Oligomer and random copolymer layer in relation to enhancement of interfacial adhesion at polystyrene/poly(styrene-*co*-acrylonitrile) interface

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Abstract: This study examines the interfacial adhesion between poly(styrene) (PS) and poly(styrene-*co*-acrylonitrile) (SAN) interfaces reinforced with poly(styrene-*co*-vinyl phenol) (PS-*ran*-PSPh) random copolymers using an asymmetric double-cantilever beam (ADCB) test. The effects of oligomer and copolymer composition on interfacial adhesion were investigated. The results showed that the interfacial adhesion of the PS/SAN interface was increased significantly after removing the residual oligomer from the SAN. The interfacial adhesion was also measured for five-purified SAN materials in the range 17–31 wt%. The highest level of PS/SAN adhesion was observed for 17% AN (acrylonitrile) materials. In addition, the interfacial adhesion of a mixture of diblock and random copolymer was measured in order to investigate which is the most effective method. The results showed that mixture systems are more cost-effective with higher adhesion, which is independent of temperature. Atomic force microscopy showed that a single craze ahead of the crack is a possible failure mode during PS/SAN interface fracture.
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Keywords: interfacial adhesion; oligomer; interfacial layer; random copolymer; block copolymer; immiscible polymer joints

INTRODUCTION

A combination of engineering plastics with different application profiles have recently become increasingly popular for several reasons.[1,2] Blending different engineering materials may increase their range of potential applications by a synergistic effect, leading to improved mechanical, electrical or thermal properties.

Many commercially available polymer blends are immiscible and form a phase-separated microstructure. In order for immiscible blends to have good mechanical properties, it is necessary to improve the interface adhesion through the addition of compatibilizers. These may react chemically with each phase, or may be miscible with each phase, thus increasing the interfacial fracture toughness. A strategy for enhancing the interfacial adhesion has been to add small amounts of block copolymers to the mixture of immiscible A and B homopolymers.[3–5] These block polymers are believed to segregate to the interfaces and, under the right circumstances, this segregation can lead to significant interface reinforcement.[6–10]

Adhesion must be understood at the molecular level in order to control the adhesion process. There are two main ways to promote adhesion in polymers. The first makes use of entanglements. It is a process where a polymer coils and bends and becomes entangled at the interface between the polymers that are being joined. Brown[8] investigated the entanglement process by measuring the strength of interfaces after copolymers were added. He reported that the entanglement process can greatly enhance adhesion. However, there is a major disadvantage with entanglements. The process requires the use of long polymers with low polydispersity. Although they work well, the chains are prohibitively expensive. Therefore, entanglement is not a practical process for adhesion.

The second process is through chemical reactions. This is just beginning to be explored and many questions remain to be explored.[11] These include: What is the relationship between adhesion and (1) the polymer structure, (2) the position of the reactive sites and (3) the number of reactive sites?

In addition, do entanglements play a role in reactive adhesion? Finally, what is the effect of polydispersity on reactive adhesion? If it is small, these materials and methods are a promising and realistic industrial choice for adhesion.

Poly(styrene-co-acrylonitrile) (SAN) is commonly used in materials such as playground equipment, which require a high impact strength and toughness with low polymer brittleness. The degree of impact strength, hardness and ductility found in SAN_X is a function of x, the acrylonitrile (AN) fraction in the polymer. The greater the AN content in the SAN, the harder the polymer. This enables the materials to be tailored according to the specifics of a given application. The AN content may also affect the adhesion of SAN to other materials. The effect on interfacial adhesion between SAN and polycarbonate (PC), interface was reported by Janarthanan et al.[12]

The main purpose of this paper was to understand the segregation of small molecules such as oligomers at the interface and its effect on interfacial adhesion between PS and SAN as a function of the interfacial layer in terms of compatibility. Adhesion was measured by ADCB (asymmetric double-cantilever beam test) in order to understand the cleaning effect in SAN. In addition, there is a need to understand the mechanism of enhancement between PS/SAN joints.

