

Thermal Expansion and Mechanical Properties of Phenolic Resin/ZrW₂O₈ Composites

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ABSTRACT: Phenolic resin/ZrW₂O₈ composites were successfully fabricated and their coefficient of thermal expansion (CTE) as well as mechanical properties was investigated. The CTE of the composites decreases from 46×10^{-6} to 14×10^{-6} K⁻¹ when the ZrW₂O₈ volume fraction increases from 0 to 52 vol %. The CTE of the composites is analyzed by some theoretical models; Schapery's upper bound provides the best estimate of the reduction in CTE. The Barcol hardness of the composites

increases with an increase in the ZrW₂O₈ volume fraction. The bending strength of the composites with 19–25 vol % of ZrW₂O₈ fillers shows a maximum value of 130 MPa, which is 45% larger than that of phenolic resin without fillers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3343–3347, 2007

Key words: resins; composites; thermal properties; mechanical properties

INTRODUCTION

Phenolic resins are utilized in a wide variety of applications because of their superior features such as low cost, good electrical and mechanical properties, very good heat resistance, and excellent moldability.¹ In applications involving an electronic package substrate, phenolic resins with a low coefficient of thermal expansion (CTE) are needed to reduce the mismatch in thermal expansion among different materials in the substrate.² Therefore, polymer-matrix composites containing low-CTE fillers such as ceramics particles and fibers are used for electronic packages. However, relatively high loading of ceramic particles and fibers is required to effect a significant reduction in the CTE.

Zirconium tungstate (ZrW₂O₈) was shown to exhibit relatively large isotropic negative thermal expansion over a wide temperature range from 0.3 to 1050 K^{3,4}; therefore, ZrW₂O₈ is considered as an attractive candidate for use as a filler material for controlling the CTE of polymers. Recently, polymer/ZrW₂O₈ composites such as polyester/ZrW₂O₈,⁵ epoxy/ZrW₂O₈,⁵ and polyimide/ZrW₂O₈,⁶ systems have been successfully fabricated. A decrease in the

CTE values of the composites has been observed when the amount of ZrW₂O₈ fillers is increased in them. However, there are no reports on the fabrication and properties of phenolic resin/ZrW₂O₈. In addition, to date, there have been few reports on the mechanical properties of polymer/ZrW₂O₈ composites, and mechanical properties such as the bending strength and hardness of the polymer/ZrW₂O₈ systems have not been investigated.

In this present study, we have successfully fabricated phenolic resin/ZrW₂O₈ composites and their mechanical properties as well as CTE have been investigated. Moreover, the CTE data obtained were compared with some theoretical equations of the thermal expansion in a composite.

EXPERIMENTAL

ZrW₂O₈ was prepared from commercially available starting materials: zirconium oxychloride octahydrate (ZrCl₂O·8H₂O; Wako Pure Chemical Industries) and ammonium tungstate para pentahydrate ((NH₄)₁₀W₁₂O₄₁·5H₂O; Wako Pure Chemical Industries). Stoichiometric mixtures of the starting powders were aged in a water bath and stirred with a magnetic stirrer at 100°C for 3 h; the mixtures were then dried. A separate burnout step was performed at 600°C for 3 h before pressing and firing to eliminate a large volume of volatile species because of the

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high weight loss associated with inorganic precursor decomposition. Powder mixtures weighing 10 g were pressed at 60 MPa into pellets (30 mm in diameter) using a hand press, and fired in air to 1200°C with a dwell time of 3 h in a Pt crucible. The heating rate was 20°C/min. The heated pellets were then rapidly quenched in liquid nitrogen. The pellets were ground to a powder using wet milling in ethanol for 24 h and the mean volume particle size as determined by laser diffraction and a scattering method (Model LA-920, Horiba, Kyoto, Japan) is 3.2 μm . Phase analysis was performed using X-ray powder diffraction (XRD; Model RINT 2500, Rigaku, Tokyo, Japan), which utilized Cu K α radiation at 40 kV and 50 mA; it was revealed that the powder shows a phase-pure cubic α -phase structure.

The phenolic resin powder used in this study was a commercially available novolac-type phenolic resin (KI-9544A) with hexamethylenetetramine (HMTA), and it was supplied by Dainippon Ink and Chemicals Incorporated (DIC, Tokyo, Japan). Stoichiometric phenolic resin and ZrW₂O₈ starting powders were mixed together using an agate mortar and pestle. The composites were prepared by curing at 170°C for 15 min in a steel die (25 mm in diameter) on a hot press.

