theories of chain scission taking place at the craze tip [4, 26, 28]. In the latter, if the chains were entangled on both the floor and ceiling of the growing craze, the chain scissioned. If it was held at neither end or only at one end, it pulled out. However, the energies involved are the same in both theories.

5. Conclusions

The fracture mechanism of polymer chains is interpreted on a molecular scale combined with the microscopic parameters of craze fibrils. The fracture mechanism on a molecular scale of polystyrene, poly(methyl methacrylate) and their latex blends was investigated with finely ground polymers by custom-built dental burr grinding instrumentation (DBGI). About 30–40% of chains in both homopolymers and the latex blends were scissioned. The scissioned chains, caught in the growing cracks, were cut many times.

The fracture energy of latex blends of polystyrene and poly(methyl methacrylate) was studied. The large interface between polystyrene and poly(methyl methacrylate) did not lead to small fracture energies of blend samples. The latex blend of two immiscible polymers primarily absorbs the fracture stress by strong continuous bulk phases even though the weak interface plays some role on a molecular scale.

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