

Thermal Pressure Coefficient of a Polyhedral Oligomeric Silsesquioxane (POSS)-Reinforced Epoxy Resin

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ABSTRACT: The thermal pressure coefficients of a neat, unfilled, epoxy resin and a 10 wt % POSS (polyhedral oligomeric silsesquioxane)-filled epoxy nanocomposite have been measured using a thick-walled tube method. It is found that just below the glass transition temperature the thermal pressure coefficient is $\sim 20\%$ smaller for the polymer composite containing 10% POSS than for the neat, unfilled resin. The

thermal expansion coefficient and thermal pressure coefficient of the uncured POSS itself are also reported. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 142–146, 2010

Key words: nanocomposites; residual stress; thermal pressure coefficient; POSS; thermoset; epoxy; polymer; high-pressure vessel

INTRODUCTION

Widespread applications of thermosetting polymer resins in composite materials call for a better understanding of their thermal and mechanical properties. One shortcoming of these resins is that residual stresses can arise in the composite because of the differences in volume changes between the resin and the reinforcing fibers or between the composite and external constraints, such as mold walls, when they are subjected to temperature changes. These residual stresses may cause early failure or sub-par performance of the composite system. In typical applications, the resin can be constrained from shrinking in one, two, or three dimensions, and these constraints lead to the build-up of potentially large stresses in the resin. The magnitude of the two-D stress build-up^{1,2} is related to the thermal stress coefficient $\alpha_L E$ (α_L is the linear coefficient of thermal expansion and E is the Young's modulus), and the three-D stress build-up^{3–5} is due to the thermal pressure coefficient γ ($\gamma = \alpha K$, where α is the volumetric coefficient of thermal expansion and K is the bulk modulus.) Recently, Li et al.⁶ investigated the thermal stress coefficient (as the product of shear modulus G and α) in a POSS/epoxy nanocomposite system, and this note expands on that work and presents the

results of an investigation of the impact of adding 10 wt % polyhedral oligomeric silsesquioxane (POSS) on the thermal pressure coefficient $\alpha K = \gamma$ of the resulting POSS/epoxy nanocomposite system.

In some instances,^{4,7,8} α and K have been considered to be nearly reciprocal (within a constant) even going through the glass transition. In such a case, $\gamma \approx \text{constant}$. If this is true in general, strategies to mitigate thermal stresses by decreasing α of a system may be thwarted if K increases by a magnitude similar to the decrease in α . However, in recent work, Alcoutlabi et al.⁹ have compiled literature data that show that γ in rubbery and glassy states of a range of polymers may differ significantly and that it varies significantly among polymer systems. This suggests that in addition to changing chemical structure of polymer resins, there may be strategies available to modify polymers through judiciously chosen reinforcing particles to reduce the thermal pressure coefficient and to, therefore, reduce thermally induced residual stresses.

The motivation for this investigation of the POSS/epoxy system is that the unique cage-like structure^{10–12} of POSS might be expected to exhibit different reinforcing effects for thermal expansion coefficient and mechanical moduli as the thermal expansion coefficients of the cage-like POSS moiety depend mainly on the bond energies, whereas the moduli of the POSS depend on the flexing/bending of the bonds in the cage. In the organic hybrid POSS used here, there are also contributions from the interatomic and intermolecular interactions. In addition, despite its unique cage-like structure, the properties of POSS have not been as extensively studied as, e.g. the cage-like structured Bucky-balls.¹³ We

