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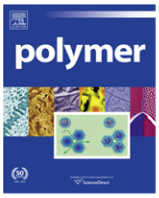

Layered structure formation in the reaction-induced phase separation of epoxy/polysulfone blends

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ABSTRACT

In an epoxy/polysulfone blend, the reaction-induced phase separation behavior and the final morphology were investigated. Three distinct morphological structures were obtained. Sea-island and nodular structures were observed at lower and higher polysulfone contents, respectively. A three-layered structure was obtained in the middle polysulfone concentration range. In order to understand the formation of three-layered structure, phase separation process was studied using time-resolved light scattering, phase-contrast optical microscope and scanning electron microscope. Bicontinuous structure formed uniformly in the whole sample at the beginning of phase separation. After the phase structure grew for a certain time, large domains formed and developed. Then, the large epoxy-rich domains gradually flew to the outer space of the sample film. This process assisted the formation of the three-layered structure. The mechanism of the formation of the three-layered structure was discussed based on the different viscoelastic properties of the components.

1. Introduction

Reaction-induced phase separation (RIPS) has been widely investigated in recent years [1–15]. Many studies focused on the reaction and phase separation mechanism [5–11]. With different component species and compositions used, varied morphological structures were obtained [10,12–15].

In an initially homogeneous epoxy resin blend, phase separation is induced as the molecular weight of the epoxy increases with curing. With different thermoplastics (TP) and curing agents added, the competition between reaction and phase separation has been qualitatively considered [11,16,17]. After the sample was cured, different morphological structures could be obtained—sea-island structure at lower TP concentration, connected globule or nodular structure at higher TP concentration and bicontinuous or double-phase morphological structure at the intermediate TP concentration [10,18–21]. Among these studies, most of the literatures focused on the final morphological structure, because of its important influence on the performance of the product materials [22–26]. However, the global structure change was normally neglected. Recently, a three-layered structure was also observed in the cured epoxy/polyimide sample in our laboratory [27,28]. We believe this global structure change is not only scientifically interesting but also has important consequences in the applications.

In this work, we used a polysulfone (PSF) to blend with epoxy monomer. The PSF has a relatively high glass transition temperature and can be commercially obtained. In this initially homogeneous system, we used phase-contrast optical microscope (PCOM) and time-resolved light scattering (TRLS) to investigate the evolution of the reaction-induced phase separation. At appropriate PSF weight fractions, large epoxy-rich domains formed during phase separation, and then flew out of the middle part of the sample. Finally, the three-layered structure was formed. This phenomenon was discussed based on the different viscoelastic properties between the components [4,29–31], especially at the beginning of the phase separation.

2. Experimental section

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA), a difunctional epoxy resin (Epon 828), with epoxide equivalent weight of 189, was supplied by Shell Chemical Co. 4,4′-diaminodiphenyl sulfone (DDS), the curing agent, was purchased from Sigma–Aldrich Chem. Co.

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Polysulfone (Udel P1700, $M_n = 38{,}000$) was provided by Solvay Co. Glass transition temperature of PSF, $T_{g,PSF}$, was about 183 °C, measured with a differential scanning calorimeter (Diamond DSC, Perkin–Elmer Co.). The formula structures are shown in Fig. 1.

2.2. Sample preparation

To prepare a homogeneous DGEBA/DDS/PSF sample, the three components were dissolved in a mixed solvent of methylene chloride and methanol (9:1 v/v). Then the transparent solution was cast and degassed under vacuum at room temperature for a few hours to remove the residual solvent and bubbles. Homogeneous blend samples with different initial PSF contents were thus obtained. The weight fraction (w) of PSF was calculated based on the sum of DGEBA, DDS and PSF. The ratio of DGEBA/DDS was fixed at 1: 0.27 w/w, i.e. 0.8 hydrogen's of amino groups per epoxy group.

2.3. Measurements

The homogeneous mixture was placed between two glass slides with a poly(tetrafluoroethylene) spacer of 100 μm in thickness. The samples were put in heating blocks controlled at the desired temperature. The cured specimens were fractured in liquid nitrogen immediately. The fractured surfaces were put in CH_2Cl_2 at room temperature for 5 min to remove the PSF-rich domains. All the sample surfaces were coated with platinum before observation by a scanning electron microscope (SEM) (JEOL JSM 6700F).

