Suppression of Phase Separation in PC/PMMA Blend Film by Thermoset Oligomer

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ABSTRACT: Phase separation of bisphenol A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) thin blend film is suppressed by addition of solid epoxy oligomer. Epoxy has strong intermolecular interactions with both PC and PMMA, while PC and PMMA are quite incompatible with each other. Consequently, phase separation in the PC/PMMA blend film pushes epoxy to the interface; at the same time, PC and epoxy react readily at the interface to form a cross-linking structure, binding PMMA chains together. Therefore, the interface between PC and PMMA is effectively reinforced, and the PC/PMMA thin blend film is stabilized against phase separation. On the other hand, only an optimal content of epoxy (i.e., 10 wt %) can serve as an efficient interfacial agent. In contrast to the traditional reactive compatibilization, here we observed that the cross-linking structure along the interface is much more stable than block or graft copolymers. Atomic force microscopy (AFM) is used to characterize the morphological changes of the blend films as a function of annealing time. Two-dimensional fast Fourier transform (2D-FFT) of AFM data allows quantitative investigation of the scaling behavior of phase separation kinetics.

Introduction

Thin polymer blend films have a broad range of technological and scientific applications, from biomedical to optics and microelectronics. Hence, experimental and theoretical investigations involving thin film blends have been a matter of considerable interest in recent years. Phase separation always takes place in blend films due to the immiscibility between blend components, resulting in film rupture. However, stable defect-free polymer films are necessary to achieve the desired properties in practical applications. Therefore, research has been focused on suppressing phase separation in thin blend films by different methods, and most attention is attracted to addition of copolymers[1−3] or introduction of chemical reactions[4−6] into the mixture. Zhu et al.[1] have reported that addition of a symmetric diblock copolymer to the polystyrene (PS)/poly(methyl methacrylate) (PMMA) binary mixture results in a completely mixed pattern by the physical effect of block copolymer confinement in a thin blend film. In other separate studies,[2,3] it was also shown that copolymer addition leads to a stability in polymer blend films due to the reduction in interfacial tension. Earlier investigations[7−11] depict that the incorporated copolymer compatibilizers always form micelles in one of the homopolymer phases before saturating the interface, thus limiting the miscibility of the blends. An alternative efficient way is introduction of chemical reactions to control the phase separation kinetics of polymer blends. Tran-Cong et al.[6] have examined the phase separation of the poly(styrene-*stat*-(chloromethyl)styrene)/poly(vinyl methyl ether) (PVME) blend accompanied by photo-cross-linking reactions. According to their results, in the presence of chemical reactions, the spinodal decomposition process is significantly suppressed.

Blends of bisphenol A polycarbonate (PC) with PMMA have received considerable attention in current research[12−15] due to their potential applications as gas separation membranes and pearl materials. PC/PMMA is known as a partially miscible binary blend with very small interaction parameter χ (∼0.04).[16] According to Kambour et al.,[17] when χ is slightly positive, the miscible blend can be achieved under particular conditions. This is the case for the PC/PMMA blend; a trapped miscible state can be obtained by solvent-casting from THF at 47−60 °C.[18] However, this is not the real equibrium state; in subsequent annealing above the thermodynamic lower critical solution temperature (LCST), the initially homogeneous PC/PMMA mixture undergoes thermal induced phase separation. In the bulk, phase separation dynamics of the PC/PMMA blend has been intensively elucidated by means of time-resolved light scattering.[19−22] It is found that phase separation in the PC/PMMA blend takes place through spinodal decomposition (SD) near the critical point in the phase diagram. At early stages, the scattering peak (corresponding to the average periodic distance of phase-separated domains), at a wavenumber of q^*, appears gradually with time and remains invariable for ca. 10 min, which can be explicated in terms of the linearized Cahn−Hilliard theory.[23] As SD proceeds to later stages, q^* shifts to lower scattering wavenumber, indicating a growth of the separated domains. The time dependence of q^* no longer obeys the linearized C−H theory but follows the power-law relationship $q^* \sim t^{-\varphi}$. Binder and Stauffer[24] predict that $\varphi = {}^1/_3$ on the basis of cluster aggregation and coalescence of domains to minimize the surface free energy, while Siggia[25] estimates $\varphi = 1$ when hydrodynamic flow is taken into consideration.

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However, in thin PC/PMMA blend films where there are two additional interfaces (polymer/air and polymer/substrate), confinement alters the thermodynamic and kinetic behavior of phase separation. Karim[26] and Viville[27] have respectively measured the phase separation behavior in PC/PMMA thin blend films. Moreover, Karim[26] has demonstrated that at elevated temperatures (above 200 °C) transesterification reactions take place simultaneously and slow down the phase separation process by generating an interfacial active copolymer layer.