EXPERIMENTAL
Materials
Samples of a random copolymer of styrene acrylonitrile (SAN) with an AN content of 17%, 24%, 26%, 29% and 31% were supplied by the Chemical Group of Monsanto-Bayer Co. Commercial grade poly(styrene) (PS) was obtained from Aldrich Chemical Company and used as received. In addition, the random poly(styrene-co-vinyl phenol) (PS-ran-PSPh) used as an interfacial layer was synthesized using mass polymerization. The chemical formulas for the polymers are shown in Fig 1.

When undergoing a chemical reaction, the OH group from the vinyl phenol group in PS-ran-PSPh, which is acidic, bonds with the CN functional group from the SAN, which is basic, forming a strong hydrogen bond.

It has been shown that oligomers at the interface between SAN and other materials are detrimental to the entanglement adhesion process.[12] This is believed to occur because the oligomers diffuse to the surface and reduce the entanglement density. To
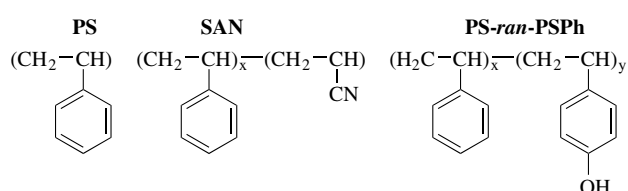
avoid this problem, the SAN must be cleaned. This process removes oligomers from the SAN. The SAN was placed into a solution of approximately 95 wt% chloroform. It was then precipitated by slowly adding the polymer while stirring in a solution of 90 vol% methanol and 10 vol% distilled water. The precipitated polymer was recovered by vacuum filtration and dried by heating at 40 °C for 3 days in an argon atmosphere so as to minimize oxidation of the SAN polymer. Since the reactive adhesion process is expected to work differently than the entanglement process, the effect of the oligomers was explored.

All the SAN and PS polymers were compression moulded in a press at 150 °C at 13.8×10^6 Pa between polished, Kevlar-covered, stainless steel moulds. The resulting samples were bar shaped and had dimensions of $5.0 \times 1.0 \times 0.2$ cm^3 using a chrome-plated mould.

The copolymer solutions were prepared by dissolving the poly(styrene-co-vinyl phenol) (PS-ran-PSPh) in toluene. Solutions of the following copolymers were prepared: (1) 3 mol%–40 mol% random vinyl phenol content in PS-ran-PSPh; (2) 10 mol% diblock brush vinyl phenol; and (3) a 50/50 ratio mixture by mass of 3.5 mol% and 10 mol% random vinyl phenol. The solutions were then spin-cast at 2500 rev min^{-1} onto pieces of silicon wafer to produce a thin film.

The film thickness was determined using an ellipsometer, as an interfacial layer to enhance at interface between the PS and SAN. When the desired thickness of 100 nm was reached, the styrene vinyl phenol (PS-ran-PSPh) solutions were then spun onto the SAN pieces.

The SAN pieces coated with the various PS-ran-PSPh solutions were then joined to the PS pieces by sandwiching them together in their respective moulds for 20 min at 150 °C. Some were joined at 180 °C in order to determine the optimal temperature for the reaction to occur while at the same time allowing PS to melt. The sandwiched samples were allowed to cool for 30 min in the mould to minimize the formation of thermal stress.

Asymmetric double-cantilever beam (ADCB) test
Once cool, the interfacial strength was measured using an asymmetric double-cantilever beam test,[6] as shown in Fig 2. A symmetric double-cantilever beam geometry would create a shear mode (K_{II})
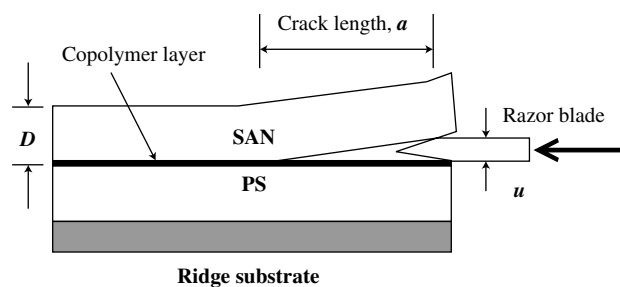

Figure 2. Geometry of the ADCB apparatus and parameters used in calculation of interfacial adhesion (fracture toughness, G_c).

