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Reactive Reinforcement of Polystyrene/Poly(2-vinylpyridine) Interfaces

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ABSTRACT: The effect of reactive compatibilization on adhesion at the interface between the immiscible polymers polystyrene and poly(2-vinylpyridine) was investigated. Reactivity was incorporated into the system by lightly sulfonating the polystyrene component, providing acid functionality which is coreactive with the basic pyridine nitrogen. The interaction between sulfonic acid and pyridine groups generates interchain cross-links and therefore compatibilizing graft copolymers. The reinforcing effects of *in-situ* copolymer generation on the interface were quantified by evaluating interfacial adhesion through measurement of interfacial fracture toughness using the asymmetric double cantilever beam test. Interfacial properties were assessed as a function of the concentration of sulfonic acid groups present. The results show that the toughness of the interface is dramatically improved by the incorporation of reactivity, increasing from ~2 J/m^2 in the unreactive system up to >150 J/m^2 in the reactive system. At long reaction times, the toughness of the reactive interface approaches that of pure polystyrene. Approximately 5−7% sulfonation was found to produce optimum mechanical reinforcement. Scaling relations between the amount of compatibilizer formed at the interface and interfacial fracture toughness suggest that the copolymers formed act to initiate interfacial crazing during failure, accounting for the enhanced adhesion.

1. Introduction

There has been significant commercial interest over the last two decades in producing improved materials through blending of readily available polymers rather than through synthesis of new polymers. Difficulties arise in the blending of polymers due to the inherent thermodynamic incompatibility of mixtures of long-chain molecules. This incompatibility often results in blends having a microscopically heterogeneous structure in which the interphase interfaces are compositionally sharp and mechanically weak. Because macroscopic blend properties, particularly mechanical properties, tend to be dependent on both the blend morphology and the interphase adhesion, development efforts are concerned with control of these aspects of blend structure.

Traditionally, morphology control has been achieved through compatibilization techniques in which block copolymers are incorporated into the blend. While the use of block copolymers for controlling the morphology of immiscible blends is well established,[1−4] the effects of block copolymer addition on interfacial adhesion have been more difficult to assess. Conventionally, only morphology effects have been routinely investigated due to the relative ease of examining blend structure using microscopy. Recently however, a method has been developed to evaluate the effect of compatibilization on the adhesion between immiscible polymers directly by isolating the interface in a model fracture geometry.[5] A series of investigations using this method have consistently shown that large improvements in interfacial adhesion result directly from the addition of suitable diblock copolymers to immiscible interfaces.[6−14] These studies have shown that interfacial adhesion may be increased by as much as 2 orders of magnitude under proper conditions of interfacial reinforcement, which include a high density of copolymer chains at the interface and reinforcement using block copolymers which are long in comparison with the entanglement molecular weight of the immiscible components.[6,7,10] Unfortunately, the conditions favoring good interfacial adhesion are often difficult to achieve in commercially processed blends where the amount of added copolymer which may be dispersed to the interfaces is limited by mixing efficiency and the formation of copolymer micelles. The compatibilization scheme also suffers from the limited availability and considerable expense of suitable block copolymers.

Due to the cost and processing difficulties of using traditional block copolymers as compatibilizers, commercial efforts have been redirected toward *in-situ* compatibilization methods, in which copolymers are formed at the interphase interfaces during processing through the interaction of functional groups incorporated onto the blend components. Reactive compatibilization may be accomplished through various types of functional group interaction, including formation of covalent, ionic, or hydrogen bonds, and potentially offers a simple and cost-efficient route to morphological control in immiscible blends.[15−17] Reactive compatibilization methods have been shown to be effective at controlling morphology in a variety of blended systems, with the degree of morphology refinement achieved dependent on the amount of reactivity introduced into the system[18−21] and the type of coreactive pair employed.[22]

Though modifications to blend morphology have been well documented, the effects of *in-situ* copolymer formation on the interphase adhesion in immiscible reactive blends has received only a little attention. Baker and co-workers[23−25] have used a novel approach to estimate the interfacial adhesive effects of reactivity indirectly by eliminating the morphology parameter by varying the processing conditions. Their investigations clearly showed that the impact strengths of reactively modified,

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rubber/thermoplastic blends were superior to those of the unreactive counterparts though the blend morphology was similar, implying that improved interfacial adhesion was responsible for the superior mechanical properties. To date, there have been only two studies published dealing with direct measurement of interfacial properties in a reactive system. In the first,[26] the adhesion at an immiscible polystyrene/polyamide interface was found to improve dramatically when a layer of a poly(styrene−8% maleic anhydride) (PS−MAn) random copolymer was added to the interface due to reaction between the anhydride and polyamide end groups. In the second study,[52] polystyrenes of various molecular weights were end-grafted into epoxy networks during curing, resulting in significant improvements to the polystyrene/epoxy interfacial adhesion. Though the potential for improving interfacial properties through reactive methods has been demonstrated clearly by these previous investigations, the role of functional group concentration, which is pivotal to morphology control, has yet to be addressed. This important issue is the subject of the current study.

