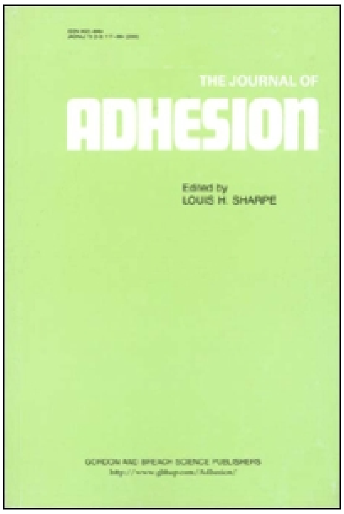

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Physical properties of a bisphenol-F epoxy containing a silica filler treated with silane coupling agents

Sandra L. Case[a]; Thomas C. Ward[a]
[a] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

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PHYSICAL PROPERTIES OF A BISPHENOL-F EPOXY CONTAINING A SILICA FILLER TREATED WITH SILANE COUPLING AGENTS

Sandra L. Case
Thomas C. Ward
Department of Chemistry,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia, USA

A model epoxy system consisting of a diglycidyl ether of bisphenol-F epoxy resin, 1,4-butanediol, and cured with 4-methyl-2-phenylimidazole has been investigated. Thermal analysis indicated that 3 parts per hundred resin (phr) is the optimum amount of curing agent for this system. The influence of silane-treated amorphous fumed silica fillers on properties of the cured epoxy was also examined. Silica particles were treated with 3-aminopropyldiethoxymethylsilane (APDS) and 3-aminopropyltriethoxysilane (APTS) coupling agents. No change in glass transition temperatures was observed with the addition of the filler (with or without coupling agents) to the epoxy. Addition of the filler led to a slight increase in the activation energy for the glass transition; however, no change in activation energy was observed when using the coupling agent. Addition of either coupling agent to the filler surface led to an increase in cooperativity. Fumed silica also did not significantly affect moisture diffusion properties, but a small decrease was observed in the moisture saturation mass with the addition of silica particles treated with APDS.

Keywords: Epoxy; Moisture uptake; Interphase; Master curves; Cooperativity; Silica filler; Silane coupling agent

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Address correspondence to Thomas C. Ward, Department of Chemistry, 2107 Hahn Hall (0344), Virginia Tech, Blacksburg, VA 24061, USA. E-mail: tward@vt.edu

INTRODUCTION

Polymeric materials are increasingly incorporated into microelectronic devices because of their low cost and high performance properties [1]. Since miniaturization is an important issue in microelectronics, direct chip attachment (DCA) technology has attracted interest. In DCAs an adhesive is added as an underfill to reinforce the physical and mechanical properties of solder joints between the chip and the substrate [1]. The underfill provides fatigue life enhancement and also protects the integrated circuit (IC) from corrosion. Filled epoxies are commonly used in flip-chip assemblies as the underfills. We briefly review mechanical and moisture uptake behavior of filled epoxies below.

Dynamic mechanical analysis has been used to study the effects of fillers in composite materials. There, introduction of an interphase has led to differences in properties, such as the temperature, or the magnitude of tan delta [2, 3] and loss modulus values [4]. The presence and type of coupling agent on the filler has also been shown to affect performance [4, 5]. The molecular mobility of coupling agents has also been investigated in composite materials using dynamic mechanical analysis. Activation energies have been shown to be useful in order to quantify changes in molecular mobility due to the filler and type of coupling agent [6, 7]. Cooperativity plots from dynamic mechanical data have also been used as another way to investigate changes in molecular mobility in epoxies reinforced with glass and were shown to be sensitive to the type of coupling agent used [8].

Water absorption in glass-reinforced composites has been widely studied. In particular, the effects of placing a coupling agent on the surface of the filler have been shown to be advantageous by decreasing moisture uptake in filled systems. The results have generally shown that incorporation of the coupling agent reduces moisture uptake in these filled systems by acting as a barrier that prevents water damage in the interphase region by reducing the number of hydrophilic sites or by increasing crosslink density [6, 8, 9].

In our work, a model epoxy system filled with silica fillers treated with different coupling agents is reported. Particles were treated with coupling agents having differing endgroups that react on the surface of the filler particle. A dialkoxysilane and a trialkoxysilane coupling agent were chosen. These produce either linear chains of the coupling agent on the filler or network formation of the coupling agent on the filler, respectively. Viscoelastic properties, mechanical properties, and moisture diffusion in the filled model system were assessed to determine if interphase differences associated with the coupling agent affected the bulk properties of the composite material.

EXPERIMENTAL

Materials

Epon 862®, a bisphenol-F resin (shown in Figure 1a), was obtained from Shell Chemical Corporation. This resin has an epoxide equivalent weight of 171 g/mole. The curing agent was 4-methyl-2-phenylimidazole (Figure 1b). In imidazole curing, the imidazole is added to the epoxy ring to form an imidazole-epoxy adduct. The hydroxy adduct then initiates the epoxy ring opening, which leads to chain propagation [10, 11]. The curing reaction is shown in Scheme 1. Since this curing agent reacts catalytically with the epoxy resin, it was added in small amounts measured as parts per hundred resin (phr). In order to increase the solubility of the curing agent and toughen the product, 10 phr of 1,4-butanediol (Figure 1c) was also added as part of the model system. The 1,4-butanediol likely toughens the epoxy through chain transfer by either (1) increasing the number of chain ends if one of the hydroxyl groups reacts or (2) chain extension when both hydroxyl groups react. Both cases lead to a crosslinked network with a lower glass transition temperature and improved flexibility.