Figure 1. The chemical formulas for polymers used in this study.

component in the stress intensity factor near the crack tip. This type of geometry was chosen because when dealing with two polymers of different hardness using a symmetrical double cantilever, a crack would propagate toward the more compliant material. In an asymmetric system, the more compliant material, in this case PS, was glued to a rigid 2-mm thick aluminum plate. A single-edged razor blade was inserted into the interface between the PS and SAN layers at a constant rate of $100 \, \mu m \, s^{-1}$ using a computer-controlled stepping motor. The length of the resulting crack was measured using a ruler with a precision of 0.05 mm. An average of six to eight measurements were then obtained for each point, and the error bars are displayed on the appropriate graphs.

When the layer is attached to a rigid substrate, the crack length can be converted to an interfacial adhesion (fracture toughness, G_c) using the equation[13]

$$G_c = \frac{3u^2}{8a^4} \frac{ED^3}{(1 + 0.64(D/a))^4} (J \times m^{-2})$$

where E and D are the Young's modulus and thickness of the top of the unattached layer (SAN), respectively, a is the crack length and u is the wedge thickness. Kanninen[13] developed this model for a single cantilever beam on an elastic foundation. This method, which was used by Brown[8] in a polystyrene/poly(methyl methacrylate) blend system, appears to fit our data because of the chosen test geometry. The equation involves the assumption that all the energy is dissipated in a very small region ahead of the crack tip. It was also assumed that the released energy only comes from the bending of the beam. For this reason, it was necessary that the blade be inserted slowly so that the crack length achieved its equilibrium value. The G_c value, which was then calculated, measures the amount of energy with which the interface was held together.

Atomic force microscopy

When the blade had been inserted as far as possible, it was then removed and the two layers were then separated. The separated pieces were then examined using atomic force microscopy (AFM) with a scanning probe microscope (SPM, Dimension SPM-3000 by Digital Instruments). AFM measures both the topography and the surface plot. The friction mode measures the plastic deformation of the polymer.

RESULTS AND DISCUSSION

The development of the thickness on the interfacial adhesion of PS/cleaned SAN is shown in Fig 3. No enhancement of G_c was observed at 31 AN content for the PS/SAN joint, irrespectively of the thickness of the interfacial layer thickness. While G_c for PS/SAN (17 AN content) increased with increasing interfacial layer thickness, and reached approximately $100 \, J \, m^{-2}$ at an interfacial layer of 170 nm. In the case of PS/SAN (24
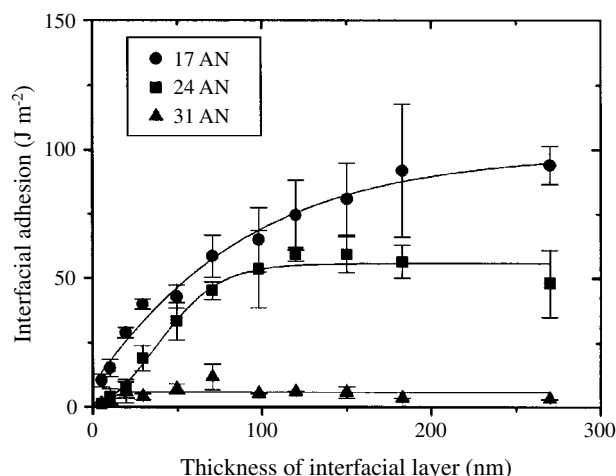

Figure 3. Thickness dependence of PS/cleaned SANs bilayer (10 mol% of vinyl phenol in PS-*ran*-PSPh, at 150 °C for 30 min).
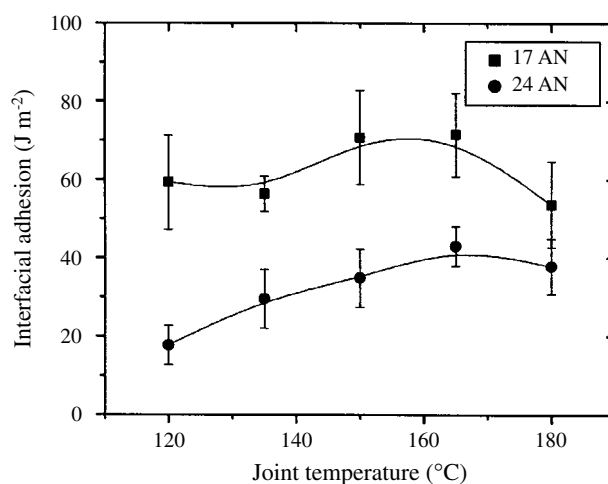

Figure 4. Temperature dependence of PS/cleaned SAN (10 mol% of vinyl phenol in PS-*ran*-PSPh).

