

Reinforcement of Polymer Interfaces with Random Copolymers

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We demonstrate that long random copolymers (monomer fraction $f = 0.48$) can be more effective than a long symmetric block copolymer in strengthening interfaces between immiscible homopolymers. The effectiveness of the random copolymer is inferred to result from each random copolymer crossing the interface multiple times, entangling with the homopolymer on either side of the interface; as f is increased from 0.48 to 0.77, the effectiveness decreases markedly as the copolymer becomes less entangled with the homopolymer (corresponding to the minor component in the copolymer) on one side of the interface.

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The very weak interfaces between immiscible homopolymers A and B may be markedly strengthened by adding small amounts of a diblock copolymer, consisting of a long block of A covalently joined to a long block of B [1–7]. These A - B diblock copolymers have been shown to organize themselves at the interface [2] to form molecular “reinforcing rods,” with the A block well anchored by entanglement of the A side of the interface and the B similarly anchored on the B side.

In practice, however, long diblock copolymers have a number of disadvantages as reinforcing agents; they are costly to produce, and they have a strong tendency to form micelles, thus drastically slowing the kinetics of their segregation to interfaces [8]. Recently Brown and co-workers [4,5] showed that a long random copolymer, made by inexpensive free radical polymerization with A and B units randomly arranged along the chain, was surprisingly effective in reinforcing polymer interfaces. Their results for a $\text{PS}_f\text{-}r\text{-PMMA}_{1-f}$ copolymer (PS = polystyrene; PMMA = polymethylmethacrylate; $f = 0.7$) at a PS/PMMA interface, while producing a fracture energy $G_c = 80 \text{ J/m}^2$, well short of their best results for long PS - PMMA block copolymers ($G_c = 330 \text{ J/m}^2$), were remarkable in light of their hypothesis that the random copolymer organizes itself so as to make multiple excursions across the interface. Such an organization, which finds some theoretical support in the recent literature [9], should be disfavored by a value of the PS fraction f that differs significantly from 0.5. We have tested Brown’s hypothesis by comparing the reinforcing effects of diblock copolymers of dPS - PVP (PVP = poly-2-vinylpyridine) at PS/PVP interfaces with those of long random copolymers $\text{dPS}_f\text{-}r\text{-PVP}_{1-f}$, where

f was varied from 0.48 to 0.77. We determine directly the number of monomers per effective crossing of the interface by the random copolymer and find that it depends markedly on monomer fraction f .

Using free radical polymerization we synthesized three random copolymers ($\text{dPS}_f\text{-}r\text{-PVP}_{1-f}$) of deuterated polystyrene (dPS) and poly-(2-vinylpyridine) (PVP): $f = 0.48$, $N_n = 7000$, $\text{PDI} = 2.5$; $f = 0.60$, $N_n = 4200$, $\text{PDI} = 2.7$; and $f = 0.77$, $N_n = 6700$, $\text{PDI} = 2.5$, where N_n and PDI are the number average polymerization index and polydispersity index ($\text{PDI} = \text{weight average}/\text{number average}$), respectively. The composition ratio f was determined by forward-recoil spectrometry (FRES), which gives a direct measure of the fraction of the deuterated component as a function of depth [10,11]. The absence of significant blockiness in the copolymers was verified by proton and ^{13}C NMR. A diblock copolymer of dPS and PVP , previously synthesized by anionic polymerization, was used for comparison [3]. The polymerization indices of its dPS and PVP blocks were 800 and 870, respectively, and its PDI was <1.1 .

Interfaces were prepared by spin casting various concentrations of copolymer in toluene solution onto a plate of PVP homopolymer ($N_n = 1000$; $\text{PDI} = 2.4$). After drying, the copolymer-coated PVP plate was welded to a plate of PS homopolymer ($N_n = 1500$; $\text{PDI} = 2.1$) by annealing for 2 h at 160°C (well above the glass transition temperature of both homopolymers) to produce samples for an asymmetric cantilever beam method [3] to measure the interfacial fracture toughness G_c . After fracture, FRES was used to measure the amount of deuterium on each surface of the fracture. Since both the random and block copolymers are labeled with deuterium on the

styrene unit, the sum of the deuterium on the two surfaces could be used to determine the areal chain density Σ of the copolymer at the interface. By analyzing the ratio of deuterium on the PS side of the fracture to the total deuterium (Σ_{PS}/Σ) we also gain important information about the fracture mechanism.

