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Double-phase morphology of high molecular weight poly(methyl methacrylate)-epoxy blend

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Abstract The double-phase morphology of 5 wt% high molecular weight poly(methyl methacrylate) (PMMA) modified epoxy system was investigated by optical and scanning electron microscopic (SEM) techniques. PMMA-epoxy blend cured at 100 °C revealed that a bicontinuous secondary phase separation was observed in both epoxy and PMMA phases in the early stages of curing. Epoxy-rich particles were dispersed in the PMMA-rich phase, while PMMA-rich particles were segregated in the epoxy-rich phase, leading to double-phase bicontinuous morphology. The spinodal decomposition mechanism could probably be responsible for this secondary phase separation. From the SEM analysis, a morphology consisting of a rough striated continuous phase along with large smooth regions was observed. Rough striated domains are ascribed to the PMMA-rich phase and the smooth domains are assigned to the epoxy-rich phase, thus confirming the secondary phase separation. The PMMA-epoxy blend showed a slight increase in flexural properties and about 20% improvement in the fracture toughness.

Introduction

Epoxy resins find significant applications in advanced composites due to their high dimensional stability at elevated temperatures, excellent thermal and chemical resistance, high mechanical strength, and easy processability. These matrices, however, are highly brittle [1] due to high crosslink densities. Blending of thermoplastics with thermosetting epoxy resins is an attractive method for improving the fracture toughness of these epoxy resins. These blends are miscible initially but as the curing progresses, they become immiscible and phase separate and the epoxy becomes highly cross-linked. Improvements of fracture toughness and other mechanical properties in epoxy resin by incorporation of thermoplastics are attributed to such phase separation and formation of small particles of thermoplastics which inhibit crack propagation [2]. Homogeneous resin/polymer blends would turn into multiphase systems with complex phase morphologies after curing with curing agents. Several studies were done on improving the toughness of epoxy resin by the incorporation of thermoplastics such as poly(ether imide) (PEI) [3], polysulfone (PSF) [4, 5], poly(ether sulfone) [6, 7], and poly(ether ketone) (PEK) [8]. High molecular weight poly(methyl methacrylate) (PMMA)-modified epoxy is the subject of the present study. Its high solubility in epoxy resin and non-reactivity with DGEBA even after prolonged heating at 220 °C [9, 10] enables one to select a high molecular weight PMMA to study its mechanical properties. Gomez and Bucknall [9] and Hseih and Woo [11] reported the blends of PMMA with epoxy resins. The former study was focused on the phase separation characteristics of a PMMA-DGEBA/cylco-aliphatic diamine blend. Morphology is a significant factor influencing the mechanical properties of modified epoxy blends [12–14]. Modifier level and curing conditions are the two key factors controlling the final morphology of the blend. Mondragon et al. [15] and Remiro et al. [16, 17] demonstrated that the morphologies of PMMA-modified epoxy

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matrices depend on PMMA content and the curing conditions.

The addition of small content of high molecular weight thermoplastics has a significant importance because the small amounts of high molecular weight polymers can lead to secondary phase separation even at the very initial stages of the curing, which will have a considerable effect on the final morphologies and various mechanical and fracture properties. The aim of the present study is to study the phase morphology of the epoxy modified with small content of the high molecular weight PMMA using optical and scanning electron microscopy (SEM). The fracture toughness and flexural properties of the resultant material will also be discussed.

Experimental

The epoxy resin used was diglycydyl ether of bisphenol-A (DGEBA) (YD-115, Kukdo Chemical, Korea), with an epoxide equivalent weight of 180–194 g. The curing agent was polyamidoamine (PAA) (G-A0533, Kukdo Chemical, Korea). Poly(methyl methacrylate) (PMMA, Mw = 120,000) was purchased from Aldrich. Dichloromethane (99.8%) was supplied by Sigma–Aldrich.

