A Highly Fluorinated Epoxy Resin: Post-Curing and Transition Behavior

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Synopsis

The post-curing and transition behavior of a highly fluorinated epoxy resin system was characterized. The material was found to have low temperature transitions similar to those found in DGEBA. The cure was discovered to be inhibited by the presence of CO_2. The glass transition was broad and near room temperature, resulting in rapid aging characteristics.

INTRODUCTION

Efforts have been made to improve the hydrophobicity of epoxy resins by halogenation of the monomer. Epoxies containing a large amount of fluorine have been synthesized by Griffith and Field,[1,2] with chemical structures of the general form shown in Figure 1. The reaction kinetics,[3] surface tension, and friction coefficients[4] of these materials have been characterized. More recently, the water uptake, dynamic mechanical, and fracture behavior of several resin compositions have been studied by Shaw et al.[5,6] The most hydrophobic resin, C8/1SA with a 0.17% moisture uptake at 20°C, was the model resin for our investigations of the post-curing and transition behavior of these materials. The C8/1SA resin is so designated for an n value of 8 for the pendant chain and employment of a silicone amine curing agent with an m value of 1, also illustrated in Figure 1. Some processing related sample history dependences of mechanical responses were qualitatively studied as well. Lack of sufficient material prevented detailed mechanical experiments.

EXPERIMENTAL

Stoichiometric amounts of C8 resin and 1SA hardener, furnished by J. Griffith, were stirred for 20 min at a temperature of 50–60°C, the window of miscibility for the two agents. Below this range, the resin and hardener are immiscible, whereas above this range the material will gel before the components can be uniformly mixed. The reacting mixture was poured onto the mold surface and degassed for 20 min at room temperature. The resin mixture was cast as thin films for differential scanning calorimetry (DSC) and thermally stimulated current (TSC) studies, and in dogbone or rectangular specimens for mechanical tests. Thin films were cast between two flat RTV 11 (General Electric) surfaces treated with Bomb Lube Yellow mold release (Price-Driscol). For bulk samples,
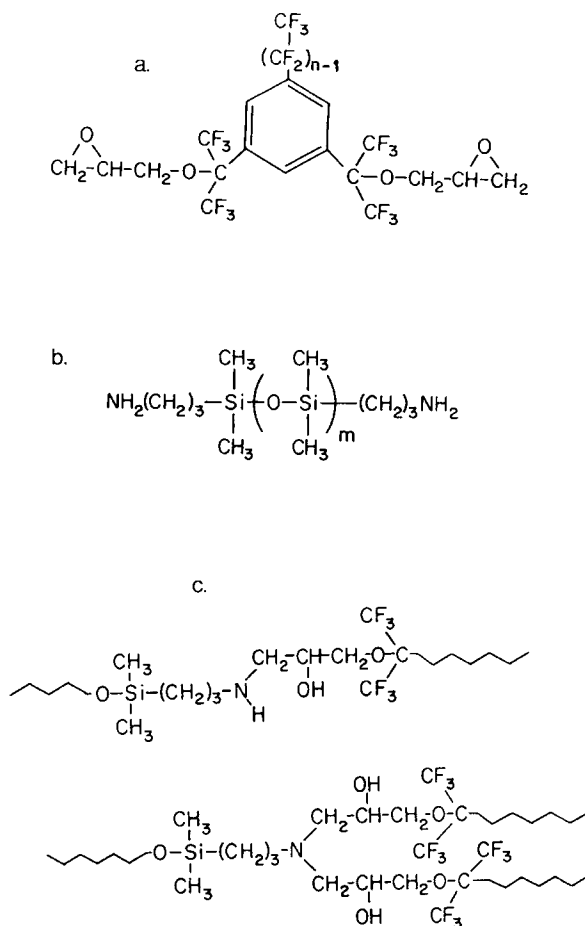
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Fig. 1. $C(n)/(m)SA$ resin system: (a) $C(n)$ type fluoroepoxy; (b) $(m)SA$ type silicone amine curing agent; (c) likely curing configurations.

one of the RTV pieces was a female mold with the desired dimensions. The pieces were allowed to cure at room temperature for at least 16 h, at which time post-curing was applied as appropriate.