Time evolution of the phase separation process was detected by a homemade time-resolved light scattering instrument with a temperature controlled hot chamber. The incident beam with a wavelength of 532 nm and a vertically polarized light was applied to the sample film. The detectable wave number, q, range was $0.2\ \mu m < q^{-1} < 4.0\ \mu m$. Light scattering profile was recorded every 10 s during the curing process. The samples for TRLS observation were prepared as described above and sandwiched between two glass slides, with a poly(tetrafluoroethylene) spacer of 50 μm thickness.

Phase-contrast optical microscope Olympus BX51 with a hot-stage, Linkam LTS-350, was also used to investigate the evolution of phase separation during the isothermal curing process. Digital micrographs were taken at several curing times by a video camera.

3. Results and discussion

Fig. 2 shows SEM images of fractured surfaces at different PSF content w, after the samples were cured at 130 °C for 1440 min. Since PSF-rich domains were removed with solvent CH_2Cl_2, they left voids at the fractured surfaces in the pictures. Three distinct morphologies were observed in different w range.

At $w = 0.10$, PSF-rich domains were separated from the epoxy matrix and formed as dispersed particles, with relatively narrow size distribution, with diameter around 1 μm.

A three-layered morphological structure was observed in the PSF weight fraction range of $0.12 < w < 0.16$. Result with $w = 0.15$ is shown in the figure. Upper and lower layers are similar. They were composed of epoxy-rich matrix and sparsely dispersed PSF-rich particles. Most of PSF-rich domains were located continuously in the middle layer. A lot of epoxy-rich particles were embedded among the PSF-rich domains (as seen from the unetched surface). Some epoxy-rich continuous structures also existed. The morphological structure in the middle layer could be called co-continuous [10].

At $w = 0.20$, epoxy-rich phase formed as nodular structure, i.e. connected particles, most of which were in the diameter of about 3 μm, with a wide size distribution; PSF-rich phase was continuous as thin walls over the whole sample film, which could be clearly observed in the unetched surface (Fig. 2b).

At $w = 0.12$, sea-island structure (similar to that at $w = 0.10$) and layered structure were both observed. Meanwhile, both layered structure and nodular structure (similar to that at $w = 0.20$) were obtained at $w = 0.16$.

In order to study the formation of the three-layered structure, we used TRLS to follow the reaction-induced phase separation process. The time evolution of scattering intensity I versus wave number q, was plotted, as shown in Fig. 3.

Typical scattering patterns, $I(q)$, of phase separation information were obtained after the sample temperature had been kept at 130 °C for a certain time, t. At $t = 227$ min, the scattering peak appeared at around $q_m = 1.6\ \mu m^{-1}$, where q_m is the peak scattering wave number at the maximum scattering intensity (I_m). When phase separation has begun, I_m increased slowly with time, while the change of corresponding q_m was not obvious at this time range (Fig. 3a). After this short time range, I_m became stronger and stronger, with q_m gradually decreasing, which illustrated the development of phase separation and coarsening of phase structures (Fig. 3b and c). However, at $t = 241$ min, another scattering peak was observed at slightly smaller $q_m = 0.42\ \mu m^{-1}$, as shown in Fig. 3f. Then the intensities, I_m, of the two peaks slowly decreased and their q_m were also decreasing with time increasing, which was probably caused by the reason that the refractive indices of the two separated domains were approaching each other and became iso-refractive as the molecular weight of epoxy increased [32]. However, from $t = 355$ min on, the two scattering peaks seemed to have merged into one peak, and this peak did not change obviously