Epoxy mixture containing 5 wt% of poly(methyl methacrylate) (PMMA) was prepared by the following method: a corresponding amount of PMMA was dissolved in dichloromethane at about 10 wt% and then diglycidyl ether of bisphenol-A, DGEBA, resin was added to the solution stirring until complete dissolution. The solvent was removed by heating at 80 °C followed by vacuo at 80 °C. The epoxy–polymer mixture at this stage was transparent. To this mixture, PAA hardener was added at 80 °C and stirred for about 8–10 min until complete dissolution. For all mixtures, epoxy/hardener ratio was taken as 2:1. The neat epoxy matrix (DGEBA/PAA, 2:1) was also cast by the same method.

For optical microscopic analysis, a drop of the mixture was placed between glass slides held together with an adhesive tape. These glass slides were placed in an oven at 100 °C for curing. Partially cured specimens were extracted at different time intervals for their phase separation analysis with an optical microscope. Two epoxy-PMMA specimens cured for 180 min were further post-cured at 150 °C for 2 h and 180 °C for 2 h, respectively.

For mechanical characterization, plaques of 5 mm thick were cast into a Teflon mold and curing was carried out at 100 °C for 3 h followed by post-curing at 150 °C for 2 h.

Dynamic mechanical thermal analysis of neat and modified epoxy blends was performed by a dynamic mechanical analyzer (DMTA, Rheometric Scientific, Mark IV, UK) using rectangular specimens (4.5 × 1 × 0.5 cm), operating at a frequency of 1 Hz in the three-point bending mode, over a temperature range 30–250 °C, at a heating rate of 5 °C min^{-1}. Storage modulus (E') and energy dissipation (tan δ) were measured as a function of temperature.

The fracture surfaces of specimens were studied by SEM (Leica Cambridge, England). Flexural tests were performed in a Materials Testing System (Model: LS Plus, AMETEK LLOYD Instruments Ltd., UK) according to the ASTM D-790 standard at a cross-head rate of 5 mm min^{-1} using 80 × 12 × 5 mm^3 specimens. Fracture toughness tests were performed following European Structural Integrity Society (ESIS) protocol [18] using single-edge-notched type samples (60 × 12 × 5 mm^3) using Instron Universal Testing Machine (Model: 8871) in a tension mode at a cross-head rate of 1 mm min^{-1}. The critical stress intensity factor, K_{IC}, was calculated from fracture toughness test.

Results and discussion

The phase separation process in DGEBA/PMMA blend cured with PAA at 100 °C was studied by optical microscopy. Figure 1 shows the development of bicontinuous phase structure in the 5 wt% PMMA-epoxy blend cured at 100 °C, followed by optical microscopy. Dark areas correspond to a PMMA-rich phase while clear domains indicate an epoxy-rich phase. As shown by Fig. 1a–c, partially cured specimens at 100 °C were extracted at 30, 90, and 150 min respectively. Figure 1d shows the morphology resulting from post-cure step at 150 °C. Not much difference was observed at this magnification with respect to the morphologies in Fig. 1a–c. Figure 2 shows the optical micrographs at a higher magnification. It is observed that from the early stages of the structure development, a double-phase morphology was formed (Fig. 2a). A droplet-type morphology composed of epoxy-rich domains of size in the order of 5–10 μm, surrounded by a PMMA-rich phase is observed. This type of morphology may be generated by an initial bicontinuous structure undergoing a very fast percolation-to-cluster transition [19, 20]. As the cure proceeds, the volume fraction of the epoxy-rich domains increases because of the continuous segregation of epoxy-rich phase from the PMMA-rich phase. These epoxy-rich domains exhibit a dispersion of PMMA-rich particles that were phase-separated from the thermosetting resin (Fig. 2b–d). Similarly, these epoxy-rich domains were dispersed in the continuous PMMA-rich phase. This segregation of the PMMA-rich domains from the epoxy is probably due to the high viscosity of the thermoplastic-rich phase. Similar secondary phase separation was reported by Marieta et al. [21] with DGEBA/DDS/PMMA blend. As reported by Clarke et al. [22], it is possible that a nucleation-growth mechanism be