Amorphous fumed silica, Cab-O-Sil M5®, with a surface area of 200 m^2/g was obtained from the Cabot Corporation. The surface of the fumed silica particles was treated with 3-aminopropylmethyldiethoxysilane (APDS) or 3-aminopropyltriethoxysilane (APTS) in aqueous solution. Each of these coupling agents contains an aminofunctional end group that can react with the epoxy resin. The

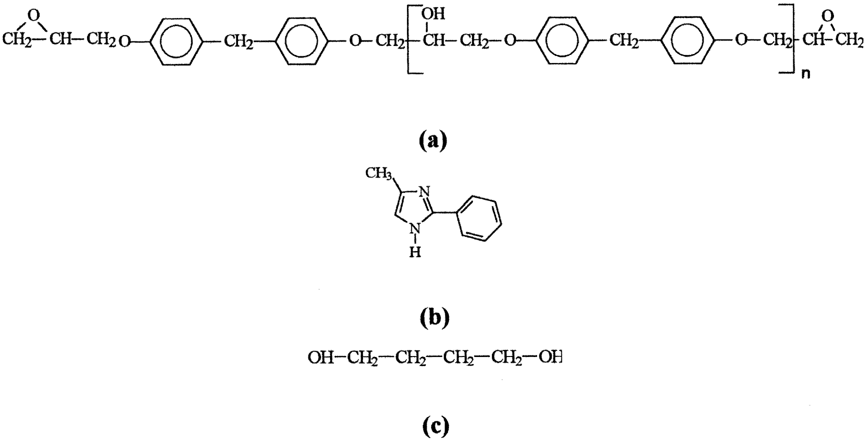
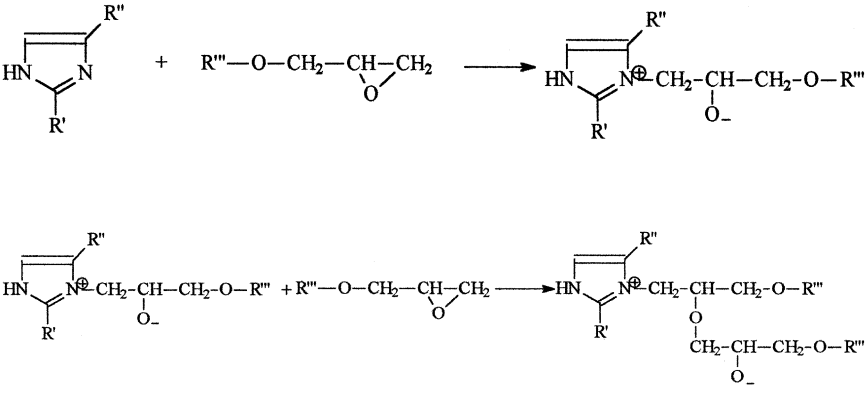


FIGURE 1 Model epoxy components: (a) Epon 862® (bisphenol-F epoxy), (b) 4-Methyl-2-phenylimidazole, and (c) 1,4-Butanediol.



SCHEME 1 Imidazole reaction mechanism.

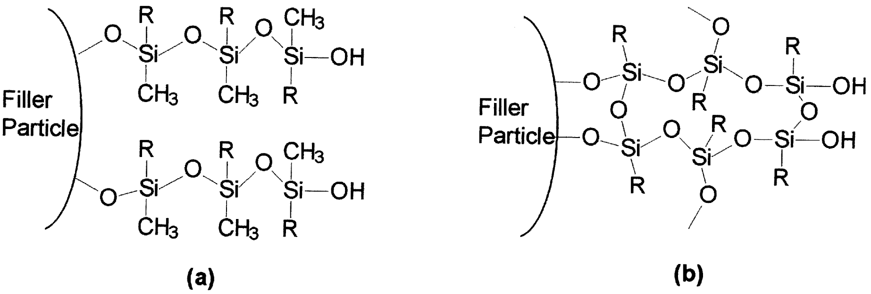


FIGURE 2 Proposed structure of coupling agent on silica particle: (a) APDS, (b) APTS.

APDS and APTS have been chosen due to the different reaction that can take place on the surface of the silica particle. Dialkoxysilanes should result in only linear siloxane sequences, while trialkoxysilanes should allow network bonding, as shown in Figure 2 [12].

Sample Preparation

Cab-O-Sil M5® fumed silica particles were: (1) left untreated, (2) treated with APDS, or (3) treated with APTS. One gram of particles was added to 25 mL of a 1% aqueous solution of coupling agent. The solution was agitated for 15 min and then filtered. The particles were placed in a forced air oven for 30 min at 100°C and then further dried in a vacuum oven at room temperature for 6 h.

Epoxy resin (10–15 g), 10 phr of 1,4-butanediol, and 3 phr of filler particles (if added) were weighed into an aluminum dish. These components were mixed on a hot plate with a magnetic stirrer for 10 min at approximately 60°C. Then the 4-methyl-2-phenylimidazole was added and stirred for 20 min at approximately 70°C.

