Toughening Method and Mechanisms for Thermosets

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ABSTRACT: A new toughening method that can be used to improve toughness for thermosets was developed. The method involved heat treatment to produce compressive residual stresses around hollow microspheres in solidified matrix. An epoxy resin system with expandable hollow microspheres for modification was adopted for demonstration. Toughening based on the method was shown to be more than twice as effective than the usual hollow microsphere toughening and its major toughening mechanism was deduced to be due to compressive residual stresses rather than cavitation. A necessary condition for cavitation in the presence of compressive residual stress was proposed and comparatively discussed for the toughening mechanisms involved. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1663–1667, 2005

Key words: thermosets; composites; fracture; toughness

INTRODUCTION

Thermosets are an important family of engineering plastics. However, thermosets are brittle compared to thermoplastics because of their crosslinked molecular structures. There has been much effort to improve such weakness, particularly for epoxies. Liquid rubber has been successfully used as a modifier to increase the fracture toughness. Its toughening mechanisms have been studied over the past 2 decades.[1] The toughening mechanisms include cavitation, shear banding, bridging, crack pinning, crack blunting, etc. In addition to liquid rubber, other modifiers such as hard particles[2] hollow microspheres,[3–6] and core-shell rubber[7] have also been used.

Another development in this area is some attempt to toughen thermosets using a similar method to that used for ceramics in which toughness increase was achieved by a volume dilation in the vicinity of the crack tip that resulted from tetragonal to monoclinic phase transformation.[8,9] Kim and Robertson[10–12] have made efforts in toughening with semicrystalline thermoplastic polymers as modifiers and as a result substantial toughening has been achieved. They thought phase transformation was the major toughening mechanism but it was inconclusive.[2,10]

A new toughening method is always desired because the applicability of toughening can be widened. Also, it can possibly lead to new toughening mechanisms, which may add additional toughness. In this paper, a new toughening method for thermosets is presented. The method involves prestressing the matrix by means of expandable hollow microspheres in conjunction with heat treatment to achieve a similar effect to that of the phase transformation of ceramics in the vicinity of the crack. The purpose of the heat treatment is to create strong residual compressive stresses around hollow microspheres to reduce the stress intensity factor when the crack is loaded.

A NECESSARY CONDITION FOR CAVITATION IN THE PRESENCE OF RESIDUAL COMPRESSIVE STRESS

Hollow microspheres can be subjected to compressive residual stresses prior to cracking, as will be shown later. When the triaxial tensile stress (σ_t) due to an external load is applied to a hollow microsphere that is under compressive residual stress (σ_r) in the vicinity of the crack tip, there will be interaction between the two stress components. In this situation, the following two different cases, depending on the magnitudes of stresses around the microsphere, can be considered:

Case I:

$$|\sigma_r| > |\sigma_t| \tag{1}$$

and

Case II:

$$|\sigma_r| < |\sigma_t|. \tag{2}$$

In the first case where σ_r is greater than σ_t, no cavitation occurs because σ_t is offset by σ_r, but this is the case where the reduction of the stress intensity

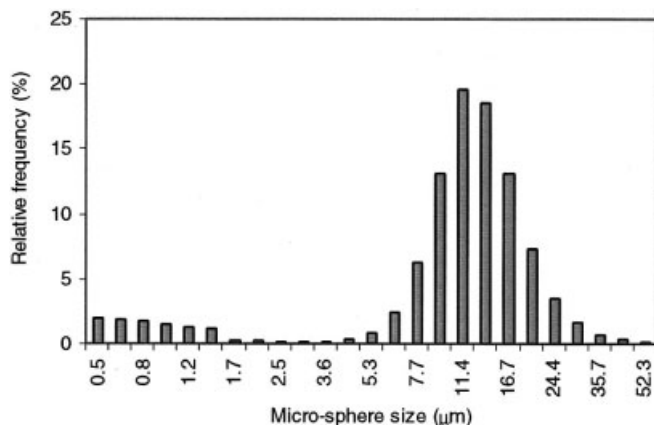*Correspondence to*: H. S. Kim (ho-sung.kim@newcastle.edu.au).

Figure 1 Hollow microsphere size distribution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

factor takes place due to the residual stress. In the second case where σ_t is greater than σ_r, the cavitation does occur but the magnitude of stress contributing to the cavitation reduces to the stress σ_{cv}, which is

$$\sigma_{cv} = |\sigma_t| - |\sigma_r|, \tag{3}$$

and still the residual stress contributes to the reduction of stress intensity factor.