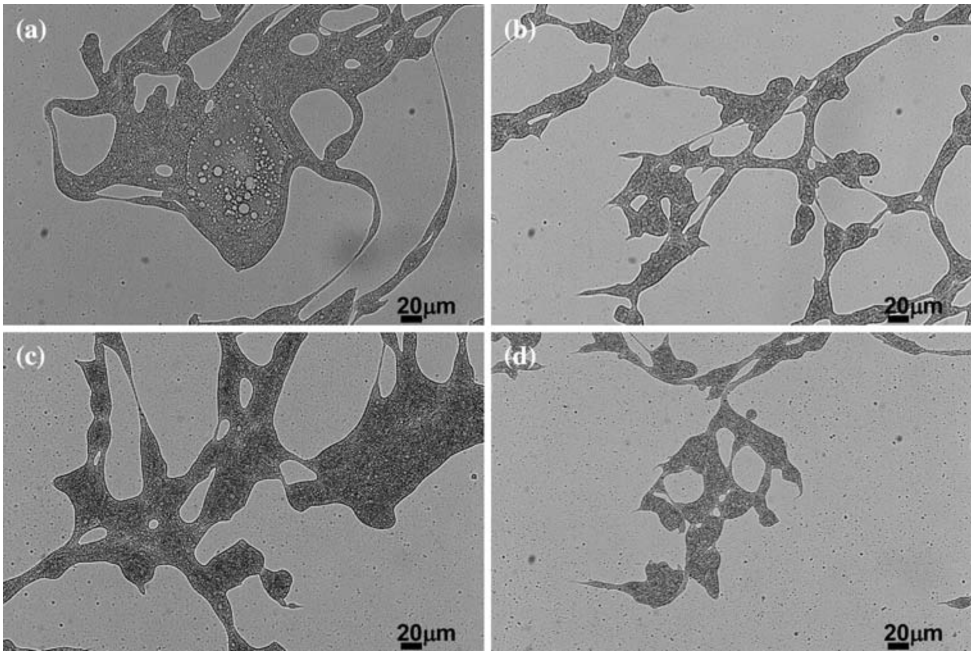


Fig. 1 Optical micrographs of 5 wt% PMMA-epoxy blend cured at 100 °C. (**a**) 30 min, (**b**) 90 min, (**c**) 150 min, and (**d**) after a post-cure at 150 °C