AN content), G_c increased with increasing copolymer layer thickness, and then remained constant at an interfacial layer thickness of 100 nm.

Figure 4 shows the relationship between G_c of PS/cleaned SAN with a 10 mol% of vinyl phenol interfacial layer and the annealing temperature at which DCBT specimens were fabricated. The interfacial adhesion for PS/SAN (cleaned 17AN) was independent of temperature, while that for the PS/SAN (cleaned 24AN) increased slightly with temperature. The interfacial adhesion of the uncleaned SAN (without extracting oligomers from SAN) with PS joints is shown in Fig 5. The interfacial adhesion (G_c) increased with decreasing AN content in the SAN, and increased with increasing vinyl phenol concentration up to approximately 18 mol%. However, G_c decreased with increasing vinyl phenol concentration. G_c was very low both at lower concentration (except 17 AN) and higher concentration of vinyl phenol.

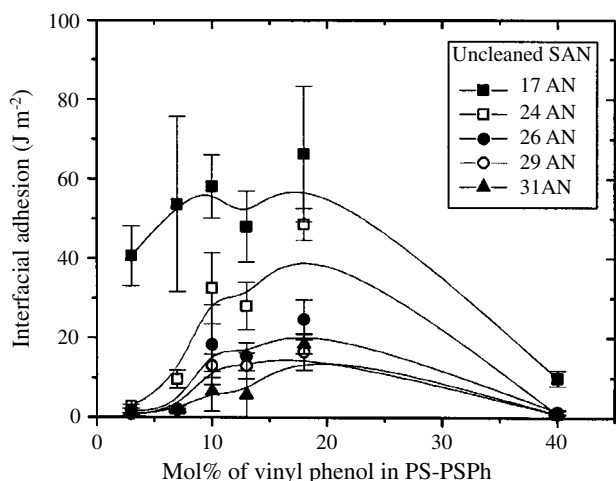The G_c value of cleaned SAN (without oligomers) with PS joints is shown in Fig 6. The interfacial

Figure 5. Interfacial adhesion as a function of content of vinyl phenol in PS-*ran*-PSPh for uncleaned SAN/PS joints.
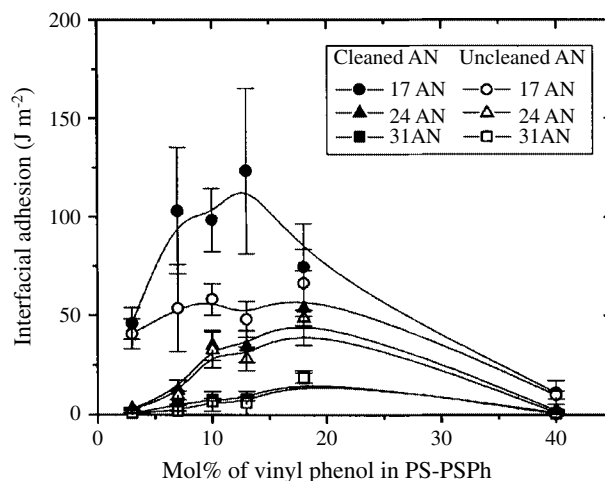

Figure 6. Interfacial adhesion as a function of content of vinyl phenol in PS-*ran*-PSPh for cleaned SANs/PS joints.

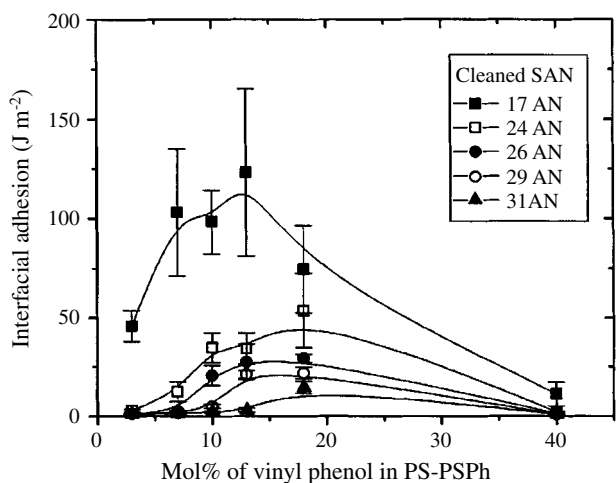**Figure 7.** Influence of the presence of oligomers on interfacial adhesion for PS/SAN.

adhesion of the cleaned SAN/PS joints shows similar features to those of uncleaned SAN/PS joints.

