한국해양공학회 2006년도 추계학술대회 논문집 pp. 233~236

Effect on the residual stress of cure conditions in an epoxy system

KYUNG HEE YU*, SANG HA SEO**, YOUNG UN KIM***, AND CHANG KWON MOON*

*Major of Materials Science and Engineering, Pukyong National University, Busan 608-739, Korea.
**Department of Computer Aided Mechanical Design, Busan Polytechnic College, Busan 616-101, Korea.
***Korea Institute of Maritime and Fisheries Technology, Busan 608-080, Korea.

KEY WORDS: Dilatometer, Shrinkage, Cure profile, Cyclic cure, Filler, Kaolin.

ABSTRACT: *A dilatometer was used to investigate the effect of cure conditions 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 number of cyclic cure. Post cured samples outside the mold led to less shrinkage compared with sample in the mold. And sample containing kaolin filler showed less shrinkage than unfilled sample.*

1.Introduction

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 (Macon, D., Prasatya, P. et al.).

Optimizing the cure temperature-time profile of the epoxy may minimize stress formation (Adolf, D. B. et al.). Slower heating rates allow more time for the polymer to relax and relieve stresses created during cure (Russel, J. D. et al.).

In the present work, the effect of cure conditions, mold constrains and filler presence have 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), obtained from Kukdo Chemical Corporation(south korea). The curing agents were Nadic Methyl Anhydride (KBH-1085) and Benzyl Dimethy Amine (KBH-1086). Kaolin was purchased from Buyeo Materials Corporation(south korea) and, if used, was placed in the epoxy at concentration 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℃ for 5min to reduce the viscosity of the epoxy 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℃ for 1hr was performed at low temperature as shown in Fig. 1. And then some of them were postcured at 120℃ for 1hr 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.

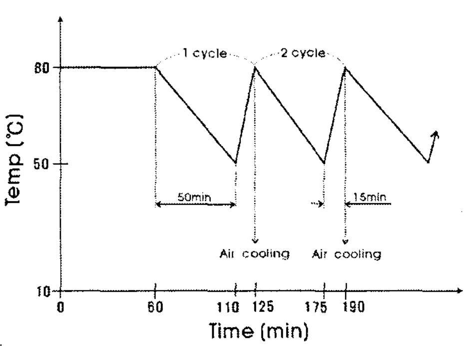

Fig. 1 Schematic of cyclic cure

교신저자 문 창권: 부산광역시 남구 용당동 산 100번지
051-620-1654 moonck@pknu.ac.kr

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 0.11N force was applied, and samples were tested from 40 to 150℃ at 5℃/min under a nitrogen gas. The samples were approximately 5mm wide, 5mm thick, and 5mm length. DSC used was Perkin-Elmer (U.S.A). All samples (10 ~13mg) were contained within sealed aluminum DSC pans and tested from 50 to 200℃ at 10℃/ 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. Schematic of cyclic cure after heating at 80 ℃ for 1hr was presented Fig. 1.

1. 80℃ for 2hrs, 120℃ for 2hrs (post cure)
2. 120℃ for 1hr (no post cure)
3. 120℃ for 2hr (no post cure)
4. 80℃ for 1hr, 1cycle
5. 80℃ for 1hr, 2cycles
6. 80℃ for 1hr, 3cycles
7. 80℃ for 1hr, 4cycles
8. 80℃ for 1hr, 5cycles
9. 80℃ forlhr, 5cycles, 120℃ for 1hr (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.

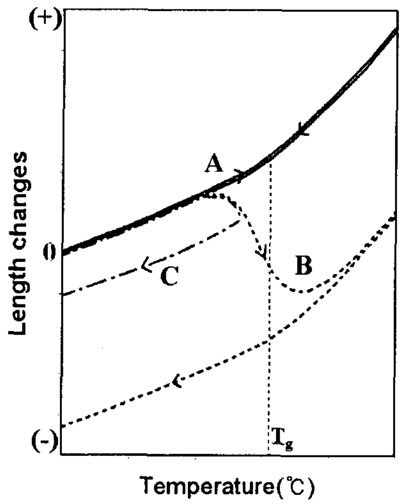

Fig. 2 Schematic of cyclic curing concept

In the Fig. 2 plot A shows the typical dilatometer result of a glassy polymer without residual stress, and plot B shows shrinkage from incomplete cure of the sample or the presence of residual stresses. So, to minimize shrinkage, cyclic cure method was applied. This is a partially cured several times at lower temperature to less shrinkage, that led to less residual stresses.

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. And the DSC analysis results are also shown in Table 1. After 80℃ for 1hr and 1cycle, the sample is 12.7% cured. After 80℃ for 1hr and 5cycles, the sample is 73% cured.