Aluminum molds were coated with a fluorocarbon mold release agent and then baked in the oven at 250°C to remove excess release agent. The epoxy was dispensed evenly into the mold. The mold was then placed in an oven that had been preheated to 175°C. The length of the cure time was 60 min. The mold containing the samples was removed from the oven and allowed to cool on the benchtop.

Equipment

Differential scanning calorimetry (DSC) was performed using a Dupont Instruments DSC 912. Ten mg samples were measured at 10°C/min under a 30 mL/min nitrogen purge.

Dynamic mechanical behavior was studied using a Netzsch DMA 242. Measurements were taken in the dual cantilever mode using frequencies of 0.33, 1, 3.33, 10, and 33.3 Hz using a 3°C step isotherm. An oscillation amplitude of 7.5 μm was employed. The sample geometry was approximately 52 mm × 6 mm × 2 mm.

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2950. Air was used as the purge gas in the experiment at approximately 30 mL/min. The sample was heated from room temperature to 850°C with a heating rate of 10°C/min.

A PHI Perkin Elmer model 5400 X-ray photoelectron spectrometer was used to examine untreated and treated fumed silica particles. Analysis was carried out using Mg K_α X-rays ($h\nu = 1253.6$ eV) at 300 watts and 14 kV. Ejected electrons were detected using a hemispherical analyzer. A 1 mm × 3 mm spot size was analyzed using a 45° takeoff angle.

Moisture uptake was evaluated using a Mettler AE200 analytical balance with a 10^{-4} g resolution. Epoxy samples (52 mm × 13 mm × 1 mm) were submerged in water at 60°C. Periodically the samples were removed from the water, the surface was blotted dry for the weight measurements, and they were returned to the water.

RESULTS AND DISCUSSION

Curing Agent Optimization

Three concentrations of 4-methyl-2-phenylimidazole were incorporated in the model epoxy system in order to determine the optimum product. Figure 3 displays DSC results, which are shown for

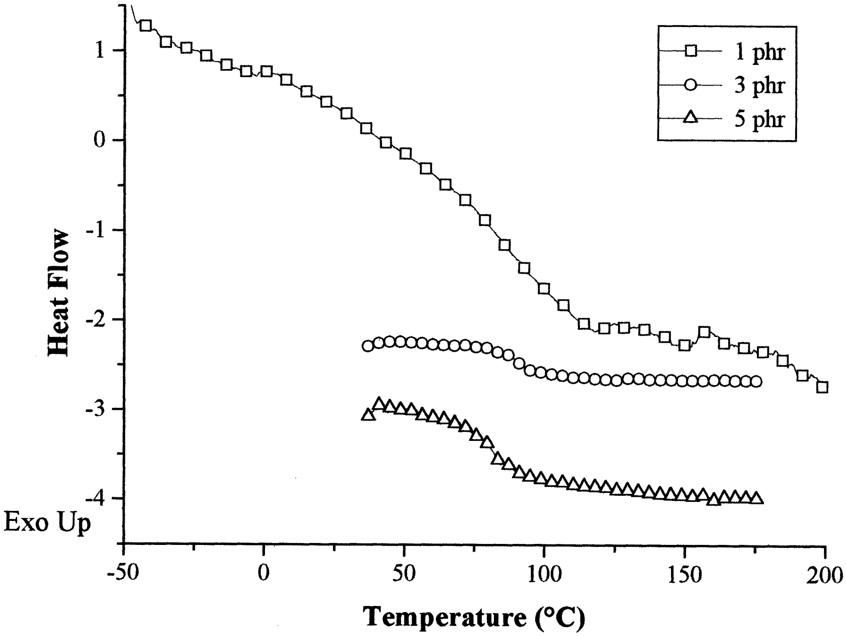


FIGURE 3 DSC results for different amounts of imidazole in the model epoxy.

the model epoxy cured at 175°C for 1 h with different amounts of 4-methyl-2-phenylimidazole (1 phr, 3 phr, and 5 phr). None of the samples produced a DSC exothermic peak, indicating complete cure. The sample containing 1 phr of the imidazole shows a broad transition with an endothermic inflection at 84°C. The broadness of this transition may result from a low crosslink density due to the lack of available imidazole. Since the imidazole acts as an initiator, low amounts lead to reduced chain initiation and chain propagation. With little chain propagation, a large distribution of small molecular weights is obtained, leading to a broad transition. Other authors have also reported that the addition of 2 wt% imidazoles to a Bisphenol A epoxy was too small to cure the epoxy fully [13]. The highest glass transition (91°C) is seen in the sample containing 3 phr of the imidazole, indicating that this may be close to the optimum concentration. The glass transition for the sample containing 5 phr of the imidazole is seen at 83°C.