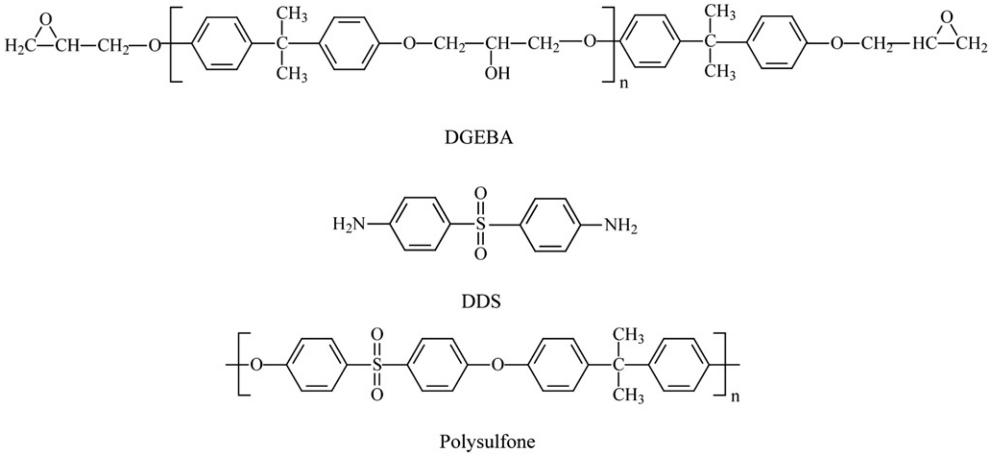


Fig. 1. Chemical structures of epoxy resin (DGEBA), 4,4′-diaminodiphenyl sulfone (DDS) and polysulfone.

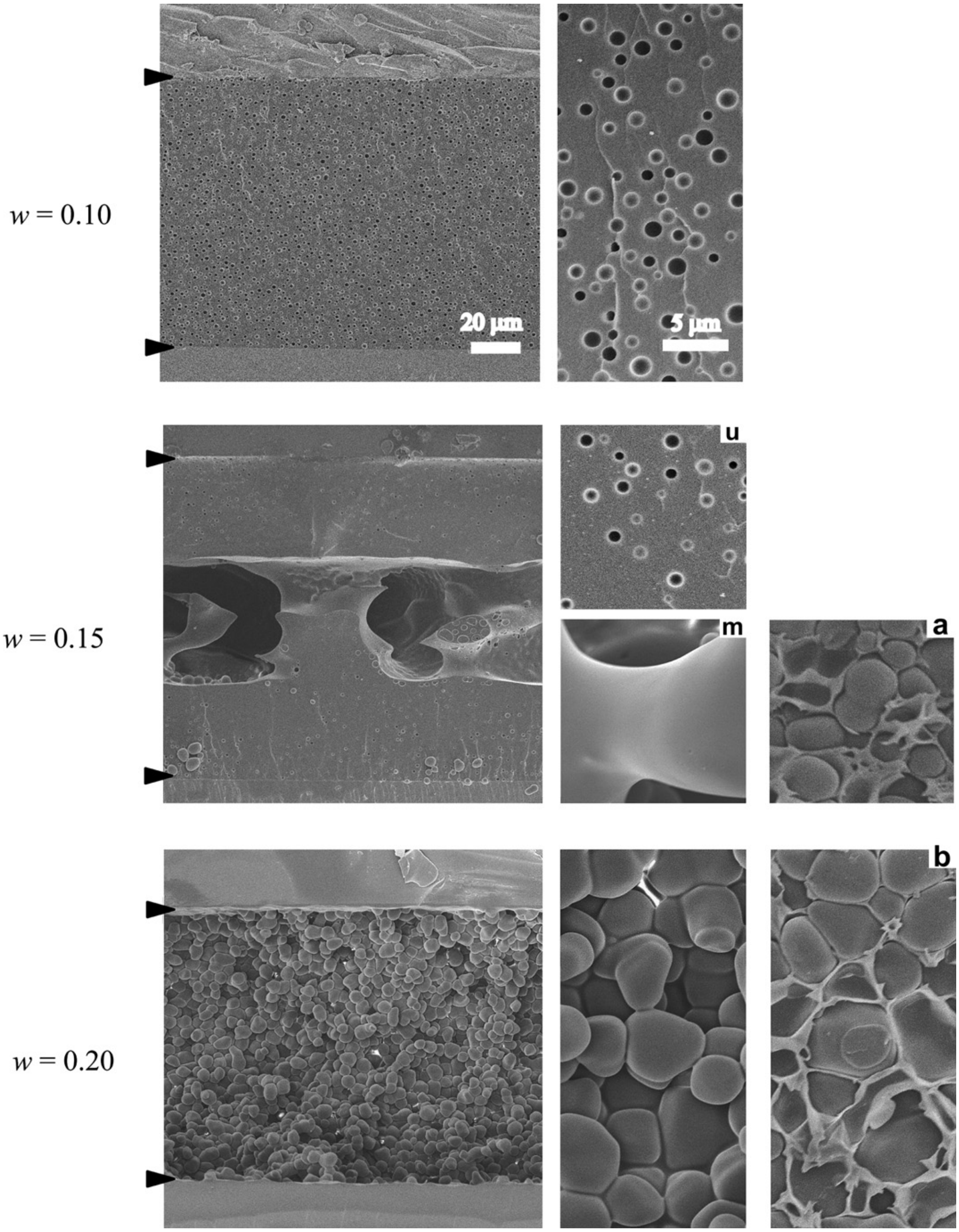


Fig. 2. SEM micrographs of fractured surfaces of epoxy/PSF blend with different PSF contents, cured at 130 °C for 1440 min. The location of the glass surfaces was indicated by arrows. The right pictures in each panel are of higher magnifications. (u) and (m) represent the upper and middle parts of the sample with $w = 0.15$, respectively. Voids in the images corresponding to the PSF-rich domains. (a) and (b) are images of unetched surfaces.