Changes in interfacial adhesion with increasing vinyl phenol concentration in PS-*ran*-PSPh are shown in Fig 6. At low (3 mol%) and high (40 mol%) vinyl phenol concentration, the interfacial adhesion was very low except with 17AN at 3 mol%. However, the interfacial adhesion increased up to 18 mol% in vinyl phenol. These changes in the interfacial adhesion between PS and SAN are reflected in the interface topography. The effect of oligomers on interfacial adhesion for PS/SAN is shown in Fig 7.

The adhesion strength of the cleaned samples was much stronger than that of uncleaned samples, particularly at lower AN concentration in the SAN. It is quite clear from the effect of the oligomers on interfacial adhesion between the PC/SAN interface by Janarthanan *et al*.[12] The interfacial adhesion decreased nonlinearly and reached a plateau beyond a certain oligomer concentration. Because the driving force results from the interfacial attraction, low molecular weight species migrate more easily and faster, and

enhance the interface in the low molecular weight fraction. This segregation effectively dilutes the entanglements between PS and SAN, and reduces the interfacial adhesion between the two components.

It is well known that commercial polymers synthesized using comonomers contain low molecular weight species such as monomers, oligomers and various other additives. Recent theories and experiments[14–16] suggest that shorter chains accumulate at the interface and lower the interfacial tension of immiscible blend systems. Hariharan *et al*[17] suggested that this preferential partitioning of the shorter chains to the interface is purely due to entropic effects, and becomes more pronounced as the difference between the molecular weights of the chain increases.

The AFM pictures of PS/SAN (cleaned 17AN) with 7 mol% vinyl phenol in the PS-*ran*-PSPh layer are shown in Fig 8. The fractured surface was observed to be quite rough on both PS and SAN sides, showing strong adhesion, as shown in Fig 6. Their failure mode was observed to be cohesive. In the case of the SAN side, most of the surface was covered by a vinyl phenol coated surface, while a fractured fibre pull-out was observed from some lines in the SAN side.

The AFM images in a very weak system such as PS/SAN (cleaned 31 AN) with 40 mol% vinyl phenol in PS-*ran*-PSPh layer are shown in Fig 9. As shown
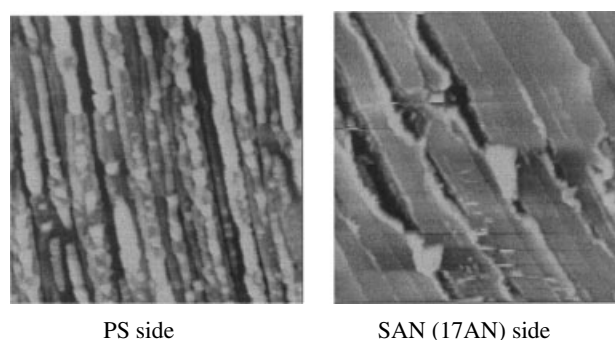

PS side SAN (17AN) side

Figure 8. AFM pictures of PS and SAN side for PS/SAN (cleaned 17AN) with 7 mol% of PS-*ran*-PSPh interfacial layer.
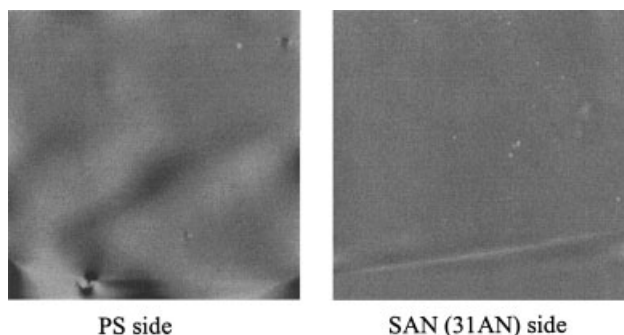
Figure 9. AFM pictures of PS and SAN side for PS/SAN (cleaned 17AN) with 40 mol% of PS-*ran*-PSPh interfacial layer.

by AFM pictures, the fractured surface such as weak adhesion reveal a smooth surface, showing very weak adhesion and an interfacial failure mode between the PS and the vinyl phenol coated SAN side.