In this work, we introduce epoxy oligomer as the interfacial agent for PC/PMMA thin blend films. Recently, we have reported that epoxy can sufficiently improve the thermal stability between PC and PMMA bilayers.[28] Epoxy resin is reported to have a strong interaction with both PC and PMMA before and after heating at high temperatures. Moreover, epoxy and PC undergo chemical reactions upon heating to form a cross-linking structure.[29,30] Therefore, epoxy resin tends to build a strong binding between PC and PMMA when treated at high temperatures and thus stabilizes the thin blend films against phase sepatation. We focus on the size evolution of domains generated upon phase separation by means of atomic force microscopy (AFM) over the treatment duration. By two-dimensional fast Fourier transform (2D-FFT) analysis of AFM images, a quantitative calculation of domain growth can be carried out, which clearly exhibits the suppression of phase separation in PC/PMMA thin film by addition of epoxy resin. In addition, selectively etching PMMA out of the film helps investigate the details at PC and PMMA interface with and without epoxy.

Experimental Section

Materials. PMMA ($M_n = 22$ kg mol^{-1}, $M_w/M_n = 1.48$) was purchased from Polyscience, and PC (Makrolon 3103, $M_n = 32$ kg mol^{-1} and $M_w/M_n = 1.59$) was from Bayer. The glass transition temperatures (T_gs) by differential scanning calorimeter (DSC) are 149 and 112 °C for PC and PMMA, respectively. Solid-state epoxy resin, diglycidyl ether of bisphenol A (E-20) with an epoxide equivalent weight of 455−500 g equiv^{-1}, was kindly supplied by Prof. X. Han (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences).

Sample Preparation. PC/PMMA (1/1, w/w) blends with different epoxy mass fractions were prepared by dissolving in cyclohexanone at a total polymer concentration of 2 wt %. Epoxy fractions in the blends were 5, 10, and 20 wt %. Thin blend films were spun-cast from cyclohexanone solutions onto polished silicon substrates at ∼40 °C. The silicon wafers used were previously treated in a piranha solution (70/30 v/v of concentrated H_2SO_4 and H_2O_2) at 80 °C for 1 h, rinsed with deionized water several times, and blown dry under compressed nitrogen gas. The as-prepared films appeared a uniform color, indicating homogeneous mixing of the components. For convenience, blend films with different epoxy mass fractions were denoted as EP0 (without epoxy), EP5, EP10, and EP20 in the following discussion. Film thickness was measured by AFM scans across a set of scratches of the samples, which provided identical values of ∼89 ± 1 nm.

Instruments. Surface topographic images of the films were investigated by atomic force microscopy (AFM) at ambient temperature. AFM measurements were carried out in a commercial SPA-300HV with a SPI 3800N controller (Seiko Instruments Inc., Japan). The probe was silicon cantilevers with a spring constant of 2 N/m and a resonance frequency lying at 70 Hz.

Quantified calculation of the evolution of average domain size and the scaling behavior of phase separation were addressed via two-dimensional fast Fourier transform (2D FFT) analysis of AFM images.

Results

1. Surface Modulation upon Phase Separation. In previous research by Viville and co-workers,[27] LCST of the PC/PMMA (50/50) blend is detected on the basis of AFM. Since AFM has a high resolution, the obtained data are very close to the real thermodynamic LCST. As mentioned above, the as-prepared homogeneous blend films of EP0, EP5, EP10, and EP20 are trapped in an out-of-equilibrium state; thermally induced phase separation can be carried out above the LCST, i.e., ∼150 °C. In our work, all the films were annealed at 190 °C, which is well above LCST but under the transesterification temperature (∼200 °C) between PC and PMMA.[26,31] Thus, the following mentioned suppression of phase separation exclusively arises from the compatibilization effect of epoxy resin.

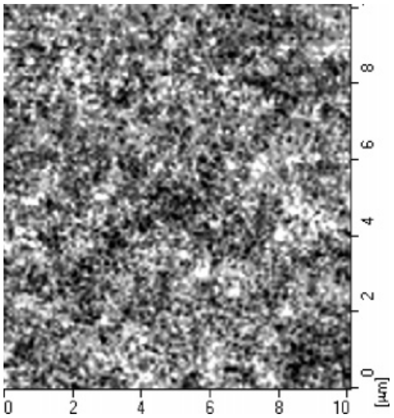

Figure 1. Surface morphology of as-prepared EP10 film.