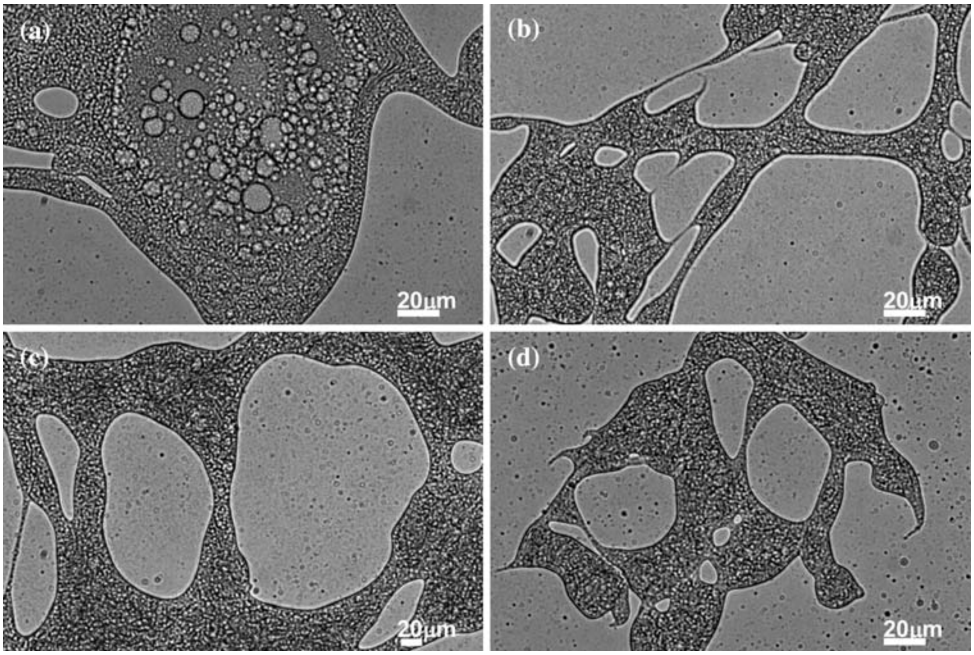


Fig. 2 Optical micrographs with higher magnification for the same 5 wt% PMMA-epoxy blend cured shown in Fig. 1. (**a**) 30 min, (**b**) 90 min, (**c**) 150 min, and (**d**) after a post-cure at 150 °C

responsible for this secondary phase separation in both the phases. However, in most of the earlier reports, the thermoplastic-epoxy systems result in localized phase inversion, in which the epoxy particles are surrounded by isolated thermoplastic domains, which in turn are surrounded by a large continuous epoxy phase. This is a co-continuous phase structure by spinodal decomposition [23–25]. A similar scenario was observed for the present PMMA-epoxy system (Fig. 2) and hence it is expected that the secondary phase separation that has occurred during the curing process is based upon the spinodal decomposition mechanism.

Dynamic mechanical thermographs of neat epoxy and PMMA-modified epoxy were shown in Fig. 3a and b, respectively. A major relaxation peak at around 90 °C with a shoulder peak at higher temperature is observed, which may be corresponding to the epoxy-rich phase (Fig. 3b). It can be observed that the PMMA modification has no major influence on the glass transition temperature of the epoxy-rich phase, indicating that the modified epoxy had a

