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Interfacial Reaction Induced Roughening in Polymer Blends

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ABSTRACT: Interfacial reaction between two immiscible polymers can cause changes in the interfacial morphology. We demonstrated this using an aliphatic amine terminated polystyrene (PS−NH_2) and anhydride terminated poly(methyl methacrylate) (PMMA−ah). Interfacial morphologies were recorded using transmission electron microscopy and atomic force microscopy. Coupling of PS−NH_2 and PMMA−ah induced flat interfaces to roughen with a magnitude of roughness around a few hundred nanometers. These morphological changes were explained in terms of the decrease of interfacial tension due to the creation of block copolymers and the thermal fluctuation induced deformations at interfaces.

Introduction

Producing polymer blends with small scale, stable microstructures in short processing times is an important research goal. One of the most popular methods currently used in industry is reactive blending which can result in polymer blends with microstructures ranging from 0.1 to 1 μm after a few minutes of mixing.[1] Recently, Orr et al. (1997) made an important discovery.[2] They blended aliphatic amine terminated polystyrene with anhydride terminated polyisoprene and found that a molecular scale microstructure evolved very quickly. Within only 2 min, the blend acquired a lamellar structure with a length scale of about 30 nm. The estimated interfacial area generation rate in this system is much higher than is possible based on simple shear alone. Orr's results imply that in addition to the classical shear induced droplet breakup there must be another mechanism that promotes interfacial area generation. The most obvious mechanism is the coupling reaction between the polymers at interfaces. However, it is difficult to separate the effects of reaction from that of shearing in the mechanical mixing procedure used by Orr. In this report, we describe experiments carried out under static conditions that demonstrate how block copolymer formation alone can lead to morphological development in polymer blends.

Experimental Section

The materials used in this study were aliphatic amine terminated polystyrene (PS−NH_2) and anhydride terminated poly(methyl methacrylate) (PMMA−ah). The synthesis of these materials was carried out by Cernohous et al.[3,4] The molecular structures of these polymers are shown in Figure 1. The polydispersities of their molecular weight distribution are 1.05 and 1.03, and the degrees of functionalization are 0.95 and 0.9 for PS−NH_2 and PMMA−ah, respectively. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to observe the morphologies of blends at different reaction times. The TEM samples of PS−NH_2 and PMMA−ah (1:1 molar ratio) were prepared by slightly mixing the two homopolymers using a cup-rotor mixer (CSI, MiniMax with rotor diameter of 13 mm) at 200 °C under nitrogen. The mixing procedure was as follows: a total polymer mass of 300 mg is dry-mixed from powder, premelted in the mixer, then subjected to a rotation rate of 30 rpm for 1.5 min, and then quenched in liquid nitrogen. The resulting blends had structures with a range of lamellar domain around a few micrometers (Figure 2). These blends were easy to microtome for TEM observation. Static reactions were carried out by annealing the samples

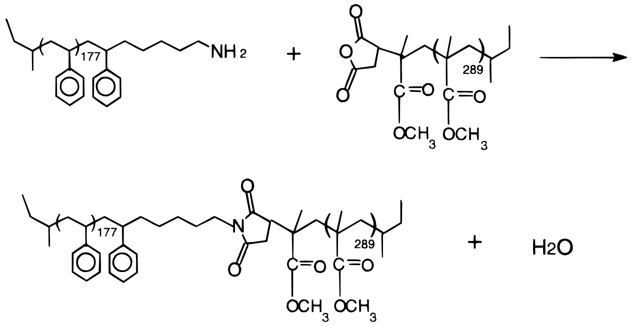

Figure 1. Schematic for coupling reaction between PS−NH_2 and PMMA−ah, leading to the formation of diblock copolymer. The numbers of monomers are from Mn as determined by GPC.