All the as-cast films with different epoxy weight fraction have smooth surfaces with root-mean-square (rms) roughness, *r*, less than 1 nm, indicating a homogeneous blending of the components. Figure 1 shows the surface morphology of as-prepared EP10 representatively. However, after annealing at 190 °C, the initially homogeneous surfaces display phase separated structures. For 720 min (Figure 2a−c), the films were perforated by a uniform distributed holes. Upon further annealing to 4320 min (Figure 2d−f), the hole diameter increases and the number decreases. Since the overall free energy of immiscible blends is lowered by minimizing the interfacial area between two phases, the phase separation process always tends to merge the neighboring domains of the same type.

In the bulk, the phase separation process in PC/PMMA blends has already been investigated in detail.[19−22] However, for thin blend films, because of the influence of confinement and spatial dimensionality, phase separation behavior always differs from that in the bulk. In blend films, the surface composition typically differs from the bulk because each component has different affinity with both the air and substrate,[32,33] and thus the critical point of polymer blends always shifts in thin films. The detailed phase separation mechanism of the PC/PMMA film will be discussed in another work. In this paper we just focus on the pattern development of PC/PMMA blend films before and after compatibilization.

Phase evolution in our experiment resembles the process described by Viville;[27] both show two distinct types of regions, darker (lower) and lighter (higher) ones. Lateral force microscopy (LFM) and infrared microscopy measurements[27] indicate that the lower areas are mostly made of PMMA and higher are PC. This topographic variation of PC and PMMA domains originates from the large vitrification temperature difference between PC (∼149 °C) and PMMA (∼112 °C), according to Viville.

To further confirm the existence of PMMA in the lower region of phase separated blends, films were immersed in acetic acid for 2 min at room temperature (note here that acetic acid

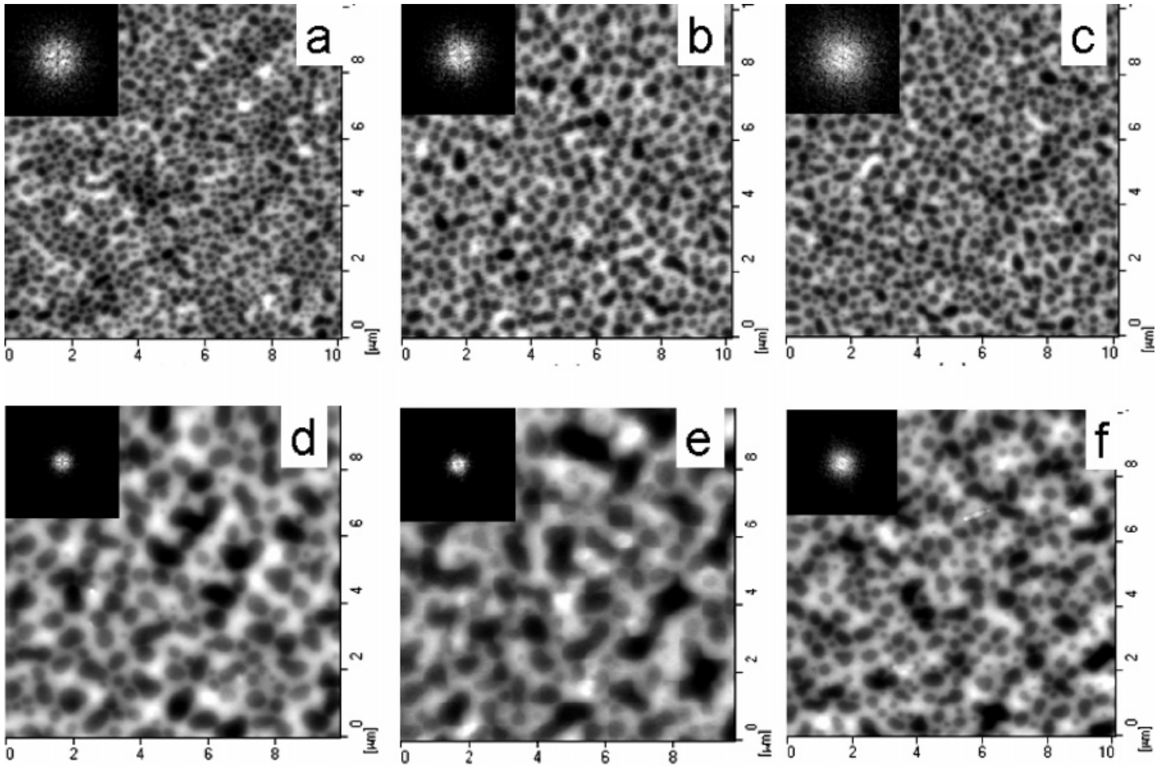

Figure 2. Series of AFM topographic images of blend films after annealing at 190 °C for various times (in min): (a) EP0, 720; (b) EP5, 720; (c) EP10, 720; (d) EP0, 4320; (e) EP5, 4320; and (f) EP10, 4320. The insets are the corresponding 2D-FFT spectra.

