tion. In addition, the phenyl ring in the center of the molecule might also reduce the extent of electron delocalization. Although the implications of such effects for the saturation behavior are uncertain, we consider that a reduction in the extent of electron delocalization would tend to reduce the chain length at which saturation occurs and therefore does not provide a satisfactory explanation of why we observe saturation at considerably greater chain lengths than theory predicts. In these longchain polyene oligomers (with terminal and central phenyl groups), it is conceivable that bond alternation is reduced, thereby increasing the chain length at which saturation occurs. However, we do not see any evidence for reduced bond alternation in the absorption spectra. In addition, the effect of the end groups on  $\gamma$  is both expected and observed to be small in such long molecules (34).

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## The Use of Graft Copolymers to Bind Immiscible Blends

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Computer simulations and experimental studies were combined to design copolymers that enhance the strength of polymer composites. These copolymers contain side chains that associate across the boundary between phase-separated regions to form a "molecular velcro" that effectively binds the regions together. This behavior significantly improves the structural integrity and mechanical properties of the material. Because the side chains can be fabricated from a large class of compounds, the technique greatly increases the variety of copolymers that can be used in forming high-strength polymer blends.

Polymer alloys or blends provide the advantage that the properties of the material can be controlled by varying the type and quantity of polymers that go into the mixture. In this way, the composite can be tailored to exhibit the desired optical, electrical, mechanical, or rheological properties for a variety of specific applications. The actual fabrication of polymer blends, however, poses significant challenges. Most polymer blends are immiscible, and thus, the components phase separate into distinct, macroscopic domains. To enhance the structural integrity and mechanical properties of the resulting material, copolymer "compatibilizers" are added to the mixture. These chains effectively act as high molecular weight surfactants: They localize at the interface between the immiscible polymers, lower the interfacial tension, and disperse the incompatible polymers into smaller domains. Consequently, the degree of adhesion between the phase-separated regions and the me-

chanical properties of the material are significantly enhanced.

Studies have demonstrated that graft copolymers act as highly effective compatibilizers (1). Graft copolymers contain a backbone and side chains ("teeth") that emanate from the backbone. We have coupled computer simulations with experimental studies to design graft copolymers that act as "molecular velcro" (2): The teeth intertwine across the polymer-polymer interface and effectively bind the two phase-separated regions (Fig. 1). As our findings show, this behavior dramatically improves the mechanical properties of the composite material. Because the teeth are chemically distinct from the phase-separated homopolymers, and may in fact be incompatible with the homopolymers, this technique significantly increases the variety of materials that can be used as compatibilizers for multiphase and multicomponent materials.

We first describe the results of the Monte Carlo computer simulations and then discuss the findings on the comparable experimental system. Simulations constitute powerful tools in such studies because the model allows the chains to self-assemble into the preferred microstructure. Consequently, the simulations can provide significant information about the morphology of the system. In addition, the computer graphics allow us to visualize the

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location and conformation of the chains within the mixture. In our study, we considered a four-component blend composed of two immiscible, phase-separated homopolymers, A and B, and two types of graft copolymers, AC and BD (Fig. 1). We represent the interface between the two homopolymers as a penetrable plane in the middle of a  $64 \times 64$  $\times$  126 cubic lattice. We introduce the following potentials to differentiate the two regions:

$$U_{A}(z) = \begin{cases} 0 & z > 63 \\ +\Delta_{A} & z < 63 \end{cases} \text{ and} \\ U_{B}(z) = \begin{cases} +\Delta_{B} & z > 63 \\ 0 & z < 63 \end{cases}$$
(1)

The parameters  $\Delta_A$  and  $\Delta_B$  represent the respective monomer-homopolymer interaction energies. The effect of the potentials is to introduce an energetic penalty for A sites being in the B region (lower half of the lattice) and, correspondingly, for B sites being in A (upper half of the lattice). As a consequence, when  $\Delta_A$ ,  $\Delta_B > 0$ , the A monomers prefer the A region, and the B monomers prefer the B region.

We introduce the AC and BD graft copolymers, which are modeled as self-avoiding random walks. The backbones of the AC copolymers are formed entirely from A segments, whereas the teeth are formed from C units. In a similar manner, the backbone of the BD chains are formed from

**Table 1.** Characteristics of the polymers. The heterogeneity index,  $M_w/M_n$ , is the ratio of the weight-averaged to the number-averaged molecular weight and indicates the distribution of chain lengths in a polydisperse sample. The nondeuterated PMMA and PEA form the backbones of the respective graft copolymers, whereas the teeth are formed from PS.