In this investigation, the effects of reactive compatibilization on the properties of the interface between polystyrene and poly(2-vinylpyridine) (P2VP) will be evaluated directly using the model interfacial geometry which has been employed previously in the study of diblock copolymer modified interfaces. Reactivity is incorporated into the system via the grafting of sulfonic acid groups to the polystyrene chains. The sulfonic acid may interact with the nitrogen of the pyridine ring either ionically or by hydrogen bonding, resulting in the *in-situ* formation of copolymers through interchain cross-linking. Previous investigations of blends containing the coreactive pair sulfonic acid/pyridine nitrogen have demonstrated that this interaction is particularly strong and readily leads to extensive interchain grafting in systems with high concentrations of reactive groups[27,28] and morphology refinement in systems with a limited concentration of functional groups.[29−33] In addition, the system PS/P2VP is ideal for study since it has been previously well characterized and information concerning the adhesion at diblock copolymer compatibilized PS/P2VP interfaces is available for comparison with the reactive system.[10]

The results of the present investigation clearly demonstrate that the interchain interaction between sulfonic acid and pyridine is highly effective at mechanically reinforcing the sPS/P2VP interface. Increases in interfacial adhesion of up to 2 orders of magnitude have been measured under optimum conditions. The degree of adhesion enhancement is found to be strongly dependent on the concentration of reactive groups in the system and affected by reaction time and material properties.

2. Experimental Section

Materials. Sulfonated polystyrenes (sPS) were prepared from a commercial polystyrene by grafting of sulfonic acid groups to polystyrene polymer chains using the method of Makowski et al.[35] The procedure involves grafting in solution by direct reaction with a sulfonating agent, such as acetyl sulfate or sulfur trioxide complexes with dioxane, tetrahydrofuran, and trialkyl phosphates. The resulting polymer structure resembles a random copolymer of styrene and styrenesulfonic acid. Sulfonated materials were prepared in styrenesulfonic acid concentrations of 0.00, 1.67, 3.37, 5.56, 6.91, 9.50, and 15.0 mol %, as measured by chemical analysis. The sulfonation procedure is not believed to alter the polystyrene molecular weight;[36] therefore all sulfonated polystyrenes are expected to have the same molecular weight as the starting material, $M_w = 212\,00$ g/mol, $M_w/M_n = 2.36$, as measured by gel permeation chromatography. Sulfonated polystyrenes will be referred to collectively as sPS, or specifically as PS-1.67SO_3H, for example, to designate the material which is a copolymer of styrene and 1.67 mol % styrenesulfonic acid.

Due to limited availability of material, it was necessary to use two different poly(2-vinylpyridine)s in this study. Both were obtained commercially and used without further modification. The first, designated P2VP-s, was purchased from Polysciences, Inc., of Warrington, PA. The second, designated P2VP-r, was obtained from Reilly Industries of Indianapolis, IN (trade name Reiline 2200). P2VP molecular weights were measured by viscometry in dimethylformamide using the Mark−Houwink parameters $K = 1.47 \times 10^{-4}$ and $a = 0.67$[34] and found to be 345 000 g/mol for P2VP-s and 190 000 g/mol for P2VP-r.

Fracture Toughness. Interfacial adhesion was quantified by measuring interfacial fracture toughness using the asymmetric double cantilever beam test (ADCB), first applied to the study of compatibilized polymer interfaces by Brown.[5] The test involves measurement of a toughness parameter, the critical energy release rate for interfacial failure (G_c), under constant displacement conditions. The displacement is achieved by inserting a razor blade into the interface of a bilayer constructed from the two immiscible polymers. An interfacial crack forms ahead of the blade and is propagated by advancing the razor blade at a constant speed. The crack is monitored until a constant length ahead of the blade is obtained, indicating that steady-state conditions have been reached. The steady-state crack length is recorded at fixed intervals during the interfacial failure and is used in conjunction with material elastic constants to calculate G_c according to the relation

$$G_c = \frac{3\Delta^2 E_1 {h_1}^3 E_2 {h_2}^3 \; E_1 {h_1}^3 {C_2}^2 + E_2 {h_2}^3 {C_1}^2}{8\alpha^4 \, (E_1 {h_1}^3 {C_2}^2 + E_2 {h_2}^3 {C_1}^2)^2} \qquad (1)$$

where a is the crack length, E_i are the Young's moduli of the two polymers, h_i are the thicknesses of the individual polymer layers, Δ is the thickness of the razor blade, and $C_i = 1 + 0.64h_i/a$.[5,37] The asymmetry in the testing geometry ($h_1 \neq h_2$) is necessary to compensate for differences in the elastic constants and deformation characteristics of the two materials on either side of the interface. A minimum occurs in the relationship between G_c and $h_1/(h_1 + h_2)$ in the region in which the asymmetry of the bilayer beam is properly balancing the asymmetry in the mechanical properties of the two polymers on either side of the interface. The value of G_c measured under these conditions most accurately reflects true interfacial properties.

In this study, the proper asymmetry ratio was determined experimentally by measuring the interfacial fracture toughness (G_c) as a function of asymmetry ratio for each PS-$x$$SO_3H$/P2VP pair. The proper asymmetry ratio, $h_{sPS}/(h_{sPS} + h_{P2VP})$, for interfacial property evaluation in the sPS/P2VP system was determined to be in the range of 0.57−0.62 for all polymer pairs, regardless of sulfonation level. This asymmetry ratio is in the same range as previously measured for unreactive PS/P2VP interfaces.[10] All data reported conform to these dimensional restrictions. Additional details about the testing procedure and the ADCB test can be found in refs 5, 10, 33, and 39.