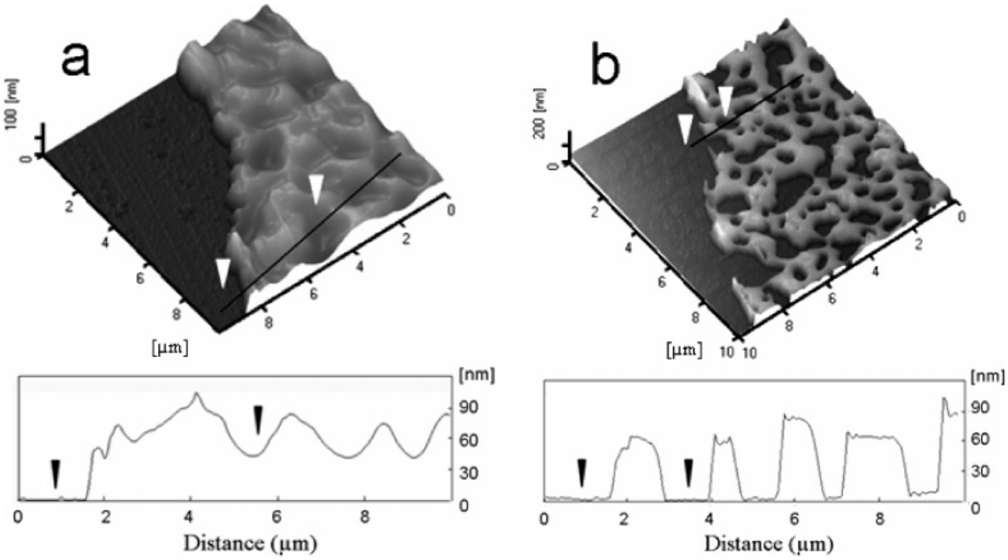

Figure 3. AFM images and the corresponding cross-section line profiles of EP0 after annealing at 190 °C for 4320 min: (a) before etching; (b) after etching in acetic acid. The dark areas at the left side of the AFM topographic images display bare Si/SiO$_2$ substrate by a scalpel scratch.

preferentially dissolves PMMA and leaves PC intact). AFM images of EP0 before and after etching are shown in Figure 3. Upon 4320 min annealing, EP0 film exhibits a surface structure with coalesenced-hole domains embedded in a continuous matrix, as depicted in Figure 3a. However, while immersing for a brief period of time (~2 min) in acetic acid, the continuous phases do not change a lot, but the embedded lower domains disappear, leaving the Si/SiO$_2$ substrate uncovered, as is evident from the cross-section profile in Figure 3b. Since acetic acid is a selective solvent for PMMA, it is obvious that the removed lower regions are corresponding to PMMA-rich domains.

2. Phase Separation Kinetics of Blend Films. We turn our attention to phase separation kinetics of PC/PMMA with different amount of epoxy upon a systematic increase in annealing duration. After 4320 min annealing, the average demixed domain size in EP0 is around 1 μm (Figure 2d); it becomes ~1.4 μm in EP5 (Figure 2e). While in EP10, although phase separation also develops during annealing, the observed domain size is much smaller than that obtained in EP0 and EP5, which is dramatically reduced to ~0.5 μm (Figure 2f). The domain size evolution is accelerated by addition of 5 wt % epoxy while considerably suppressed by 10 wt % epoxy. Further increasing epoxy fraction to 20 wt %, phase separation is markedly increased again (figure is not shown here). Therefore, only an optimal content of epoxy can play an effective role in compatibilizing PC/PMMA blend. In our previous work,[34] cross-

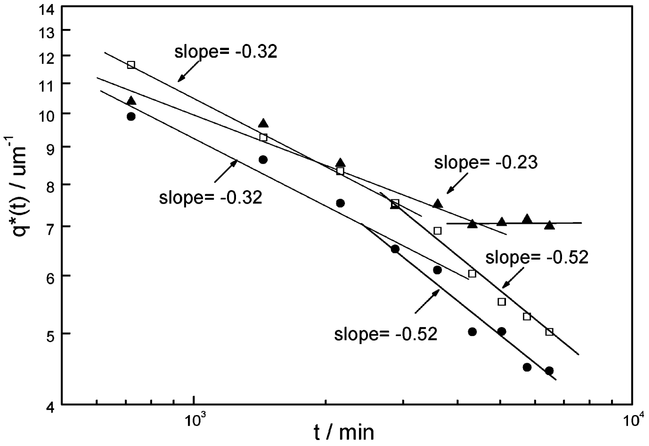

Figure 4. Annealing time dependence of characteristic wavenumbers $q^*(t)$ on a log−log scale: □, EP0; ●, EP5; ▲, EP10. All films display a two-stage evolution pattern.