EXPERIMENTAL

Materials used

An epoxy system was adopted as a model material for this study. The system consisted of West System Epoxy 105 (a blend of Bisphenol A and Bisphenol F) and West System Slow Hardener 206 (a blend of aliphatic amines and aliphatic amine adducts based on diethylene triamine and triethylenetetramine) as curing agent. An average density of five measurements was 1.1 for the epoxy system.

The modifier used was hollow microspheres (Expancel, 551 DU40, Akzo Nobel), which consist of copolymer shell and gas. The microspheres were analyzed for chemical structure using a Perkin-Elmer Fourier transform infrared spectrometer (Paragon 1000) and found to be $(C_5H_8O_2\text{-}C_3H_3N\text{-}C_2H_2Cl_2)x$. The average density of microspheres from three measurements at room temperature, using an air comparison pycnometer (Beckman 930), was 1.2. The hollow microsphere sizes were measured using a laser particle analyzer (Malvern 2600C) and their distribution is given in Figure 1.

The microspheres expand when heated. As part of the characterization for volume expansion of 551 DU40, 10 mL microspheres was put in a 100-mL measuring cylinder and tapped for 5 min and then placed

in an oven preheated to 70 °C. Further heating followed every 5 to 6 min for an increment of 10 °C until the temperature reached 200 °C. The volume expansion as a function of temperature is shown in Figure 2. The volume reaches its maximum and then decreases because some hollow microspheres explode when the temperature is high.

Preparation of test specimens

Two types of specimens for microsphere modification were prepared—one without heat treatment (ME) and the other with heat treatment (MEH). The reason for ME was that there would be toughening effect caused by microspheres themselves without heat treatment and thus its purpose was to isolate the heat treatment effect.

Mixing of control epoxy and curing agent was conducted by stirring for 5 min. The amount of curing agent was 17 phr (by weight) for all specimens. The resulting mixture was poured into an aluminum mold with a 6-mm-thick cavity and left for curing at room temperature at least for 1 day. Temperature rise in the mold due to exothermic reaction was monitored using a thermocouple and found to be about 8 °C, which would not affect the expansion of hollow microspheres (see Fig. 2).

For both ME and MEH, various amounts (by mass) of 551 DU40 were added to epoxy and stirred for about 10 min. The mixtures were heated to about 80 °C for 30 min to reduce the viscosity for easy stirring and then allowed to cool gradually in a water bath for about half an hour. The hardener was then added and stirred for 5 min. The casting and curing were conducted in the same way as for the control epoxy system.

The heat treatment was conducted for all the cured specimens of MEH in an oven at 135 °C for 2 h and then allowed to cool down to room temperature.

Mechanical testing

All specimens for mechanical testing were machined into dimensions of 12 × 60 × 6 mm for edgewise
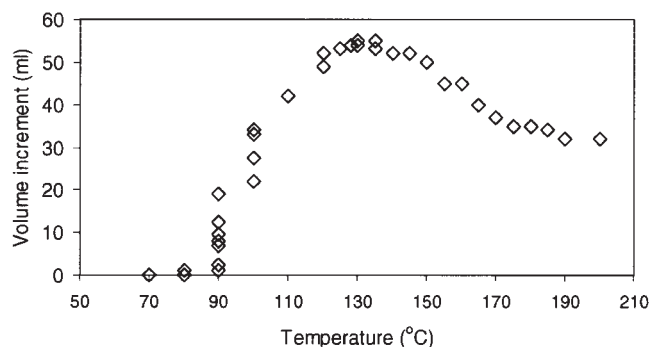

Figure 2 Volume expansion measurement of 551 DU40 as a function of temperature.
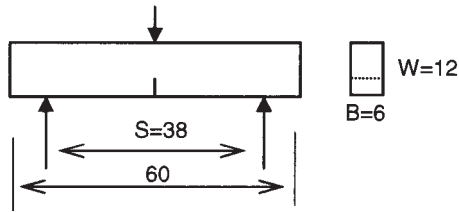
Figure 3 Three-point loading for both flexural and fracture tests but without the notch for flexural tests.

placement as shown in Figure 3. Three-point bending tests on a universal testing machine (Shimadzu 5000) were conducted for elastic modulus, strength, and fracture toughness. A crosshead speed of 10 mm/min was adopted for tests of flexural properties and 0.5 mm/min for the fracture toughness measurements at a room temperature of 21 °C.