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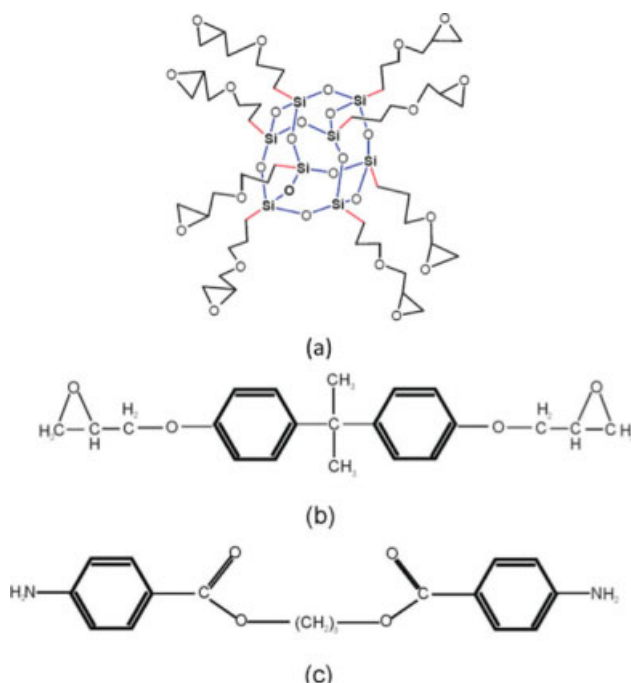


Figure 1 (a) Structure of POSS molecule used in present study; (b) diglycidyl ether of bisphenol A (DGEBA); (c) trimethylene glycol di-paminobenzoate. (After Ref. 6). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

base this work on the hypothesis that using POSS in an epoxy resin provides the opportunity to mitigate the bulk thermal stresses by reducing α without a proportional change in K . The work is complementary to the recent work by Li et al.⁶ from these laboratories that the thermal stress coefficient $\alpha_L G$ can be reduced (above room temperature) by addition of POSS to an epoxy, consistent with this hypothesis that the thermal pressure coefficient $\gamma = \alpha K$ can also be changed. This report provides results of the measurement of the thermal pressure coefficient $\gamma = \alpha K$ for a neat epoxy resin and the resin with 10 weight % POSS added.

MATERIALS AND METHODS

The epoxy resin used in this study was diglycidyl ether of bisphenol A (DGEBA) (DER332 Dow Chemical), the POSS was polyepoxyglycidyl silsesquioxane (EP0409 Hybrid Plastics), and the curing agent was tetrafunctional aromatic diamine (Versalink 740 AirProducts). The structures of the POSS, the epoxy, and the curing agent are shown in Figure 1. Epoxy, aromatic diamine, and POSS (or epoxy and diamine) were mixed in a stoichiometric ratio of functional groups and stirred at 100°C for at least 30 min until the mixture was homogeneous. Dissolved gas was removed before cure by pumping in vacuum at

room temperature for 30 min and then at 100°C for ~ 1 h until air bubbles were no longer observed. (Based on the results of Wisanrakkit and Gillham¹⁴ for the epoxy resin and from Merzlyakov et al.,¹⁵ this would result in partial reaction but would not result in gelation of the system).

Measurement of the thermal pressure coefficient γ was performed using the thick-walled tube method of Merzlyakov et al.¹⁶ developed in the laboratories of Texas Tech University. Here, we briefly describe the method and modifications we have made to the original procedure for this study. The thick-walled tube in this method is a stainless steel pressure nipple from High Pressure Equipment Co. (60-HM4-2.75-316). On the outer wall of the tube a strain gage is attached to measure the stresses of the sample inside the tube. As it was already shown¹⁶ that stresses measured using axial and hoop gages are the same, here, we used only the hoop gage for our measurement because of its greater sensitivity. In addition to the FSM-series gages (Vishay) mentioned in Ref. 16, we also used general purpose strain gages from Vishay with equal success although the FSM gages are more robust and thus last longer. The strain gage is placed in one arm of a Wheatstone bridge with three other fixed-value resistors at the other arms. Here, we replaced the trim-pot from Ref. 16 with a resistor (S102C Vishay) whose value (350 Ω) matches very closely to that of the strain gage. As a result, the bridge condition is slightly more unbalanced at the outset (i.e. at room temperature, zero pressure), but this is acceptable as we are ultimately measuring how much the bridge gets out of balance from this baseline; whether the baseline is about 0.1 μ V (balanced with a trim-pot) or about 10 μ V (with 350 Ω fixed-value resistor) does not affect the measured stress. The pressure response of the strain-gaged tube at room temperature was calibrated by pressurizing the tube with vacuum-pump oil and recording the bridge voltage as a function of pressure. Similarly, the temperature response was calibrated by recording the voltage response as a function of temperature for the empty tube in a temperature-programmable oven. We remark that, as shown below, the present measurements of γ for the neat resin are somewhat higher than those obtained by Merzlyakov et al.¹⁶ The reasons for this seem to be related to the details of the experimental procedures used. However, all experiments reported here are for a single thick walled tube device and are considered to be valid within the set of experiments performed here. Reasons for the differences between sets of experiments run on different tubes and by different investigators remain to be established.