linking reaction between PC and epoxy has been verified by FTIR and DSC. Additionally, Su and Woo[35] have reported that the degree of cross-linking between PC and epoxy depends on the initial blend compositions. In the EP10 blend film, epoxy first migrates to the interface between PC and PMMA domains due to thermodynamic driving force and then reacts readily with PC upon heating, resulting in an interlinked structure. At the same time, PMMA chains adjacent to the interface might also be bound into the network through special molecular interactions with epoxy; therefore, the interface between PC and PMMA is stabilized and phase separation is suppressed. While for EP5, the chemical reactions occurring between PC and epoxy are probable very limited, with PC chains cleaved,[36] which results in an accelerated phase separation between PC and PMMA. However, in EP20, the incorporated epoxy serves not only as a compatibilizer but also as a plasticizer for the PC/PMMA blend. The excessive epoxy accelerates the macromolecular chain motions of both components,[37] and phase separation of PC/PMMA is enhanced.

Insets in Figure 2 show that the corresponding 2D-FFT patterns are circular, consistent with a laterally isotropic morphology. The FFT transformed data exhibit a maximum intensity at a characteristic wavenumber q^*. Figure 4 shows the time dependence of q^* on a log−log plot. Phase evolution kinetics of all the three blend films involves two distinct processes. For EP0 and EP5, $q^*(t)$ can be characterized by a power law of $t^{-0.32}$ at the early stage and then follows $t^{-0.52}$ in the second regime. The two stages cross at 2880 min. Karim et al.[26] have also shown that φ exponent for PC/PMMA ultrathin film changes from 1/3 to a larger value in their work. Phase separation dynamics in blend films have been examined widely in literature. For instance, Sung et al.[33] investigated phase evolution of polystyrene (PS)/polybutadiene (PB) film by optical microscopy. The scaling exponent exhibits 1/3 pattern growth first and then followed by a slope near unity. It is well-known that phase separation is much more complicated in thin blend films since it depends not only on the surface energy of the components but also on the substrate properties and film thickness. Consequently, though various theories and simulations[38,39] and many experiments[40,41] have been focused on describing the phase separation kinetics of thin blend film, there are no consistent results.

The phase coarsening process in EP10 is of particular interest because the power exponent is 0.23 for $q^*(t) \sim t^{-\varphi}$ in early stage and then approaches zero at a later time, which indicates that phase separation of the PC/PMMA blend film eventually freezes by addition of 10 wt % epoxy.

3. Interface Morphologies. To gain detailed insight into the interfacial structure of these thin blend films in the phase-separated state, acetic acid was again used to remove the PMMA-rich domains out of the film, revealing the interfaces between PC and PMMA. As depicted in Figure 5, the interface is smooth in EP0 and EP5, while it becomes much rougher when 10 wt % epoxy was incorporated in the blend. According to Rice,[42] any third component that increases the phase stability of a binary mixture must be present in excess at the interface between coexisting phases. In EP10, the roughened interface between PC and PMMA domains is probably due to enrichment and reaction of epoxy at the interface. On the other hand, EP10 treated with acetic acid before annealing just demonstrates a unsmoothed surface morphology (inset in Figure 5c) compared to the as-prepared film, since PMMA and epoxy are all dissolved in the solvent before reaction. This further confirms that the reactive compatibilization of epoxy can only occur upon heating.

Discussion

Phase Separation Kinetics of Blend Films. Phase separation of polymer blends in the presence of chemical reactions has been studied widely.[6,43−47] Simple chemical reactions have been suggested to dramatically affect the dynamics of phase separation in binary mixtures and can be used to stabilize and tune patterns of phase-separated blends. Tran-Cong and co-workers have reported that the spinodal decomposition process of P(S-*stat*-CMS)/PVME[6,43] and poly(2-chlorostyrene)/poly(vinyl methyl ether) (P2CS/PVME)[44] blends was eventually arrested by photo-cross-linking reactions. Computer simulations[47] have shown that the domain growth freezes in ternary mixtures coupled with an interfacial reaction. The reactively generated