Polymer	M <sub>w</sub> /M <sub>n</sub>	M <sub>w</sub>
d-PEA	1.1	149,000
d-PMMA	1.1	182,000
PMMA	2.5	145,000
PEA	2.5	150,000
PS	1.06	14,600

**Table 2.** Mechanical properties of the materials. The Young's modulus is the initial stress/strain ratio in the material, the stress at break is the value of the applied stress that causes the material to break, and the tensile strength is a measure of the resistance to stretching. Measurements were made on six optically uniform tensile specimens. The standard deviation from the average value is  $\pm 5\%$ .

Sam- ple	Young's modulus (kPa)	Stress at break (kPa)	Tensile strength (mJ)
S1	26,500	3,260	0.90
S2	63,500	9,530	2.5

B segments, and the D segments are the teeth. In the experimental system, the high interfacial tension between the immiscible homopolymers drives the grafts to the A-B boundary. In our computer model, this effect is simulated by introducing an attractive interaction,  $\Delta_{CD}$ , between the C and D teeth. All other interaction energies were set equal to zero.

The graft copolymers can move about the lattice through the bond fluctuation algorithm (3). To determine whether a move is accepted, we invoke the Metropolis algorithm (4). In particular, moves that reduce the energy of the system are accepted with unit probability, and moves that increase the energy of the system are weighted by the probability  $\exp(-\Delta E/kT)$ . The parameter  $\Delta E$  is the change in energy associated with the movement of a monomer, k is the Boltzmann constant, and T is temperature.

The graphical output from the simulation, which provides a "snapshot" of the equilibrated system, is shown in Fig. 2. The C-D attraction drives the graft copolymers



**Fig. 1.** A diagram of the interlocking teeth at the interface between two immiscible homopolymers, A and B. The backbones of the respective graft copolymers are also formed from A and B monomers. The teeth, on the other hand, are made up of C and D monomers.

to associate, but the A-B repulsion prevents entire chains from crossing the boundary. Consequently, the chains are localized at the interface, with the C and D teeth intertwining across the A-B layer. The localization of the graft copolymers can also be observed in the polymer density profiles, which display a significant peak at the interface (Fig. 2B).

Because the simulations reveal that the teeth thread through and bind across the interface, we predict that these side chains will reinforce the interface and improve the overall mechanical properties of the blend. The simulations provide guidelines for synthesizing such interfacially active graft copolymers. Specifically, the respective backbones can be fabricated from the incompatible polymers, A and B. The teeth, however, should be highly compatible. The latter condition can also be achieved by having chemically identical teeth on both copolymers, that is, using AC and BC graft copolymers in the A-B mixture. Because this prescription involves fewer chemical species and therefore facilitates the experimental studies, we adopted this system for testing our predictions.

The immiscible A and B homopolymers chosen for the experiments are deuterated poly(ethyl acrylate) (d-PEA) and deuterated poly(methyl methacrylate) (d-PMMA). Graft copolymers of PEA-polystyrene (PS) and PMMA-PS were synthesized as described (5) and consisted of a polydisperse PMMA or PEA backbone and an average of one monodisperse, randomly positioned PS tooth on each backbone. For experimental contrast, only the homopolymers were deuterated. The characteristics of these polymers are summarized in Table 1. We note that PS is





Fig. 2. (A) "Snapshot" from the computer simulation. The respective backbones are red and green, whereas the teeth are yellow and violet. The diagonal line through the figure represents the boundary between the A and B regions. The length of the backbones was fixed at 20 segments. All graft copolymers contain three teeth, each seven segments in length. The sys-

tem contains 120 copolymers. The parameters are  $\Delta_A = \Delta_B = 1.0$  and  $\Delta_{CD} = -1.2$ . The simulation was run for  $10^{12}$  time steps. (**B**) The density profiles for the C and D teeth versus distance from the interface (z = 63). Solid line, D monomers; dashed line, C monomers.

also immiscible with both PEA and PMMA (6), so all of the polymeric components are incompatible. Furthermore, PEA is a rubbery polymer [the glass transition temperature,  $T_g = -40^{\circ}$ C (7)], whereas PMMA and PS are brittle [ $T_g =$ 100° and 105°C, respectively (7)]. The mechanical properties of the d-PEA-d-PMMA-PEA-PS-PMMA-PS mixture (referred to as a thermoplastic elastomer blend) will depend on the successful intermixing of these different components.

