Effect on the Residual Stress of Cure Profiles, Fillers and Mold Constraints in an Epoxy System

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ABSTRACT: *A dilatometer was used to investigate the effect of cure conditions, mold types and the presence of filler in an epoxy system. These studies showed shrinkage in the cured epoxy when heating it through the glass transition temperature region. The magnitude of the shrinkage, related to stress build up in the epoxy during curing, was influenced by the processing conditions, filler presence and the nature of the mold used to contain the resin. Cure and cyclic cure at a lower temperature, prior to a post cure, decreased the magnitude of observed shrinkage. Cure shrinkage decreased with the number of cyclic cures. Post cured samples outside the mold led to less shrinkage compared with samples in the mold. Sample cured in a silicon mold represented less shrinkage than sample cured in an aluminum mold. Sample containing kaolin filler showed less shrinkage than unfilled sample.*

1. Introduction

It is more essential to apply and use new materials properly together with the development of new materials than any other things during the recent and rapid industrial development in a highly sophisticated industrial society. Fiber reinforced plastics (FRP) are composite materials composed of heat hardening resin among new materials and are advanced composite materials (ACM) with the matrix of epoxy resin that has relatively excellent chemical properties. Composite materials as new materials have excellent light weight, heat resistance, mechanical characteristics, and control characteristics, and therefore, the uses are increasing broadly as materials of structures in relevant areas such as space and aviation industry for airplane and artificial satellites and transportation industry for ships and railroad, sporting goods, medical instrument parts, and mechanical parts. Especially, the excellent adhesion to carbon fibres and the low shrinkage on curing provide epoxy resins advantages over other resin systems for being used as the matrix materials for advanced composites. However, the cross-linked structure results in brittleness of epoxies which limits their application in circumstances where higher toughness is required.

Since residual stresses are inherently present in virtually all composite materials and influence the properties of the composite structures significantly (Favre, 1988; Unger and Hansen, 1998; Kim and Mai, 1998; Adams, et al., 1991), it is of utmost importance that the residual stresses are taken into account in both design and analytic modelling of composite structures (Johnston et al., 1991; Manson and Seferis, 1992). Predictive models for residual strains and stresses in composites require verification and validation with experimental results. Many experimental techniques for residual stress determination in polymer matrix composites have been developed in the past (Eijpe, 1997; Favre, 1988; Schulz et al., 2005).

In many adhesive applications, epoxies are geometrically constrained during cure, leading to residual stresses. These residual stresses are undesirable because they may lead to premature debonding of the epoxy from a substrate. Volume changes that occur in an epoxy during the cross-linking process are known to produce curing stresses (Prasatya et al., 2001). Optimizing the cure temperature-time profile of the epoxy may minimize stress formation (Adolf et al., 1998). Slower heating rates allow more time for the polymer to relax and relieve stresses created during cure (Russel et al., 2000).

In the present work, the effect of cure conditions, mold constrains and filler presence has been investigated to understand their role in stress development in an epoxy system.

2. Experimental

2.1 Materials

An epoxy system was chosen based on diglycidyl ether of bisphenol A (YD-127) epoxy resin, obtained from Kukdo Chemical Corporation (South Korea). The epoxy curing agents were Nadic Methyl Anhydride (KBH-1085) and Benzyl

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Dimethy Amine (KBH-1086). Kaolin was purchased from Buyeo Materials Corporation (South Korea) and, if used, was placed in the epoxy at concentrations of 36 wt.%.

2.2 Sample preparation

Samples of the epoxy and the epoxy/kaolin (36 wt.%) composites were prepared as follows. Epoxy resin and dried kaolin were mixed after heating at 60°C for 10 min to reduce the viscosity and cured according to given cure profiles. Sample size was approximately 15 mm wide, 5 mm thick and 160 mm length. In additions, cyclic cure after heating at 80°C for 1 h was performed at low temperature as shown in Fig. 1. And then some of them were postcured at 120°C for 1 h in and out of mold.

2.3 Thermal analysis

Dilatometer and differential scanning calorimeter (DSC) were employed to measure thermal properties of the epoxy resin and its composites according to given cure profiles.

Length changes of specimen as a function of temperature were measured using a Perkin-Elmer (U.S.A) thermal mechanical analyzer (TMA). The instrument was outfitted with a flat tipped expansion probe. A 0.11 N force was applied, and samples were tested from 40 to 150°C at 5°C/min under a nitrogen gas. The samples were approximately 5 mm wide, 5 mm thick, and 5 mm length.

