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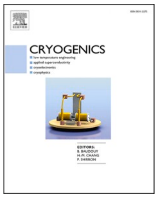

Specific heat of epoxies and mixtures containing silica, carbon lamp black, and graphite

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ABSTRACT

We present specific heat measurements in the 2 – 20 K range of several commercially available epoxies (Stycast 1266, Stycast 2850FT, EPO-TEK 377, and EPO-TEK 377H) and mixtures of one of these epoxy binders and fillers such as silica, carbon lamp black, and graphite. The results are briefly described in the context of the Debye model.

1. Introduction

Thermosetting polymers are widely used in cryogenic instrumentation to form strong, permanent, and reliable bonds between dissimilar materials. It is also well established that the thermodynamic and electro-optical properties of this class of material can be tailored by adding particulate fillers to the base polymer matrix to form mixtures. For example, Stycast 2850FT contains alumina particles that appropriately match the coefficient of thermal contraction (CTE) of the resulting epoxy mixture to metal substrates of interest. Similarly, the complex dielectric function of a thermosetting polymer can be tuned with ferromagnetic or electrically conductive fillers to tailor the wave impedance and electromagnetic loss of the resulting medium [1]. A variety of cryogenically useful electromagnetic structures can be realized by casting and machining a thermosetting mixture, including broadband free-space absorbers [2–4] and blackbody calibrators [5], and impedance-matched absorptive transmission line filters [6,7]. These structures are regularly used in cryogenic microwave through far-infrared astronomical instruments that employ extremely sensitive superconducting sensors, where exquisite control of the background radiation environment is needed to avoid saturating the detectors.

As assembly and formulation methods of thermosetting polymers advance, so does the proliferation of the applications and end use for this class of material. It is therefore important to characterize the thermal properties of new mixtures to aid the design process and ensure proper cryogenic functionality. As an example, knowledge of the specific heat of these mixtures would be helpful in the design and specification of the thermal response time of blackbody calibrators [5,4,8]. A response time that is long compared to the hold time of a single-shot cryogenic cooling stage can be undesirable, while a short response time compared to the detector time constant can be obfuscating as the blackbody temperature tends to fluctuate.

In this communication, the specific heat of several commercially available epoxies (Stycast 2850FT, Stycast 1266, EPO-TEK 377, and EPO-TEK 377H) and epoxy-based mixtures is presented (see Table 1). The mixtures contain silica powder to prevent setting of the mixture during cure, better match the coefficient of the thermal expansion of the epoxy binder to a metallic substrate (e.g., Cu and Al), and carbon in the form of graphite or lamp black to increase and control the extent of the electromagnetic loss in the resulting media. These considerations, along with the pre-cure viscosity and bond strength largely set the range of useful mixtures that can be realized for thermal control in cryogenic applications. As an example, increasing the filling fraction of carbon lamp black increases the pre-cure viscosity, the electromagnetic loss in the mixture, and the surface reflectance (due to the increase in the index of refraction with conductive loading [1]). A 10% volume filling fraction is a compromise between these properties. Above a 15% volume filing fraction, the pre-cure sample is too viscous (with a putty-like texture), which is difficult to mix uniformly, degas, and cast. Fig. 1 shows the measured specific heat data for the mixtures investigated.

2. Sample preparation and measurement methodology

The samples were prepared by mixing the recommended mass ratio of a polymer resin (part A), which acts as a binder in a mixture, and a catalyst (part B) to initiate curing. The mass ratios shown in Table 1 were

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Table 1
Samples measured. Carbon content is represented by sC for graphite (crystalline) and aC for carbon lamp black (amorphous). EPO-TEK 377H is a mixture of EPO-TEK 377 and graphite, with an estimated 377(86):sC(14) volume filling fraction based on the density of its uncured components.