The measured interfacial adhesion values (fracture toughness, G_c) were found to depend on the amount of AN in the SAN composition. Figure 10 shows the interfacial adhesion between PS and SAN as a function of AN composition. As shown in that figure, the adhesion decreases monotonically with increasing AN content, irrespective of the interfacial layer containing vinyl phenol. It is natural that the adhesion force of PS/PS (pure PS, without AN content) be up to approximately $500\,J\,m^{-2}$ (for the same joint conditions). Therefore, the adhesion force of the 17% AN in the SAN with a PS joint was lower than that of the PS/PS joint. The order of the interfacial adhesion was 13 mol% > 7 mol% (and 10 mol%) > 18 mol% > 3 mol% > 40 mol% vinyl phenol in the PS/SAN (cleaned 17AN) joints, as shown in Fig 10. There are two processes in relation to vinyl phenol, the reaction rate and diffusion competition. It is interesting to note the combined effects of diffusion and reaction at the interface since the vinyl phenol layer reacts with both AN in SAN and diffuses at different vinyl phenol compositions. Diffusion and reaction are the two competing driving forces for enhancing the
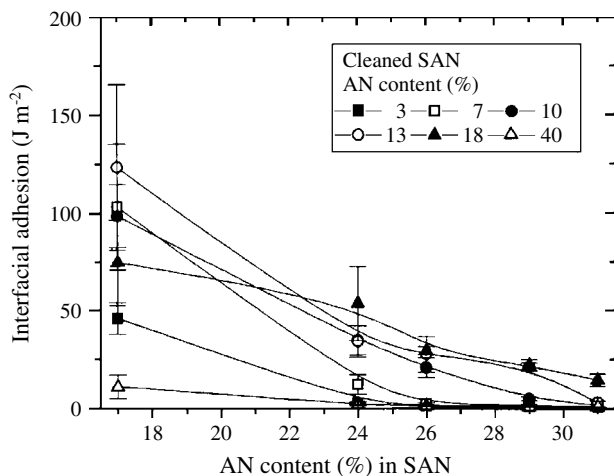
interfacial adhesion for different levels of the vinyl phenol composition layer.

However, in the case of the PC/SAN system reported by Janarthanan *et al*,[12] adhesion between SAN and PC reached a maximum for 24 wt% AN content. This is because of optimal thermodynamic interactions for an AN content of 25 wt% in the SAN.[18] In addition, Guest and Dally[19] recently observed a shift in the T_g of PC/SAN blends and attributed this shift to a partitioning of the oligomers.

The molecular weight is a significant factor in reactive adhesion. It has been previously reported that SAN must be cleaned prior to the entanglement process because of the adverse effects of oligomers. However, in this experiments, a SAN with the same AN content but a different molecular weight reacted with random copolymers to adhere to PS with similar G_c values. Therefore, the molecular weight is not a significant factor in the reactive process. As a result, there is no need to clean the SAN when it is used with reactive random copolymers.

The adhesion of an immiscible blend joint with a block copolymer interface layer is generally much higher than that with a random copolymer. However, Kramer *et al*[20] recently reported that a long symmetric random copolymer can be more effective as a coupling agent than a diblock copolymer. Figure 11 shows that the random copolymer has a larger fracture toughness than the diblock for the three most commonly used AN concentrations of SAN: 17AN, 24AN and 26AN. The 17AN-concentration SAN had the highest G_c value and the most significant difference between the random and diblock copolymers.