These partially cured samples were examined in a linear 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. 3 and Fig. 4.

Table 1. DSC Residual Heats of Reaction

Sample	ΔH (J/g)	% cure
No cure	188.917	0
80℃ 1hr, 1cycle	164.898	12.7
80℃ 1hr, 2cycles	70.048	62.9
80℃ 1hr, 3cycles	67.486	64.3
80℃ 1hr, 4cycles	60.517	68.0
80℃ 1hr, 5cycles	50.942	73.0
120℃ 1hr	0	100
120℃ 2hrs	0	100

The samples exhibit shrinkage on heating through the glass transition temperature. And glass transition temperature increased and cure shrinkage decreased with number of cyclic cure after heating at 80℃ for 1hr. It was known that epoxy 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 work in the literature has demonstrated that in volumetrically

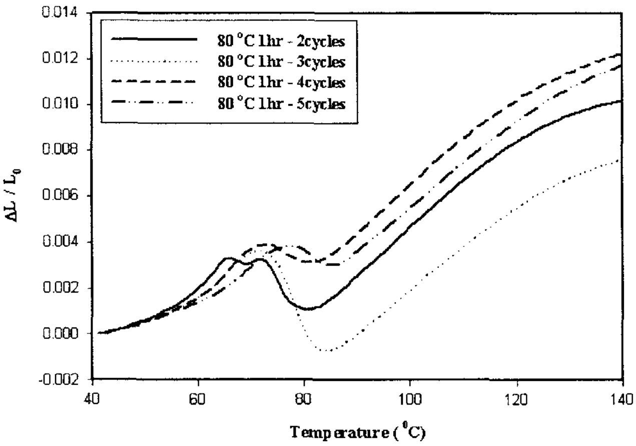

Fig. 3 Dilatometer results for samples cured at 80℃ for 1hr each cycle

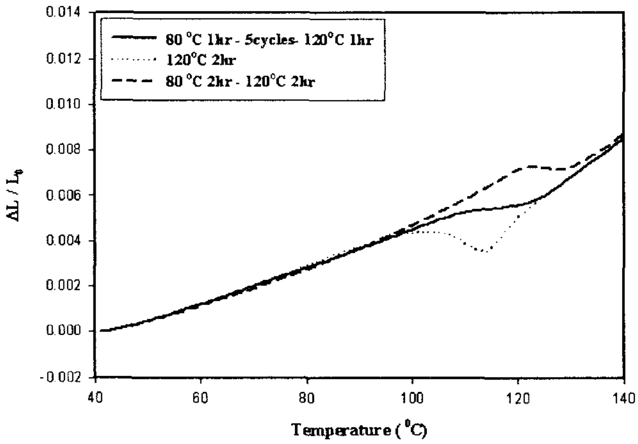

Fig. 4 Dilatometer results for standard cure samples versus cyclic cure

constrained epoxies large stresses develop due to cure shrinkage and thermal expansion/ contraction (Plepys, A. et al.). Therefore, the effects of mold constrains on stress relief were studied by heating the epoxy samples after cure (80℃for 1hr, 5cycles and then 120℃for 1hr post cure) above the glass transition temperature either in the mold or out of the mold. The dilatometer results are shown in Fig. 5 and Fig. 6. 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 relieved; therefore greater shrinkage was observed in the dilatometer.

3.3 Effect of kaolin filler presence

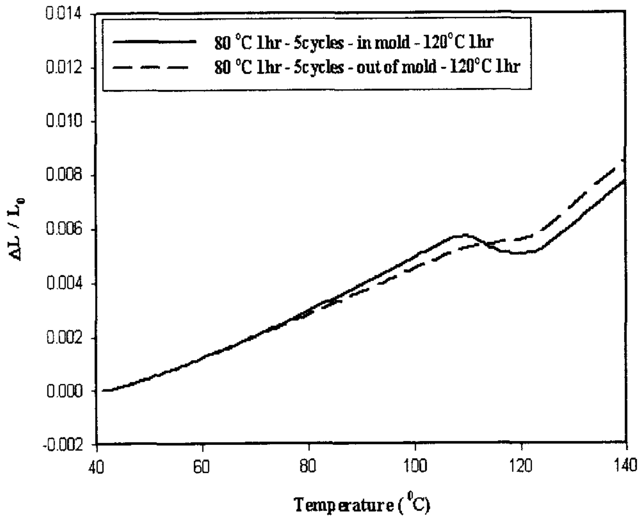

Fig. 5 Dilatometer results for samples cured at 80℃ for 1hr, 5cycles and post cured at 120℃ for 1hr (without kaolin)