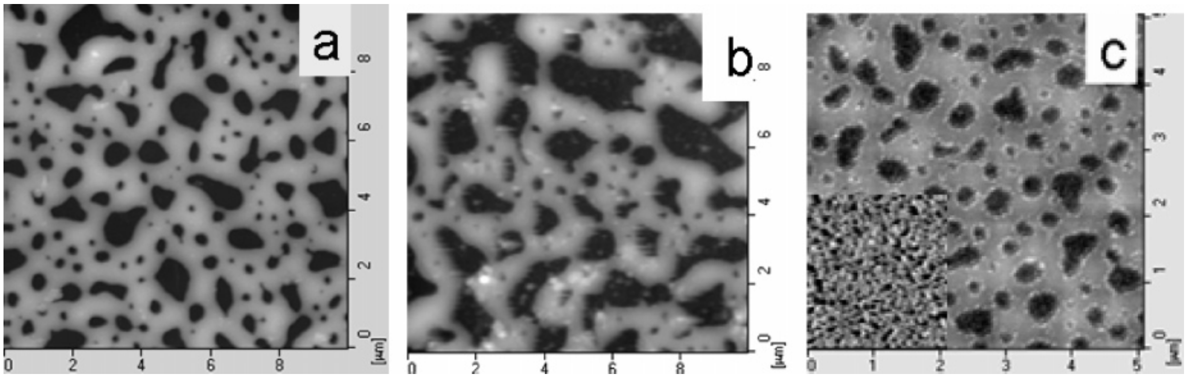

Figure 5. AFM height images of films annealed at 190 °C for 4320 min and then etched by acetic acid (∼2 min): (a) EP0, (b) EP5, and (c) EP10 (note the changes in horizontal scale). Inset in (c) is EP10 treated with acetic acid before annealing for comparison (2 × 2 μm).

copolymers at the interface are believed to promote mixing between the blend components and slow down the coalescence rate of droplets of one phase dispersed in another through steric repulsion.

In our case, addition of 10 wt % epoxy oligomer to PC/PMMA binary mixture has been shown to enhance the phase stability of PC/PMMA film during annealing. Epoxy is relatively compatible with both PC and PMMA, whereas PC and PMMA are quite incompatible with each other; as a consequence, phase separation between PC and PMMA pushes epoxy to the interface. Concurrently, PC and epoxy undergo chemical reactions upon annealing to form a cross-linking structure, trapping PMMA chains together and thus stabilizing the thin blend film against coarsening.

Glotzer and co-workers[48] have proposed a scaling function for the time evolution of phase separation in polymer blends undergoing chemical reactions:

$$\xi(t) = t^n G(x)$$

and

$$x = kt$$

where $\xi(t) = 2\pi/q^*(t)$, which is the characteristic length scale of structures, k is reaction rate, and n is an exponent of the scaling law.

When the reaction follows first-order kinetics ($k = 1$), the scaling function $G(x)$ has the following features:

$$G(x) = \text{constant} \quad (x \ll \infty)$$

$$G(x) \propto t^{-n} \quad (x \rightarrow \infty)$$

In view of $\xi(t) = 2\pi/q^*(t)$, $q^*(t)$ can be written as

$$q^*(t) \propto t^{-n} \quad (x \ll \infty)$$

$$q^*(t) = \text{constant} \quad (x \rightarrow \infty)$$

In EP10, $q^*(t)$ follows the $t^{-0.23}$ power law in the early stage of phase separation, as shown in Figure 4, and then there are almost no changes in $q^*(t)$ with annealing time after 2880 min, which is in full agreement with the scaling function mentioned above. The phase separation kinetics in EP10 with a power exponent of 0.23 proceeds much slower than that in uncompatibilized EP0, suggesting a case of weak phase separation. This result implies that the network formed by PC and epoxy at the interface has effectively decreased the chain mobility of both PC and PMMA components and thus suppressed the phase separation of the blend. Upon further annealing, the separation process is pinned by the interfacial reaction, with $q^*(t)$ being independent of annealing time t.

Interface Morphologies. Numerous studies[49,50] have shown that interface topography plays an important role in determining polymer−polymer interactions. The common consensus is that increasing interfacial roughness improves polymer adsorption and thereby enhances the interactions between two phases. The usual understanding for this effect is that the interfacial area is somehow being increased.