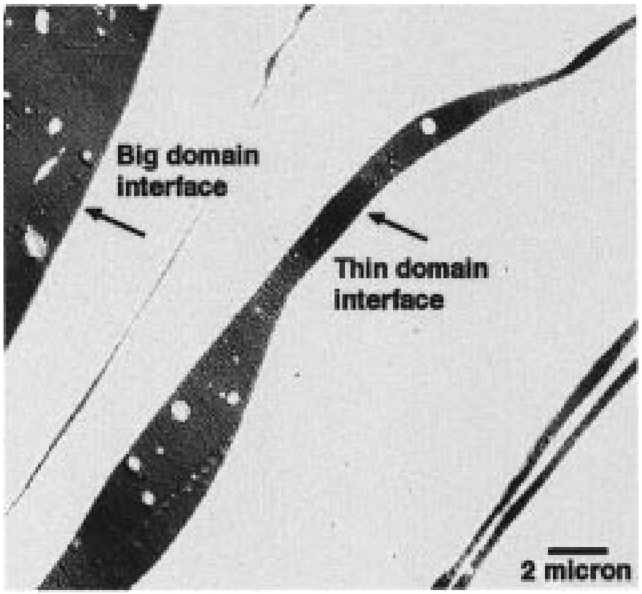

Figure 2. A representative TEM picture of the morphology of slightly mixed blends. PS and PMMA appear dark and light, respectively. These samples represent the starting point for static interfacial polymer reaction during annealing.

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under vacuum (lower than 10 mTorr) at 200 °C for various times. After annealing, the samples were microtomed at room temperature into approximately 50 nm films using a diamond knife with a Reichert Ultracuts microtome. The PS phase was selectively stained with ruthenium tetraoxide vapor, and the interfacial morphologies were imaged with a JEOL 1210 TEM using an acceleration voltage of 120 kV. In TEM pictures PS appears black due to reaction with stain, while PMMA appears lighter.

AFM was used to examine the 2-dimensional interfacial topology. AFM specimens were formed from two polymer layers that were separately solvent-cast onto the surface of a piece of 3 × 1 in.^{2} aluminum foil under an argon atmosphere. A PMMA film was cast first from 1 wt % tetrahydrofuran (THF) solution followed by PS that was cast from 1 wt % cyclohexane on top of the PMMA layer. Each layer thickness was about 10 μm. As with the TEM samples, the coupling reaction occurred during annealing of the layered specimen at 200 °C under vacuum. After reaction, the samples were dipped in cyclohexane for 15 min. The top PS layer was washed away. To confirm that all the PS−NH_2 was removed, we washed an unreacted layered specimen with cyclohexane for the same time and analyzed the remaining sample with gel permeation chromatography (GPC). Within the GPC detection limit we did not observe any PS signal. The interfacial topology was then studied with AFM (Digital Instruments NanoScope III atomic force microscope) using silicon probes in the tapping mode.

Results

Figures 3 show the development of interfacial morphology with annealing in the slightly mixed blends. Before annealing, the interfaces between PS and PMMA are smooth and flat (Figure 3a). Surprisingly, after annealing the sample for only 20 min, the interface is quite rough (Figure 3b). Some parts of the PS domain appear to have pinched off at the interface and moved into the PMMA. Apparently, the interfaces become unstable although we could not identify a dominant wavelength during roughening. After annealing the sample for 1 h (Figure 3c), the interfacial roughness increases further. We approximately localize the roughening zone using two dashed lines in Figure 3c. The magnitude of the width of the roughening zone is about 0.5 μm.

There is an interesting relationship between interfacial roughening and the initial domain size. Figure 3a−c shows the interfaces between large domains of PS and PMMA. Interfaces separating smaller domains (Figure 3d−f) seem to roughen more quickly, propagating from both sides of the thin domains. After 1 h of annealing, lamellae appear throughout the thin domains. The appearance of these lamellar structures indicates the formation of PS−PMMA block copolymer.

We used GPC to assess the extent of reaction in these mixtures.[5] This confirmed that diblock copolymer was formed upon annealing. The extent of reaction after 1 h of annealing was about 25% in the slightly mixed blend. However, after annealing the slightly mixed PS−NH_2 and PMMA−ah for 10 h or longer, GPC analysis revealed new products with molecular weights higher than that of the diblock copolymer. We have not identified these products although they are probably multiblock or grafted copolymers formed through side reactions.

AFM images confirmed the presence of interfacial roughening observed in the slightly mixed samples. Figure 4a,b shows the interfacial topologies between PS and PMMA before and after reaction. Before reaction the interface is flat. After 1 h of annealing the interface becomes rough. The magnitude of the width of the roughening zone (between two dashed lines in Figure 4b) is approximately 0.2 μm. Qualitatively, the rough interfacial topology confirms the occurrence of corrugated cross sections seen by TEM in the annealed blends (Figure 3).

Here we note from GPC measurement that some amount of coupling between PS−NH_2 chains occurred during annealing of the layered specimen. For example, there was about 4% PS−PS coupling after 1 h of annealing of a PS−NH_2 and nonfunctionalized PMMA layered sample. Coupling was not significant during annealing the slightly mixed blends. GPC measurement showed that the PS−PS coupling was less than 1% after annealing a blend of PS−NH_2 and nonfunctionalized PMMA for 1 h at the same temperature. Surface area per unit volume of the layered specimen was much larger than that of the slightly mixed blends. Probably oxygen adsorbed on the surfaces of these samples caused PS−NH_2 to couple with itself.