Further studies were performed to verify the optimum amount of curing agent for the model epoxy. The glass transition temperature (T_g) was measured for three curing agent concentrations (1 phr, 3 phr, and 5 phr) using dynamic mechanical analysis and dilatometry, and compared with the results from DSC. Figure 4 shows the results of

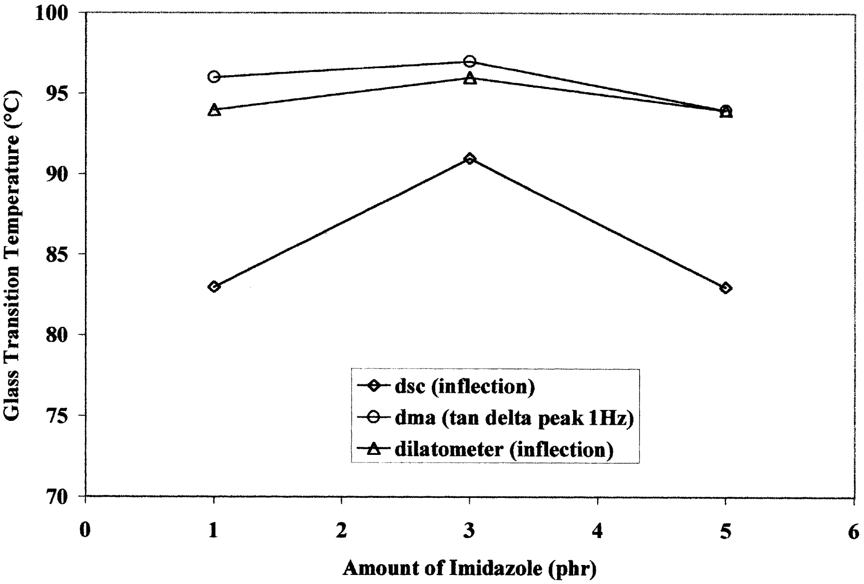


FIGURE 4 Glass transition temperature as a function of curing agent amount in the model epoxy.

the glass transition temperature as measured by dynamic mechanical analysis, DSC, and dilatometry. The trend is the same for all techniques; however, the values are different. It is not surprising that the values are different, though, as the glass transition is a second order-transition. A physical property can be used to locate the transition temperature, but the precise value will depend on the measurement technique and the rate of measurement [14]. The glass transition temperature was again highest for the epoxy containing 3 phr of curing agent. The lowering of the glass transition temperature of the 5 phr sample (as compared with the 3 phr sample) results from each molecule of imidazole acting as a chain endgroup, thus reducing the length of each polymerizing chain [10, 15]. This results in more free volume, and lower crosslink density, which produces a lower glass transition temperature. From these results, 3 phr was selected as our optimum curing agent concentration.

Silica Particle Characterization

X-ray photoelectron spectroscopy (XPS) was used to analyze the fumed silica before and after treatment with the coupling agents. The particles should contain no nitrogen before treatment with the coupling agent. Both APDS and APTS contain nitrogen; thus, after treatment of the particle with the coupling agent, the presence of nitrogen can be used to verify the presence of the coupling agent on the surface of the particle. Table 1 shows the atomic concentration results, and nitrogen is not detected on the particles before treatment with the coupling agent. After treatment of the particles with APDS and APTS coupling agents, nitrogen is detected and is present at 2.2% and 2.7%, respectively. This indicates that the particles were successfully treated with the coupling agent.

Thermogravimetric analysis (TGA) was also used to analyze the fumed silica before and after treatment with the coupling agents—the sample weight percent as a function of temperature for the average of three samples is shown in Figure 5. At 100°C, the particles treated with APTS show a larger decrease in weight ($0.8 \pm 0.2\%$) than the untreated and APDS-treated particles ($0.4 \pm 0.1\%$), indicating that the APTS particles contained more residual moisture or ethanol from the treatment process. A loss in weight, not observed in the untreated particles, is also observed between 300–400°C for the APDS- and APTS-treated particles. This is possibly degradation of the coupling agent on the surface of the particle and may be another way to verify that the coupling agent is present on the surface of the particle. The weight loss was calculated to be $1.5 \pm 0.1\%$ and $1.8 \pm 0.03\%$ for particles treated with APDS and APTS, respectively. The slight increase in weight above 600°C is due to an observed weight difference of the sample pan due to a decreased density of the purge gas and increased buoyancy of the sample pan [16].

A rough estimate of the thickness of the silane layer can be calculated using the weight loss data [17]. Assuming the coupling agent occupies 50Å^2, for a particle surface area of $200\,\text{m}^2/\text{g}$, the aforementioned weight loss indicates a surface coverage of approximately 10%.

TABLE 1 Atomic Percent Concentration of Silica Particles

Element	Neat (%)	APDS (%)	APTS (%)
C	14.8	22.7	28.2
O	57.8	50.1	46.7
Si	27.4	25.0	22.4
N	nd	2.2	2.7

nd, not detected (< 0.2%).

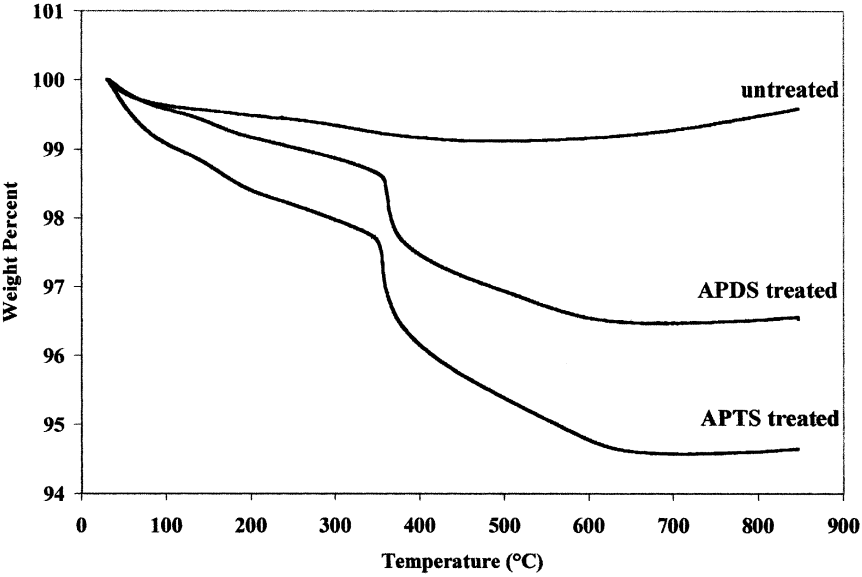


FIGURE 5 TGA results for fumed silica particles.