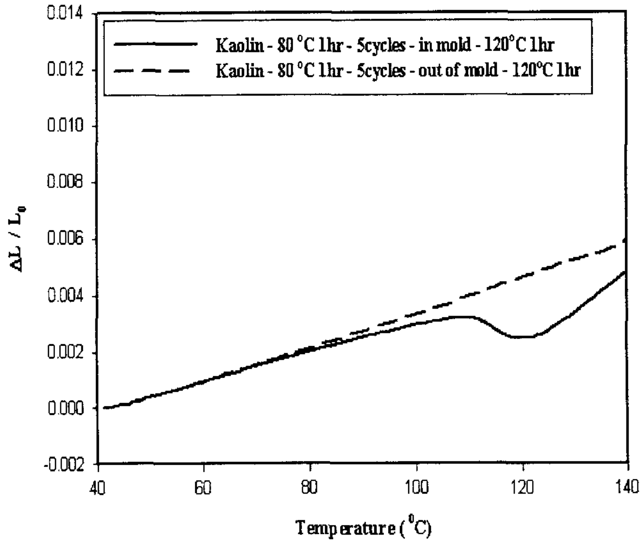

Fig. 6 Dilatometer results for samples cured at 80℃ for 1hr, 5cycles and post cured at 120℃ for 1hr (kaolin of 36wt%)

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 constrain the polymer chains.

Dilatometer was used to investigate the epoxy system filled with kaolin. The results are plotted in Fig. 7 and Fig. 8. The sample containing kaolin of 36 wt% has 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.

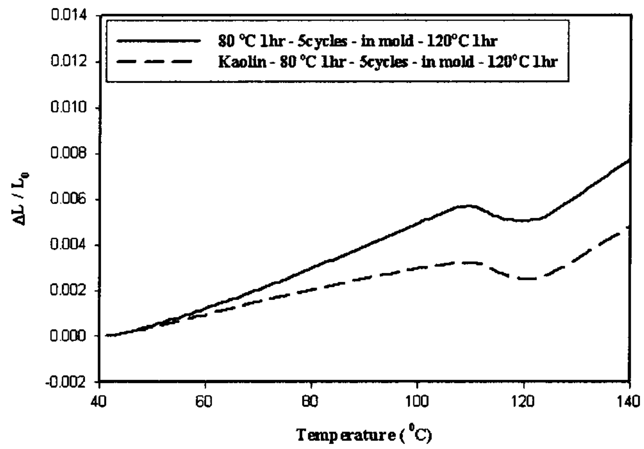

Fig. 7 Dilatometer results for samples cured at 80℃ for 1hr, 5cycles and then post cured in mold at 120℃ for 1hr

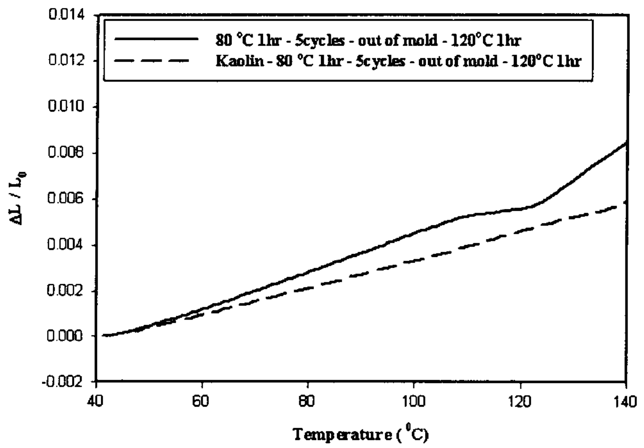

Fig. 8 Dilatometer results for samples cured at 80℃ for 1hr, 5cycles and then post cured out of mold at 120℃ for 1hr

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 number of cyclic cure. Post cured samples outside the mold led to less shrinkage compared with sample 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. And sample containing kaolin filler showed less shrinkage than unfilled sample.

Reference

Macon, D. J. (2001). polymer 42, pp 5285-5291.

Prasatya, P., McKenna, G. B., and Simon. (2001). S. L., Comp. Mater. 35, pp 826-848.

Adolf, D. B., Martin, J. E., Chambers. R. S., Burchett. S. N., and Guess, T. R. (1998). J. Mater. Res., 13, pp 530-550.

Russel, J. D., Madhukar, M. S., and Lee, A. Y. (2000). J. comp. Mater. 34, pp 1926-1947.

Plepys, A., Vratsanos, M. S., and Farris, R. (1994). J., Compos. Structures 27, pp 51-56.

Kan, K. N., Nikolayevich, A. F., and Miilen, E. A. (1975). polym. Sci. USSR 17, pp 518-519.