We compare the fracture toughness G_c of the PS/PVP interface as a function of areal chain density Σ of the diblock copolymer in Fig. 1(a) with that for the $f = 0.48$ random copolymer in Fig. 2(a). At small values of Σ , G_c hardly increases at all with increasing Σ for both random copolymer and block copolymer additions. Above $\Sigma = 0.004$ chains/nm², the G_c of the interface reinforced by the random copolymer increases rapidly, eventually attaining a value close to 150 J/m². The G_c of the interface reinforced by the block copolymer also shows an increase but only above a $\Sigma = 0.03$ chain/nm², and this increase occurs over a wider Σ regime than for the random copolymer [3]. The G_c from adding the optimum amount of copolymer is also less for the block copolymer [6] than for the random copolymer.

A plot of the ratio of the deuterium on the PS side after fracture to the total deuterium as a function of Σ helps to clarify the failure mechanisms that operate. Figure 1(b)

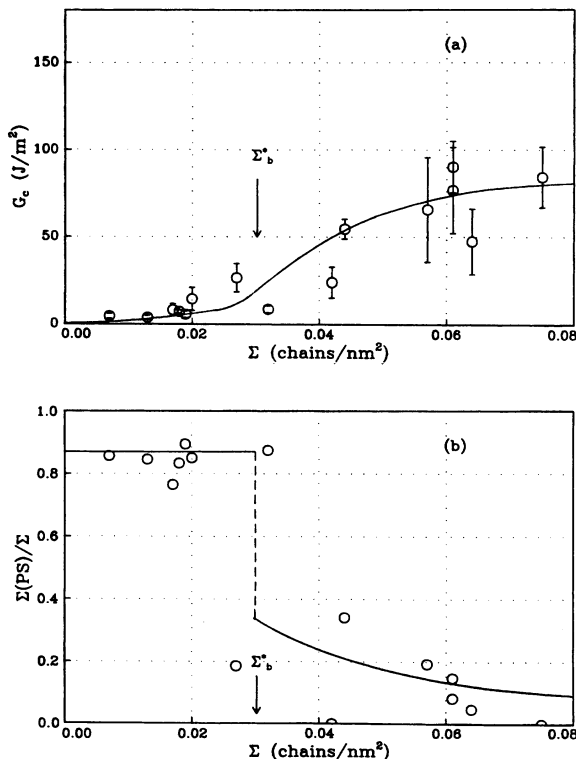


FIG. 1. Reinforcement of PS/PVP interface by a long diblock copolymer dPS-b-PVP. (a) Fracture toughness G_c versus areal chain density Σ . (b) The fraction of dPS found on the PS side of the fracture versus areal chain density Σ . Data from Ref. [3].

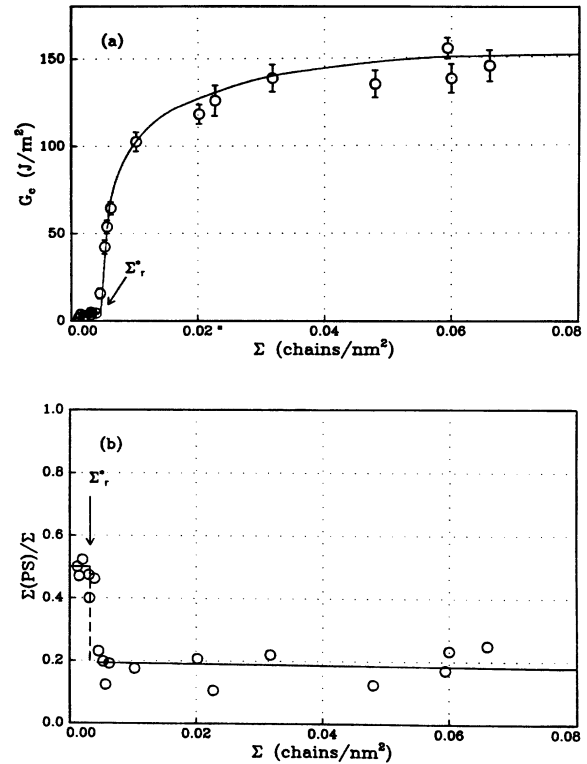


FIG. 2. Reinforcement of PS/PVP interface by a long random copolymer dPS_{0.48}-r-PVP_{0.52}. (a) Fracture toughness G_c versus areal chain density Σ . (b) The fraction of dPS found on the PS side of the fracture versus areal chain density Σ .