The thermal expansion was measured on composites bars (4 × 4 × 20 mm³) using a thermal mechanical analyzer (Thermoflex, Rigaku, Tokyo, Japan) in air with a heating rate of 2°C/min over the temperature range of 20–90°C. The CTE was determined from the slope of the plot between the thermal expansion and the temperature in the temperature range of 20–90°C. The Barcol hardness tester (GYZJ-934-1, Eurotherm, VA) according to ASTM D2583 standard test method was used for testing the hardness of the composites at 23°C. The three-point bending test (AL-50KNB, Minebea, Tokyo, Japan) was carried out at a span of 15 mm and at 23°C. Samples (3 × 4 × ~22 mm³) were tested at a cross-head speed of 0.5 mm/min. Fractured surfaces were observed with a scanning electron microscope (model JSM-6460LA, JEOL, Tokyo, Japan) at 20 kV with a working distance of 20 mm. Phase analysis was performed using XRD, which utilized Cu K α radiation at 40 kV and 50 mA. Phase identification was accomplished by comparing the experimental XRD patterns to standards that have been compiled by the international center for diffraction data (ICDD).

RESULTS AND DISCUSSION

Figure 1 shows the thermal expansion of the phenolic resin/ZrW₂O₈ composites. The thermal expansion of phenolic resin/ZrW₂O₈ composites increases linearly with the temperature and decreases with an

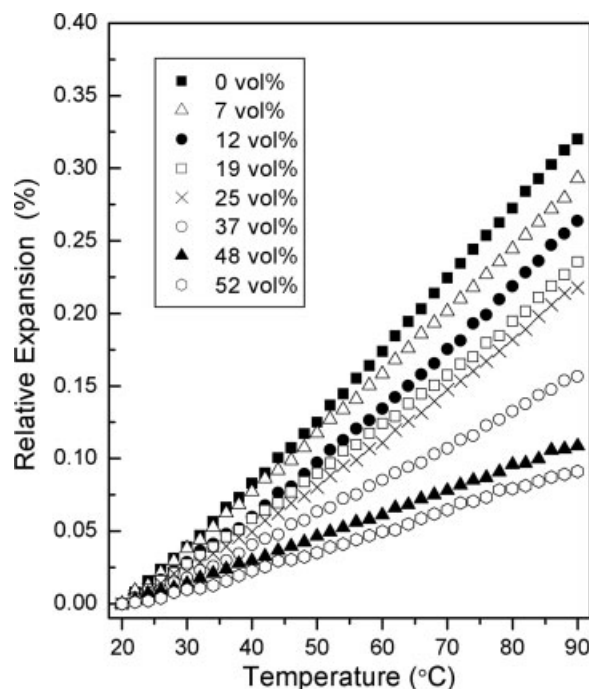


Figure 1 Thermal expansion of phenolic resin/ZrW₂O₈ composites.

increase in the ZrW₂O₈ filler content. The thermal expansion from 20°C to 90°C shows an increase of 0.32% for phenolic resin without fillers, whereas that of phenolic resin/ZrW₂O₈ composites at 7, 12, 19, 25, 37, 48, and 52 vol % ZrW₂O₈ shows an increase of 0.29, 0.26, 0.24, 0.22, 0.16, 0.11, and 0.09%, respectively. This result indicates that ZrW₂O₈ fillers contribute to the decrease in the thermal expansion of the composites and the CTE of phenolic resin/ZrW₂O₈ composites decreases with an increase in the amount of ZrW₂O₈ fillers in the composites. The CTE of phenolic resin/ZrW₂O₈ was determined from the slope of the experimental plots between the thermal expansion and the temperature in the range of 20–90°C.

Figure 2 shows the CTE experimental plots as well as the calculated curves by assuming the rule of mixtures (ROM),⁷ Turner model,⁸ and Schapery's model⁹ as a function of the volume loading for ZrW₂O₈ fillers.

The ROM serves as the first-order approximation to the overall calculation of the CTE of the composites.

$$\alpha_c = \alpha_f \phi + \alpha_m(1 - \phi) \quad (1)$$

where α_c , α_f , and α_m represent the CTEs of the composites, filler, and matrix, respectively, and ϕ is the volume fraction of the filler.