(Fig. 3d and e). Since $q \sim 2\pi/L$, where L denotes the dimension of structures, evolution of the scattering peaks indicated that larger domains were formed after the phase separation developed for some time. The large domains coexisted with the smaller domains (the initial one) for a while. Then the two size scale domains merged together or one of them disappeared. Finally only the domains in one size scale can be detected. This phenomenon seems puzzling at this point, but after more detailed PCOM and SEM studies are carried on the cross-section images of the sample, physics of this phase separation mechanism can be explained and understood.

PCOM observation of phase separation process was shown in Fig. 4. Since light traversed through the sample, we focused our microscope on the middle depth of the sample. After the sample was placed at 130 °C for about 170 min, phase separation was observed. Detailed structure was difficult to be distinguished at this time because of the low resolution of the optical microscope. With reaction and phase separation continuing, phase structures grew in size slowly. At $t = 195$ min, the morphological structure could be discerned as bicontinuous. Phase structures gradually coarsened. From $t = 205$ min on, coalescence of the domains became more and more obvious; many large domains were gradually formed. The large domains continuously grew in size (up to 20–30 μm), coalesced and converged into channels. However, at about 320 min, the large domains seemed to have disappeared from our visual

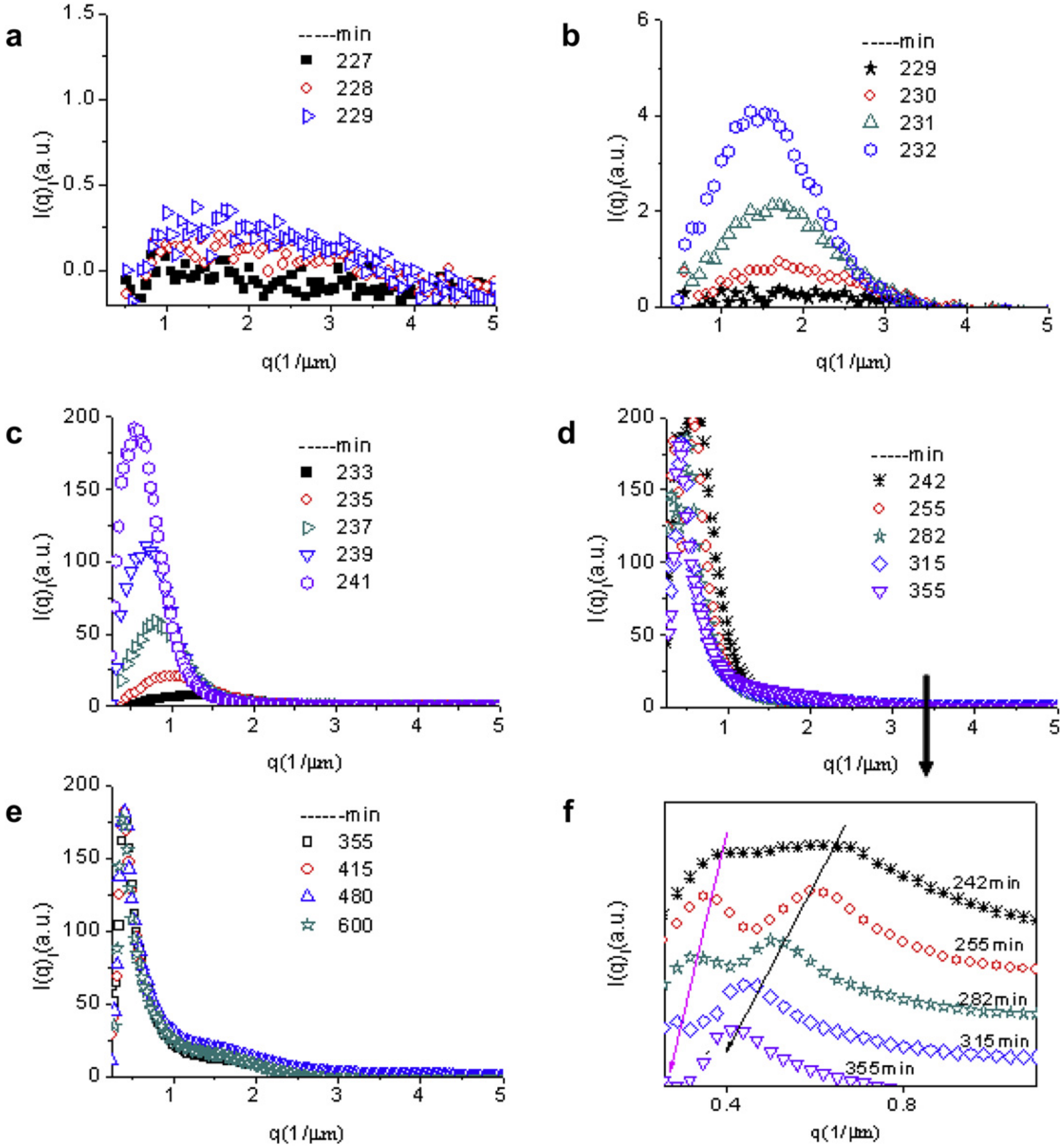
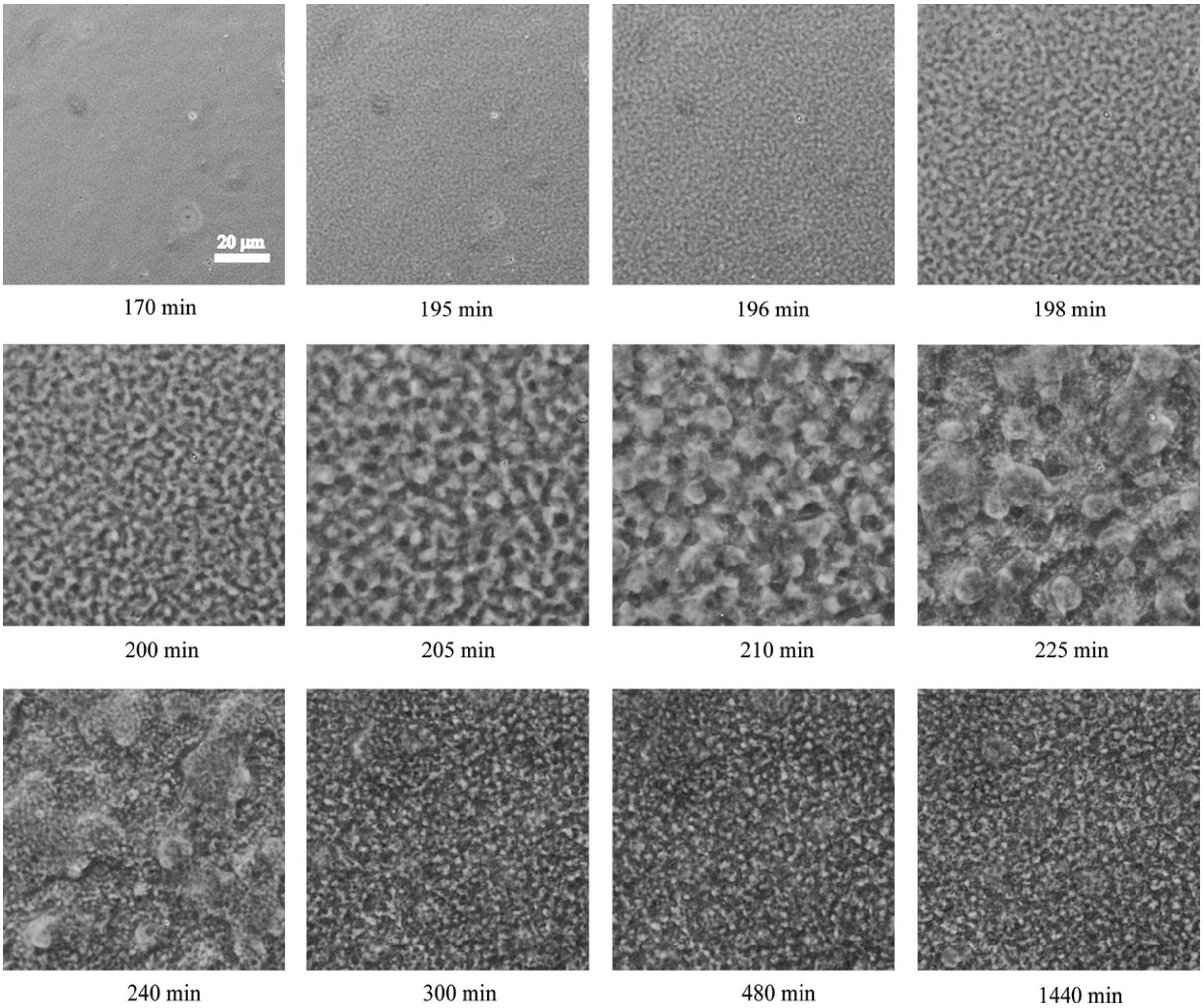


