

Structural and Material Properties of a Rapidly Cured Thermoplastic-Toughened Epoxy System

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ABSTRACT: Thermoplastic-toughened epoxy resins are widely used as matrices in modern composite prepreg systems. Rapid curing of thermoplastic-toughened epoxy matrix composites results in different mechanical properties. To investigate the structure–property relationship, we investigated a poly(ether sulfone)-modified triglycidylaminophenol/4,4'-diamino diphenyl sulfone system that was cured at different heating rates. An intermediate dwell was also applied during the rapid heating of the thermoplastic-modified epoxy system. We found that a higher heating rate led to a larger domain size of the phase-separated macrostructure and also facilitated more complete phase

separation. The intermediate dwell helped phase separation to proceed even further, leading to an even larger domain size of the macrostructure. A carbon-fiber-reinforced polymer matrix composite prepreg based on the poly(ether sulfone)-modified multifunctional epoxy system was cured with the same schedule. The rapidly heated composite laminates exhibited higher mode I delamination fracture toughness than the slowly heated material. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 485–491, 2009

Key words: curing of polymers; morphology; phase behavior; thermoplastics

INTRODUCTION

Carbon-fiber-reinforced polymer matrix composites have been widely used for secondary structures on aircraft to reduce weight. Rising oil prices and pressure to reduce carbon emissions require the aircraft industry to use even more of these materials. Boeing is aiming to incorporate composites into its new 787 passenger aircraft to the extent of about 50% of the total airframe by weight. Airbus 350 will require around 41% of aircraft construction to be composites.¹ Under these circumstances, the development of composite manufacturing technologies has become one of the key requirements for meeting the increasing demand for high-performance composite structures. Traditionally, advanced polymer matrix composites are produced by autoclave technology, which employs relatively low heating rates (1–2°C/min) to ensure uniform heating and to avoid runaway exothermic reactions in the thermosets. Various rapid composite fabrication technologies have been developed and used recently for processing polymer matrix composites of a quality similar to aerospace grade but in a shorter time and at a lower

cost.^{2–7} Microwaves, electron beams, Quickstep (a process that uses fluid as a heat-transfer medium), and other out-of-autoclave technologies have enabled much faster heating of composite components, and this reduces production costs significantly.

Thermoplastic additives have been proven to be very effective in toughening brittle epoxies without significantly compromising the high modulus and high glass-transition temperature of epoxies.^{8,9} The toughening mechanism of thermoplastic modification involves phase separation of an initially homogeneous blend of thermoplastics and epoxies.^{10,11} The phase-separation process of thermoplastic/epoxy blends has been studied extensively. Nucleation and growth (NG), spinodal decomposition (SD), or a mixed mode of both can occur during the separation process. When there is a low concentration of the thermoplastic modifier, it tends to segregate from the matrix by the NG mechanism; for blends containing higher thermoplastic contents, phase separation proceeds by the more complex SD mechanism and leads to epoxy particles dispersed in the matrix. These epoxy particles grow and become connected to form epoxy-rich macrophases with irregular shapes. In the mean time, small thermoplastic particles appear within the dispersed epoxy-rich macrophase, and small epoxy particles appear within the continuous thermoplastic-rich macrophase. After that, phase inversion can occur, resulting in the transformation of the epoxy-rich macrophase from

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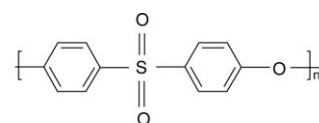
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being dispersed to continuous. Further secondary phase separation can occur within the thermoplastic-rich macrophases. Chen and Chang¹² demonstrated the NG and SD mechanisms in detail by providing illustrative graphs. The rate at which the temperature is increased to the final cure temperature can play an important role in affecting the phase-separation process, therefore resulting in different mechanical properties.¹³ In this work, a poly(ether sulfone) (PES)-modified triglycidylaminophenol (TGAP)/4,4'-diamino diphenyl sulfone (DDS) system was investigated. The polymer blend was heated at a low rate of 1.5°C/min and a high rate of 10°C/min, which simulate autoclave curing and rapid curing, respectively. The morphology of the phase-separated structure in the thermoplastic/epoxy blends and the mode I delamination fracture toughness of the composite specimens were studied. To improve surface finish and mechanical performance, an intermediate dwell is often used during the rapid heating of composite components for degassing when the resin is at its lowest viscosity.¹⁴ This work also investigated the influence of intermediate dwell on the phase structure of the thermoplastic/epoxy blends and the end properties of their fiber-reinforced composites.