Sample	Composition	Density (g/cm^3)	Vol. Fraction	Mass Fraction
A) 2850FT	Stycast 2850FT^{a}	2.4	1.00	1.000
B) 2850FT(90): aC(10)	Carbon Lamp Black Stycast 2850FT^{a}	2.0 2.4	0.10 0.90	0.085 0.915
C) 1266	Stycast 1266^{b}	1.1	1.00	1.000
D) 1266(60): SiO$_x$(30): aC (10)	Carbon Lamp Black SiO$_x$ Stycast 1266^{b}	2.0 2.2 1.1	0.10 0.30 0.60	0.131 0.431 0.438
E) 377	Epotek 377^{c}	1.2	1.00	1.000
F) 377H	Epotek 377H^{c}	1.3	1.00	1.000
G) 377(65): SiO$_x$(30): sC(5)	Graphite SiO$_x$ Epotek 377^{c}	2.0 2.2 1.2	0.05 0.30 0.65	0.065 0.428 0.507
H) Thomas Keating RAM	Polypropylene & carbon^{d}	0.96	1.00	1.000

[a] Manufactured by Henkel Loctite (formerly Emerson & Cuming). Catalyst 23LV was used to cure the 2850FT resin with a 100: 7.5 Resin: Hardener mass ratio.
[b] Manufactured by EPO-TEK. A Resin: Hardener mass ratio of 100: 28 was used.
[c] Manufactured by EPO-TEK. A Resin: Hardener mass ratio of 100: 100 was used.
[d] The exact composition of the commercially available TK RAM sample is unknown. [9,10].

used in formulations where a base epoxy is mixed with a filler such as silica and carbon lamb black. The fused silica powder [12] was filtered with a 400 mesh to limit the particle size to ~ 40 μm and smaller. Although not employed here, fumed silica is another choice that is commonly used in epoxy-based mixtures to better CTE match the binder to the substrate, control the pre-cure viscosity, and prevent settling of the mixture during polymerization. The carbon lamp black was produced by Acros Organics (Part Number: 612475000) and is estimated to have a particle size in the range of $\sim$ 30 to 120 nm. Sample G is made by diluting EPO-TEK 377H, which contains graphite particles, with EPO-TEK 377. The graphite-to-377 mass ratio of 377H is estimated to be 0.21: 0.79. Sample H was taken from a Thomas Keating Radar Absorbing Material (TK RAM) tile that has low reflectance at terahertz and millimeter wavelengths [9]. The base matrix or binder of a TK RAM is polypropylene (a thermoplastic) and the lossy conductive filler is carbon [10]. A TK RAM can be cryogenically cycled and has been shown to have low outgassing.

After hand stirring the uncured epoxy mixture sample for greater than 20 min, it is placed in a vacuum chamber and de-gassed to remove trapped air. During this step, the vacuum chamber is vented periodically to control the boil off rate. The process of degassing and venting is repeated until the surface of the pre-cure sample is smooth and stopped before the pressure in the chamber drops below $\sim$ 50 Torr (the latter ensures the hardener/catalyst is not boiled off). The samples were then cured in a temperature controlled oven for the duration and at the temperature recommended by the epoxy manufacturer. The final mass of the uncured mixture was generally tens of grams to ensure homogeneity throughout the resulting sample volume. Approximately 10 mg of the cured substance was used to measure the specific heat.

The specific heat of the samples was measured in a Quantum Design Physical Property Measurement System (PPMS – www.qdusa.com), which utilizes thermal relaxation calorimetry to extract the specific heat of a sample under test [13]. Each sample was attached and thermally anchored to a platform using a thin layer of Apiezon-N grease. The platform is suspended with wires from a frame that constitutes the bath of the system in the PPMS. Measurements were performed under vacuum and start with the application of a heat pulse that raises the temperature of the sample by 2–3% above the bath temperature. The pulse duration is about twice the time constant of the suspended system, which includes the platform, thermal grease and sample when present. The temperature of the sample was recorded as a function of time, after which fitting algorithms were used to extract the sample heat capacity from the heating and cooling curves. This measurement was performed before and after the sample was installed in order to remove the contributions from the thermal grease and platform (addenda). The fractional error in each measurement of the specific heat is less than 1%.