Epoxy Characterization

DSC data was obtained for the unreacted epoxy containing 3 phr of 4-methyl-2-phenylimidazole with and without the fillers. The average of three samples of each type is shown in Figure 6. The data have been offset on the y-axis for clarity. Upon heating, the uncured epoxies exhibit an exothermic peak due to curing that appears at 117 ± 2°C and peaks at 127 ± 1°C. Integration of the exothermic peak results in a value of 294 ± 27 J/g. No significant differences exist with the presence of filler or type of coupling agent.

Multifrequency Dynamic Mechanical Analysis (DMA) data were obtained on the model epoxy with 3 phr of 4-methyl-2-phenylimidazole both with the treated and the untreated fumed silica filler. Representative data for each sample are shown in Figures 7–10. The glass transition temperature for each sample (average of three) was determined from the tan delta peak at a frequency of 1 Hz and is shown in Table 2. No significant differences were observed among the different samples. Master curves and shift factor plots were generated using the glass transition temperature as the reference temperature. The Williams, Landel, Ferry (WLF) equation [18]

$$\log(a_T) = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)} \tag{1}$$

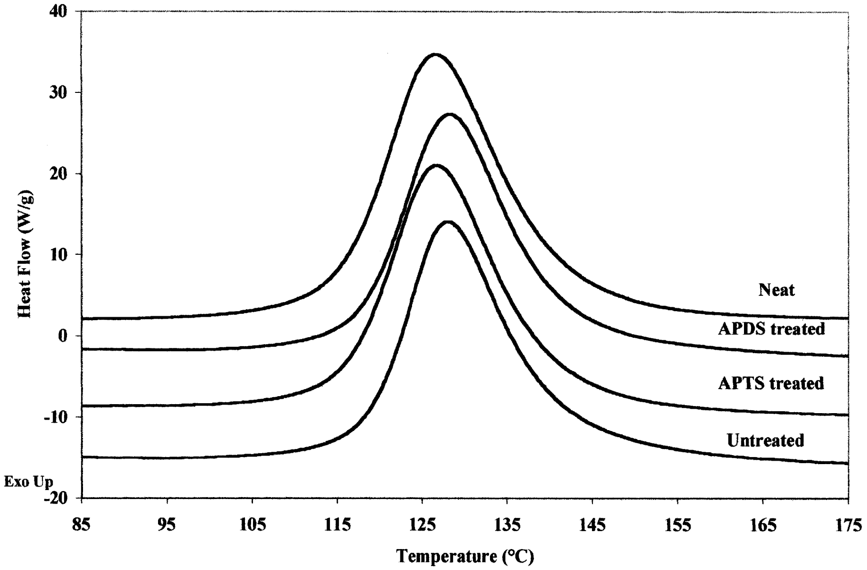


FIGURE 6 DSC data for the unreacted model epoxy with differing filler types.

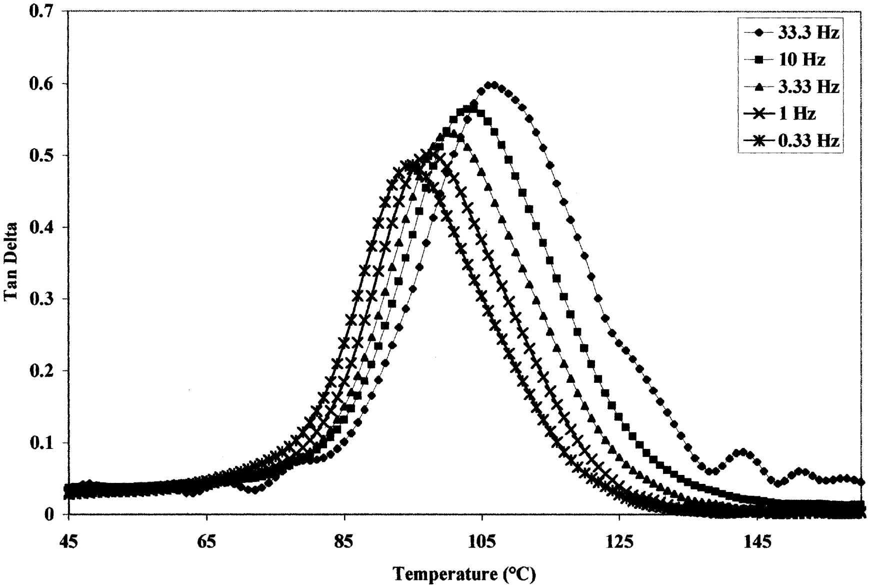


FIGURE 7 Multifrequency DMA curves for the neat model epoxy.