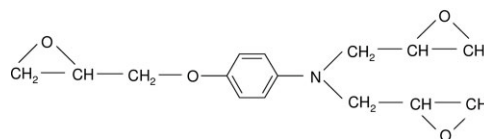
In general, the objective of this study was to clarify the effects of curing conditions such as the heating rate and intermediate dwell on the phase structure and fracture toughness of thermoplastic-modified epoxy systems. A polymer blend (100/30/30 TGAP/PES/DDS) was studied as a model system for the study of the cure kinetics and *in situ* phase structure observation. A commercial thermoplastic-toughened composite system (Hexply914) was cured with the same schedules. The mode I delamination fracture toughness of the composite laminate specimens was tested, and the phase structure of the delaminated fracture surface was investigated with scanning electron microscopy (SEM). Because Hexply914 and the studied polymer blend are both PES-modified multifunctional epoxy systems, the results indicate a general trend of the influence of the heating rate and intermediate dwell.

EXPERIMENTAL

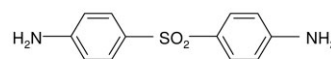
The thermoplastic modifier PES (Ultrason E1010 natural; 20,000 < number-average molecular weight < 30,000) in a granular form was purchased from BASF (Melbourne, Australia), the epoxy resin TGAP (Araldite MY0510) with an epoxy equivalent of 95–106 was provided by Hunstman (Melbourne, Australia), and the hardener DDS was purchased from Sigma–Aldrich (Sydney, Australia) (purity > 97%). The chemical formulas of the individual components can be illustrated as follows:



polyether sulphone (PES)



Triglycidylaminophenol (TGAP)



4,4'-diaminodiphenyl sulfone (DDS)

The epoxy/thermoplastic blends were prepared by solution casting from methylene chloride at room temperature. The blends were placed onto glass slides for *in situ* optical observation of the phase morphology. The solvent was allowed to evaporate slowly at room temperature. To remove the trace solvent, the blends were dried in a vacuum oven at 50°C for 15 h. A Nikon (Melville, NY) Eclipse 80i microscope equipped with a Linkam LTS 350 (Surrey, UK) hot stage was used for optical observation, and a Leo 1530 (Oberkochen, Germany) field emission scanning electron microscope was employed to examine the microstructures of the cured blends. The *in situ* optical images were taken with ACT-2U software in the DIC/PH mode. The fracture surfaces of the cured blends were immersed in methylene chloride at room temperature for 10 h. The thermoplastic phase was preferentially etched by the solvent, whereas the epoxy phase remained unaffected. Etched specimens were then dried and coated with gold/palladium before SEM observation. An SEM in-lens detector was used for imaging. The aperture size was 30.00 μm, and the electrical high tension was 5 kV. Nonisothermal cure kinetics were studied with real-time Fourier transform infrared spectroscopy. Polymer blends were coated onto KBr disks for monitoring the epoxy conversion. A Bruker (Ettlingen, Germany) Vertex 70 Fourier transform infrared spectrometer equipped with a Specac 20730 electrical heating cell (London, UK) was used in the absorption mode with a resolution of 4 cm⁻¹.

A polymer blend (100/30/30 TGAP/PES/DDS) was used for investigation in this work. It was cured according to three different schedules. Cure A used a heating rate of 1.5°C/min, whereas cure B and cure C used a heating rate of 10°C/min. The curing temperature of the blend was 175°C, and the isothermal curing time was 130 min. An intermediate dwell at 110°C for 30 min was adopted for cure C. The cure schedules are displayed in Figure 1.