Elastic moduli (E) and flexural strengths (σ_y) were calculated using the following equations given in ASTM D 970M-93:

$$E = \frac{S^3 m}{4BW^3} \tag{4}$$

and

$$\sigma_y = \frac{3PS}{2BW^2}, \tag{5}$$

where S is the support span, B is the thickness, W is the width, m is the slope of the tangent to the initial straight-line portion of the load-deflection curve, and P is the load.

The critical stress intensity factor (K_{IC}) expression[13] used was

$$K_{IC} = \frac{3PS\sqrt{\pi a}}{2BW^2} Y, \tag{6}$$

where a is the crack length and Y is a geometry factor given by

$$Y = \frac{1}{\sqrt{\pi}} \frac{1.99 \frac{a}{W}\left(1 - \frac{a}{W}\right)\left(2.15 - 3.93 \frac{a}{W} + 2.7\left(\frac{a}{W}\right)^2\right)}{\left(1 + 2\frac{a}{W}\right)\left(1 - \frac{a}{W}\right)^{3/2}}$$

A precrack, 4 to 5 mm long, was produced by a tapping a razor blade into the tip of a saw-cut notch, 2 mm long, of each fracture test specimen and its length was measured with a pair of Vernier calipers.

Specific fracture energy values for mode I were approximated using

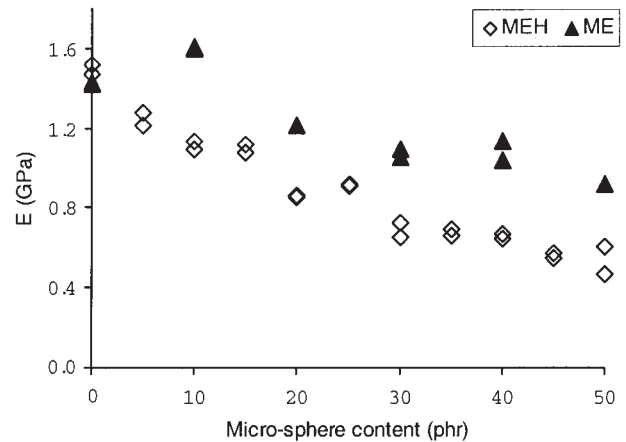$$G_{IC} = \frac{K_{IC}^2}{E}. \tag{7}$$

Figure 4 Flexural modulus of elasticity vs. microsphere content.

Microscopy

Scanning electron microscopic work (Oxford-XL30, Philips) was conducted for specimens coated with gold. The specimens were cleaned with water using a Bran Sonic 52 and dried in an oven at 30 °C for 30 min before being coated for SEM. Fracture surfaces for photos were taken from midsections in the vicinity of precracks. Also, thin sections of midplane from broken specimens of ME and MEH were prepared for transmission microscopy (Axioplan 2, Carl Zeiss). The thicknesses of thin sections were about 19 μm.

RESULTS AND DISCUSSION

Results of the two types of specimens (ME and MEH) for flexural elastic modulus and flexural strength are plotted as functions of microsphere content in Figures 4 and 5, respectively. Elastic modulus and flexural strength of both ME and MEH appear to generally decrease with increasing microsphere content, which
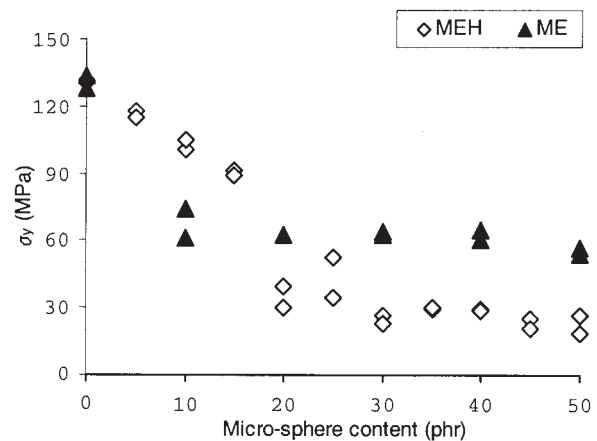