In Turner's model,⁸ the mechanical interaction between the different materials in the composites is

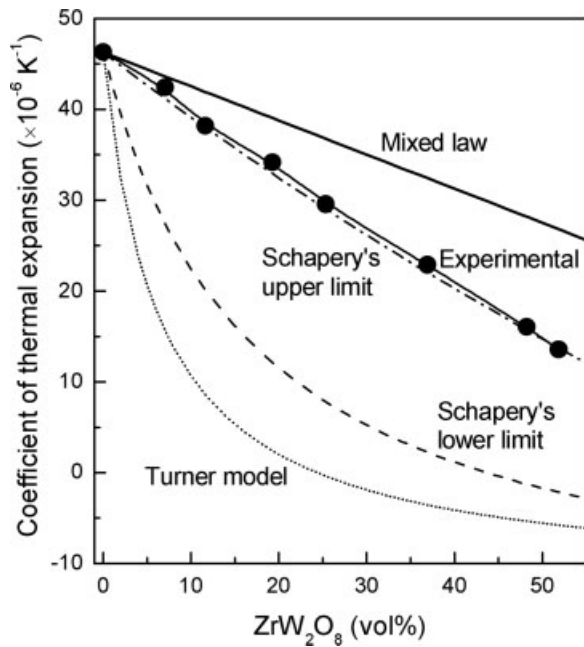


Figure 2 CTE experimental plots as well as calculated curves by assuming mixed law, Schapery's model, and Turner model as a function of volume loading for ZrW₂O₈ fillers.

taken into account. Turner's equation is given as follows:

$$\alpha_c = \frac{(1 - \phi)K_m\alpha_m + \phi K_f\alpha_f}{(1 - \phi)K_m + \phi K_f} \quad (2)$$

where K_m and K_f represent the bulk moduli of the matrix and filler, respectively.

Schapery⁹ developed a model to predict the upper and lower bounds of the CTE of a composite. The two bounds are given as follows:

$$\alpha_c^l = \alpha_m + \frac{K_f (K_m - K_c^u)(\alpha_f - \alpha_m)}{K_c^u (K_m - K_f)} \quad (3)$$

$$\alpha_c^u = \alpha_m + \frac{K_f (K_m - K_c^l)(\alpha_f - \alpha_m)}{K_c^l (K_m - K_f)} \quad (4)$$

where the superscripts "u" and "l" refer to the upper and lower bounds, respectively. K_c^l and K_c^u are the upper and lower bounds of the bulk modulus of the composites, respectively.

$$K_c^l = K_m + \frac{1}{\frac{1}{K_f - K_m} + \frac{3(1 - \phi)}{(3K_m + 4G_m)}} \quad (5)$$

$$K_c^u = K_f + \frac{1 - \phi}{\frac{1}{K_m - K_f} + \frac{3\phi}{(3K_f + 4G_f)}} \quad (6)$$

Here, G_m and G_f represent the shear moduli of the matrix and filler, respectively. The bulk and shear

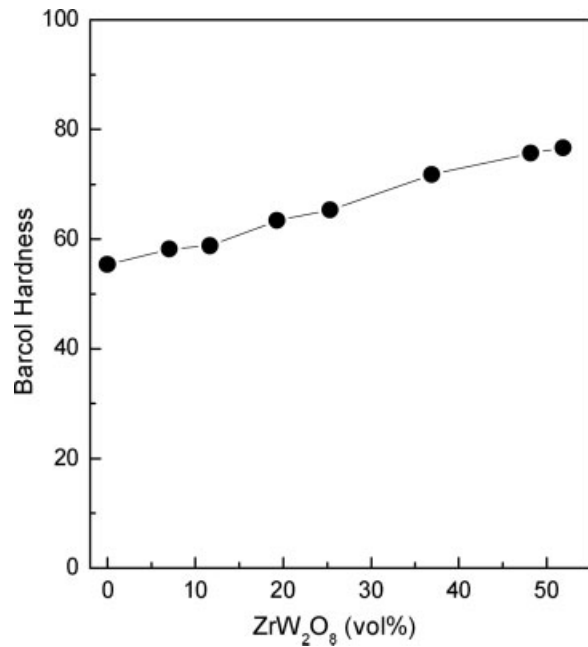


Figure 3 Barcol hardness of phenolic resin/ZrW₂O₈ composites as a function of volume loading for ZrW₂O₈ fillers.

