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Tailoring the Global Properties of Nanocomposites. Epoxy Resins with Very Low Coefficients of Thermal Expansion

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Introduction. Cubic silsesquioxanes (see Figure 1) are unique molecules that combine three-dimensional cubic symmetry with single nanometer diameters and a core that is the smallest single crystal of silica. Symmetry places a functional group on each vertex in a different octant in Cartesian space providing the opportunity to form covalent bonds accordingly, such that the potential exists to construct materials in 1-, 2-, or 3-dimensions nanometer by nanometer. In principle, this permits manipulation of global properties by tailoring structures at nanometer length scales, allowing the finest control possible. It also provides access to materials with highly reproducible properties and the potential to predict and design them for specific applications.[1−10]

Results and Discussion. We recently began exploring the chemistries and properties of epoxy resins and polyimides made with octaaminophenylsilsesquioxane, $[NH_2PhSiO_{1.5}]_8$, OAPS.[11−14] In early studies we demonstrated that global silsesquioxane nanocomposite properties can be tailored by controlling the structure of the organic tether linking cube vertices, at nanometer length scales.[15−19]

We report here efforts to develop single-phase materials that offer control of the coefficients of thermal expansion (CTE) of silsesquioxane epoxy resins over an order of magnitude. Control of CTE is of considerable importance in multiple materials applications (e.g., coatings that offer resistance to abrasion, corrosion, photooxidation, hydrophobicity, staining, etc.) where the polymer coating is applied to glass, ceramic, or metal substrates with quite dissimilar CTEs. In such instances, thermal cycling often leads to loss of adhesion followed by coating failure via chemical and/or mechanical mechanisms.[20]

CTE mismatches are also quite problematic in electronic applications, for example, in interlayer dielectrics and flip-chip underfills.[21] In the latter case, the underfill epoxy must match the CTEs of silicon-based ICs (CTEs of 2−3 μm/°C) with substrates (CTEs of 20−40 μm/°C) to ensure good thermal management. Current epoxy materials require silica fillers to adjust CTEs to ≥20 μm/°C. Such CTEs are intermediate between substrates and silicon to minimize fatigue at solder joints. These fillers raise resin viscosities to levels near 50 000 mPa•s, making processing very difficult. Likewise, corrosion-resistant epoxy resin coatings on Al alloys for aircraft bodies must minimize environmental corrosion and offer good abrasion resistance and curing at temperatures <50 °C but also have CTEs close to those of the alloys, typically 22−24 μm/°C. Such values were heretofore unknown for simple epoxy systems and especially for primer coats on aircraft fuselages that are typically DGEBA/DDM materials (60−70 μm/°C).[22]

Epoxy resin thermosets studied here were produced from a series of epoxys (see Table 1 and Figure 2) formulated using OAPS as the curing agent. The formulations chosen were made according to our original model systems, wherein the ratio of NH_2:epoxy groups was either 0.5 or 1.0. The first composition is that typically used for commercial resins. The second composition was chosen because our original studies found that resins cured with this composition led to better control of the tether structures between cube vertices and generally better tensile strengths and fracture toughness.[17,18]

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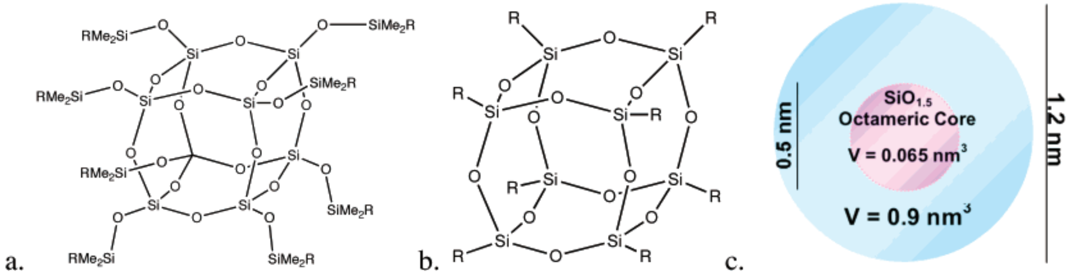

Figure 1. Silsesquioxanes. (a) Q_8 ($Q = SiO_{2/2}$); R = H, vinyl, epoxy, methacrylate, etc. (b) R_8T_8 ($T = R{-}SiO_{3/2}$); R = alkyl, alkene, acetylene, acrylate, R′X (X = halogen, −CN, amine, epoxy, ester, etc., R′ = R same or mixed). (c) Typical sizes/volumes.

Table 1. CTEs of Selected Epoxy Resins Where N = Number of NH_2s/Epoxy Groups[a]

epoxy	molar ratio, N	wt % OAPS	CTE (ppm/°C) below inflection	inflection point[b] (°C)	CTE (ppm/°C) above inflection
TGMX	0.5	41.3	55	120	103
TGMX	1.0	55.6	25 ± 2	110	46
TGMX	1.0/10 wt % Al_2O_3	50.5	22 ± 2	135	33
ECHX	0.5	36.3	91	110	191
ECHX	1.0	50.3	55	110	92
DGEBA	0.5	27.9	80	95	176
DGEBA	1.0	43.7	72	115	145
OG	0.5	32.8	196	100	179
OG	1.0	35.9	141	100	162
OC	0.5	21.1	185	120	240
OC	1.0	34.6	220 ± 10	100	329

[a] All samples cured 20 h/200 °C/N_2 as done previously.[4,12] [b] No true T_gs were observed for any of the above resins by TMA or DSC. Inflection points were observed and measured as the intersection of slopes on the extreme ends of TMA plots.