Samples for fracture toughness measurements were prepared by first molding individual polymers into plates and subsequently joining a P2VP plate to an sPS plate in a separate step. Individual plates were prepared by compression molding using frame molds with thicknesses of 1−2.5 mm. Typical molding temperatures for polystyrenes were 150−185 °C. Higher temperatures were necessary for molding of highly sulfonated materials due to the increase of the glass transition temperature with sulfonation level. P2VP plates were molded at 150 °C. Bilayers for interfacial fracture testing were made by joining sPS and P2VP plates under slight contact pressure at 150 °C for times ranging from 6 min to 3 h. Joining temperatures were limited to 155 °C or less due to degradation of P2VP. After the desired joining period was complete, the

Table 1. Room Temperature Flexural Properties

	P2VP-s	P2VP-r	PS	PS-1.67s	PS-3.37s	PS-5.56s	PS-6.91s	PS-9.50s	PS-15.0s
strength (MPa)	71.5 ± 6.37	76.3 ± 6.03	47.9 ± 8.4	59.9 ± 2.1	50.8 ± 3.1	59.4 ± 3.0	62.9 ± 0.35	42.2 ± 9.1	29.9 ± 7.5
modulus (GPa)	4.12 ± 0.31	4.00 ± 0.22	3.5 ± 0.12	3.57 ± 0.26	3.40 ± 0.19	3.40 ± 0.23	3.72 ± 0.15	3.08 ± 0.23	3.49 ± 0.12

pressure was released and the laminates were allowed to cool slowly in the molds over a period of 1−1.5 h. All plates were dried for a minimum of 16 h at 50−70 °C under vacuum immediately prior to the bonding step. After cooling, the edges of the plates were trimmed off and the remaining material was cut into strips ~9−10 mm wide for testing.

Interfacial failure was achieved by inserting a razor blade at the bilayer interface at a constant speed of 3×10^{-6} m/s using a stepping motor with a programmable microstepping indexer. Crack growth was monitored through the transparent P2VP beam from above the sample via a video camera. This procedure typically allowed for 20 measurements of crack length per sample. Interfacial fracture toughness, G_c, was calculated according to eq 1 from the measured crack lengths and values of the elastic constants determined by flexure tests, discussed below. Values of G_c reported are an average of 10−20 measurements per sample in the steady-state regime. All error bars represent ±1 standard deviation.

Failure Analysis. The fracture surfaces of bimaterial beams were examined using a JEOL 840 scanning electron microscope. Surface chemical analysis was also performed in the SEM using wavelength-dispersive spectroscopy (WDS). Under the conditions employed, WDS is expected to be able to detect elements with atomic number ≥8 which are present in concentration of at least ~0.5% by weight probing a depth of ~1 μm from the sample surface.

Flexural Properties. Mechanical properties were measured for all materials in three-point bending according to the geometry defined in ASTM D790[40] using a SINTECH 20 testing machine. Samples for flexural testing were made by compression molding into window frame molds in a procedure identical to that described above for making the individual plates used to form bilayers. Tests were performed at a crosshead speed corresponding to a strain rate in the outer fiber of 1.2×10^{-5} m/s, which is a good approximation to the strain rates imposed on the bilayers during interfacial fracture testing[10] of 10^{-5}−10^{-7} m/s. The room temperature flexural modulus of sPS was found to be independent of sulfonation level within the accuracy of the measurement and not significantly different from the room temperature modulus of the unmodified PS. Values of the flexural modulus and strength, which are averages of 2−4 tests per material, are summarized in Table 1. Modulus values used in the calculation of G_c were $E_{P2VP-s} = 4.1$ GPa, $E_{P2VP-r} = 4.0$ GPa, and $E_{PS\ or\ sPS} = 3.5$ GPa.

3. Results and Discussion

The addition of reactivity to the PS/P2VP system results in substantial reinforcement of the interface. For example, functionalization of PS with only 1.67 mol % of styrenesulfonic acid results in a three- to tenfold increase in the interfacial adhesion. More significantly, the adhesion continues to improve as the functionality of the PS increases, reaching as high as ~350 J/m² for the toughest interface measured, as compared to only ~2 J/m² for the unreactive PS/P2VP interface and ~400 J/m² for virgin polystyrene[51] (Figures 1 and 2). This behavior implies the formation of reinforcing copolymers due to interaction of the functional groups.

The success of the reactive scheme employed in this study in promoting interfacial toughening may be attributed to favorable characteristics of the sPS/P2VP system. The interaction between sulfonic acid and pyridine exploited in the sPS/P2VP system is known to occur readily in solution without the need for thermal activation[27−33] and should also occur spontaneously at the interface between the two polymers in the melt. In addition, the probability of contact between reactive groups at an sPS/P2VP interface is high due to the full reactivity (one reactive group per monomer) of P2VP, so that any SO_3H moiety making contact with the interface should encounter a coreactive site. The probability of reaction at an sPS/P2VP interface should also be enhanced by monomer−monomer interactions. The attraction between styrenesulfonic acid and pyridine may promote segregation of reactive groups to the interface, a situation which has been observed for systems in which hydrogen bonding is involved.[44] Similarly, repulsive interactions between styrenesulfonic acid and styrene,[42] which are believed to be stronger than those between styrene and vinylpyridine,[42,43] should promote segregation of styrenesulfonic acid groups to the interface and/or diffusion of P2VP into sPS. This diffusion mechanism may account for the higher efficiency of the lower molecular weight P2VP-r relative to P2VP-s in reinforcing interfaces at low reactivity level (Figure 2) though it is important to note that extensive diffusion cannot occur due to the pinning of molecules by their grafting sites to the interfacial region.