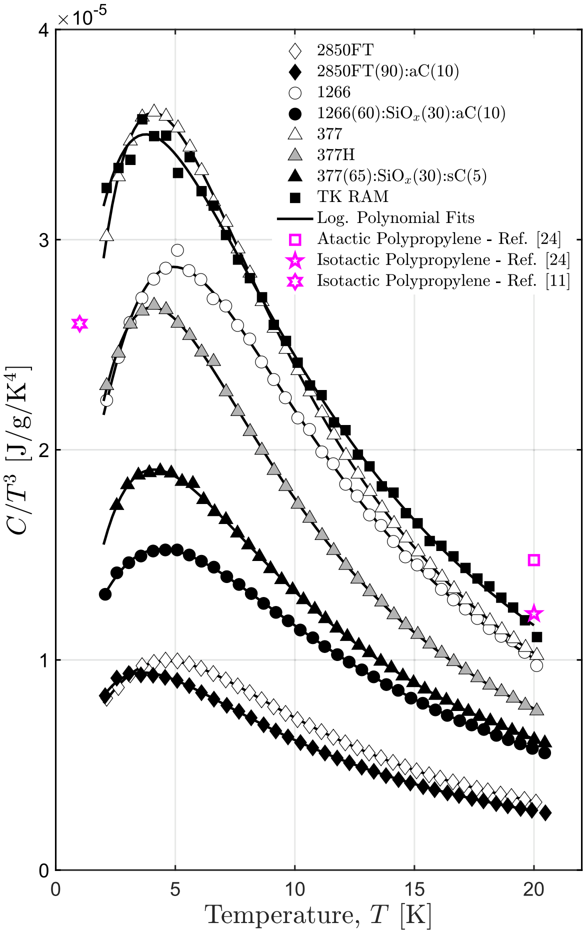

Fig. 1. Specific heat of various epoxies and epoxy mixtures, scaled by T^3. An idealized Debye material has a constant C/T^3 with temperature (a straight horizontal line in this plot). The notation M$_1$(x):M$_2$(y) indicates a volume filling fraction of x:y expressed as a percentage for the two part material that is a mixture of materials M$_1$ and M$_2$. The carbon filler is represented by sC for graphite (crystalline) and aC for lamp black (amorphous). EPO-TEK 377H is a mixture of EPO-TEK 377 and graphite, with an estimated 377(86):sC(14) volume filling fraction based on the density of its uncured components. The TK RAM sample is commercially available and composed of polypropylene mixed with carbon [9,10] (exact composition is unknown). The polypropylene sample measured in Ref. [11] is assumed to be isotactic (semi-crystalline) given commercially available stock is commonly of this form. The solid lines are generated from a fourth order logarithmic polynomial fit to the data. The fit coefficients are presented in Table 2 and can be used to interpolate the data in the 2–20 K range.

3. Results

The behavior of the specific heat of the samples shown in Fig. 1 is consistent with expectations for amorphous solids [14,15]. The measurements of Stycast 2850FT agree to less than 10% at 9 K (3% at 2 K) with data found in [16]. For Stycast 1266, the discrepancy is at most 4% with the data found in [17], which covers 0.5 to 7 K. These differences could stem from variability in the mixture compositions and are not necessarily associated with measurement systematics. To our

Table 2

Logarithmic polynomial coefficients. A logarithmic polynomial of the form $\log_{10}(C) = \sum_{i=0}^{4} a_i \log_{10}(T)^i$ is fit to the specific heat data shown in Fig. 1. The fit coefficients can be used to interpolate the specific heat of the samples in the 2–20 K range.