A Perkin-Elmer DSC 4 was used to study the change in glass transition of the material as a function of post-cure time at 80 and at 120°C. Griffith recommended a room temperature cure for 16 h followed by a post-cure of 3 h at 120°C.[7] To resolve the nature of an unidentified peak in the above experiments, DSC scans of the 1SA hardener in both the pure state and crystallized by the presence of CO_2 were run, as were FTIR scans of the non-post-cured sample using a Nicolet 7199 1180 E spectrometer. Aging studies were also run using the DSC.

For TSC studies, thin films (1.5 cm^2 × 0.2 mm thick) of fluoroepoxy with 20 min of post-curing at 120°C were used. Gold electrodes with 1 cm diameter were evaporated onto both sides of each specimen. In order for these samples to be satisfactory, a surface resistance of less than 5 Ω and an infinite resistance through the sample were required. For the low temperature transition study

the sample was polarized for 30 min at room temperature using a 10,000 V/cm field. The high temperature transition samples were polarized in a 10,000 V/cm field at 120°C for various times, the total post-cure being the sum of the original post-curing period and the length of polarization at 120°C.

Dogbone samples 2.5 × 0.5 × $\frac{3}{8}$ in. (length × width × thickness) with a 1.5 × 0.25 in. (l × w) gauge dimension were cast and fully post-cured (120°C, 3 h). The room temperature aging histories of these samples were removed by heating to 120°C for over 0.5 h, followed by slow cooling. The samples were tested in tension in an Instron 1551. Initial strain measurements were made using a knife edge extensometer with a 0.5 in. gauge length. The Instron was fitted with a thermocouple controlled oven. The tensile behavior was recorded for both 28 and 45°C.

Rectangular samples 2.5 × 0.5 × $\frac{1}{8}$ in. were cast and fully cured, then aged at room temperature for 1 year. The samples were tested at 28°C in tension using an MTS 180.

RESULTS AND DISCUSSION

The 120°C post-cured fluoroepoxy showed a subambient transition by DMA in Shaw's work.[5] This peak is resolved into three peaks in the TSC scan shown in Figure 2. The γ peak is present as a shoulder at a temperature of −125°C. This peak is located in the same range as the γ peak seen by Pangrle et al.[8] in DGEBA epoxies ascribed to the onset of motion of the diether linkage. Assuming the assignment in Pangrle et al. is correct, we suggest that this motion may be
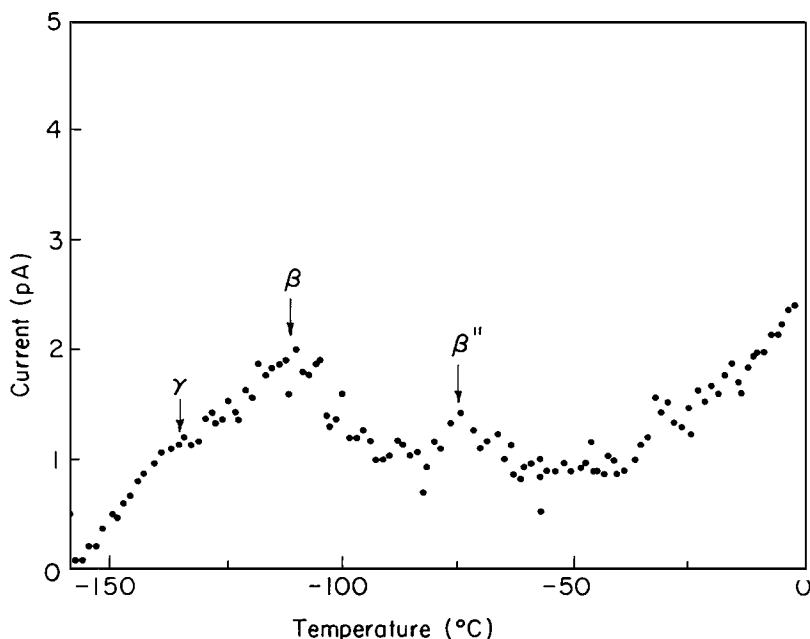

Fig. 2. Subambient TSC scan of C8/1SA. Note the three peaks at −125°C (γ), −112°C (β), and −25°C (β″).

associated with the onset of motion of phenyl–CF_3 groups. There is also a β peak located at $-112°C$. This peak is consistent with the β_{OH} peak found in the work by Pangrle et al. to be due to the crankshaft motions of the hydroxy-ether linkages. In the fluoroepoxy resin system, such groups form during cure, as illustrated in Figure 1. The highest temperature β'' peak ($-25°C$) has been assigned as an interaction with CO_2, which we have found to be associated with undercured fluoroepoxy samples when no precautions have been taken to avoid CO_2 absorption during cure. This is consistent with the interaction of water assigned to a similar peak in the DGEBA resins studied by Pangrle et al.