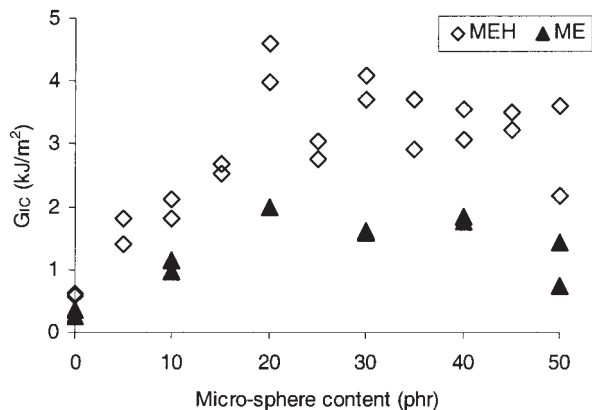**Figure 5** Flexural strength vs. microsphere content.

Figure 6   Specific fracture energy vs. microsphere content.

is not unexpected. A noticeable difference in flexural modulus and flexural strength between heat-treated and non-heat-treated specimens is seen, while the control epoxy system is not much affected by the heat treatment. Elastic modulus of modified epoxy system (Figure 4) appears to decrease due to heat treatment. The same is true for flexural strength (Fig. 5) of those with microsphere content ranging from 20 to 50 phr except at a low microsphere content of 10 phr.

As shown in Figure 6, fracture toughness (or specific fracture energy), G_{IC}, of both ME and MEH increases as microsphere content increases up to a microsphere content of 20 phr and thereafter tends to be more or less flat. It should be highlighted that the maximum increase of MEH is about 13 times that of the control epoxy system but only about 6 times that of the control epoxy system for ME. Some increase of the control epoxy in fracture toughness after heating may be due to postcuring effect, the interest of which is beyond the scope of this work.

Microscopic work was conducted to identify toughening mechanisms of ME and MEH responsible for the

increase in fracture toughness. Figure 7 shows typical SEM images of fracture surfaces for a microsphere content of 20 phr. A major difference between ME and MEH appears to be in the interface between the microspheres and the matrix. No gaps between the microspheres and the matrix are seen in MEH and it is evident that the crack passed through the microspheres without pullouts of microspheres. In contrast, in ME microspheres are debonded or pulled out from the matrix. There are two possibilities for the creation of the gaps between the microspheres and matrix in ME—one is due to the cavitation[14] and the other is due to shrinkage of epoxy during curing.[15] The latter possibility can be rejected because no gaps were found in fast cracking regions for not only ME but also MEH. As for MEH, no evidence was found for cavitation, although one can argue that the absence of gaps in MEH does not necessarily indicate that no cavitation occurred, because if bonding between microspheres and matrix is sufficiently strong, the gap would not appear on the fracture surfaces. However, the bonding strength in the interface of MEH would not be any higher than that of ME because no chemical reaction is expected between the microspheres and the matrix when they are heat treated. Therefore, it can be deduced that the compressive residual stress in MEH is stronger than the tensile cavitation stress, which is Case I, $|\sigma_r| > |\sigma_t|$ (see A Necessary Condition for Cavitation in the Presence of Residual Compressive Stress).

When MEH is heated, it is obvious that microspheres naturally expand against the matrix and both matrix and microspheres would permanently deform if deformation is sufficiently high. Consequently, residual compressive stresses/strains around microspheres would be created when cooled down. To confirm the residual compressive stresses/strains in the matrix, thin sections of MEH were examined and the
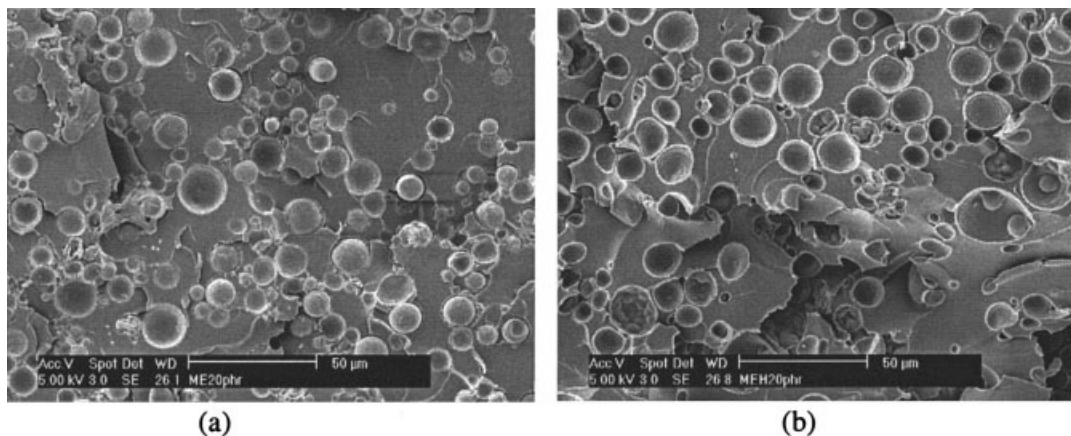