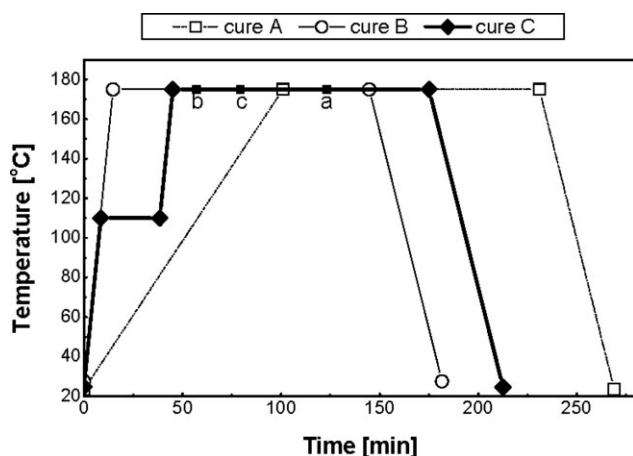


Figure 1 Three cure schedules employed for the cure of the TGAP/PES/DDS (100/30/30) blend: cure A (heating rate of 1.5°C/min and cure temperature of 175°C), cure B (heating rate of 10°C/min and cure temperature of 175°C), and cure C (heating rate of 10°C/min, 30 min of intermediate dwell at 110°C, and cure temperature of 175°C). The points at which phase separation starts for (a) cure A, (b) cure B, and (c) cure C are indicated.

The commercial composite prepreg Hexply914 was cured with the same schedules used for the polymer blends with both autoclave and Quickstep processes. The low heating rate (1.5°C/min) cure was conducted with an American Autoclave (Alpharetta, GA) MB-2036-415-315-800 minibonder at Australian National University, and the high heating rate cures (10°C/min) were conducted with a Quickstep QS5 (Perth, Australia) at Deakin University. The Quickstep technology is a rapid out-of-autoclave composite production process that uses fluid as the heat-transfer medium to achieve heating rates as high as 10°C/min. A detailed description of this technology can be found in refs. 15 and 16. The mode I delamination fracture toughness tests were performed in accordance with the protocol of the

European Structural Integrity Society.¹⁷ The delaminated fracture surfaces of the mode I delamination test specimens were etched by methylene chloride before SEM observation. The secondary electron detector was used. The aperture size was 30 μm , and the electrical high tension was 5 kV too.

RESULTS AND DISCUSSION

The starting point of phase separation for each cure schedule is indicated by points a, b, and c in Figure 1, which correspond to cure A, cure B, and cure C. Because of the different curing conditions, the time required for phase separation to occur is different for each cure schedule. When phase separation starts to happen, the optical morphology changes from homogeneous to heterogeneous, as can be seen in Figure 2 (the difference can be detected in the optical micrographs taken at 56 and 70 min). For cure A, phase separation occurs when the polymer blend is cured at 175°C for 21 min; for cure B, phase separation occurs when the blend is cured at 175°C for 42 min; and for cure C, phase separation starts when the blend is cured for 34 min at 175°C following a 110°C intermediate dwell. The phase separation at 175°C occurs too quickly for the optical micrographs to distinguish different stages of the separation process. Consequently, the cure temperature was lowered to 160°C so that the phase-separation process could be slowed; this facilitated the *in situ* optical micrograph capture. Figure 2 shows optical micrographs illustrating the phase-separation process at 160°C. The blend remains homogeneous until it is cured for 70 min at 160°C. Then, a cocontinuous structure appears, indicating that phase separation takes place by the SD mechanism.¹⁸ After 74 min, the periodic distance of the structure increases with time, and this results in a phase structure with irregular macrophases dispersed in a continuous matrix. With the growth of the macrophases, small