If our predictions concerning the effect of the graft copolymers are correct, the mechanical properties of the three-component blend should be better than the binary homopolymer mixture. To test this assertion. bulk samples of the compounds were prepared by blending in tetrahydrofuran (THF) for 24 hours. Two samples were prepared: a 1:1 weight percent mixture of d-PEA and d-PMMA (S1) and a 0.3:0.3:0.2:0.2 mixture of d-PEA, d-PMMA, PMMA-PS, and PEA-PS (S2). After evaporating the solvent and drying in a vacuum at 60°C, thin strips (0.042 mm thick) of each compound were compression molded at 160°C and cut into tensile bars. The stress-strain measurements were performed at 25°C on an Instron at a rate of 0.51 mm/min. The results (Table 2) show that the three-component blend does indeed have superior properties to the binary mixture. The Young's modulus, stress at break, and tensile strength are increased by a factor of 3 by the addition of graft copolymers. (We note that similar results were obtained in the case where the PEA-PS

Α



**Fig. 3.** Optical micrographs showing the d-PEAd-PMMA homopolymers (**A**) without the graft copolymers and (**B**) with the copolymers.

copolymers contained an average of three PS teeth.)

Further insight into the role of the graft copolymers can be obtained by examining the bulk samples with optical microscopy (Fig. 3). The micrographs show that d-PEA-d-PMMA samples have large domains of different optical scattering contrast. On the other hand, the samples containing the graft copolymers appeared optically homogeneous.

Although the mechanical and optical microscopy results confirm that graft copolymers can enhance blend properties, we must examine the interface to determine the physical basis for this behavior. We used dynamic secondary ion mass spectrometry (SIMS) to probe the composition at the phase boundaries. Thin films of the three-component blend were prepared. In particular, a 788 Å thick film of volume fraction  $\phi = 0.85$  d-PMMA and  $\phi = 0.15$  PMMA-PS copolymer was spin-coated from toluene solution onto a native oxide-covered silicon wafer. The film was annealed in a vacuum  $(10^{-4})$ torr) at 175°C for 24 hours. Because the surface tension of PS is lower than that of PMMA (8), annealing this layer causes the PMMA-PS graft copolymers to segregate to the surface. The sample was then covered with another layer, 817 Å thick, of d-PEA ( $\phi$  = 0.85) and PEA-PS ( $\phi$  = 0.15) graft copolymer floated from the surface of water. The sample was further annealed for 24 hours at 175°C. This procedure facilitates the segregation of the PEA-PS copolymer to the now PSrich interface.

The SIMS results are shown in Fig. 4, where we plot the volume fraction of d-PEA and d-PMMA and the graft copolymers as a function of distance from the vacuum interface. A significant fraction



**Fig. 4.** SIMS profiles of the volume fraction of d-PEA (open circles) and d-PMMA (open circles) and the graft copolymers (open triangles) as a function of distance from the vacuum surface. The large peak at the polymer-polymer interface arises from the graft copolymers. For clarity, the graft copolymer trace is multiplied by a factor of 3.

of the graft copolymers segregates to the polymer-polymer interface, in agreement with the predictions from the simulations. Because PS is highly immiscible with both PEA and PMMA, the peak at the interface must arise from the PS teeth associating across the d-PEA-d-PMMA boundary. The graft copolymers that do not reside at the interface can be assumed to form micelles with PS cores. [The ratio of the copolymer at the interface versus the amount present as micelles can in principle be calculated by using the above Monte Carlo simulations (9).]

The SIMS results confirm the prediction that the teeth form a "molecular velcro" at the interface. The optical results reveal that the "velcro" not only interlinks the phaseseparated regions, but also reduces the interfacial tension and effectively intersperses the domains of the two immiscible homopolymers. Both effects contribute to the observed enhancement in the mechanical properties of the three-component blend.

As noted above, all of the polymeric components in the system are immiscible. However, by placing one of the incompatible components in the teeth of both graft copolymers, we can fabricate a highstrength blend. Because the teeth can be formed from a broad class of polymers and graft copolymers can be easily and inexpensively synthesized, this prescription greatly increases the variety of copolymers that can be used for enhancing the structural integrity and mechanical properties of polymer composites.

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