RESULTS AND DISCUSSION

A typical test is run by first loading the uncured sample into the strain-gaged tube at 100°C in a vacuum oven (under vacuum) using a shortened-pipette with one end closed. After filling the tube with the sample, the other end of the tube is also closed. Next, a thermocouple is attached to the pressure nipple, which is then put in an oven, and the stress and temperature are recorded as the oven temperature is changed according to a preset temperature profile. To compare our results with the previous data of Merzlyakov et al.,¹⁶ we followed the curing schedule reported in that study: the filled tube is heated to the curing temperature at 1 K/min in an oven and then held at that temperature for 10 h. The device is then allowed to cool back to room temperature. The cooling rate is below 1 K/min and the rate slows as the oven temperature approaches room temperature. The results for the neat resin are shown in Figure 2. The zero value of the pressure at room temperature is defined for each run by shifting the data vertically. This does not affect γ_{app} as it is determined from the slope of the pressure–temperature plot.

As the sample is heated from room temperature, a hydrostatic compression (pressure) develops in the resin due to the fact that it cannot expand due to the constraining tube walls. At $\sim 100^\circ\text{C}$, the resin begins to cure, which results in a decrease in volume as van der Waals bonds are converted to covalent bonds. In Figure 2, this manifests itself in a decrease in the initially linear P vs. T profile. As temperature continues to increase, the reaction rate accelerates, and at $\sim 120^\circ\text{C}$, the rate of shrinkage due to cure overtakes the rate of thermal expansion and the compressive pressure in the resin decreases (becomes less negative). At the end of the 10-hour

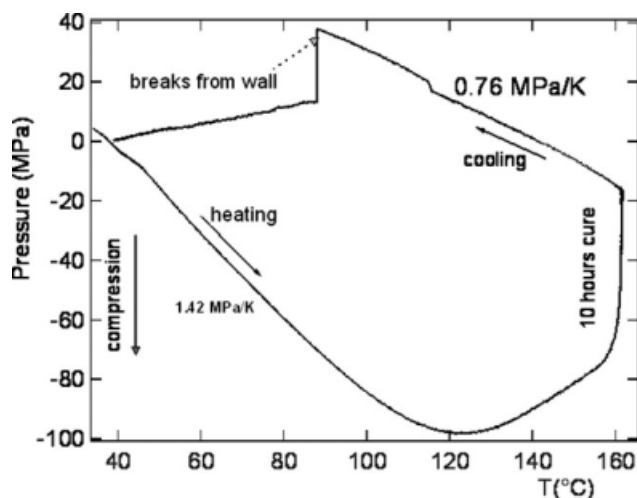


Figure 2 Pressure vs. temperature during heat-hold-cool cycle for the neat epoxy resin.