shows that almost all the dPS block is found on the PS side up to a $\Sigma_b^* = 0.03$ chain/nm² at which point a transition occurs and beyond which most of the dPS is found on the PVP side. In Fig. 2(b) we see that a similar transition occurs for the PS/PVP interface, reinforced by the random copolymer. In this case, however, the value of Σ at the transition $\Sigma_r^* = 0.004$ chain/nm² is much lower than for the diblock copolymer. Moreover, for $\Sigma < \Sigma_r^*$ only half the dPS is found on the PS side of the fracture.

The fracture transition for the diblock copolymer has been examined in detail previously [3], resulting in the following conclusions which are consistent with the way the diblock copolymer is thought to organize itself at the interface, as shown schematically in Fig. 3(a). For $\Sigma < \Sigma_b^* = 0.03$ chain/nm² fracture occurs near the PS/PVP interface and the diblock copolymers are broken near, but not exactly at, the joint between the dPS and PVP blocks. For $\Sigma > \Sigma_b^* = 0.03$ chain/nm², crazing (a cavitation mode of plastic deformation resulting in a fine fibrillar polymer/void microstructure) occurs on the PS side of the interface, followed by failure of the craze fibrils where the dPS block and the homopolymer PS meet. Since the stress on the interface required to fracture all the block copolymers is given by $\sigma_{break} =$

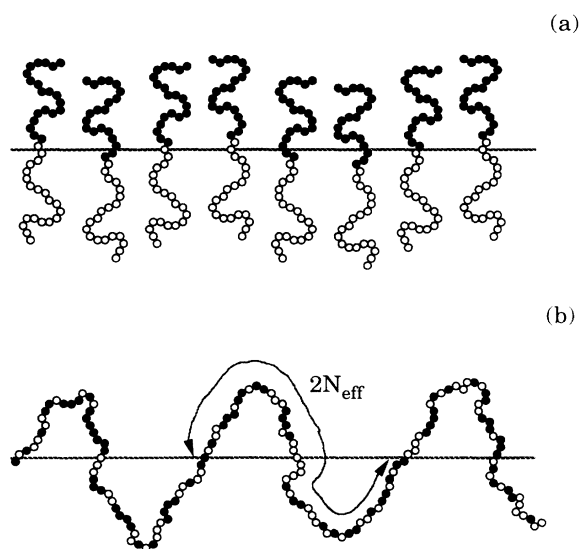


FIG. 3. Schematic illustration of the organization at the interface of (a) the diblock copolymer, which has one crossing per chain, and (b) the random copolymer, which has N_{eff} monomer units per effective crossing of the interface.

Σf_b , where f_b is the force to break a single C-C bond along the backbone, this stress will exceed the crazing stress σ_{craze} of PS above a critical areal chain density $\Sigma_b^* = \sigma_{\text{craze}}/f_b$. From the experimental values of Σ_b^* and σ_{craze} (≈ 55 MPa) we derived an estimate [3] of $f_b \approx 2 \times 10^{-9}$ N in essential agreement with theoretical predictions, indicating that each diblock copolymer chain effectively crosses the interface only once, as expected.

Exactly the same kind of fracture transition from chain scission (without crazing) to crazing followed by craze failure is to be expected for the random copolymer [12]. We used optical microscopy of the fracture surfaces to verify that a wide craze does not form on the PS side for $\Sigma < \Sigma_r^*$ but does form for $\Sigma > \Sigma_r^*$. However, the decrease in Σ_r^* to 0.004 chain/nm² from 0.03 chain/nm² for the diblock copolymer and the fact that equal amounts of deuterium are found on each side of the fracture mean that the random copolymer weavers back and forth across the PS/PVP interface, with each effective crossing forming entangled loops (or ends) in both phases as shown schematically in Fig. 3(b). Such a morphology is consistent both with our result that half of the dPS is found on each side of the fracture for $\Sigma < \Sigma_r^*$ and with a recent theory of the segregation of random copolymer to a fluid-fluid interface [9]. [The fact that half of the dPS is found on each side for $\Sigma < \Sigma_r^*$ also rules out explanations of the reinforcement as due to a nonrandom distribution of dPS and PVP units along the copolymer chain. If the copolymer were so ‘‘blocky’’ (in contradiction to the architecture found by our NMR results) that placing the dPS blocks on one side and the PVP blocks on the other