moduli values for ZrW₂O₈¹⁰ corresponding to 74.5 and 33.9 GPa, respectively, have been used. The bulk modulus (K) and Poisson's ratio (ν) for phenolic resin are reported to be 4.5 GPa and 0.37, respectively.¹¹ Therefore, the shear modulus (G) value of 1.28 GPa for the phenolic resin is determined by the following equation¹²:

$$G = \frac{3K(1 - 2\nu)}{2(1 + \nu)} \quad (7)$$

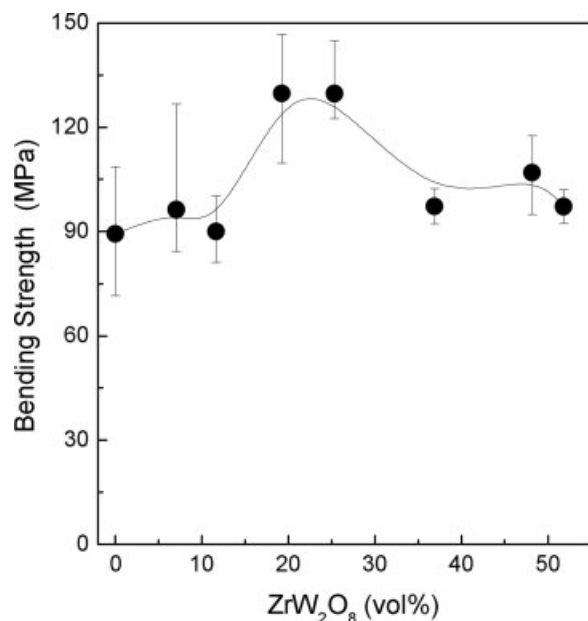


Figure 4 Bending strength of phenolic resin/ZrW₂O₈ composites as a function of volume loading for ZrW₂O₈ fillers.

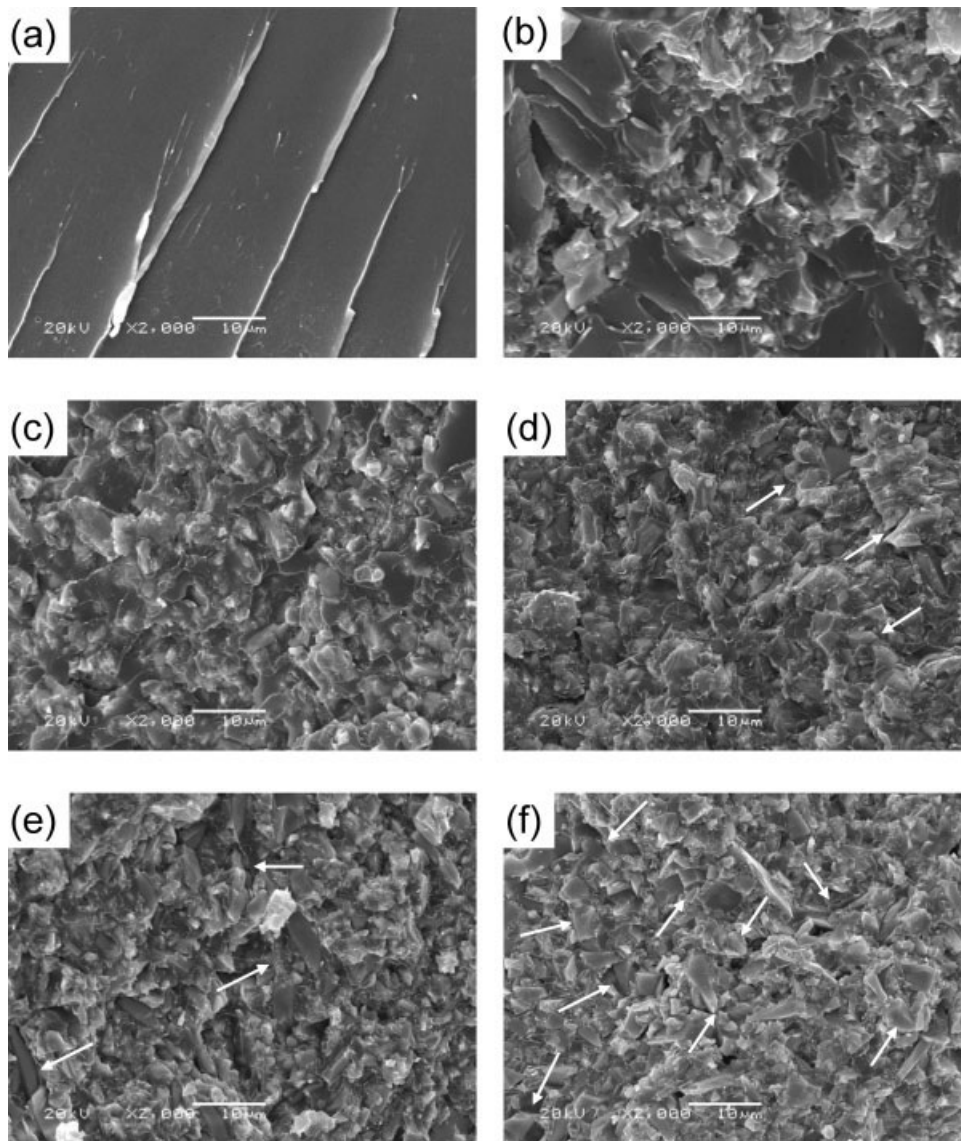


Figure 5 SEM micrographs of the fracture surfaces of phenolic resin/ ZrW_2O_8 composites at a volume loading for ZrW_2O_8 fillers: (a) 0 vol %; (b) 12 vol %; (c) 25 vol %; (d) 37 vol %; (e) 48 vol %; and (f) 52 vol %. Arrows in (d), (e), and (f) point to the aggregation of ZrW_2O_8 fillers.