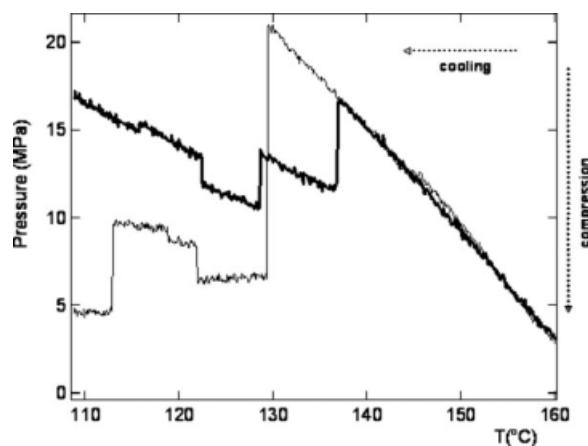


Figure 3 Cooling curves after curing the epoxy and POSS mixture. Different lines represent separate samples.

cure at 160°C, the sample is cooled to room temperature, and the pressure decreases and becomes “positive” as the sample goes into hydrostatic tension. One sees a rapid drop in the hydrostatic tension at $\sim 90^\circ\text{C}$ as the sample debonds and/or breaks from the transducer (tube) wall. For the temperature range of 140–155°C, the slope of the cooling curve gives the apparent thermal pressure coefficient of the cured resin, γ_{app} as 0.76 MPa/K; this is greater than the result of 0.64 MPa/K obtained earlier for the same material.¹⁶ The discrepancy may be due to our use of a different pressure vessel, strain gage attachment, and/or minor modification of the electronics. However, all experiments in this study were performed using a single thick-walled tube device and are considered to be consistent within this set of experiments.

In Figure 3, we show the cooling response after curing for the epoxy + 10% by weight POSS nanocomposite. The two traces correspond to two different samples. From the figure, we see that the hydrostatic tension develops nearly identically for the two samples until the cured samples break from the transducer walls at ~ 17 and 21 MPa, respectively. For the temperature range of 140–155°C, we find that the apparent thermal pressure coefficient γ_{app} is 0.60 and 0.59 MPa/K for the two different runs. Hence, the nanocomposite has a lower thermal pressure coefficient than the neat resin, consistent with the original hypothesis of the work and consistent with the prior work by Li et al.⁶ for the thermal stress coefficient.

Because the type of POSS we use (EP0409) is a viscous liquid at ambient conditions, it was also possible to determine the thermal pressure coefficient of the POSS. Figure 4 shows two cooling curves for the POSS; γ_{app} is found to be 1.05 and 1.02 MPa/K, for the two tests in the temperature range 140–155°C that is in the liquid state. We also measured the

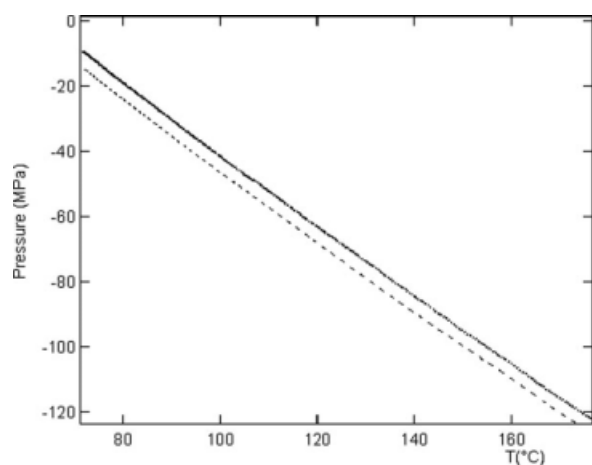


Figure 4 Pressure-temperature plot from cooling of POSS (EP 0409). Two lines representing two samples are offset vertically for clarity.

nominal value of α for the liquid POSS itself for the temperature range 25–150°C to be $2.6\text{--}3.8 \times 10^{-4}/\text{K}$. This value is expected to be between that of silica for which it is very small ($1\text{--}10 \times 10^{-6}/\text{K}$) and the organic group for which it would be larger. Our measured value is much higher than that of silica indicating that the thermal behavior of the organically modified POSS is dominated by its organic component. Li et al.⁶ have measured α for neat and POSS-filled resin at 150°C to be $4.2 \times 10^{-4}/\text{K}$ and $4.0 \times 10^{-4}/\text{K}$, respectively.