Figure 7   SEM images of fracture surfaces: (a) ME 20 phr, (b) MEH 20 phr. Fracture propagation direction is from bottom to top.
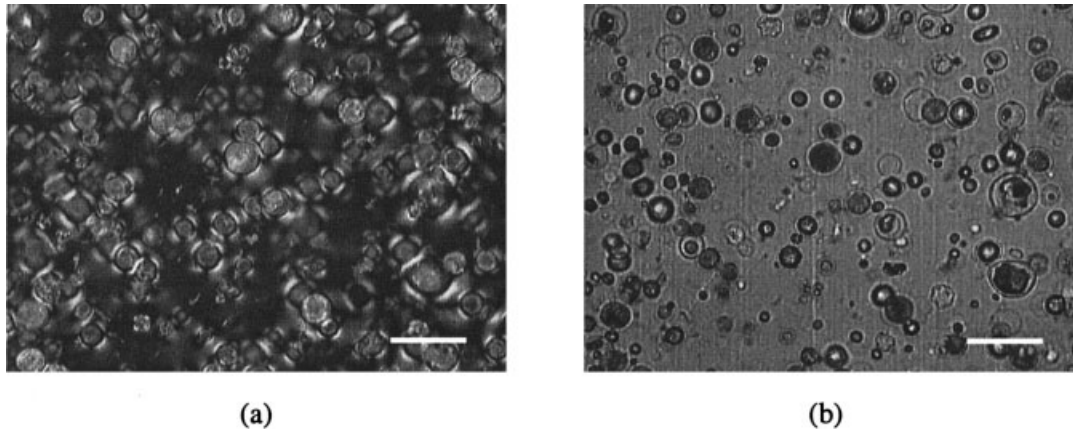
Figure 8 A thin section of MEH with a microsphere content of 20 phr showing heat treatment effect: (a) polarized, (b) unpolarized. The polarized image displays strong fringe patterns around microspheres representing residual stresses. Scale bar, 30 μm.

residual stresses/strains were indeed found to exist around microspheres as shown in Figure 8. Both cross-polarized and nonpolarized images, under a transmission optical microscope, of a thin section taken from the midplane of a MEH specimen with a microsphere content of 20 phr are shown in Figure 8. The fringe patterns around microspheres in Figure 8a is the evidence for the residual stresses/strains. The effect of compressive stress in the vicinity of a crack tip is well known.[16] A difference, though, between ceramics toughening and the current one is noted. In the case of ceramics toughening, the compressive stress produced by volume dilation is localized in the vicinity of crack.[16] In the case of MEH, however, the compressive stresses/strains are distributed around microspheres throughout the whole specimen although only microspheres in the vicinity of the crack tip would play a role for toughening.

Further, to check whether the residual stress/strain in MEH is due solely to heat treatment, thin sections of ME were also examined and relatively weak residual stresses/strains around microspheres were also found. An epoxy shrinks during curing[15] and thus it is likely that the residual stresses/strains were caused by shrinkage in this case since it was not subjected to heat treatment. Consequently, it appears that the toughness increase in both ME and MEH is due partially to the contribution of the compressive residual stresses/strains. However, cavitation occurred in the case of ME as discussed above and thus this indicates that the tensile cavitation stress is stronger than the compressive residual stress, which is Case II, $|\sigma_r| < |\sigma_t|$ (see A Necessary Condition for Cavitation in the Presence of Residual Compressive Stress).

CONCLUSIONS

A new toughening method involving the creation of compressive residual stress/strain by heat treatment in an epoxy system, using expandable hollow microspheres, has been demonstrated.

Toughening mechanisms involved in modified epoxy systems, both with and without heat treatment, have been identified and comparatively discussed in relation to the necessary condition for cavitation in the presence of compressive stress.

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