Fig. 3. Time-resolved light scattering patterns (a–e) of sample $w = 0.15$ cured at 130 °C (a.u.: arbitrary unit). Pattern f is the magnification of the scattering peaks part of pattern d, where each curve is vertically shifted.

field. After $t = 360$ min, when gelation of the epoxy curing reaction has already occurred [33], the morphological structure stopped changing any more.

Neglecting the experimental uncertainties and resolution differences from different instruments, development of the morphologies obtained in PCOM was consistent with phase separation evolution detected by TRLS. After phase separation was observed, it developed in the usual phase separated structures firstly. Phase structures gradually coarsened and coalesced to form large domains. The large domains, even up to 20–30 μm size, coexisted with the small domains, around several microns. This two-domain structure was consistent with the two scattering peaks in the TRLS experiment. These large domains gradually coalesced, formed channel structures, then flew out of the middle part (our view field in the PCOM observation) and formed the outer layers. Thus the scattering peak at smaller wave number became weaker and weaker and finally disappeared in the TRLS measurement.

SEM information of the samples cured at different time intervals can also support our explanation, as illustrated in the fractured surfaces shown in Fig. 5. At the beginning of phase separation, homogeneous structure formed in the whole sample film, like the image at $t = 160$ min. With the phase separation proceeding, both PSF- and epoxy-rich phases were more and more concentrated. At $t = 180$ min, three layers were observed, with the middle layer consisted of bicontinuous domains. Outer layers were relatively thin, and they were mainly composed of epoxy-rich phase. In the middle part, both PSF-rich and epoxy-rich phases were continuous. The PSF-rich phase has a trend to be more aggregated, moving to the center part of the film. This process could be described as “shrinking”. Before gelation of the epoxy resin occurred, the continuous PSF-rich phase continued to shrink and the epoxy-rich phase could gradually flow to the outer layer. Finally three parallel layers were formed in the sample film, like the image at $t = 300$ min and $t = 1440$ min. If the large epoxy-rich domains did not flow out before the gelation occurred, they could be trapped in the middle layer. At higher curing temperature, e.g. 200 °C, cure reaction was faster than at lower temperatures. Three-layered structure also formed, with detailed morphological structure being somewhat