Theoretical analysis of the polymer−polymer interface has always been explored in relatively simple cases, i.e., at the planar interface. Schematic illustrations are presented in Figure 6 to describe the interface formation between PC and PMMA in compatibilized blend film(EP10). PC, PMMA, and epoxy were initially homogenously mixed. Upon annealing at 190 °C, phase separation took place between PC and PMMA, with epoxy migrating to the interface simultaneously. PC and epoxy at the interface reacted readily to form a cross-linking structure; meanwhile, a small amount of PMMA would also be bound into PC−epoxy interlinks. Such a structure may be thought of as a network at the PC/PMMA interface. This network can be penetrated by PC and PMMA free chains at both sides. Kerle et al.[51] have investigated the penetration/adsorption of a cross-linked substrate by chemically similar but non-cross-linked melt. A theoretical treatment of such interactions is also provided by Leibler.[52] Enthalpic interactions are neglected in this model because of the chemical identity between cross-linked substrate and the free melt. Consequently, the penetration/adsorption energy is uniquely dominated by the entropy balance between the gain of translational entropy by free chains and the loss of conformational entropy by tethered chains due to stretching. Upon further annealing, cross-linking proceeds to a higher extent, which leads to an increase in interfacial roughness. This roughening will then be the dominant effect on penetration or adsorption of the free chains.[51] First, interfacial roughening increases the effective area for more free PC or PMMA chains to adsorb at the interface; second, polymer adsorption would occur more readily on roughened surfaces, since it is accompanied by less entropic loss, according to Douglas.[49] As a consequence, the interface between PC and PMMA phases is greatly reinforced and phase separation is significantly suppressed.

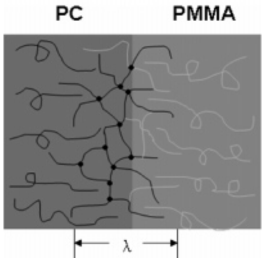

Figure 6. Schematic illustration of roughened interface between PC and PMMA. λ represents the interfacial layer.

Conclusions

We investigated the phase separation morphologies and kinetics of PC/PMMA thin blend films coupled with an interfacial chemical reaction. Bisphenol A epoxy oligomer serves as an effective interfacial agent for PC/PMMA blend, but only at an optimal content. When 5 and 20 wt % epoxy were incorporated in the binary mixture, domain size evolution is accelerated in comparison with that of PC/PMMA blend without epoxy. With the addition of 10 wt % epoxy, the phase separation process of PC/PMMA is dramatically suppressed. 2D-FFT of AFM images gives a quantitative analysis of the scaling behavior of phase separation. For EP0 and EP5, phase separation follows a power law of $q^*(t) \sim t^{-1/3}$ at early stage and then accelerated to $t^{-0.52}$. However, in EP10, the scaling behavior can be characterized by $q^*(t) \sim t^{-0.23}$ in the first regime, while at a later time, phase separation is suppressed completely. This was believed to be attributed to the cross-linking structure at the interface. Epoxy has strong intermolecular interactions with both PC and PMMA, while PC and PMMA are relatively incompatible. Upon annealing, epoxy oligomers prefer migrating to the PC/PMMA interface and react with PC readily. At proper compositions and times, the reaction between epoxy and PC would build a cross-linking structure. Meanwhile, PMMA chains can also be bound into the network at the interface through their attractive interactions with epoxy.

As a result, the incompatibility between PC and PMMA is considerably reduced, which is responsible for the suppression of phase separation in PC/PMMA thin blend films.