To determine the amount of block copolymer formed in the layered specimen, the PS layer was washed off with cyclohexane. The PMMA layer was dissolved in THF, and block copolymer was measured by GPC. Owing to the small amount of interfacial area per unit volume of sample, block copolymer detected was roughly equal to only 0.1% of the total amount of the layered specimen. Based on this value, the magnitude of block copolymer coverage at the interface was calculated to be approximately 0.2 chain per nm^2 of interfacial area, which is similar to the values obtained in reactive blending by Guégan et al.[5] The block copolymer coverage in pure PS−PMMA lamellar structure was estimated to be about 0.3 chain per nm^2 based on the results by Russell et al.[6]

Discussion

Jiao also observed interfacial roughing in a system of reactive polystyrene and styrene−maleic anhydride random copolymer (PSMA).[7] He suggested that a microemulsion was formed when the interfacial tension was driven negative due to the creation of graft copolymer at interface. Our experiments are different from Jiao's in two respects. First, in Jiao's experiments the product is randomly grafted copolymer due to the high maleic anhydride content (28 wt %) in the PSMA. In our experiment, well-defined PS−PMMA diblock copolymer was formed within short reaction time. (Only diblock copolymer was detected in the slightly mixed blends within annealing of at least 3 h though there were new products formed after longer time of reaction.) Second, in Jiao's experiments the PS phase is actually a mixture of benzylamine terminated PS and nonreactive PS of different molecular weight. Our system contains nearly monodispersed and nearly completely functionalized PS−NH_2 and PMMA−ah. In addition, the contrast in our TEM pictures is much greater than Jiao's due to the more selective staining of PS relative to PMMA. Finally, the magnitude of roughness of our results is as much as a few hundreds of nanometers, which is almost an order of magnitude greater than was observed by Jiao. These better controlled experiments provide unambiguous evidence of interfacial roughening.

An important conclusion that can be drawn from our experiments is that the interfacial polymer coupling can cause interfacial roughening. Jiao argued that this