The values of the thermal pressure coefficients measured from the slope of the pressure vs. temperature plots in Figures 2–4 are only apparent values because the confining tube both has a mechanical compliance and its own coefficient of thermal expansion, i.e., the measurements are not performed under ideal isochoric conditions. Merzlyakov et al.¹⁶ derived an equation to obtain the actual γ from the apparent values (γ_{app}) determined from the measurements of pressure and temperature for a filled and instrumented tube

$$\gamma = \gamma_{\text{app}}(1 + K/K_T)/(1 - \alpha_T/\alpha) \quad (1)$$

Equation (1) involves two dimensionless numbers: α_T/α and K/K_T where the subscript T indicates the value for the steel tube. We take¹⁶ $\alpha_T = 4.86 \times 10^{-5}/\text{K}$ and $K_T = 55.6 \text{ GPa}$. We estimate K by using γ_{app} and the value of α cited above and find that $K = 1.79 \text{ GPa}$ and 1.50 GPa for the neat resin and the POSS-filled resin, respectively. It is interesting that the value of the bulk modulus obtained for the POSS filled resin is $\sim 26\%$ lower than that of the neat resin, consistent with the hypothesis that the cage structure might flex somewhat in a mechanical

deformation. This comment is made with caution, however, because the complex structure of the organically modified POSS may also be a major contributor to this behavior and because the POSS particles are chemically bonded through the epoxide linkages to the polymer network and the nanocomposite is not a simple mixture of the particles and the matrix. Using these values for K in eq (1), we estimate that $\gamma = 0.88 \text{ MPa/K}$ for the neat resin and 0.70 and 0.69 MPa/K for the POSS-filled resin (Table 1).

Although we have measured only a relatively small change in γ , such a change may still be very important. McKenna and Penn^{17,18} and Crissman and McKenna,¹⁹ for example, found that failure lifetime of polymers follows a very strong power law in the applied stress. For example, assuming¹⁹ $t_{\text{failure}} \propto \sigma^{-19}$ where σ is the residual stress and the reduction in stress on the order of 20% as found above for γ , we find that t_{failure} increases by nearly a factor of 70.

FUTURE WORK

The present thick-walled tube method requires somewhat more correction for the tube's thermal expansion and mechanical compliance than is desirable. As seen in eq (1), the dominant correction (for a sample with comparable properties to the resin studied here) comes in the thermal expansion coefficient term that contributes about 25% whereas the structural stiffness or compliance term contributes less than 10%. Increasing the tube wall thickness, while feasible, reduces the sensitivity of the device that already required the use of a lock-in amplifier to measure the small strains in the tube wall.¹⁶ On the other hand, using a material like Invar that has a very low thermal expansion coefficient combined with a structural stiffness comparable to the steel used in the current device configuration offers the opportunity to improve the thick walled tube method of thermal pressure coefficient determination.

TABLE I
Thermal Pressure Coefficients of POSS-Filled Resin and Its Constituents from 140–155°C. To Determine the Actual Thermal Pressure Coefficient γ of Pure Poss We Use eq (1), Our Measured Value of $\alpha = 3.2 \times 10^{-4}/\text{K}$ and the Bulk Modulus $K = 7.5 \text{ GPa}$ from Molecular Simulations²⁰ for a Similar POSS

Material	γ_{app} (MPa/K)	γ (MPa/K)
Neat epoxy resin	0.76	0.88
10 wt % POSS/resin	0.59, 0.60	0.69, 0.70
Liquid POSS	1.02, 1.05	1.36, 1.41

CONCLUSIONS

This work has shown that the glassy state thermal pressure coefficient γ is $\sim 20\%$ smaller for a 10 wt % POSS-filled epoxy resin nanocomposite compared to the value of γ for the neat resin over the temperature range 140–155°C, i.e., just below the glass transition temperature. The value of γ for the POSS alone has also been determined, and we report estimates of the values of the bulk modulus for the epoxy neat resin and for the POSS-filled system as well.

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