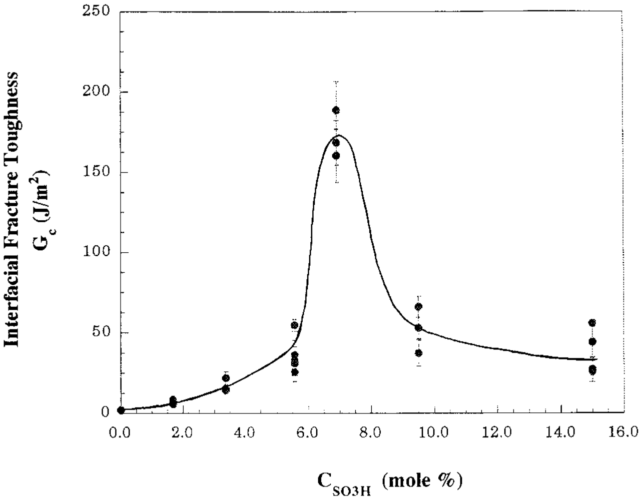

Figure 1. Interfacial toughness versus reactivity for the sPS/P2VP-s system.

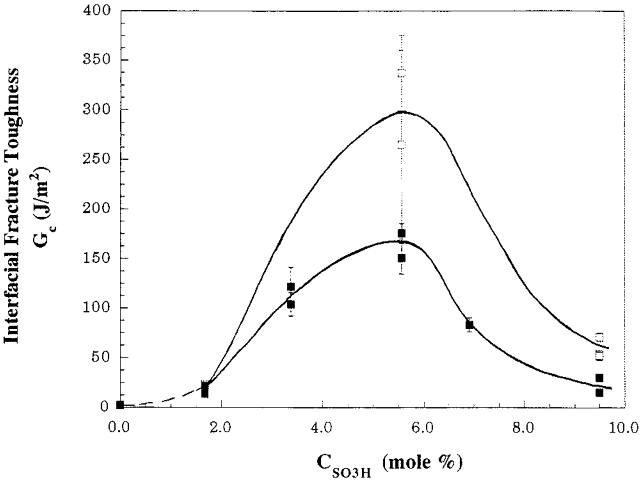

Figure 2. Interfacial toughness versus reactivity for the sPS/P2VP-r system: (□) bonding under pressure for 180 min; (■) bonding under pressure for 6 min.

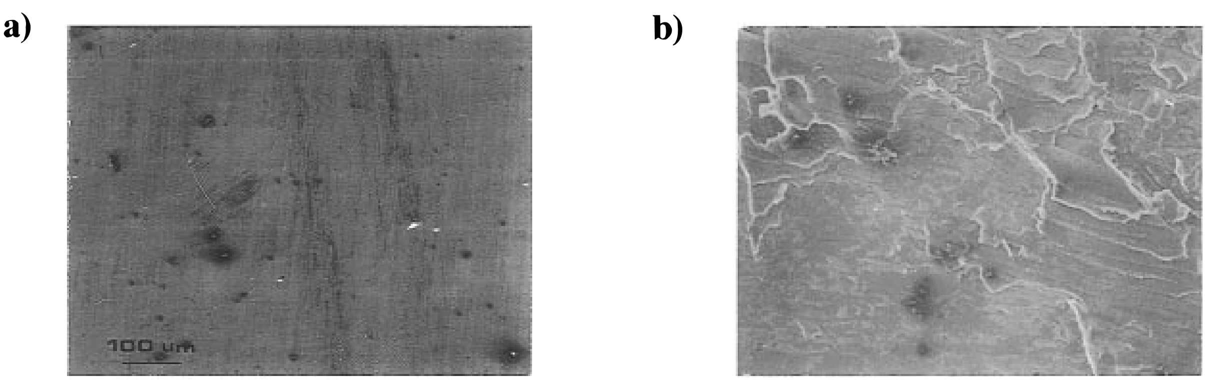

Figure 3. SEM fractographs of the P2VP side of (a) an unreactive PS/P2VP-s interface and (b) a reactive PS-6.91SO$_3$H/P2VP-s interface. Both images are at the same magnification.

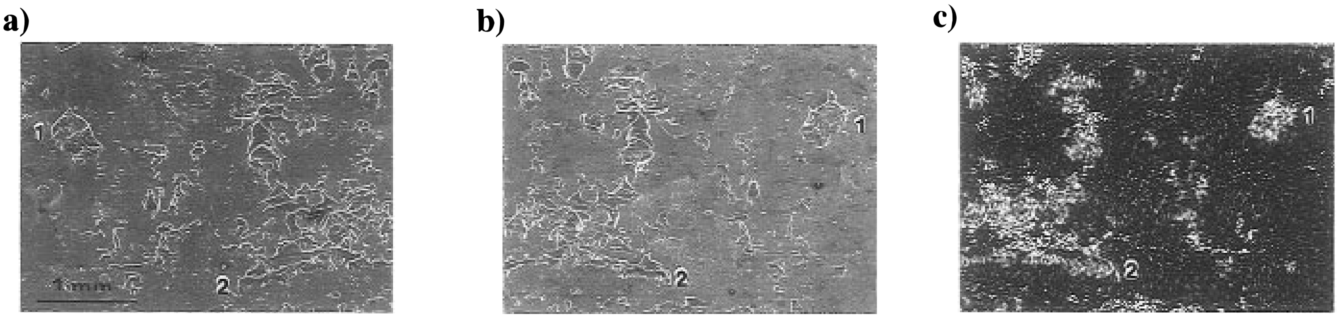

Figure 4. SEM fractographs of matching sides of a failed PS-6.91SO$_3$H/P2VP-s interface: (a) sPS surface; (b) P2VP-s surface; (c) WDS sulfur map of (b). Numbers indicate corresponding features. All images are at the same magnification.