The effects of 80°C post-curing are illustrated in Figure 3. As can be seen, T_g hardly changes at all, contrary to expected behavior.[9] There is also a peak at approximately 80°C, which lowers slightly with increased post-cure at 80°C. The origin of this peak was at first unknown. However, the expected residual exotherm,[9] characteristic of an undercured epoxy above its T_g, is not evident until this peak has been passed. This suggested that the peak represented the freeing (melting) of some form of structure that blocked any curing at or below 80°C. FTIR studies of the un-post-cured specimen reflected the presence of few of the $-NH_2$ and $-NH-$ groups which should be present if unreacted curing agent were present. DSC was run on crystalized silicone amine formed in the presence of CO_2. The crystals "melted," the CO_2 coming off, predominantly in a range from 85 to 100°C, although some portion was still melting at as high a temperature as 130°C, which is consistent with the unidentified peak. This peak was not present in CO_2-free 1SA. So it seems that when the initial cure is conducted in the presence of CO_2, the hardener will absorb CO_2, which
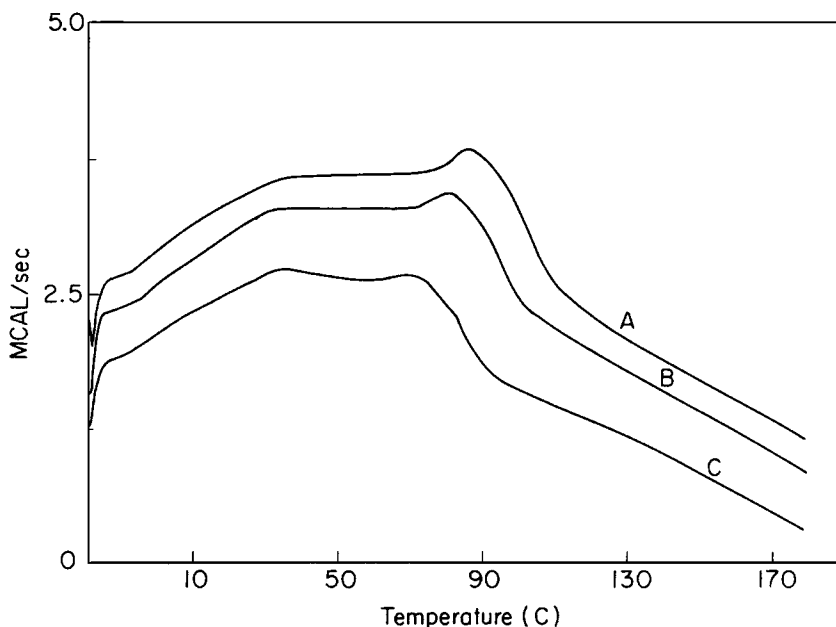

Fig. 3. DSC scans illustrating the effects of post-curing at 80°C for various times: (A) no post-curing; (B) 1 h post-cure; (C) 4 h post-cure.

will inhibit both further curing and post-curing at temperatures below the "melting" range.

The TSC curves illustrated in Figure 4 show the progress of T_g as a function of extent of 120°C post-cure. The lowest curve, having a minimum of post-curing, shows a T_g of 35°C with a possible shoulder at 15°C due to a less densely crosslinked "phase." As post-curing progresses, both peaks shift to higher temperatures, the main T_g peak shifting to 65°C. The change in shape indicates that a significant portion of the material retains a much lower T_g, as is shown by the shoulder of the completely cured specimen scan at approximately 45°C; i.e., there are domains representing two degrees of crosslinking. The higher temperature peak that shifts from 60 to 75°C has been assigned as a ρ peak. A ρ peak often occurs about 30°C above the glass transition, the result of heterogeneous charge injection.[10] Despite the near disappearance at full cure, such an assignment seems most reasonable at this time. The height of this peak is known to vary considerably from sample to sample, even in supposedly identical samples.