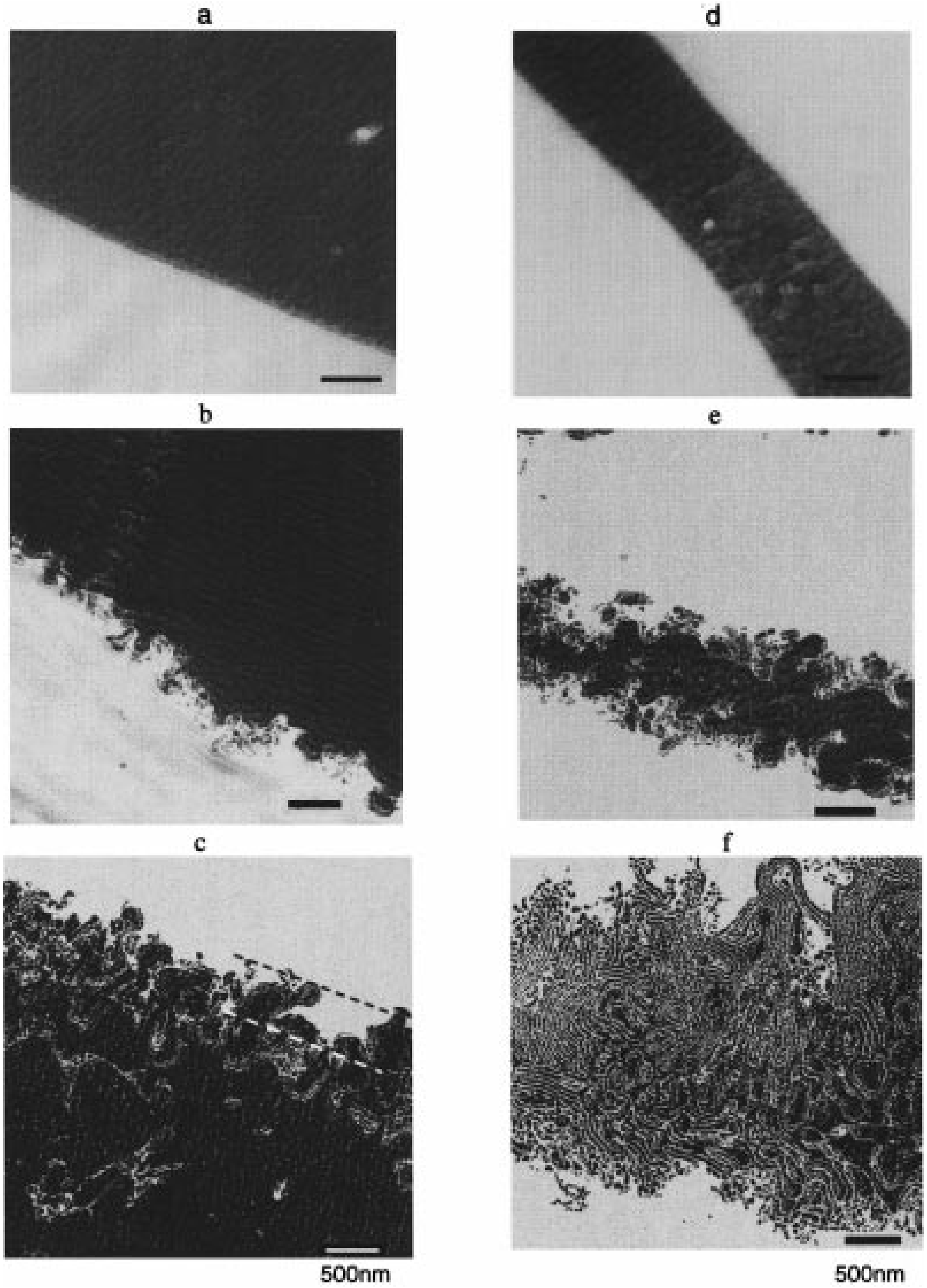

Figure 3. Representative morphologies of PS$-$NH$_2$/PMMA$-$ah blends after static reaction of (a) 0, (b) 20, and (c) 60 min at large domain interface and after static reaction of (d) 0, (e) 20, and (f) 60 min at thin sheet interface at 200 °C. All scale bars are 500 nm. Two dash lines in (c) approximately indicate the roughening zone. The magnitude of its width is roughly 0.5 μm.

roughening is a type of instability resulting from negative interfacial tension, arising from copolymer formation at the interface.[7] However, Milner has suggested that the reduction in interfacial tension due to the presence of block copolymers may have been overestimated.[8] Here we do not attempt to determine the magnitude of the decrease in interfacial tension. However, we speculate that this decrease, due to the formation of block copolymers, is the main cause of interfacial roughening.

This hypothesis can be explained by considering a flat interface saturated by block copolymers (Figure 5a). Thermal fluctuations will induce slight deformations at random locations along the interface. The associated increased interfacial curvature will be accompanied by an increase in the interfacial area (Figure 5b), leading to a local increase in interfacial tension due to a decrease in block copolymer coverage. Together, these effects will increase the total interfacial free energy. If block copolymer does not form, the curved interface will

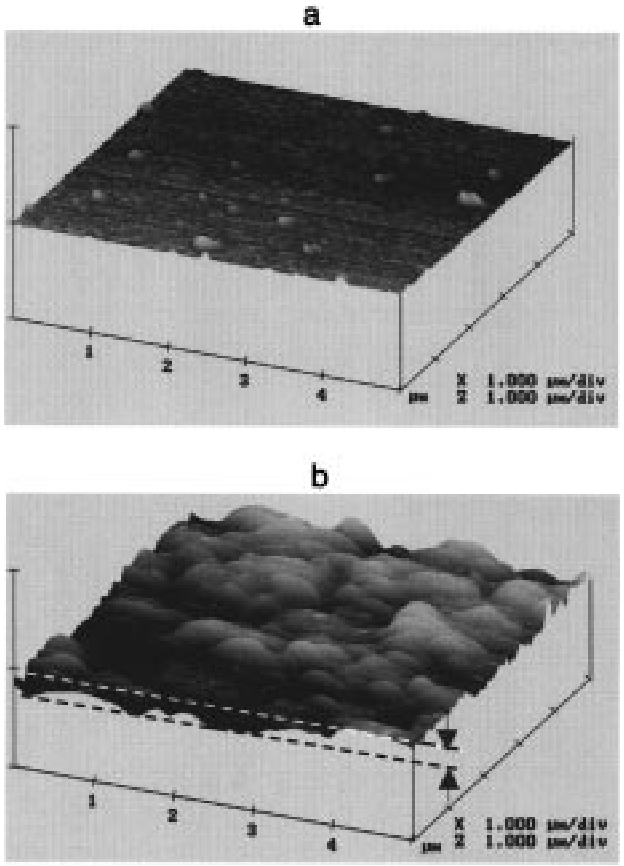

Figure 4. AFM topological images of the interface between PS−NH$_2$/PMMA−ah bilayer. The thickness of each layer is about 10 μm. (a) Before annealing; (b) after annealing for 1 h. The magnitude of the width of the roughening zone between two dash lines is roughly 0.2 μm.