This study of sPS/P2VP interfaces has shown that G_c is dependent on several properties of the system, specifically reactivity, molecular weight of the P2VP component, and reaction time. The effect of increasing reactivity on the toughness of sPS/P2VP-s interfaces is illustrated in Figures 1 and 2. There is clearly an optimum reactivity level for reinforcement. The interfacial toughness improves with increasing reactivity up to styrenesulfonic acid levels of ~5−7 mol %, after which there is a rapid decline into a regime where the toughness levels out to a value which is approximately 10−20 times that of the unreactive counterpart. The latter region of the G_c versus reactivity relationship will be designated the increasing toughness regime or regime I, while the former will be referred to as the postoptimum toughness regime or regime II. Toughness in the postoptimum regime is relatively insensitive to changes in sulfonic acid concentration. The optimum reactivity level differs between the sPS/P2VP-s system and the sPS/P2VP-r system. This behavior is believed to reflect the sensitivity of adhesion to the molecular weight of the reinforcing polymers which has been observed previously.[6,10,52] The optimum reactivity level does not appear to be strongly affected by the reaction time; however, the magnitude of the toughness is clearly affected by this parameter, increasing as reaction time increases (Figure 2). The reaction time dependence of G_c appears to be a function of sulfonic acid concentration—the change in G_c with bonding time is negligible at 1.67% styrenesulfonic acid while it is pronounced at higher reactivity levels.

The fracture surfaces of sPS/P2VP interfaces were examined by scanning electron microscopy in order to gain some insight into the failure mechanism. Fracture surfaces from unreactive and lightly sulfonated interfaces do not show evidence of large-scale plastic deformation (Figure 3a). Once the sulfonic acid concentration becomes high enough to generate an interfacial toughness of ~50 J/m^2 or greater, large-scale plastic deformation is evident on the fracture surfaces (Figure 3b). This characteristic persists in samples out to the 15.0% sulfonation level. Examination of matching sides of a given interfacial fracture show common features (Figure 4a,b), suggesting that the fracture path in sPS/P2VP pairs of higher reactivity may wander away from the interface. This possibility was investigated by wavelength-dispersive spectroscopy (WDS) to determine the chemical composition of the fracture surfaces from which the fracture path may be evaluated. Comparison of Figure 4b, which shows the P2VP surface of a PS-6.91SO$_3$H/P2VP bilayer after fracture toughness testing, with Figure 4c, which shows the WDS sulfur map of this surface, clearly demonstrates the presence of sPS adhered to the regions of the P2VP surface in which large-scale deformation is evident. This evidence coupled with the correspondence of damaged regions on the sPS and P2VP surfaces indicates that the crack formed between the sPS and P2VP layers during the fracture toughness test wanders from the interface and into the sPS layer at some points during the failure. Crack path wandering into the sPS side as opposed to the P2VP side is expected since P2VP has a higher crazing stress.[10] Thus, the fractography results indicate that once the interface becomes strong enough, failure occurs both adhesively and cohesively, as the crack propagates both along the interfacial plane and into the material adjacent to it.

The magnitude of the reinforcing effect observed coupled with the evidence of plastic deformation on the fracture surfaces implies that a major energy dissipating mechanism has been activated during the failure. The origin of the mechanical reinforcement and the activation of energy dissipating mechanisms may be understood in terms of a recent conceptual model of failure which has been used successfully to explain the behavior of block copolymer reinforced interfaces.[6−10,45,47] This

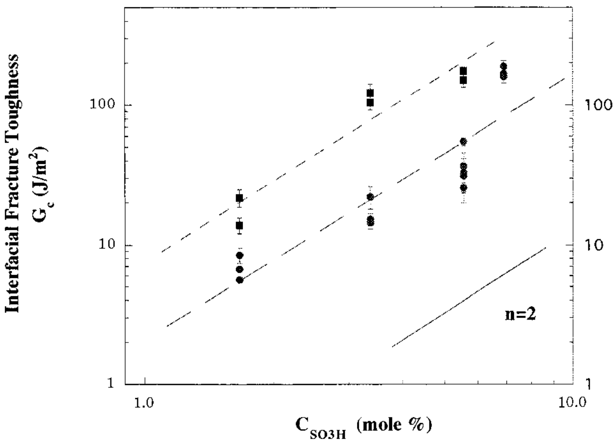

Figure 5. Power law fit of interfacial toughness versus system reactivity: (●) sPS/P2VP-s, 1 h bonding; (■) sPS/P2VP-r, 6 min bonding.