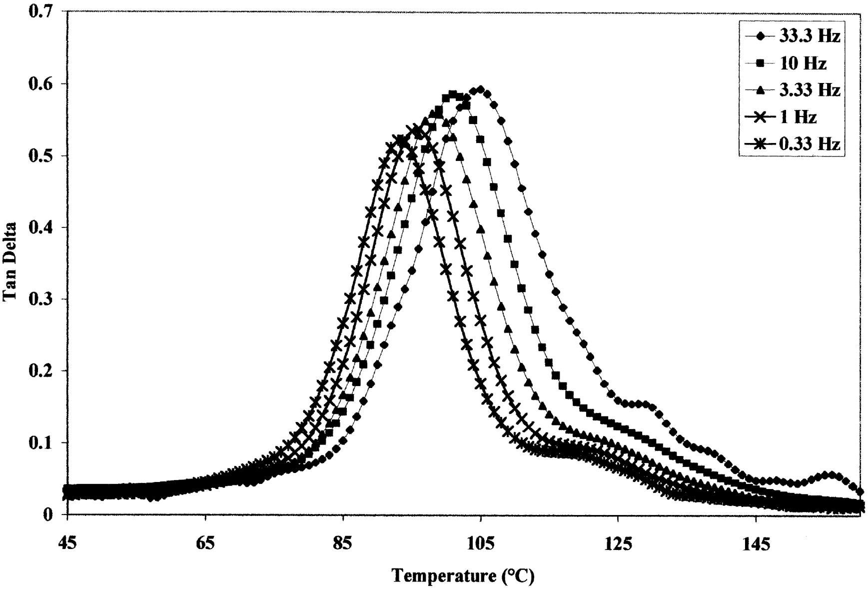


FIGURE 8 Multifrequency DMA curves for the model epoxy with untreated filler.

can be used to describe the temperature dependence of the superposition, where a_T is the WLF shift factor. The constants, C_1 and C_2, were extracted from plots of 1/(log a_T) versus $1/(T - T_R)$ and are shown in Table 2. Using these constants, an activation energy can be calculated from [18]

$$E_a = 2.303R\frac{C_1 T_R^2}{C_2} \tag{2}$$

The WLF equation is nearly always applicable for the glass transition region of most polymers [19]. However, due to the subjectivity and the amount of error introduced from the shifting process, activation energies were also calculated using an Arrhenius fit which is typically more appropriate for sub-T_g relaxations [19] but still provides a good estimate (and values with less error):

$$\ln(\omega) = -\frac{E_a}{R}\frac{1}{T} + \ln(A) \tag{3}$$

where ω is the test frequency, R is the universal gas constant, and T is the temperature at which the peak maximum of tan delta occurs for

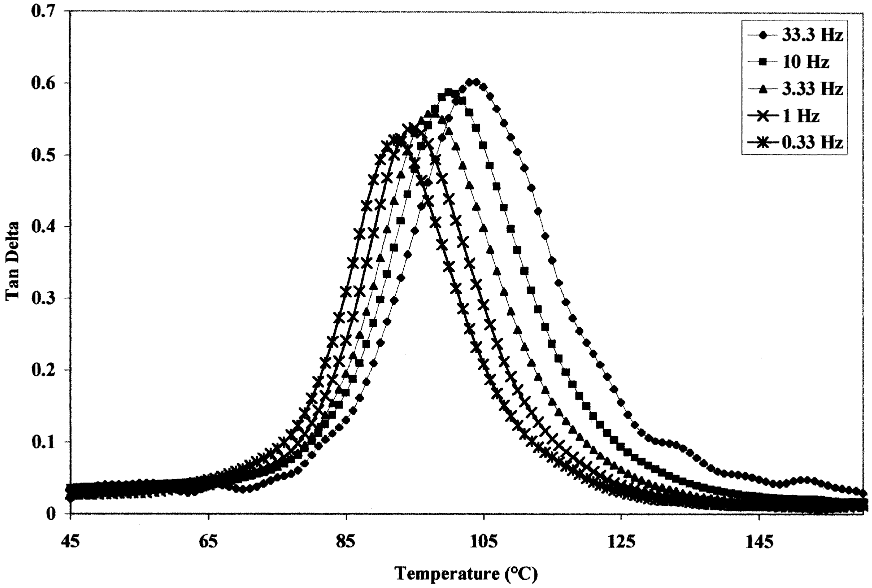


FIGURE 9 Multifrequency DMA curves for the model epoxy with APDS-treated filler.

each frequency. The values of E_a (shown in Table 2), using Equations (2) and (3), were greater for the filled epoxy than for the unfilled. Hence, addition of the filler led to a reduction of chain mobility. It was expected that the coupling agent type would also influence the chain mobility, with the trialkoxysilane leading to a greater reduction in chain mobility than the dialkoxysilane due to the crosslink formation. However, the values were not sensitive to the presence or type of coupling agent.