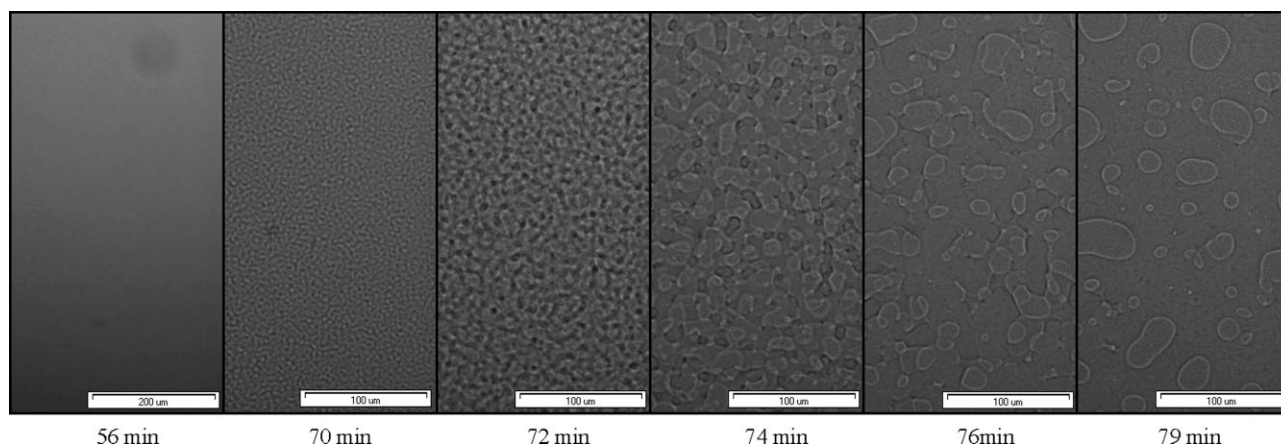


Figure 2 Process of phase separation of the TGAP/PES/DDS (100/30/30) blend monitored with an optical microscope at 160°C.

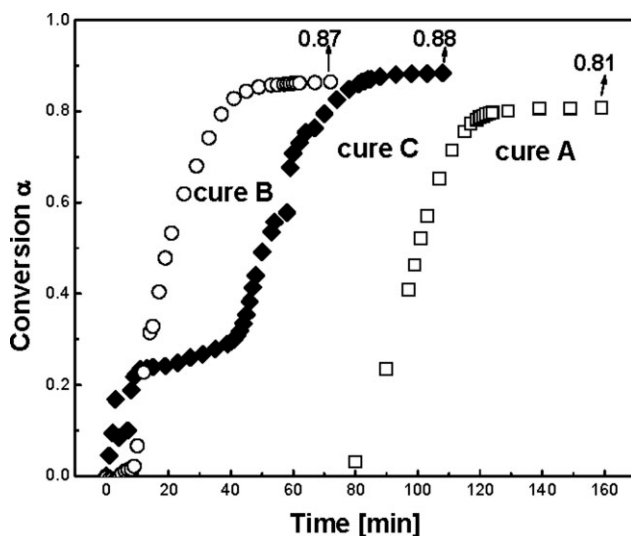


Figure 3 Nonisothermal kinetics for TGAP/PES/DDS (100/30/30) following temperature programming of different cure schedules.

particles appear in both the dispersed macrophases and the continuous matrix (76 min). The morphology stabilizes at 79 min.

The cure kinetics were investigated via the monitoring of the intensity changes at the 908-cm^{-1} band¹⁹ (the oxirane ring stretching mode). The epoxy conversions, followed by different cure schedules up to 60 min at 175°C , are shown in Figure 3. Because of the low heating rate of cure A, the epoxy does not show obvious conversion until 80 min after the cure is started. The conversion curve for cure C displays an intermediate step when the blend is heated isothermally at 110°C . The higher heating rate results in a higher epoxy conversion. The epoxy conversion after 60 min of curing at 175°C is 0.88 for cure C and 0.87 for cure B, and these values are higher than the conversion of 0.81 for slowly heated cure A. Although cure A takes a much longer time than the other two cure schedules, the final epoxy conversion is actually lower than that of the other cure schedules. The epoxy conversion is higher for cure C than for cure B because of the extra curing time at 110°C .