Figure 5 shows the stress–strain behavior in tension of C8/1SA resin at 28 and 45°C. The 28°C test showed a modulus of 194 ksi, whereas the 45°C ex-
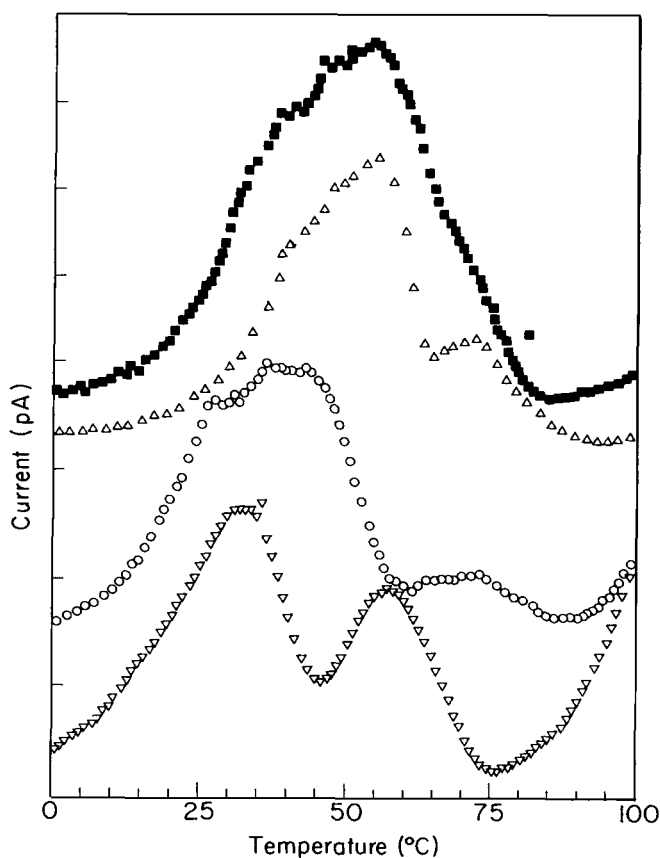

Fig. 4.   TSC scans illustrating the effects of post-curing at 120°C for various times: (∇) 20 min; (○) 1 h; (△) 3 h; (□) 3.25 h.
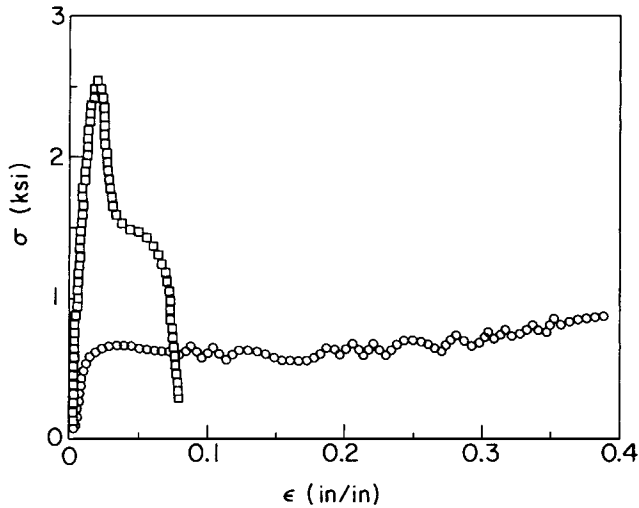
Fig. 5.   Stress–strain behavior of C8/1SA at (□) 25°C and (○) 45°C.

periment showed a significant drop in modulus to 46 ksi. The 28°C modulus is consistent with that measured by Shaw. Although the material yielded in a ductile fashion at both temperatures, it behaved much more plastically at the elevated temperature. The 28°C sample yielded at the extensometer knife edge, whereas the higher temperature sample yielded and drew uniformly up to the maximum stroke range (2 in.) of the Instron, making it impossible to measure the failure stress and strain. The noise in the high temperature signal is due to the small scale of the signal relative to the load cell available (200 lbf).