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References and Notes

(1) Zhu, S.; Liu, Y.; Raifailovich, M. H.; Sokolov, J.; Gersappe, D.; Winesett, D. A.; Ade, H. *Nature (London)* **1999**, *400*, 49.
(2) Akpalu, Y. A.; Karim, A.; Satija, S. K.; Balsara, N. P. *Macromolecules* **2001**, *34*, 1720.
(3) Wang, P.; Koberstein, J. T. *Macromolecules* **2004**, *37*, 5671.
(4) Tran-Cong. Q.; Nagaki, T.; Nakagawa, T.; Yano, Q.; Soen, T. *Macromolecules* **1989**, *22*, 2720.
(5) Tran-Cong, Q.; Nagaki, T.; Yano, Q.; Soen, T. *Macromolecules* **1991**, *24*, 1505.
(6) Harada, A.; Tran-Cong, Q. *Macromolecules* **1996**, *29*, 4801.
(7) Ibuki, J.; Charoensirisomboon, P.; Chiba, T.; Ougizawa, T.; Inouea, T.; Weberb, M.; Kochb, E. *Polymer* **1999**, *40*, 647.
(8) Charoensirisomboona, P.; Chibaa, T.; Solomkoa, S. I.; Inouea, T.; Weberb, M. *Polymer* **1999**, *40*, 6803.
(9) Charoensirisomboona, P.; Inouea, T.; Weberb, M. *Polymer* **2000**, *41*, 4483.
(10) Charoensirisomboona, P.; Inouea, T.; Weberb, M. Polymer **2000**, *41*, 6907.
(11) Hu, W.; Koberstein, J. T.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1995**, *28*, 5209.
(12) Wei, M.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 4061.
(13) Marin, N.; Favis, B. D. *Polymer* **2002**, *43*, 4723.
(14) Ray, S. S.; Bousmina, M. *Macromol. Rapid Commun.* **2005**, *26*, 450.
(15) Bonzanini, R.; Girotto, E. M.; Goncalvesb, M. C.; Radovanovica, E.; Muniza, E. C.; Rubira, A. F. *Polymer* **2005**, *46*, 253.
(16) Kim, W. N.; Burns, C. M. *Macromolecules* **1987**, *20*, 1876.
(17) Kambour, R. P.; Gundlach, P. E.; Wang, I-C. W.; White, D. M.; Yeager, D. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1987**, *28−2*, 140.
(18) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* **1991**, *32*, 272.
(19) Kyu, T.; Saldanha, J. M. *J. Polym. Sci., Polym. Phys.* **1990**, *28*, 97.
(20) Lim, D.-S.; Kyu, T. *J. Chem. Phys.* **1990**, *92*, 3944.
(21) Lim, D.-S.; Kyu, T. *J. Chem. Phys.* **1990**, *92*, 3951.
(22) Kyu, T.; Lim, D.-S. *Macromolecules* **1991**, *24*, 3645.
(23) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(24) Binder, K.; Stauffer, D. *Phys. Rev. Lett.* **1975**, *33*, 1006.
(25) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.
(26) Karim, A.; Douglas, J. F.; Satija, S. K.; Han, C. C.; Goyette, R. J. *Macromolecules* **1999**, *32*, 1119.
(27) Viville, P.; Biscarini, F.; Brédas, J. L.; Lazzaroni, R. *J. Phys. Chem. B* **2001**, *105*, 7499.
(28) An, N.; Li, Y.; Yang, Y.; Yu, F.; Dong, L. *Macormol. Rapid Commun.* **2006**, *27*, 955.
(29) Woo, E. M.; Wu, M. N. *Polymer* **1996**, *37*, 2485.
(30) Woo, E. M. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 781.
(31) Rabeony, M.; Hseih, D. T.; Garner, R. T.; Peiffer, D. G. *J. Chem. Phys.* **1992**, *97*, 4505.
(32) Chung, H.-J.; Wang, H.; Composto, R. J. *Macromolecules* **2006**, *39*, 153.
(33) Sung, L.; Karim, A.; Douglas, J. F.; Han, C. C. *Phys. Rev. Lett.* **1996**, *76*, 4368.
(34) For review, see supporting information in ref 28.
(35) Su, C. C.; Woo, E. M. *Macromolecules* **1995**, *28*, 6779.
(36) Woo, E. M.; Wu, M. N. *J. Polym. Sci., Polym. Phys.* **1996.** *34*, 789.
(37) Woo, E. M.; Wu, M. N. *Polymer* **1996**, *37*, 1907.
(38) Wu, Y.; Alexander, F. J.; Lookman, T.; Chen, S. *Phys. Rev. Lett.* **1995**, *74*, 3852.
(39) Toxvaerd, S. *Phys. Rev. Lett.* **1999**, *83*, 5318.
(40) Wang, H.; Composto, R. J. *Macromolecules* **2002**, *35*, 2799.
(41) Liao, Y.; Su, Z.; Ye, X.; Li, Y.; You, J.; Shi, T.; An, L. *Macromolecules* **2005**, *38*, 211.
(42) Rice, O. K. *J. Chem. Phys.* **1976**, *64*, 4362.
(43) Toshikazu, T.; Imagawa, A.; Tran-Cong, Q. *Macromolecules* **1994**, *27*, 7486.
(44) Imagawa, A.; Tran-Cong, Q. *Macromolecules* **1995**, *28*, 8388.
(45) Glotzer, S. C.; Stauffer, D.; Jan, N. *Phys. Rev. Lett.* **1994**, *72*, 4109.
(46) Glotzer, S. C.; Di Marzio, E. A.; Muthukumar, M. *Phys. Rev. Lett.* **1995**, *74*, 2034.
(47) Tong, C.; Zhang, H.; Yang, Y. *J. Phys. Chem. B* **2002**, *106*, 7869.
(48) Glotzer, S. C. In *Annual Reviews of Computational Physics*; Stauffer, D., Ed.; World Scientific: Singapore, 1995; Vol. II, p 1.
(49) Douglas, J. F. *Macromolecules* **1989**, *22*, 3707.
(50) Baumgärtner, A.; Muthukumar, M. *J. Chem. Phys.* **1991**, *94*, 4062.
(51) Kerle, T.; Yerushalmi-Rozen, R.; Klein, J. *Macromolecules* **1998**, *31*, 422.
(52) Leibler, L.; Ajdari, A.; Mouran, A.; Coulon, G.; Chatenay, D. In *Ordering in Macromolecular Systems*; Teramoto, A., Norisuya, T., Eds.; Springer-Verlag: Berlin, 1994.

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