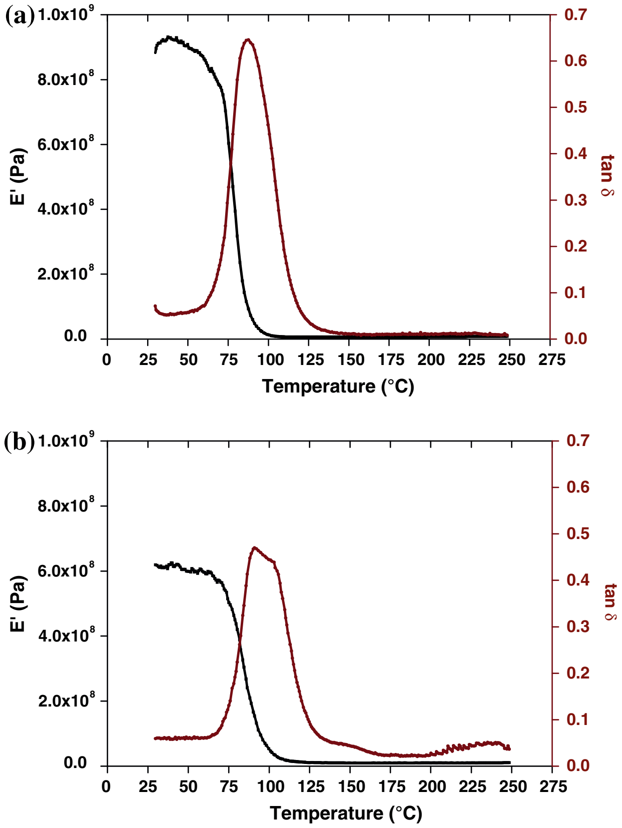


Fig. 3 DMTA spectra of (**a**) neat epoxy and (**b**) 5 wt% PMMA-modified epoxy

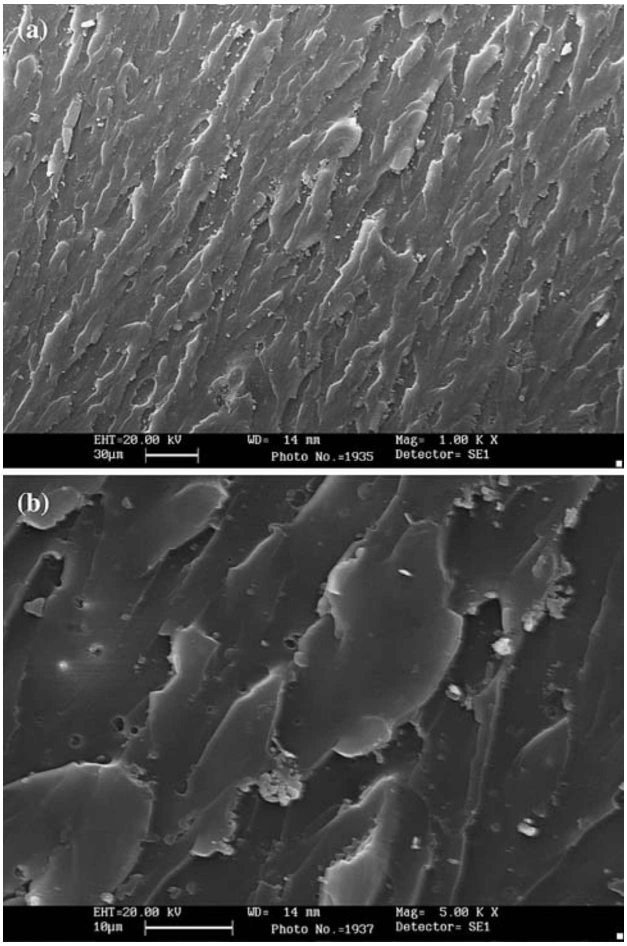


Fig. 4 SEM micrographs of fracture surfaces of 5 wt% PMMA-modified epoxy. (**a**) 1,000× and (**b**) 5,000×

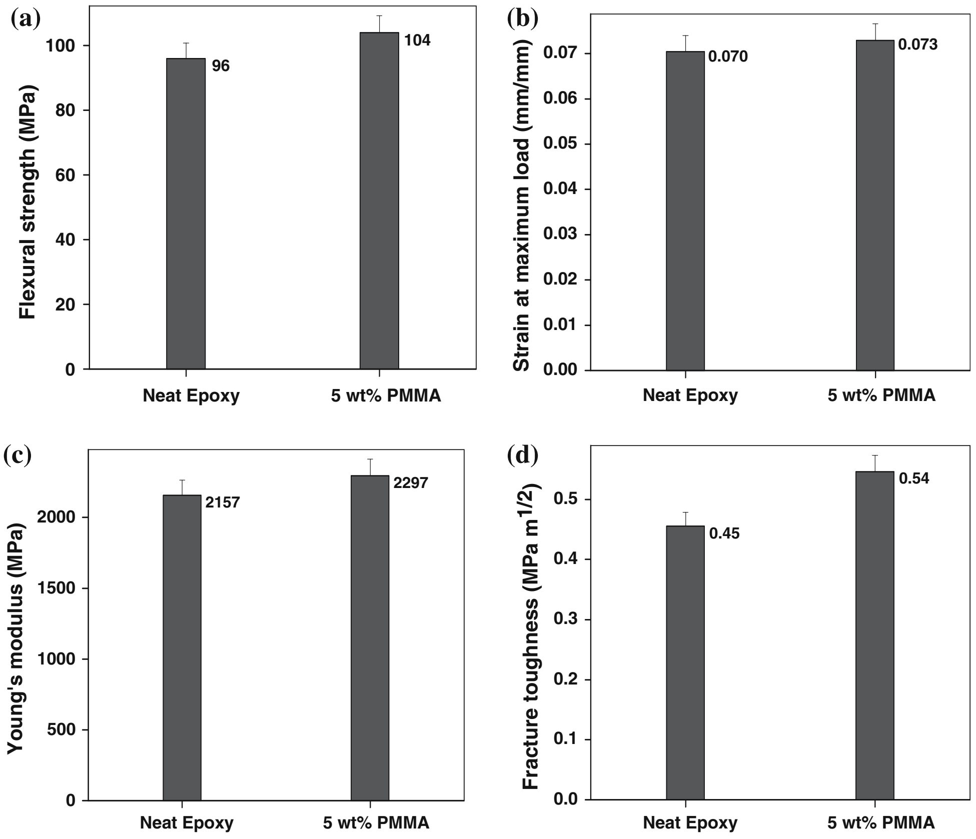
crosslinking density similar to that for the cured neat epoxy.