Figure 6 demonstrates the change in stress–strain behavior in tension of the C8/1SA resin as a function of sample age. The 1-year-old sample showed a
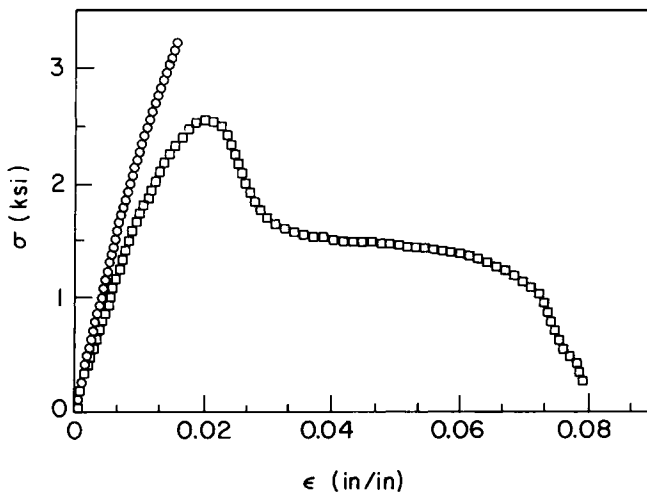

Fig. 6.   Stress–strain behavior of C8/1SA both (□) fresh and (○) aged for 1 year.

modulus of 260 ksi, a distinct increase over the 194 ksi seen in a fresh sample. Note that the two modulii measured for a fresh sample and a fully aged sample bracketed the modulus reported by Shaw of 241 ksi.[5] The largest effect by far, however, is the radical change from ductile to brittle failure in just 1 year. Clearly, in the early days in the C8/1SA lifetime, the mechanical behavior will change from day to day, an effect which can be reversed by heating above T_g.

Figure 7 shows the progress of physical aging as observed by DSC. In a fresh, fully post-cured sample there is a slight change in baseline at approximately 65°C indicative of T_g, as would be expected for a fully cured, tightly crosslinked sample. As time progresses, however, a peak develops at the T_g, increasing rapidly, until after only 77 days it reaches approximately 95% of its total equilibrium height, that is, 95% of the peak height of a 1-year-old specimen. This peak is indicative of physical aging.[11]

CONCLUSIONS

Processing must be conducted under an inert atmosphere to avoid absorption of CO_2 with the subsequent termination of post-curing reactions below 80°C and the slowing of post-curing at higher temperatures. The material has a reasonable strength, but the T_g is broad and starts as low as 40°C, with a commensurately low deflection temperature. This low T_g also gives rise to a predictably rapid aging rate at room temperature. Three low temperature transitions have been observed, and the toughness associated with these transitions for DGEBA resins will be present in the fluoroepoxy resin systems as well. The
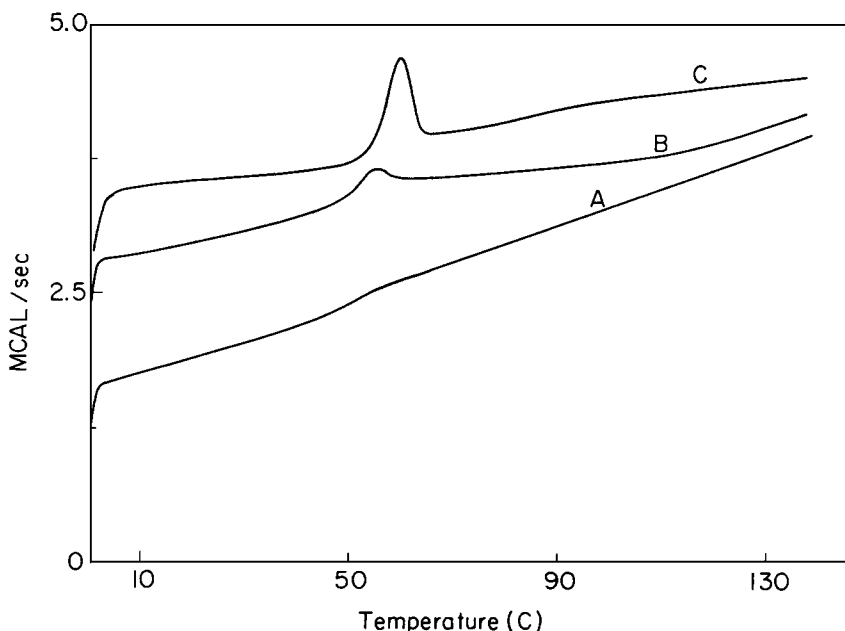

Fig. 7. DSC scans illustrating the progress of sample aging: (A) fresh sample; (B) aged 16 days; (C) aged 77 days.

results of using this resin as a component in a blend with DGEBA and as a matrix or fiber coating will be examined in future papers.

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