DSC used Perkin-Elmer (U.S.A). All samples (10~13 mg) were contained within sealed aluminum DSC pans and tested from 50 to 200°C at 10°C/min under a nitrogen atmosphere.

2.4 Cure profiles

The influence of different cure conditions on dilatometric behavior was studied by investigating nine different cure profiles. A schematic of cyclic cure after heating at 80°C for 1 h is presented in Fig. 1.
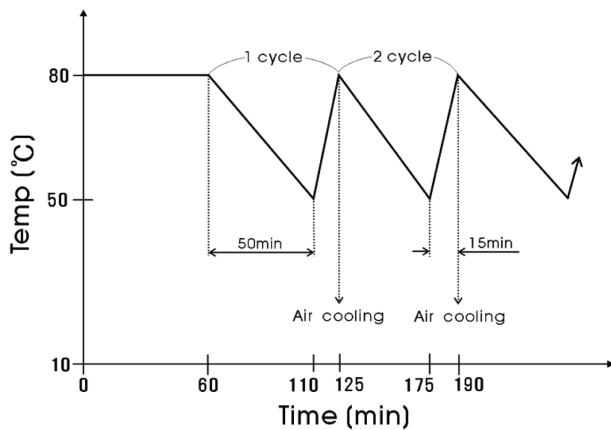

Fig. 1 Schematic of cyclic cure

1. 80°C 2 h, 120°C 2 h (post cure)
2. 120°C 1 h (no post cure)
3. 120°C 2 h (no post cure)
4. 80°C 1 h, 1 cycle (80°C → 50°C: 50 min, 50°C → 80°C: 15 min)
5. 80°C 1 h, 2 cycles
6. 80°C 1 h, 3 cycles
7. 80°C 1 h, 4 cycles
8. 80°C 1 h, 5 cycles
9. 80°C 1 h, 5 cycles, 120°C 1 h (post cure)

For the various cure profiles, the epoxy was dispensed in a mold and placed in an oven that had been preheated to the desired cure temperature for the specified time. For samples containing a post cure, the oven was immediately ramped to the desired post cure temperature following the initial cure step.

3. Results and Discussion

3.1 Effect of cyclic cure

DSC was used to determine the difference in extent of cure for each cure condition. Exothermic peak was observed in subsequent DSC isotherms. The areas of the exothermic peak are shown in Table 1.

Comparison of this exothermic peak area to the exothermic peak area of a sample with no cure can be used to determine the degree of cure of the specimen using the following relationship:

$$x = 1 - \frac{\triangle H_t}{\triangle H_0} \tag{1}$$

Where, Δt is the residual heat evolved for a partially cured material, ΔH_0 is the total heat of reaction evolved for the sample with no cure, and χ is the degree of cure. The DSC analysis results are also shown in Table 1. After 80°C for 1 h and 1 cycle, the sample is 12.7% cured. After 80°C for 1 h and 5 cycles, the sample is 73% cured.

These partially cured samples were examined in a linear

Table 1 DSC residual heats of reaction

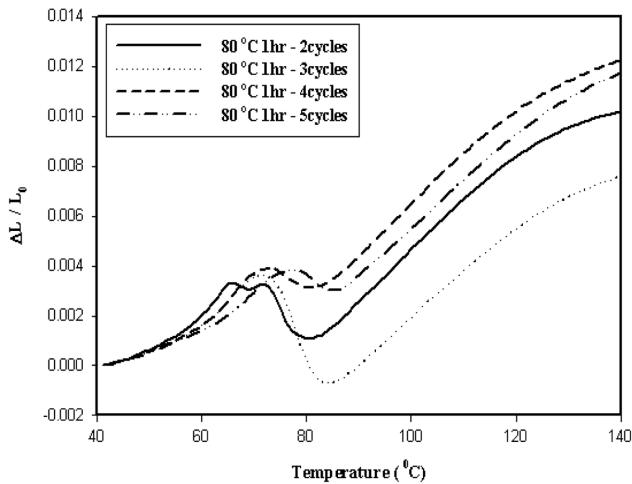| Sample	ΔH [J/g]	Cure [%]
No cure	188.917	0
80°C 1 h, 1 cycle	164.898	12.7
80°C 1 h, 2 cycles	70.048	62.9
80°C 1 h, 3 cycles	67.486	64.3
80°C 1 h, 4 cycles	60.517	68.0
80°C 1 h, 5 cycles	50.942	73.0
120°C 2 h	0	100