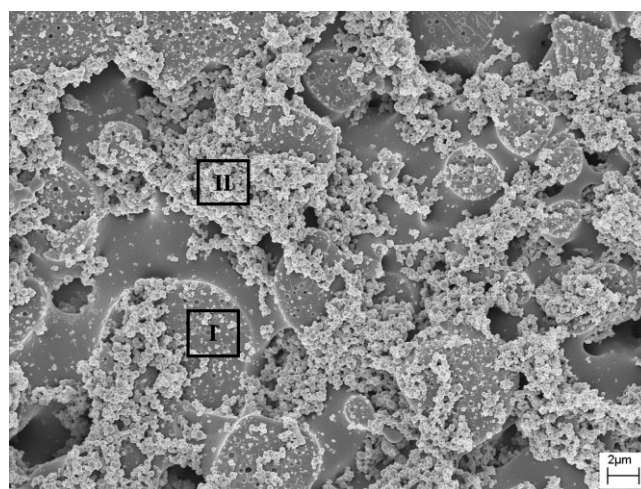


Figure 4 SEM morphology of the phase-separated structure of the cured TGAP/PES/DDS (100/30/30) blend: (I) the epoxy-rich macrophase and (II) the thermoplastic-rich macrophase.

Figure 4 shows the SEM morphology of the phase-separated structure. Two different regions exist: I and II. Region I is the epoxy-rich macrophase containing dispersed thermoplastic-rich particles, and region II is the thermoplastic-rich macrophase containing numerous epoxy particles. To correlate the optical morphology with the SEM morphology, the cover for an optical glass slide specimen was carefully removed, and the exposed material was etched by methylene chloride. SEM micrographs were taken of the dispersed macrophases in the optical specimen, as shown in Figure 5. Because the thermoplastics were etched away, the epoxy particles were exposed. This suggests that the dispersed macrophase is a thermoplastic-rich macrophase composed of epoxy particles embedded within a continuous thermoplastic phase. It also implies that phase inversion takes place in this composition.

To study the influence of the heating rate and intermediate dwell on the morphology of the phase structure, optical micrographs and SEM micrographs are compared in Figures 6 and 7. Figure 6 shows

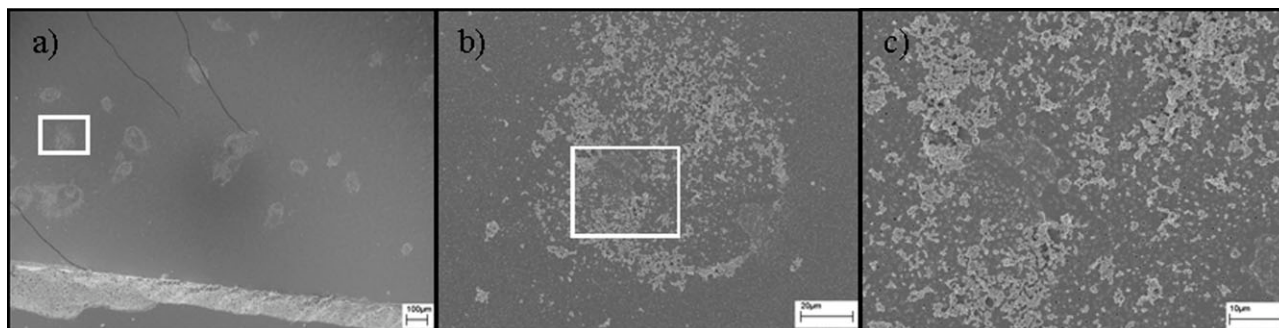


Figure 5 (a) SEM morphology of the dispersed macrophase in an optical specimen, (b) an enlargement of the area framed in panel a, and (c) an enlargement of the area framed in panel b.