Cooperativity plots were also generated from the multifrequency DMA data. Plazek and Ngai [20] report that for thermorheologically simple dispersion mechanisms the cooperativity can be derived as in Equation (4)

$$(1-n)\log a_T = \frac{-C_1(T-T_g)}{C_2+(T-T_g)/T_g} \tag{4}$$

where C_1 and C_2 were found to be 5.49 and 0.141, respectively, for a wide variety of polymers. In Equation (4), log a_T is the shift factor, T is the measurement temperature, and T_g is the glass transition

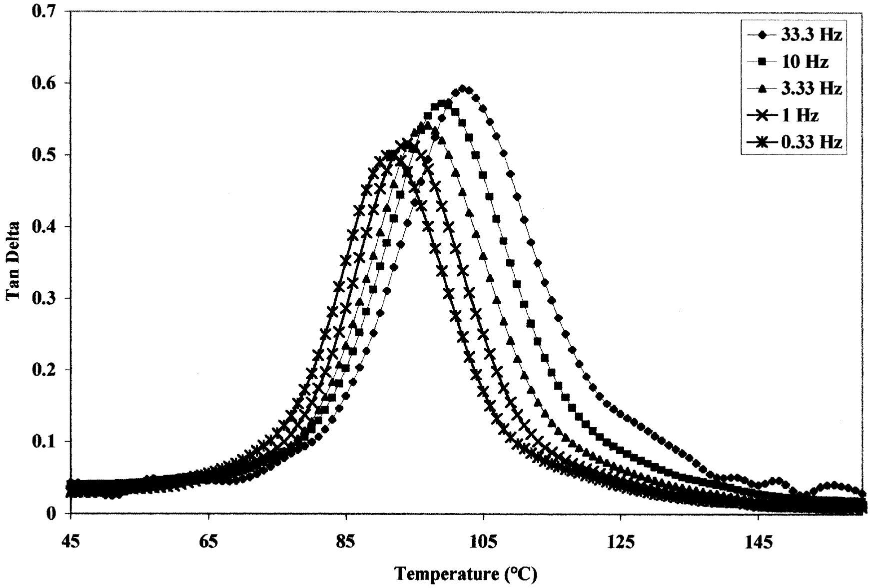


FIGURE 10 Multifrequency DMA curves for the model epoxy with APTS-treated filler.

TABLE 2 Glass Transition Temperatures, Activation Energies, and Coupling Constants

	T_g(°C)	E_a (kJ/mol) (Arrhenius)	C_1	C_2(°C)	E_a(kJ/mol) (WLF)	n
Neat	96.9 ± 0.6	425 ± 24	5.5	30.0	480 ± 18	0.45 ± 0.02
Untreated	96.8 ± 1.6	472 ± 2	9.6	46.0	542 ± 43	0.46 ± 0.01
APDS treated	95.4 ± 1.2	483 ± 7	10.6	53.0	517 ± 51	0.53 ± 0.02
APTS treated	94.6 ± 0.6	484 ± 21	9.2	46.7	509 ± 27	0.50 ± 0.01

temperature chosen as the reference temperature for shifting. The coupling constant, n, ranges from 0 to 1.0. The value of n describes the cooperativity, with larger n indicating more cooperative motions. Larger cooperativity is associated with a larger volume of segments undergoing rearrangements, with a broader distribution of relaxation times. In order to determine n, a plot of $\log a_T$ versus $(T - T_g)/T_g$ is constructed, and a fit to the data is performed using Equation (4).

In order to determine the shift factor to calculate the cooperativity, master curves were generated from the multifrequency DMA data.

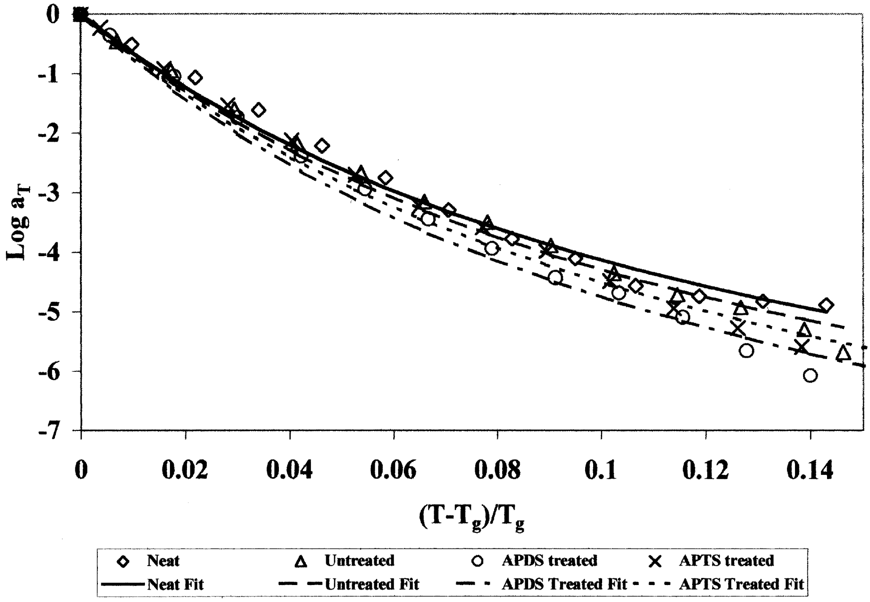


FIGURE 11 Cooperativity plot for the model epoxy with differing filler treatments.

Isothermal tan delta curves were plotted as a function of frequency. The glass transition temperature was chosen as the reference isotherm, and the remaining curves were shifted horizontally to generate a smooth curve. The cooperativity results for the model epoxy containing 3 phr of the filler with different surface treatments are shown in Figure 11. The values determined for n ranged between 0.45 and 0.50 and are shown in Table 2. These values lie within the range of 0.45–0.75 that Plazek and Ngai [20] reported for several polymers. Incorporation of the silane led to a slight increase in the coupling constant, indicating that cured polymer became more heterogeneous with a broader relaxation time distribution. Since the silane coupling agent presumably leads to covalent bonding of the filler to the epoxy matrix, it is expected that this would lead to an additional constraint on the system and increase the amount of cooperativity required for segmental motion. It was also expected that the trialkoxysilane would lead to an increase in cooperativity over the dialkoxysilane due to the network formation, leading to a reduction in segmental motion. However, no difference could be detected between the two types of coupling agents.