Fig. 2 Dilatometer results for samples cured at 80°C for 1 h under each cycle
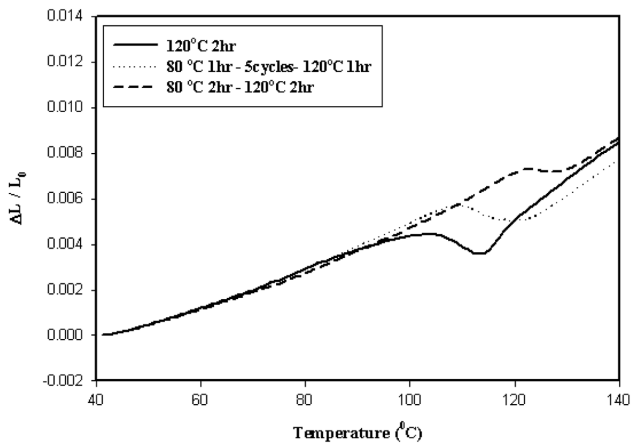
Fig. 3 Dilatometer results for standard cure samples versus cyclic cure

Fig. 4 Dilatometer result for samples cured at 80°C for 1 h, 5 cycles and post cured at 120°C for 1 h (without kaolin)

Fig. 5 Dilatometer result for samples cured at 80°C for 1 h, 5 cycles and post cured at 120°C for 1 h (kaolin of 36 wt.%)

dilatometer. The average change in length normalized by the initial length is plotted as a function of temperature for each processing condition and is shown in Fig. 2 and Fig. 3. The samples exhibit shrinkage on heating through the glass transition temperature. As the glass transition temperature increased the cure shrinkage decreased with number of cyclic cure after heating at 80°C for 1 h. It is known that epoxies contract during curing.

3.2 Influence of post cure in or out of mold

It was postulated that the mold surfaces were constraining the samples during polymerization, thus causing the stress buildup and later shrinkage of the epoxy resin system in the dilatometer. Other studies in the literature have demonstrated that in volumetrically constrained epoxies large stresses develop due to cure shrinkage and thermal expansion/contraction (Plepys et al., 1994). Therefore,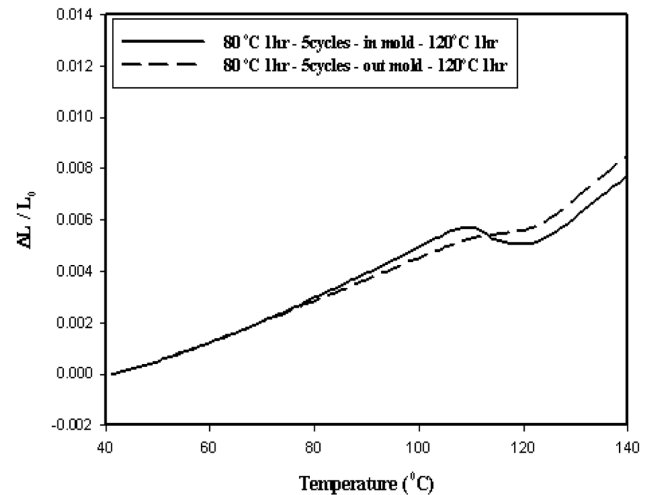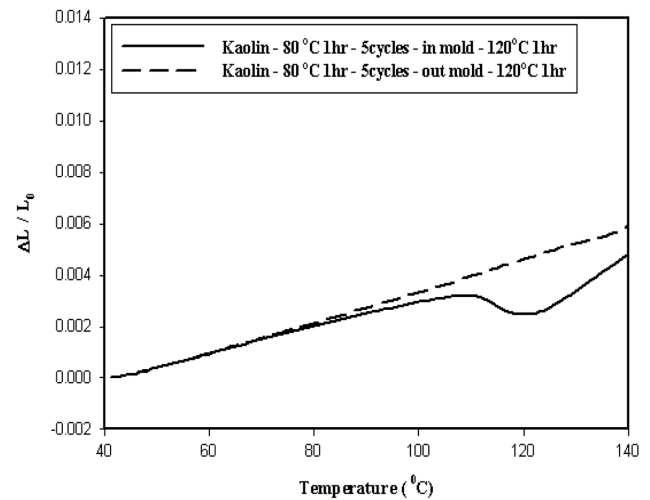 the effects of mold constraints on stress relief were studied by heating the epoxy samples after cure (80°C for 1 h, 5 cycles and then 120°C for 1 h post cure) above the glass transition temperature either in the mold or out of the mold. The dilatometer results are shown in Fig. 4 and Fig. 5. Heating samples out of the mold allowed stresses that developed during the curing to be reduced, leading to less shrinkage observed in the dilatometer. However, samples reheated in the mold were constrained and stresses generated during cure could not be retarded; therefore greater shrinkage was observed in the dilatometer.