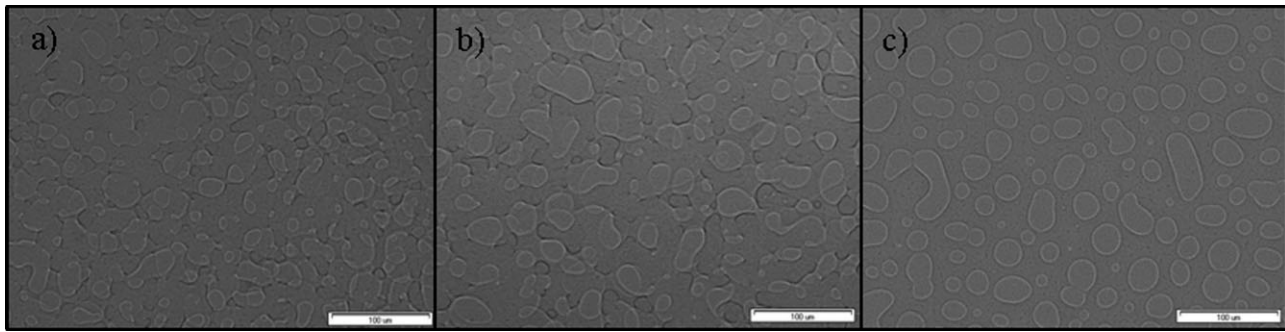


Figure 6 Optical morphology of the phase-separated structure: (a) cure A, (b) cure B, and (c) cure C.

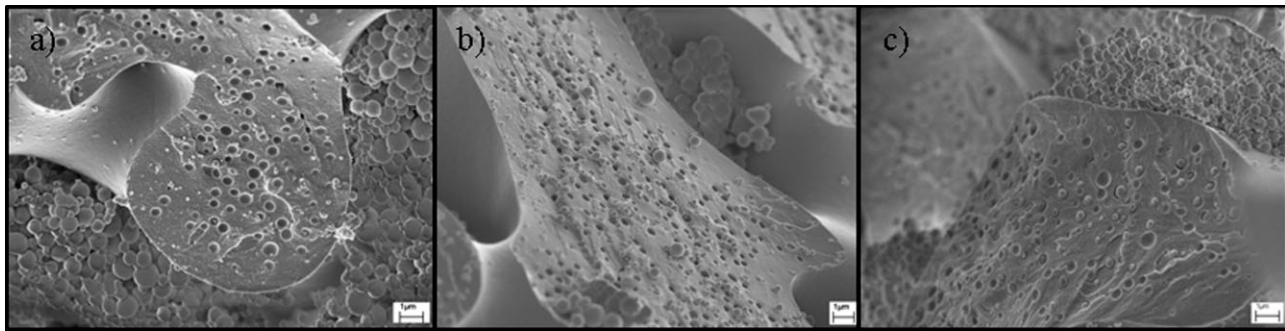


Figure 7 SEM morphology of the phase-separated structure of the cured TGAP/PES/DDS (100/30/30) blend: (a) cure A, (b) cure B, and (c) cure C.

TABLE I
Comparison of the Thermoplastic Macrophase Distributions in the Optical Micrographs of the TGAP/PES/DDS (100/30/30) Blend Cured with Different Cycles

		Number of samples	Mean diameter (μm)	Length (μm)	Width (μm)	Mean area (μm^2)	Per area (%)
Cure A	Average	202	9.67	12.30	8.08	107.80	14.94
	SD	15	0.64	0.76	0.64	11.22	1.33
Cure B	Average	167	11.41	14.60	9.35	162.75	18.74
	SD	17	0.62	0.60	0.66	11.87	1.98
Cure C	Average	117	18.23	20.97	16.14	340.02	27.54
	SD	9	0.93	1.29	0.71	28.08	2.24

Cure A: heating rate of 1.5°C/min and cure temperature of 175°C; cure B: heating rate of 10°C/min and cure temperature of 175°C; and cure C: heating rate of 10°C/min, 30 min of intermediate dwell at 110°C, and cure temperature of 175°C.