model predicts that the failure mechanism at an immiscible, A-*b*-B diblock copolymer reinforced, A/B interface is a function of both the molecular weight of the "A" and "B" copolymer blocks and the number of copolymer chains which cross the interface. For systems in which the copolymer segments are long with respect to the entanglement molecular weight of the corresponding polymers, the force required to break the copolymer chains during the interfacial fracture generates a stress on the interface equivalent to the breaking force per chain times the number of copolymer chains per unit interfacial area (Σ). If the stress generated on the interface exceeds the crazing stress of either polymer, the crazing mechanism will be activated, contributing the energy necessary to create and propagate a craze to the failure energy, thereby increasing interfacial fracture toughness. The degree of toughening ultimately achieved is dependent on the molecular weight of the reinforcing copolymer blocks and on Σ. The signature of crazing failure at compatibilized interfaces is an $n = 2$ power law relation between the interfacial fracture toughness and the areal density of copolymers crossing the interface ($G_c \sim \Sigma^2$).[7,8,10,45-47]

The relationship between toughness and the concentration of interfacial copolymers formed at the sPS/P2VP interface in regime I may be considered in light of this failure mechanism model. The relation between G_c and graft concentration breaks down in regime II, for reasons which will be discussed below. All polymers employed in this study have average molecular weights well in excess of the corresponding entanglement molecular weights for P2VP ($M_e \sim 27\,000$ g/mol) and PS ($M_e \sim 18\,000$ g/mol) and consequently interchain reaction should generate copolymers having at least one segment on either side of the interface with $M > M_e$.[10,53] Therefore, sPS-*g*-P2VP copolymers will generate interfacial stress during failure, the magnitude of which increases with Σ, and may eventually result in crazing as described above. Since the density of copolymers (Σ) formed should be directly proportional to the concentration of reactive groups ($[C_{SO_3H}]$), one would expect a power law relation, $G_c \sim [C_{SO_3H}]^n$, with $n = 2$ if interfacial failure by crazing was occurring in the sPS/P2VP system. The best power law fit to the interfacial toughness versus reactivity data, shown in Figure 5, gives $n = 1.9 \pm 0.3$ for both the sPS/P2VP-r and sPS/P2VP-s interfaces, in reasonable agreement with the predicted exponent $n = 2$ for interfacial failure by crazing. The assertion that the *in-situ* generation of sPS-*g*-P2VP copolymers reinforces immiscible sPS/P2VP interfaces by inducing interfacial crazing during failure is further supported by the evidence of plastic deformation apparent on the fracture surfaces (Figures 3 and 4) and by the magnitude of G_c. Previous studies in block copolymer reinforced systems have shown that fracture toughness does not exceed ~15 J/m^2 unless crazing has been activated.[7,10] All of the evidence collected in this study indicates that the mechanism responsible for the large increases in interfacial toughness which have been measured at the sPS/P2VP interfaces is the activation of crazing during interfacial failure.

Although the mechanical behavior of reactively reinforced interfaces in regime I may be qualitatively understood in terms of block copolymer reinforcement models, it is important to remember that the architecture of the reinforcing copolymers in the reactive system and a diblock copolymer compatibilized system is quite different. Because the grafting site between a randomly sulfonated polystyrene chain and a fully reactive P2VP chain has an equal probability of occurring at any position along either molecule, the copolymer formed has an architecture similar to a four-armed star. Thus the grafting reaction generates up to four reinforcing strands per copolymer bond. The graft architecture leads to a higher density of reinforcing strands at a reactive interface than may be achieved at a diblock copolymer reinforced interface and appears to yield more efficient strengthening; the highest toughness reached with diblock copolymer reinforcement of a PS/P2VP interface[10] was ~120 J/m^2, while the toughness of optimally reinforced sPS/P2VP interfaces in this work reached as high as ~350 J/m^2 under conditions where the average length of reinforcing strands in the graft copolymer should be similar to those of the diblock copolymers, as described in the literature.

Finally, the factors responsible for the decline of toughness at high reactivity levels (regime II) deserve some comment. The appearance of an optimum reactivity level was somewhat unexpected, and the reasons for its occurrence in a reactively reinforced system are not intuitively obvious. A qualitatively similar relationship between G_c and Σ has been observed previously for PPO/PMMA interfaces reinforced with PS-*b*-PMMA diblock copolymers[7,8] in which the toughness decline at higher Σ in this system was attributed to the formation of copolymer lamellae at the interface. However, the formation of lamellae or organized structures at reactive sPS/P2VP interfaces is unlikely due to the complicated architecture of sPS-*g*-P2VP copolymers. In the reactive system considered here, factors such as property changes due to sulfonation and excessive interfacial grafting, discussed below, are believed to be responsible for the decline in toughness observed at high acid levels.