ZrW_2O_8 has two cubic phases at the ambient pressure (α -phase below 423 K and β -phase above 423 K) and one orthorhombic phase at high pressures (γ -phase). The CTEs of all the three phases are negative but vary in magnitude beginning from $\text{CTE}_\alpha = -8.7 \times 10^{-6} \text{ K}^{-1}$, $\text{CTE}_\beta = -4.9 \times 10^{-6} \text{ K}^{-1}$, and $\text{CTE}_\gamma = -1.0 \times 10^{-6} \text{ K}^{-1}$.^{3,4,13} X-ray diffraction analyses revealed that only the cubic α -phase of ZrW_2O_8 exists in the phenolic resin/ ZrW_2O_8 composites. The CTE of the phenolic resin/ ZrW_2O_8 composites varies in the range from 46×10^{-6} to $14 \times 10^{-6} \text{ K}^{-1}$, with ZrW_2O_8 filler from 0 to 52 vol %. The CTE of the phenolic resin/ ZrW_2O_8 composites is lower than the values obtained by assuming the mixed law behavior, and Schapery's upper bound provides the best estimate for the CTE of the phenolic resin/ ZrW_2O_8 composites.

Figure 3 shows the Barcol hardness of the phenolic resin/ ZrW_2O_8 composites as a function of the volume loading for ZrW_2O_8 fillers. The room-temperature Barcol hardness increases linearly with an increase in the ZrW_2O_8 filler content because the ZrW_2O_8 particles have a considerably greater elastic modulus as compared to that of the phenolic resin matrix. The Barcol hardness value of the phenolic resin/ ZrW_2O_8 composite at 52 vol % ZrW_2O_8 is 75.7, which is 36.6% greater than that of phenolic resins without fillers-55.4.

Figure 4 shows the bending strength of the phenolic resin/ ZrW_2O_8 composites as a function of the volume loading for ZrW_2O_8 fillers. The bending strength of the composites increases by adding ZrW_2O_8 fillers. The bending strength of the compo-

sites with 19–25 vol % of ZrW_2O_8 fillers shows a maximum value of 130 MPa, which is 45% greater than that of the phenolic resin without fillers—89.4 MPa. Therefore, ZrW_2O_8 particles will play an important role in increasing the bending strength of the composites. The bending strength of the composites with 37–52 vol % of ZrW_2O_8 fillers shows values of 97–107 MPa, which is slightly greater than that of the phenolic resin without fillers.

Figure 5 shows the SEM micrographs of the fracture surface of the phenolic resin/ ZrW_2O_8 composites. The fracture surface of the unfilled phenolic resin shows a smooth pattern, while that of the composites shows a rougher pattern. In composites with ZrW_2O_8 fillers below 25 vol %, good dispersion of ZrW_2O_8 particles is observed. As discussed earlier, the elastic moduli such as the bulk and shear moduli of the ZrW_2O_8 particles is considerably greater than those of the phenolic resin. Therefore, the bending strength will be improved by an increase in the elastic modulus and from the formation of uniform microstructure composites. However, at a high filler volume loading of 37–52 vol %, the aggregation of ZrW_2O_8 , which increases with an increase in the ZrW_2O_8 fillers, appears to decrease the bending strength of the phenolic resin/ ZrW_2O_8 composites.

CONCLUSIONS

Phenolic resin/ ZrW_2O_8 composites were successfully fabricated and their CTE as well as mechanical properties was investigated. The CTE of the composites decreases from 46×10^{-6} to $14 \times 10^{-6} K^{-1}$ when the ZrW_2O_8 volume fraction increases from 0 to 52 vol %.

The CTE of the composites is analyzed by some theoretical models; Schapery's upper bound provides the best estimate of the reduction in CTE. The Barcol hardness of the composites increases with an increase in the ZrW_2O_8 volume fraction. The bending strength of the composites with 19–25 vol % of ZrW_2O_8 fillers shows a maximum value of 130 MPa, which is 45% larger than that of phenolic resin without fillers.

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