SEM studies were also carried out for modified epoxy containing 5 wt% PMMA, cured at 100 °C and post-cured at 150 °C. The corresponding micrographs are shown in Fig. 4. Figure 4a shows micrograph of large area of fracture surface. A morphology consisting of a rough striated continuous phase along with large smooth regions was observed. Rough striated domains are ascribed to the PMMA-rich phase and the smooth domains are assigned to the epoxy-rich phase. Figure 4b shows the higher magnification of these domains. PMMA-rich particles with sizes in the micrometer range are dispersed in the epoxy-rich phase, which is a clear evidence of secondary phase separation. Plastic drawing of PMMA-rich particles may be observed together with crack-path deflection. The complex morphology of the rough phase might possibly be arising from a spinodal decomposition mechanism.

The influence of thermoplastic addition in mechanical behavior was also studied. Figure 5 shows the flexural properties and fracture toughness of the neat epoxy and the 5 wt% PMMA-modified epoxy. As shown in Fig. 5a–c, the inclusion of 5 wt% PMMA in the epoxy matrix led to a slight increase in flexural properties. The flexural strength, strain at maximum load, and Young's modulus of epoxy were increased by 8.3, 4.2, and 6.5%, respectively, with an addition of 5 wt% PMMA. Probably the small particles segregated from the epoxy matrix at such a low PMMA amount of 5 wt% did not influence practically the yield strength of these materials.

Figure 5d shows the fracture toughness of the neat and modified epoxies. The values of stress intensity factors at the onset of crack growth were $K_{IC} = 0.45$ MPa m$^{1/2}$ for the neat epoxy and $K_{IC} = 0.54$ MPa m$^{1/2}$ for the blend containing 5 wt% PMMA. The thermoplastic addition led to an improvement of about 20% in fracture toughness of the resulting material. This increase is probably related to the partial purification of the PMMA-rich phase as revealed by the increase in its T_g and also because of the large fractional area covered by the PMMA-rich phase. As it is evidenced from SEM analysis (Fig. 4), the plastic drawing of the PMMA-rich particles in the epoxy-rich phase, together with crack-path deflection and the debonding of the epoxy-rich particles in the thermoplastic-rich phase could be the toughening mechanisms that explain this increase of the fracture toughness.

Fig. 5 Mechanical properties of neat epoxy and 5 wt% PMMA-modified epoxy. (**a**) Flexural strength, (**b**) strain at maximum load, (**c**) Young's modulus, and (**d**) fracture toughness



Conclusions

The addition of small content of high molecular weight PMMA has a significant importance because the small amounts of high molecular weight PMMA will lead to secondary phase separation even at the very initial stages of the curing which will have a considerable effect on the final morphologies and various mechanical and fracture properties. In the present study, the double-phase morphology and mechanical properties of high molecular weight PMMA-epoxy blend were investigated. Morphological features of 5 wt% PMMA modified epoxy mixture were investigated by optical and SEM techniques. A secondary phase separation was observed in both epoxy and PMMA phases at initial stages of curing. Epoxy-rich particles were dispersed in the PMMA-rich phase, while PMMA-rich particles were segregated in the epoxy-rich phase, leading to double-phase bicontinuous morphology. The formation of this secondary phase separation could probably be attributed to the spinodal decomposition mechanism. The PMMA-epoxy blend showed a slight increase in flexural properties and an improvement of about 20% in the fracture toughness.

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