3.3 Effect of kaolin filler presence

Kaolin particles were added to the epoxy resin system. The fillers may lead to lower conversion and thereby lower the cross-link density of the epoxy resin, but the filler may still
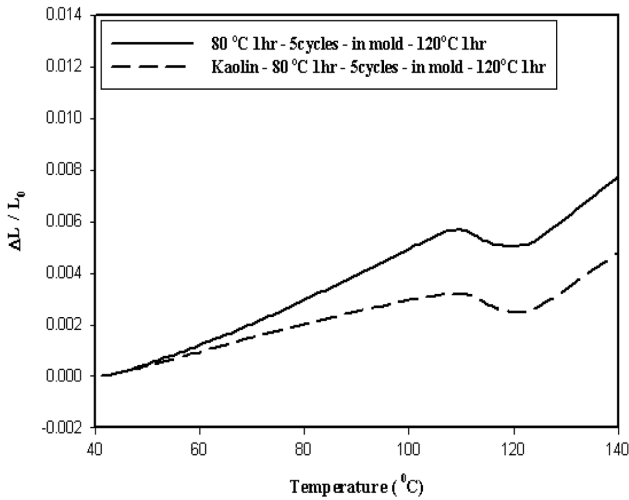
Fig. 6 Dilatometer results for samples cured at 80°C for 1 h, 5 cycles and then post cured in mold at 120°C for 1 h
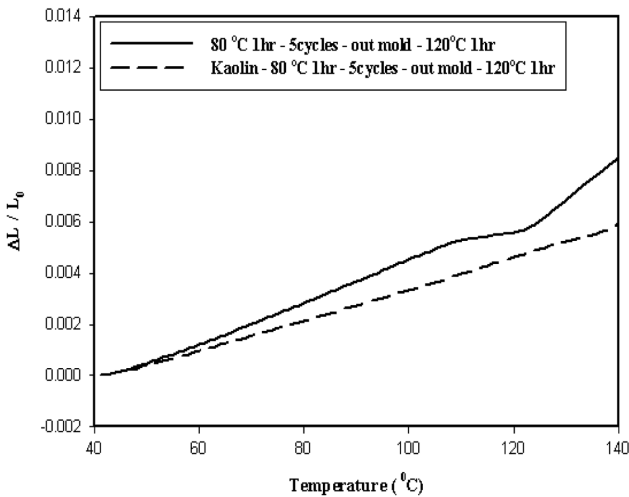

Fig. 7 Dilatometer results for samples cured at 80°C for 1 h, 5 cycles and then post cured out of mold at 120°C for 1 h

constrain the polymer chains.

A dilatometer was used to investigate the epoxy system filled with kaolin. The results are plotted in Fig. 6 and Fig. 7. The sample containing kaolin of 36 wt.% had less shrinkage than unfilled epoxy. This behavior could be attributed to restricted molecular mobility of the reactive species induced by the presence and reactivity of kaolin.

3.4 Influence of mold type

To examine further the effects of mold constraints, specimens were cured in a silicone mold and compared with otherwise identical ones cured in an aluminum mold. We note that specimens cured in the silicone mold exhibited less shrinkage on heating than those cured in the aluminum mold. Some of the reasons for this effect could be as follows: (1) the surface

energy of the silicone is lower, and thus the poorly adhering epoxy is not constrained as it contracts on polymerization; (2) the silicone is more compliant than the epoxy resin, thus allowing stress relief. All of these factors would lead to greater constraints and higher stresses in the epoxy when the aluminum mold was utilized, thus creating more measured shrinkage in the dilatometer. These results are consistent with their research (Kan et al., 1975), who have also indicated anomalous dilatometer curves as a result of stresses introduced during processing due to adhesion of the polymer to the side of the mold.

4. Conclusions

Based on the results obtained and discussed previously, the following conclusions may be drawn: Cure and cyclic cure at a lower temperature, prior to a post cure, decreased the magnitude of observed shrinkage. Cure shrinkage decreased with the number of cyclic cures. Post cured samples outside the mold led to less shrinkage compared with samples in the mold. Samples reheated in the mold were constrained and stresses generated during cure could not be relieved; therefore greater shrinkage was observed in the dilatometer. Samples cured in a silicone mold represented less shrinkage than samples cured in an aluminum mold. And samples containing kaolin filler showed less shrinkage than unfilled samples.

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