The sulfonation of polystyrene has consequences which may directly influence the toughness of an sPS/P2VP interface. Ionic aggregation of [SO_3^-] and [H^+] groups is known to occur in sulfonated polystyrenes at increased acid levels. Small-angle X-ray scattering results have shown that ionic aggregation becomes significant in the sulfonated polystyrenes used in this study above ~7% styrenesulfonic acid.[33] These aggregates may compete with the interface as preferred segregation sites for SO_3H groups, effectively lowering the concentration of acid available for the grafting reaction and consequently the interfacial toughness. In addition, the work of Hara and co-workers[48] has shown

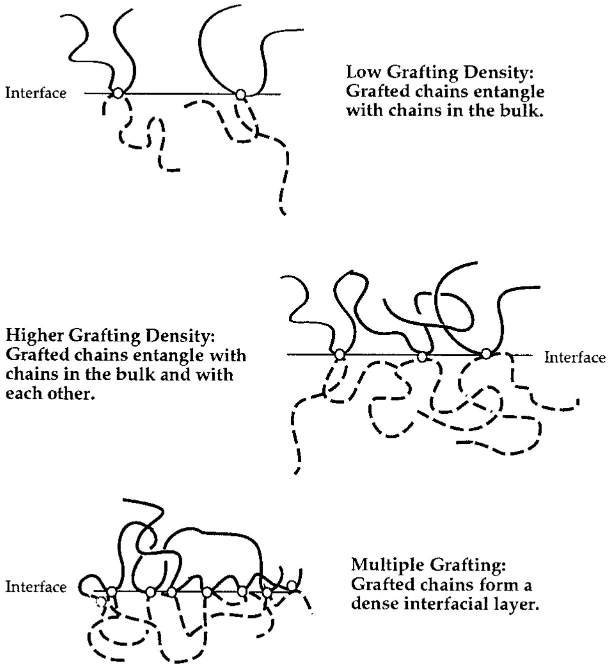

Figure 6. Schematic illustration of graft copolymer entanglement at reactive interfaces.

that sulfonated PS ionomers have increased crazing stress relative to unmodified PS. Since G_c is known to be inversely proportional to crazing stress,[46,47] increased crazing stress due to aggregation would result in decreased toughness, as observed.

Though property changes resulting from ionic aggregation probably contribute to the occurrence of a maximum in the toughness versus reactivity relationship, they cannot sufficiently explain all of the observed behavior. If changes in polystyrene properties with sulfonation were solely responsible for the drop in G_c in regime II, one would not expect the maxima to occur at different reactivity levels for sPS/P2VP-r and sPS/P2VP-s, as has been observed (Figure 2). Therefore, excessive interfacial grafting, which may account for the molecular weight dependence, is also believed to be contributing to the observed G_c versus reactivity behavior.

As the functionality of sulfonated polystyrene increases, the total number of grafts formed at an sPS/P2VP interface increases as does the probability of multiple grafts along a given sPS chain. The density of the grafted layer therefore increases with increased sulfonation and so does the probability that grafted chains will entangle with each other rather than with chains in the bulk polymer on either side of the interface (Figure 6). Graft–graft entanglements fail to transfer load across the interface and are ineffective at reinforcing it. This type of ineffective copolymer–copolymer entanglement has been predicted by the numerical simulations of Shull and Kramer.[10,49] Their simulations also indicated that the Σ at which ineffective entanglement becomes significant would be higher for longer copolymer chains than for shorter chains. This is in qualitative agreement with the behavior observed in the sPS/P2VP system, where the end of the increasing toughness regime was reached at a lower sulfonation level (grafting density) for P2VP-r than for the higher molecular weight P2VP-s (Figures 1 and 2). Multiple grafting along a single chain may also result in diminished toughness at high sulfonation levels. The net result of multiple grafts forming along a single chain is a decrease in the molecular weight of the PS reinforcing segments between bonds (Figure 6). In cases where the distance separating grafting points is less than the entanglement molecular weight of PS, the loops between grafts will be too short to support entanglement, and these segments may be ineffective in promoting toughening.[26] Future studies of sPS/P2VP bilayers using depth profiling methods are planned to examine the development of chemical composition in the interfacial region and possibly correlate the development of the grafted layer with the observed properties.

4. Conclusions

The effect of reactive compatibilization on the mechanical properties of sulfonated polystyrene/poly(2-vinylpyridine) interfaces has been investigated, and the incorporation of reactivity into the PS/P2VP system was found to improve interfacial mechanical properties dramatically. Fracture toughness at the reactive interface was increased by up to 2 orders of magnitude relative to its unreactive counterpart. Under optimum conditions of reactivity and bonding time, the fracture toughness of the reactive interface approached that of pure polystyrene. The enhancement in the interfacial adhesion reflects the formation of reinforcing copolymers at the interface through interchain interaction between sulfonic acid and pyridine groups.

The relationship between the functionality of the polystyrene and interfacial fracture toughness was evaluated systematically over a range of styrenesulfonic acid concentrations from 0 to 15.0 mol %. An optimum level of reactivity was found, in the range of ~5–7 mol % styrenesulfonic acid, which provides maximum toughening. The occurrence of an optimum level of reactivity has been used to divide the relationship between interfacial toughness and concentration of styrenesulfonic acid into two regimes: regime I in which G_c is continuously increasing with reactivity, and the postoptimum toughness regime (regime II) in which the toughness is relatively insensitive to changes in sulfonic acid concentration and has a value which is ~10–20 times that of the unreactive interface but only about one-third of the optimum toughness. Failure mechanisms were evaluated in regime I using recent conceptual and theoretical models of failure at compatibilized interfaces. Scaling relations predicted by these models between interfacial fracture toughness and the concentration of copolymers at the interface were extended to the reactive case and used to establish agreement between the observed behavior and that which would be expected for interfacial toughening due to the initiation of crazing during failure. Regime II behavior is believed to be a consequence of several factors, including ionic aggregation and excessive interfacial reaction at high sulfonation levels.

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References and Notes

(1) Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978; Vol. 2.
(2) Rudin, A. *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C19*, 267.