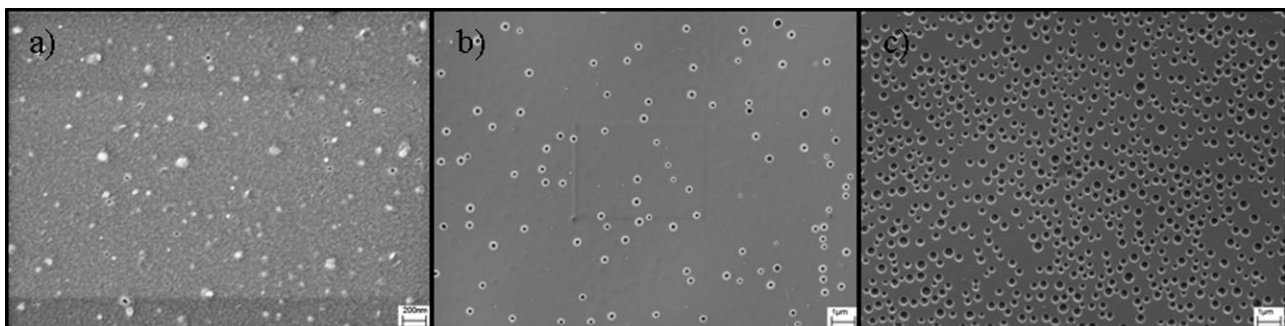


Figure 8 SEM morphology of the unfractured surface of the cured TGAP/PES/DDS (100/30/30) blend: (a) cure A, (b) cure B, and (c) cure C.

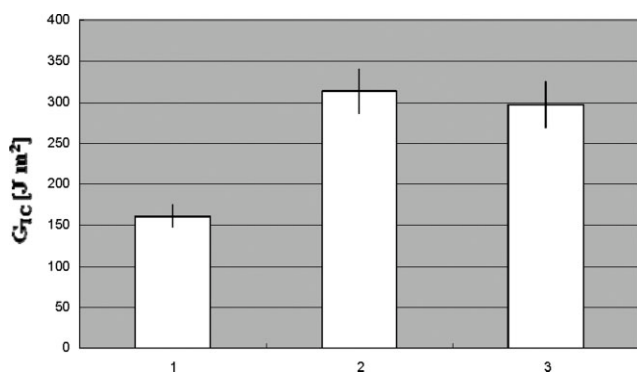


Figure 9 Comparison of the mode I delamination fracture toughness (G_{IC}) for composite specimens cured with the same schedule: (1) cure A, (2) cure B, and (3) cure C.

that these curing conditions affect the size and shape of the dispersed thermoplastic-rich macrophases in the continuous matrix macrophase. With the increase in the heating rate, the size of the dispersed macrophases increases. The dispersed macrophases spheroidize more for the blend cured with an intermediate dwell, and this signifies more complete phase separation. Image analysis software (Image-Pro Plus 4.5.1) was used to measure the domain size and the area percentage occupied by the dispersed thermoplastic-rich macrophases. The comparison results are summarized in Table I. With the increase in the heating rate, the number of dispersed macrophases decreases, but the average size of the dispersed macrophases increases in both length and width. The area percentage occupied by the dispersed thermoplastic-rich macrophases increases with the increase in the heating rate. The domain size and the area percentage occupied by the thermoplastic-rich macrophases are largest for the cure that incorporates an intermediate dwell. It is expected that a higher cure temperature will provoke an increase in the average size of the dispersed phase and a decrease in the concentration of the dispersed phases.^{18,20} When blends are cured with a

higher heating rate, they experience a shorter curing time at a low temperature.

Figure 7 displays the SEM morphology of the blend cured with different schedules. It is difficult to detect the differences in the microstructure of the cured blend. However, the SEM micrographs (Fig. 8) of the unfractured surface showed a difference in the number and size of the thermoplastic-rich particles. Both the number and size of the thermoplastic-rich particles increase clearly with the increase in the heating rate. The number and size of the thermoplastic-rich particles are even larger for the cure that incorporates an intermediate dwell. This compares well with Chen and Chang's work,¹² which found that no or incomplete phase separation can result from a high viscosity of the blend. Previously, Davies et al.⁴ compared the viscosity of the commercial Hexply 6376 prepreg heated at rates of 2, 5, 10, and 15°C/min. They found that the minimum viscosity in the 6376 resin decreased with an increase in the heating rate. Therefore, it can be suggested here that a higher heating rate results in a lower resin viscosity, which further promotes a higher degree of phase separation.