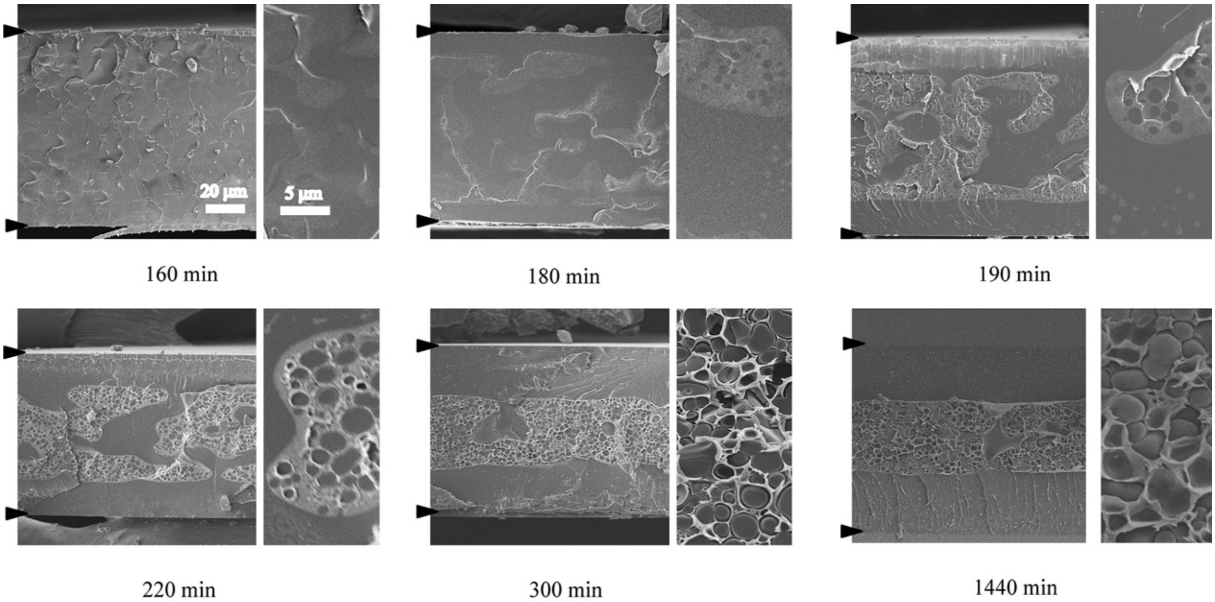


170 min 195 min 196 min 198 min

200 min 205 min 210 min 225 min

240 min 300 min 480 min 1440 min

Fig. 4. Phase-contrast optical microscopy images of blends $w = 0.15$ cured for different time at 130 °C.



160 min 180 min 190 min

220 min 300 min 1440 min

Fig. 5. Scanning electron micrographs of the fractured surfaces with sample $w = 0.15$ cured at 130 °C for different times. The right pictures in each panel are the higher magnification pictures for the middle part of the sample.

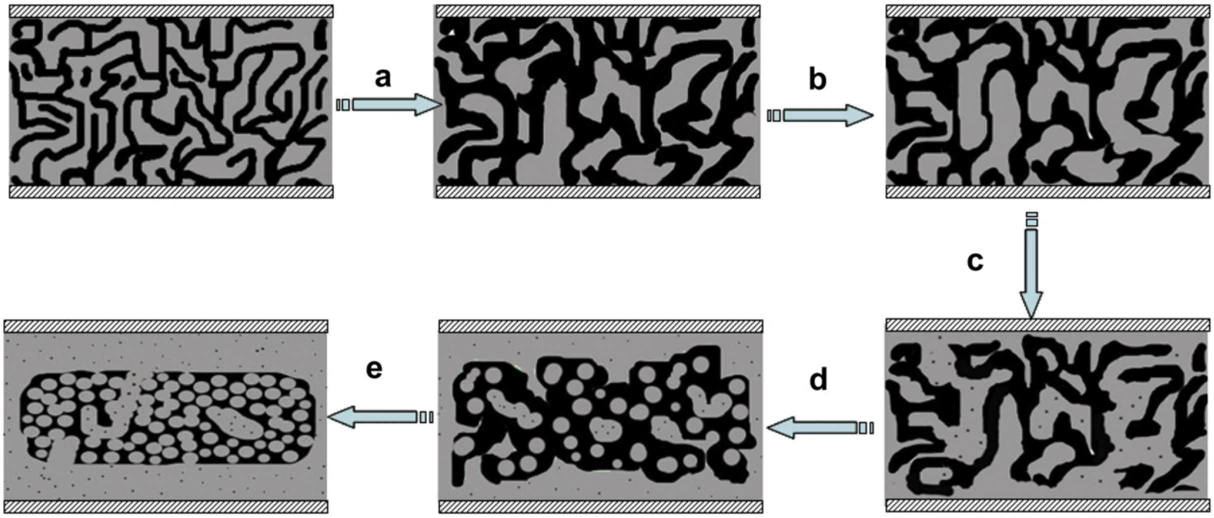


Fig. 6. Schematic model of the three-layered structure formation process. Epoxy-rich phase: ▨ (gray), PSF-rich phase: ■ (dark). Bicontinuous structure growing in size, a; PSF-rich domains shrinking (becoming thinner and thinner), b; Epoxy-rich phase converging as channels, c; Large epoxy-rich domains flowing out, d; and PSF-rich domains shrinking further towards the center, e.

different. The higher the curing temperature was, the more large epoxy-rich domains existed in the middle layer.