Diffusion studies at 60°C in distilled water were conducted for the model epoxy via mass uptake measurements. The percent moisture content M (percent weight gain) was measured as a function of time (t).

$$M = M(t) = \frac{\text{Weight of moist material} - \text{Weight of dry material}}{\text{Weight of dry material}} \times 100 \tag{5}$$

The percent moisture content as a function of time (M_t) can be analyzed using the following equation derived from Fick's second law:

$$M_t = G(M_\infty - M_i) + M_i \tag{6}$$

where M_i is the initial percentage of moisture content in the sample, M_∞ is the percentage of moisture at equilibrium content, and G is a time-dependent parameter given as follows [21]:

$$G = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp\left[-(2j+1)^2\pi^2\left(\frac{Dt}{b^2}\right)\right]}{(2j+1)^2} \tag{7}$$

The diffusion coefficient (D) can be calculated from a plot of weight percent versus square root of time and by applying the following equation:

$$D = \pi\left(\frac{sb}{4M_\infty}\right)^2 \tag{8}$$

where s is the slope of the initial linear portion of the plot and b is the sample thickness.

A plot of weight percent versus the square root of time/thickness (hours$^{1/2}$/cm) is shown in Figure 12 for the various epoxy samples. The symbols represent the experimental data (average of three samples) and the solid lines indicate the fit using Equation (7) (with an upper limit of $j = 200$). The agreement of the fit with the data indicates that the diffusion was Fickian. The diffusion coefficients were calculated for these samples using Equation (8), taking the slope from the data points below 1% mass uptake. The results are shown in Table 3. Within the experimental error, there is very little difference in the saturation mass and diffusion coefficients for the different types of samples. Since increasing crosslink density leads to a decrease in free volume, it was expected that the samples with the trialkoxysilane coupling agent would exhibit a lower mass uptake than the samples with the dialkoxysilane. However, treatment of the particles with the APDS coupling agent led to a small decrease in the saturation mass as compared to the other samples.

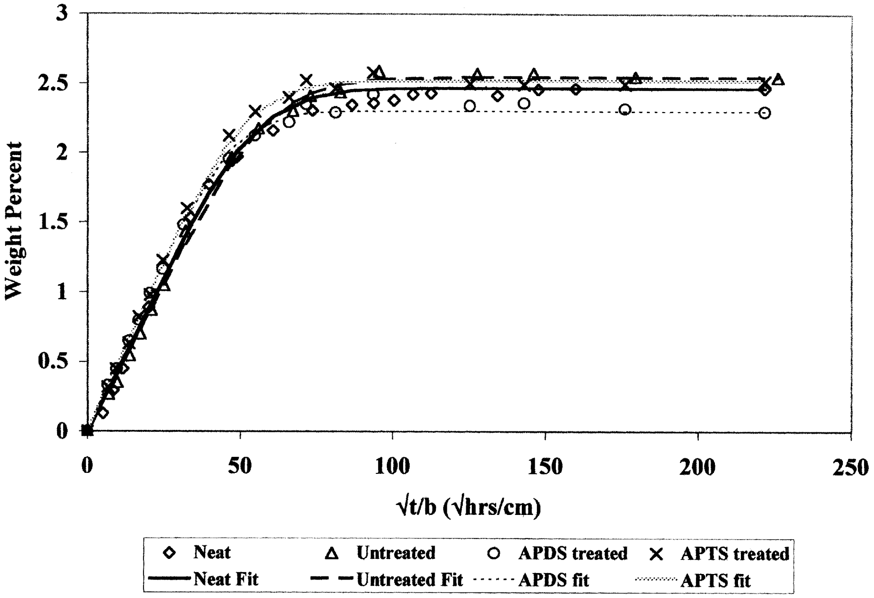


FIGURE 12 Moisture uptake results at 60°C for the model epoxy with differing filler treatments.

TABLE 3 Saturation Mass and Diffusion Coefficients

	M_{∞}(%)	D*10^8(cm^2/sec)
Neat	2.46 ± 0.09	1.74 ± 0.28
Untreated	2.55 ± 0.02	1.49 ± 0.29
APDS	2.30 ± 0.03	2.41 ± 0.72
APTS	2.52 ± 0.13	2.00 ± 0.14

CONCLUSIONS

A model epoxy system containing a bisphenol-F resin, 1,4-butanediol, and 4-methyl-2-phenylimidazole was found to have an optimum curing agent concentration of 3 phr. Amorphous fumed silica, with and without coupling agents, in the epoxy led to no changes in the glass transition temperature and very little change in moisture uptake properties. Addition of the filler did lead to an increase in the activation energy for the glass transition region, but no changes were observed for different coupling agent treatments. However, addition of coupling agents did lead to changes in the cooperativity of the epoxy, which should also show up in changes in other mechanical properties such as toughness. Larger differences would likely be observed at higher filler loadings and greater surface coverage of the filler with the silane coupling agent. However, the high surface area of the fumed silica leads to rapid increases in viscosity when it is added to the epoxy and prevents the addition of filler loading much beyond 5% by weight.

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