The PS and SAN pieces were then separated and examined by AFM. This showed that crazing resulted from the crack. The random copolymer had a seemingly wavy surface with a peak closely associated. This type of tight crazing has been shown to present strong adhesion. The diblock copolymer system had a smoother surface of circular sections. This type of crazing usually represents a weaker bond.[6]

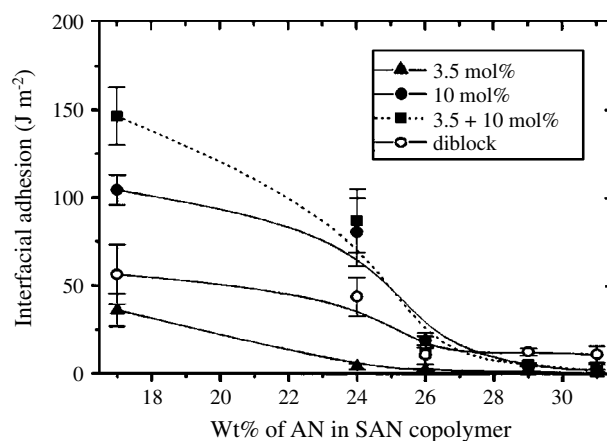The diblock copolymer system was held together by micelles at the interface. It is the point where part A of

Figure 10. Interfacial adhesion as a function of AN content for cleaned SAN/PS.

Figure 11. Interfacial adhesion of PS/SAN with random (PS-*ran*-PSPh) and diblock copolymer (PS-*block*-PSPh) layer.
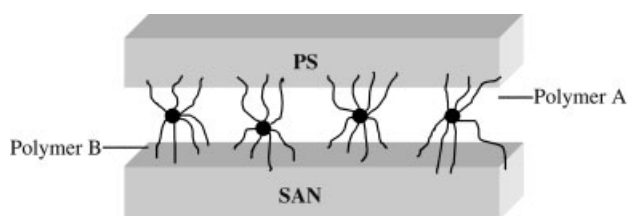
Figure 12. Micelles formed by diblock copolymer.

the copolymer is entangled with polymer A and part B is entangled with polymer B, as shown in Fig 12.

However, the micelles are not adequate for holding the whole system together. They are not deep, which indicates that the diblock copolymer is only at the surface of the PS and SAN. In the random copolymer system, the entire interface is active, which leads to much stronger adhesion. The copolymer was entangled with the PS going very deep into the materials, which is evident from the depth of the cracks left when the system was separated. The random copolymer was also able to react more often with the SAN. This is why the waves are so close together, as shown in Fig 13.

It is evident from the experiments above, that the random copolymer represents a much more effective method of adhesion. This is because (1) it is temperature independent; (2) it is molecular weight independent; and most importantly (3) the vinyl phenol (PS-*ran*-PSPh) was able to undergo mechanical bonding, entanglement with the PS, and hydrogen bonding and a reaction with the SAN, leading to a much stronger interface. The much more effective random copolymer is also the less expensive of the two. Since the random copolymer is a combination of entanglement and reactions, it is important to determine the optimal number of reactive groups of the SAN and vinyl phenol (PS-*ran*-PSPh).

For this, the system was made of PS and SAN at five AN concentrations and various vinyl phenol levels in the PS-*ran*-PSPh. The systems that had a 17AN concentration had the greatest fracture toughness (adhesion) for their respective vinyl phenol levels. This is because, if there is too much AN in the SAN, the PS-*ran*-PSPh makes very small loops in order for the vinyl phenol to react with the AN. This results in very few entanglements on the PS side. Systems consisting of 3.5 mol% and 40 mol% vinyl phenol (PS-*ran*-Ph) did not exhibit strong adhesion. The 3.5 mol% vinyl phenol entangled itself in the PS in very large loops because the groups that reacted
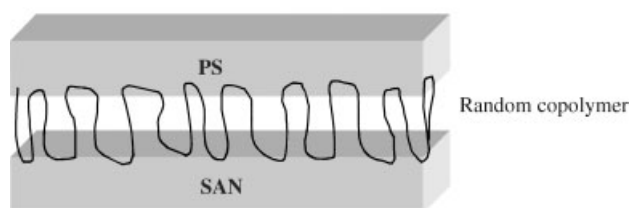
with the AN were wide spread. The 40 mol% PS-*ran*-PSPh mainly reacted with the SAN side because of the proximity and abundance of phenol groups in the vinyl phenol (PSPh). Therefore, the loops were small and were only on the SAN side.