Sample	a_0	a_1	a_2	a_3	a_4
A) 2850FT	−2.11494050	2.51709056	2.59374465	−2.99675188	0.86125486
B) 2850FT(90): aC(10)	−2.25445368	3.69064400	−0.24899678	−0.54512700	0.14941590
C) 1266	−1.72272035	2.74684260	2.20865182	−2.62360390	0.73084529
D) 1266(60): SiO_x(30): aC(10)	−1.94985355	3.00757091	1.09039993	−1.44253505	0.36037169
E) 377	−1.73020906	3.65343010	0.30871953	−1.22590643	0.37382964
F) 377H	−1.77036189	3.21084905	1.13701708	−1.91294933	0.58275509
G) 377(65): SiO_x(30): sC(5)	−2.01595217	3.76306112	−0.02265842	−0.87695966	0.27510453
H) Thomas Keating RAM	−1.58913775	3.23175162	0.48169058	−0.97484268	0.23920503

knowledge, the cryogenic specific heat of EPO-TEK 377 and 377H has not been published in the literature. The solid lines in Fig. 1 are logarithmic polynomial fits to the data. The fit coefficients are presented in Table 2 and can be used to interpolate the data in the 2 – 20 K range.

Examining the pairs of data {A, B} and {E, F} suggests the specific heat of B and F is a non-linear function of the specific heat of the respective components of these mixtures. This behavior is associated with the mixture-specific surface states that arise from the adhesion of the polymer matrix to the filler surface – carbon lamp black and graphite in B and F, respectively. For reference, the specific heat of graphite and carbon lamp black is proportional to T^n [18,19], where n varies from $\sim 2-3$ across the $1-20$ K range and has contributions from electrons and phonons. Silica in the glassy state exhibits a similar behavior to polymers with a characteristic bump in C/T^3 at ~ 10 K [15] that is higher than the peaks in Fig. 1. Thus, the specific heat of the mixtures explored here is dominated by the amorphous polymer matrix as suggested by both the functional form and magnitude of the reduction in specific heat due to the displacement of the polymer between the respective samples {A, B}, {E, F}, {C, D}, and {E, G}.

The deviation of the specific heat from a T^3 functional dependence signifies that the phonon density of states of a thermosetting polymer is more complex than assumed in the Debye approximation. This behavior is common to amorphous polymers [14,15,20] and is characterized by a peak in C/T^3 below ~ 20 K. The Tarasov model [21] generalizes the behavior of an amorphous polymer with the assumption that the phonon density of states is three-dimensional at low-frequencies ($\propto f^2$, where f is the phonon frequency) and one-dimensional ($\propto f^0$) at high-frequencies where the optical phonon wavelength is smaller than the physical length of a polymer chain. However, as pointed out by Reese [14], only a density of states derived from lattice dynamics calculations, which is tractable for a crystalline material, can accurately account for the functional form and magnitude of the specific heat at low temperatures. For the samples shown in Fig. 1, the peak in C/T^3 is indicative of an excess of low frequency phonon modes above the Debye prediction [14,15,20]. The peak in C/T^3 occurs over a temperature range of a few Kelvins across the samples tested. This robust signature can be partially attributed to the averaging effect of the specific heat parameter over many phonon modes. Recent theoretical developments and large-scale numerical vibrational mode analysis of amorphous structures are shedding light on both the nature and universality of this anomalous signature in glassy solids [22,23].

For the polypropylene, published specific heat data is available below 1 K [11] and above 20 K [24]. As shown in Fig. 1, this data suggests the specific heat of the TK RAM mixture is dominated by the polypropylene binder and further indicates the binder is amorphous (atactic) in its final form in the mixture.

We note that in Table 1, both volume and mass filling fractions of the samples tested are shown for completeness. The mass filling fraction is most relevant when considering the specific heat (i.e., mass is a proxy for the number of particles and phonon density of states per volume), whereas to determine the dielectric properties of a mixture, the volume filling fraction (in the spirit of the Clausius–Mossotti relation) is used to quantify the strength of dielectric polarizability of each constituent in the media [25].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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