(3) Paul, D. R.; Barlow, J. W. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1986; p 399.
(4) Liebler, L. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 1.
(5) Brown, H. R. *J. Mater. Sci.* **1990**, *25*, 2791.
(6) Washiyama, J.; et al. *Macromolecules* **1994**, *27*, 2019.
(7) Creton, C.; Brown, H. R.; Deline, V. R. *Macromolecules* **1994**, *27*, 1774.
(8) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, *26*, 4164.
(9) Brown, H. R.; et al. *Macromolecules* **1993**, *26*, 4155.
(10) Creton, C.; et al. *Macromolecules* **1992**, *25*, 3075.
(11) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* **1991**, *24*, 1846.
(12) Washiyama, J.; Creton, C.; Kramer, E. J. *Macromolecules* **1992**, *25*, 4751.
(13) Reichert, W. F.; Brown, H. R. *Polymer* **1993**, *34*, 2289.
(14) Brown, Hugh R. *Macromolecules* **1993**, *26*, 1666.
(15) Brown, S. B. In *Reactive Extrusion, Princioples and Practice*; Xanthos, M., Ed.; Hanser Publishers: New York, 1992; p 75.
(16) Liu, N. C.; Baker, W. E. *Adv. Polym. Tech.* **1992**, *11*, 249.
(17) Xanthos, M.; Dagli, S. S. *Polym. Eng. Sci.* **1991**, *31*, 929.
(18) Liu, N. C.; Baker, W. E.; Russell, K. E. *J. Appl. Polym. Sci.* **1990**, *41*, 2285.
(19) Angola, J. C.; et al. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 807.
(20) Fowler, M. W.; Baker, W. E. *Polym. Eng. Sci.* **1988**, *28*, 1427.
(21) MacKnight, W. J.; et al. *Polym. Eng. Sci.* **1985**, *25*, 1124.
(22) Song, Z.; Baker, W. E. *J. Appl. Polym. Sci.* **1992**, *44*, 2167.
(23) Liu, N. C.; Baker, W. E. *Polymer* **1994**, *35*, 989.
(24) Liu, N. C.; Baker, W. E. *Polym. Eng. Sci.* **1992**, *32*, 1695.
(25) Liu, N. C.; Baker, W. E. *PMSE Preprints* **1992**, *67*, 305.
(26) Lee, Y.; Char, K. *Macromolecules* **1994**, *27*, 2603.
(27) Huglin, M. B.; Rego, J. M. *Polymer* **1990**, *31*, 1269.
(28) Huglin, M. B.; Rego, J. M.; Gooda, Shaban R. *Macromolecules* **1990**, *23*, 5359.
(29) Douglas, E. P.; Sakurai, K.; MacKnight, William J. *Macromolecules* **1991**, *24*, 6776.
(30) Zhang, X.; Natansohn, A.; Eisenberg, A. *Macromolecules* **1990**, *23*, 412.
(31) Sakurai, K.; Douglas, E. P.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4506.
(32) Eisenberg, A.; Smith, P.; Zhou, Z.-L. *Polym. Eng. Sci.* **1982**, *22*, 1117.
(33) Beck Tan, N. C. Ph.D. Thesis, University of Maryland, 1994.
(34) Arichi, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 439.
(35) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent No. 3 870 841, 1975.
(36) Lundberg, R. D.; Makowski, H. S. *Ions in Polymers*; Advances in Chemistry Series 187; American Chemical Society: Washington, DC, 1980; p 25.
(37) Kanninen, M. F. *Int. J. Fracture* **1973**, *9*, 83.
(38) Cho, K.; Brown, H. R.; Miller, D. C. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 1699.
(39) Xiao, F.; Hui, C.-Y.; Kramer, E. J. *J. Mater. Sci.* **1993**, *28*, 5620.
(40) *Standardized Test Method ASTM D790-90*; ASTM: Philadelphia, PA, Vol. 8.01, p 272.
(41) Guégan, P.; et al. *Macromolecules* **1994**, *27*, 4993.
(42) Beck Tan, N. C.; et al. *Polymer* **1995**, *36*, 1995, 1969.
(43) Shull, K. R.; et al. *Macromolecules* **1990**, *23*, 4780.
(44) Dai, Kevin H.; et al. *Macromolecules* **1994**, *27*, 5187.
(45) Xu, D.-B.; et al. *Mech. Mater.* **1991**, *11*, 257.
(46) Hui, C. Y.; et al. *Macromolecules* **1992**, *25*, 3948.
(47) Brown, H. R. *Macromolecules* **1991**, *24*, 2752.
(48) Bellinger, M.; Sauer, J. A.; Hara, M. *Macromolecules* **1994**, *27*, 1407.
(49) Shull, K. R.; Kramer, E. J. *Macromolecules* **1990**, *23*, 4769.
(50) Di Marzio, E.; McCrackin, F. L. *J. Chem. Phys.* **1965**, *43*, 539.
(51) Wool, R. P.; Yuan, B.-L.; McGarel, O. J. *Polym. Eng. Sci.* **1989**, *29*, 1340.
(52) Norton, L. J.; et al. *Macromolecules* **1995**, *28*, 1999.
(53) The relation between sulfonation and entanglement molecular weight is undocumented. For the purpose of this study, the entanglement molecular weight of sPS is assumed to be less than or equal to that of PS.

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