The Hexply914 prepreg is a high-temperature-resistant, high-performance system used for primary aircraft structures. PES is used in this prepreg as a thermoplastic modifier to toughen the multifunctional epoxies tetraglycidyl diamine diphenylmethane and TGAP.²¹ Composite laminates were manufactured with the same heating schedules applied to the TGAP/PES/DDS (100/30/30) blend. The isothermal curing time at 175°C was 1 h for the composite laminates. A postcure at 190°C for 4 h was applied after each cure schedule. The mode I delamination fracture toughness results for the composite laminate specimens are shown in Figure 9. The rapidly heated specimens exhibited much higher fracture toughness than the specimens heated at a lower rate. The SEM morphology of the delaminated fracture surface can be seen in Figure 10. A connected-globule phase-separated structure was generated by this composite

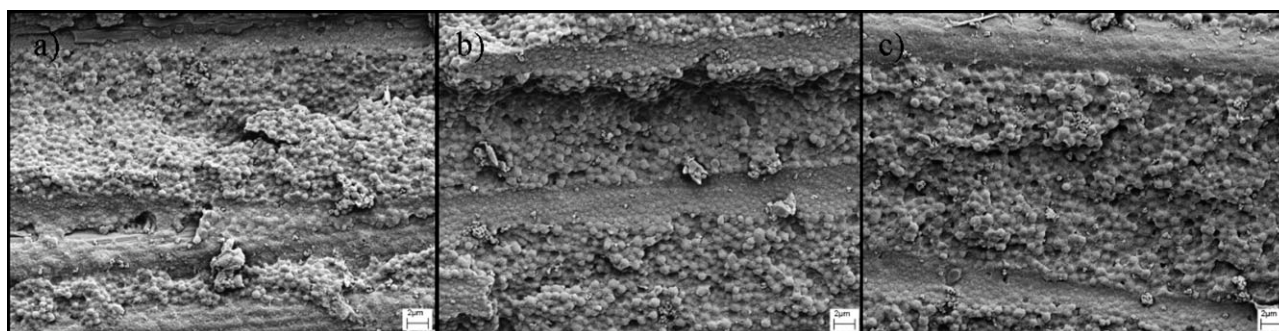


Figure 10 SEM morphology of the phase-separated structure of the cured Hexply914 composite: (a) cure A, (b) cure B, and (c) cure C.

system. The domain sizes of the composites cured with different cure cycles exhibited a difference. With analysis software (Soft Imaging System Co.), the average domain size of the epoxy globules was measured. The average domain size was 0.80 μm for composites processed by cure A, 0.88 μm for composites processed by cure B, and 0.93 μm for composite samples processed by cure C. It showed a trend similar to that of the optical morphology observed in the TGAP/PES/DDS (100/30/30) blend.

CONCLUSIONS

The phase structure and nonisothermal cure kinetics of the rapidly heated (10°C/min) PES-modified TGAP/DDS system have been investigated by comparison with a system cured at a slow heating rate of 1.5°C/min. It has been shown that the increase in the rate at which the temperature rises to the final cure temperature results in a larger domain size of the dispersed thermoplastic-rich macrophases. The area percentage occupied by the thermoplastic-rich macrophases in the optical images increases with the increase in the heating rate too. An intermediate dwell leads to an even larger domain size of the dispersed macrophases, a more spherical shape of the dispersed macrophases, and an even larger area percentage occupied by thermoplastic-rich macrophases. Rapidly heated systems exhibit higher epoxy conversions than the slowly heated system. SEM observation reveals that higher heating rates lead to a larger degree of phase separation. The rapidly heated thermoplastic-toughened commercial composite system Hexply914 showed higher mode I delamination frac-

ture toughness than the slowly heated materials. The influence of the curing conditions on the phase structure of the cured Hexply914 exhibited a trend similar to that of the thermoplastic-modified epoxy blend.

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