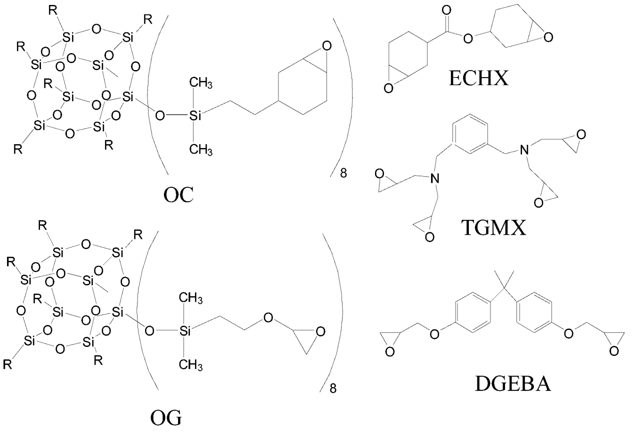

Figure 2. Sets of epoxies tested in OAPS resins.

The specific amino and epoxy compounds of the system to be investigated together with solvent (THF) and nano-δ-alumina (Degussa, when used) are placed in a vial and magnetically stirred until the system is homogeneous. Solvent is removed by vacuum, and the mixture is then poured into a circular PTFE mold and heated at 50 °C/12 h to remove residual solvent. The system is then heated at 20 °C/h to 200 °C and cured for 20 h/N_2. The cured resin is cooled, and samples for thermomechanical analysis (TMA) are cut and polished to ≥1.5 × 5.5 × 5.5 mm with 400C grade sandpaper. CTE data are acquired using a Perkin-Elmer TMA7 (Boston, MA) heated at 10 °C/min/He from 30 to 230 °C.

Measured linear CTEs of the epoxy resins are given in Table 1. In almost all systems, those made using $N = 1.0$ compositions offer better CTEs than those with $N = 0.5$. To our knowledge, a CTE of 25 ppm/°C has not previously been reported for an “unfilled” liquid epoxy resin system cured under similar conditions. We believe it reflects the nature of our “nanofilled” system. However, there are other considerations here because on addition of 10 wt % nano-δ-alumina particles the CTE drops only another 2−3 ppm (≥10%). The incorporation of nanofillers can introduces pores (even nanopores) and aggregates and, therefore, may not produce the expected decreases in CTE.

In related studies, TEM was used to demonstrate a high degree of dispersion for cube epoxy systems with no obvious aggregation for the $N = 1$ composition.[18] In contrast, work done by Mather et al. does show by TEM that in related systems some aggregation can occur that can strongly affect the mechanical properties of these materials.[23] These materials are brittle because of the high cross-link-density. Although there are mechanisms for reducing their brittle behavior,[19] the exact causes, which could result from at least partial aggregation, require further study.

The epoxy systems examined here exhibit cure behavior typical of commercial epoxy resins. However commercial, low-viscosity epoxy resins, especially those made with DGEBA, usually exhibit CTEs in the 60−200 ppm/°C range, which contrasts with our observations.

Our rationale for the observed behavior is twofold. First, because of steric effects in the silsesquioxane cage system, fewer amine hydrogens are available for reaction at the $N = 0.5$ stoichiometry. Once the silsesquioxane cage is locked into the epoxy network early in the reaction, the accessibility of the remaining unreacted amine hydrogens diminishes, leading to incomplete curing of the resin and to high CTE values for the cured material. Second, in the system where $N = 1$, many more amine hydrogens are available for reaction than in the $N = 0.5$ composition, leading to higher cross-link density or more complete curing. Furthermore, at $N = 1$, the mole fraction of the “nanofiller” silsesquioxane cage in the cured material is twice as high as in the $N = 0.5$ system, hence the lower CTE. Finally, it is likely that the $N = 1$ stoichiometry also provides lower viscosities, which in turn should lead to higher degrees of curing. Indeed, the viscosities of all of the coating resin systems are less than about 1000 MPa•s as determined using a parallel plate Rheometric RDS II E system at a shear rate = 10/s, gap = 1 mm.

In addition to offering very low CTEs, these materials are all robust offering $T_{d5\%} \geq 300$ °C (air). Furthermore, no true T_gs are observed only slight inflections in the TMA, typically near 110 ± 10 °C. However, the CTEs before and after do not reflect those expected for a material that is above its T_g. As we will report in another paper shortly, these same low CTE materials offer good to excellent oxygen barrier properties that speaks to the uniformity of these nanostructured materials.[24]

Conclusions. Cubic silsesquioxanes offer the potential to tailor global properties in nanocomposite systems nanometer by nanometer because such control occurs at the finest length scales possible. Building on previous work with epoxy resins, we demonstrate here that by judicious choice of short-chain, polyfunctional epoxies combined with nontraditional resin stoichiometries it is possible to control epoxy resin CTEs over an order of magnitude. An additional important point is that we can obtain these very low CTEs starting from a low-viscosity resin system.

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