The systems containing the 10 mol% vinyl phenol random copolymer PS-*ran*-PSPh had the strongest interfacial adhesion at almost all AN concentrations in the SAN. The weight-average molecular weight of the PS-*ran*-Ph was 100 000 g mol^{-1}. Each monomer is 104 g mol^{-1}. This means that there were 961.5 monomers, of which 10% were reactive. Thus, there were 96.2 reactive groups per chain. That is sufficient to react with the SAN while still having large enough loops in between the reactive groups that can entangle in the PS. The typical reaction to make a random copolymer will have a natural distribution of both molecular weight and number of functional groups. Since a narrow distribution is difficult to obtain, the effects of polydispersity must be tested. The molecular weight has already been shown to have little effect on a random copolymer system as was expected. This is because, no matter how long or heavy the polymer chain may be, the presence of functional groups and the spacing between them will remain the same for a given mol% in vinyl phenol.

Polydispersity in terms of vinyl phenol content mixed with 10 mol% would occur if the off-peak mol% vinyl phenol is mixed the 10 mol% containing an off-peak 3.5 mol% vinyl phenol in a 50/50 ratio by mass. The G_c of the system was then calculated. As shown in Fig 11, not only did the existence of the off-peak copolymer not have a detrimental effect on the fracture toughness, the polydispersity actually resulted in an enhancement of the interfacial adhesion. This is a highly valuable finding. The reason for the enhancement is as follows. As previously stated, 3.5 mol% vinyl PS-*ran*-Ph entanglements with PS formed very large loops. The 10 mol% PS-*ran*-Ph reacts quite well with the SAN forming slightly smaller loops, which also entangle with the PS. As shown in Fig 14, the large 3.5 mol% loops then connect with the 10 mol% loops in a Velcro-like entanglement forming an even stronger bond between the two originally immiscible polymers.
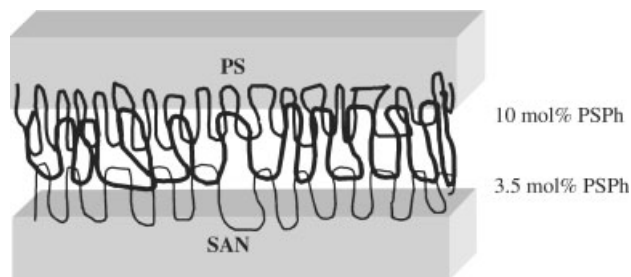

Figure 13. Tight wave crazing formed by random copolymer.

Figure 14. Velcro-effect of random copolymer mixtures of 3.5 mol% and 10 mol% vinyl phenol.

CONCLUSIONS

The effect of oligomers and vinyl phenol on the interfacial adhesion of fraction PS/SAN interfaces was investigated. The incorporation of a mixture of random copolymers was found to improve dramatically interfacial adhesion.

Adhesion of a cleaned SAN was much stronger than that of an uncleaned SAN, showing an oligomer effect in PS/SAN interfaces. The maximum adhesion was observed at the PS/cleaned 17AN with 7–13 mol% vinyl phenol, while adhesion was observed both at low and high vinyl phenol concentrations in PS-*ran*-PSPh layer, reflecting the competition between diffusion and reaction rate.

As shown in a prior study, Brown *et al*[7] demonstrated that a random copolymer is less effective in increasing interfacial adhesion than a block copolymer. The random copolymer used in this study, PS-*ran*-PSPh, was also less effective than a block copolymer. However, the random copolymer was more effective than the black copolymer in increasing adhesion with the same reactive sites of 10% of PS-*ran*-PSPh and PS-*block*-PSOH. In particular, the interfacial adhesion of the mixture of 3.5 mol% of the random copolymer with low adhesion, and of the 10 mol% random copolymer with higher adhesion, was dramatically enhanced.

The results of the above experiments have significant applications. It has been shown that the less expensive (by a factor of four), reactive random copolymers are better for a number of reasons. Besides being more cost-effective, they perform the necessary adhesion that is independent of temperature and molecular weight, which allows them to be used as received. They also facilitate the process by undergoing both chemical and mechanical bonding, which allows for very large fracture toughness. The random copolymers can be also produced in large quantities because the polydispersity, which results from the natural distribution during the production process, actually enhances interfacial adhesion. Therefore, the least expensive method of adhesion is also the most efficient.

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