return to its equilibrium flat state. However, at the interface between two highly reactive polymers, block copolymers may form as soon as the block copolymer coverage decreases below the saturation level. These recently formed block copolymers will compensate for the decreased interfacial coverage, returning it to saturation (Figure 5c). This in turn will decrease the interfacial tension and the total interfacial energy. As interfacial fluctuations continue further curvature will develop, eventually forming a very rough interface.

In our explanation, we do not assume that negative or zero interfacial tension is achieved. Theoretical studies show that as the block copolymer coverage increases with reaction time an energy barrier to the diffusion of homopolymer to an interface may develop. The energy barrier is due to the entropy loss involved in the localization of the end of the chain at the interface and the stretching of the copolymer blocks.[9−12] This energy barrier increases with molecular weight of the block copolymer (N). It is expected to dramatically suppress the coupling rate before the interfacial tension is diminished. Therefore, we expect roughening to occur only for low molecular weight samples. In our experiment, χN was estimated to be about 13. (Here χ is the segment−segment interaction parameter. It was estimated to be 0.027 for PS−PMMA at 200 °C based on the results by Shearmur et al.[13]) We have repeated the same experiments with higher molecular weight PS−PMMA systems with their χN being up to 34. Significant interfacial roughening was not observed, which is in qualitative agreement with theory. On the other hand, if the molecular weight is reduced so that $\chi N < 10$, the system would become homogeneous,[14] thereby eliminating the interfaces.

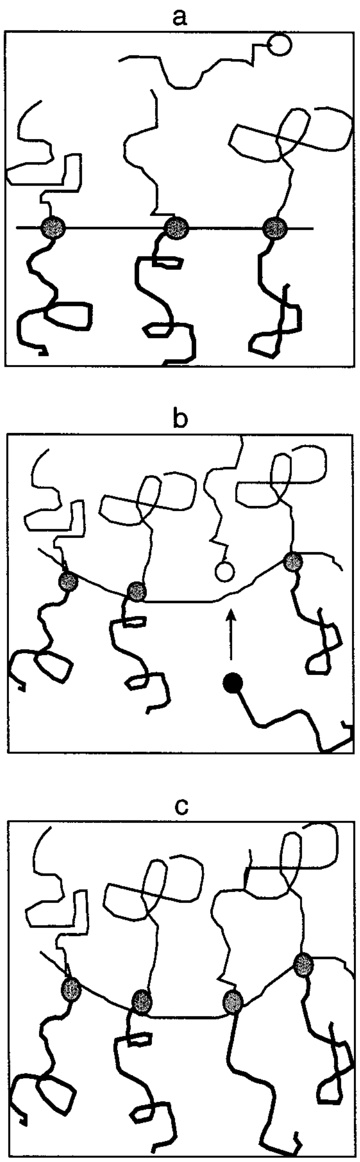

Figure 5. Suggested mechanism for interfacial roughening induced by reactive coupling. (a) Interface is saturated by block copolymers; (b) interface curves due to thermal fluctuations leading to decreased block copolymer coverage; (c) additional block copolymers are formed, saturating the interface and stabilizing the increased interfacial area.

If we further assume that the chemical reaction is very fast compared to the time required for homopolymers to diffuse to the interfaces, our explanation suggests that the rate of interface roughening might be correlated with the diffusion of homopolymers and the interfacial roughness could be of the same order of magnitude as the diffusion length of the slowest homopolymer. We estimated the diffusion of PS and PMMA into PS−PMMA diblock copolymer matrix based on the results of Green et al.[15] The diffusion coefficient of PMMA with a molecular weight similar to that used in our study is roughly 10^{-12} cm^2/s while that of PS is roughly 10^{-11} cm^2/s. Thus, these chains could move around 1 μm in 1 h, comparable to the 0.5 μm interfacial roughness observed after 1 h of annealing.

On the basis of these results, we speculate that Orr's fast interfacial area generation is directly related to reaction induced interfacial roughening. Under static conditions we believe that interfacial reaction together with thermal fluctuations causes the interface to become rough. Vigorous mixing then enhances the creation of fresh interfacial area, thereby greatly accelerating the process.

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