is responsible for the multiple crossings, we would expect to see more dPS than 50% on the PS side of the fracture in this regime.] On the basis of this morphology we can also explain the decrease in Σ_r^* from the corresponding value for the diblock copolymer. Since the stress to break the random copolymer chain $= \Sigma f_b n_{\text{cross}}$, where n_{cross} is the average number of crossings per chain that are effectively entangled across the interface, the criterion for the transition from chain scission to crazing followed by craze failure becomes

$$\Sigma_r^* = \sigma_{\text{craze}}/(n_{\text{cross}} f_b) = \Sigma_b^*/n_{\text{cross}}. \quad (1)$$

We can therefore estimate the average number of effective crossings per random copolymer chain to be eight, or one about every $N_{\text{eff}} = 900$ units along the chain.

Our results for the less symmetric random copolymers add useful detail to the picture sketched out above. We also observe a transition from chain scission to crazing followed by craze failure for the $f = 0.60$ copolymer, but this transition occurs at $\Sigma_r^* = 0.011$ chains/nm², which corresponds to one effective crossing every $N_{\text{eff}} = 1400$ units. The value of G_c at large Σ (in the craze failure regime) decreases from its value of ~ 150 J/m² for the $f = 0.48$ copolymer to ~ 60 J/m² for the $f = 0.60$ one. For the most asymmetric copolymer, $f = 0.77$, we observe no chain scission to crazing transition at all. Essentially all the dPS is found on the PS side of the fracture at all values of Σ , indicating that if loops were formed on the PVP side of the interface, they were too short to entangle effectively, and thus N_{eff} for this copolymer is greater than $N_n = 6700$. The G_c we observe for interfaces reinforced with the $f = 0.77$ random copolymer is always less than 5 J/m².

Long, symmetric, random copolymers thus can be remarkably effective in reinforcing immiscible polymer interfaces. We have demonstrated that this effectiveness comes about because the random copolymer crosses the interface multiple times, forming loops which entangle effectively with the homopolymer on both sides, thereby confirming the original hypothesis of Brown *et al.* [4]. Of equal importance, we have developed a method, based on measurement of Σ_r^* at the transition from chain scission to crazing, for determining the number of units per effective loop N_{eff} and have used this method to show that N_{eff} increases rapidly as f increases from its symmetric value of 0.5.

PS and PVP are highly immiscible polymers, with a Flory parameter $\chi \approx 0.12$ at the annealing temperature [13]. One might expect that the random copolymer would form a condensed thin film at the interface, penetrating only a little into either homopolymer, leading to a very weak interface. Our results in combination with those of Brown *et al.* show this expectation is misleading. A possible counter argument for the case of small Σ is that a strongly confined film would require that the random copolymer chains be flattened into thin pancakes along the

interface, producing a large loss in entropy. For the small molecule fluid-fluid interface studied by Yeung *et al.* [9], the minimum free energy is achieved by a compromise structure in which the random copolymer is confined to the vicinity of the interface and forms relatively large loops into either phase. While their model is clearly too simplified to give us anything but qualitative guidance [14], the fact that it predicts large excursions from the interface indicates that further theoretical work on the problem, to develop a more realistic model for the random copolymer at a polymer/polymer-melt interface, may be useful.

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- [14] The necessity to maintain a roughly constant polymer density near the interface is a complication in our problem that is not present in the fluid-fluid case of Ref. [9]. Furthermore, the fact that we observe that G_c saturates, and does not decrease, as Σ is increased to very large values, well beyond those shown in Fig. 2, that correspond to random copolymer film thicknesses larger than the radius of gyration of the random copolymer chain, means that the simple confinement argument given here cannot explain all our results.