In this system, viscoelastic properties between the components were quite different, especially at the beginning of phase separation. The PSF has a high molecular weight and high glass transition temperature, while both molecular weight and glass transition temperature of epoxy are very low at the early stage of phase separation. The initial coexistence curve is quite asymmetrical, with the critical concentration located at a low polysulfone concentration. As the reaction proceeded, molecular weight of epoxy was increasing and the binodal line was also moving [1,10,28]. With reaction and phase separation continuing, PSF- and epoxy-rich phases were both moving toward their more concentrated coexisting compositions corresponding to the phase diagram at that moment. Thus, after the initial growth, PSF-rich phase would continuously decrease its volume fraction [28,30]. When the curing temperature (T_{cure}) is lower than $T_{\text{g,PSF}}$, PSF-rich phase would behave like glassy solid; at $T_{\text{cure}} > T_{\text{g,PSF}}$, PSF-rich phase would behave like a polymeric elastomer. At the same time, molecular weight of epoxy gradually increased, which could not be very high before gelation occurred. Compared with the PSF-rich phase, the epoxy-rich phase has a faster dynamics before it is gelled. Therefore, asymmetric phase separation occurred based on the different viscoelastic properties of the components.

At certain composition, e.g. $w = 0.15$, bicontinuous structure formed at the early stage of phase separation. However, they changed to three layers after the sample film was cured. Formation of the three-layered structure could be understood with the help of the schematic model shown in Fig. 6. The process was roughly divided into 5 stages. In the first stage (a), bicontinuous structure formed and grew in size, according to the initial stage of phase separation. After the initial increase, volume fraction of PSF-rich phase would decrease, which could be described as stage b. Asymmetrical phase separation continued. The PSF-rich phase became more PSF rich and domain structures became thinned or shrinked. In this process, each phase was more and more concentrated (moving toward the higher concentration of the majority component). The large molecular weight entangled network of the PSF-rich phase could start to shrink inwards due to the elasticity of the network, the low viscosity of epoxy oligomers and the negative driving force of Gibbs free energy, ΔG, towards its coexisting composition. Due to the different viscoelastic properties between the two phases, shrinking process could continue and the PSF-rich phase moved towards the middle part of the sample, as shown in stage c. With phase separation going on, relaxation of PSF-rich network was also happening. As the epoxy-rich domains grew, the stress on the slow dynamic PSF-rich network also grew. Since the PSF-rich domain was only an entangled network instead of a permanently cross-linked network, the relaxation motion of PSF chains could cause some break-ups in the network, i.e. the network chains partially disentangled. The break-up of the PSF-rich network could form channels or pockets like voids for epoxy-rich domains and finally the fast dynamic component (epoxy-rich phase) could flow out and coalesced into larger domains. With the shrinking process of the PSF-rich network continuing, more and more epoxy-rich domains converged to form larger channels, and eventually flew out to the outer part of the sample, as shown in stage d. This process would continue before the epoxy-rich phase was gelled. Thus, layered structure was gradually formed based on the dynamic asymmetrical phase separation and hydrodynamic flow process. When the epoxy-rich phase could not flow any more, phase separation can only continue locally. The final morphological structure was pinned by the gelation and later vitrification of epoxy.

4. Conclusion

We investigated the reaction-induced phase separation process in the epoxy/DDS/PSF blends. Three distinct morphological structures were observed at different PSF compositions. Sea-island structure formed in the lower PSF *w* sample, while nodular structure formed at higher PSF *w*. In the middle PSF *w* range, a three-layered structure can be formed.

Formation process of the three-layered structure was studied through microscopic observation and time-resolved light scattering measurements. Bicontinuous structure formed at the beginning of phase separation. Then the phase domains coarsened quickly after the initial growth. Epoxy-rich domains gradually grew in size and coarsened. While the PSF-rich domain network became thinner and thinner in order to continuously decrease its volume fraction.

Difference in viscoelastic properties between the two components was very large in this system. At the beginning of phase separation, epoxy-rich phase showed good fluidity, while the PSF-rich phase behaved as the slow dynamic component. Being more and more concentrated with the phase separation continuing, the continuous PSF-rich phase (network) would shrink towards the middle part of the sample. Meanwhile the fast dynamic component, epoxy-rich phase, kept its fluidity. With the shrinking process of PSF-rich phase, epoxy-rich domains gradually converged to become large domains, broke some part of the PSF-rich thin walls, grew to be even larger, formed channel like structures and flew out to the outer space. This period related to the double-peak phenomenon in the TRLS experiment. With the asymmetric phase separation continuing, the three-layered structure was eventually formed.

Acknowledgement

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[33] According to the gelation theory deduced by Flory, gelation in this system would occur at the epoxy conversion $\chi = 0.65$, corresponding to the time $t = 340$ min in our DSC measurement.