

Electronic Supplementary Information

Phase Change Nanocomposites with Tunable Melting Temperature and Thermal Energy Storage Density

Minglu Liu¹ and Robert Y. Wang^{1,*}

¹ Mechanical Engineering, Arizona State University, Tempe, USA.

1. Experimental details:

Materials and Equipment:

The polyimide resin was purchased from Alfa Aesar. All other reagents and solvents were purchased from Sigma Aldrich. The Bi NPs were characterized by transmission electron microscopy (TEM, Tecnai F20) and x-ray diffraction (XRD, Siemens D5000). The nanocomposite was analyzed by TEM and DSC (TA Instrument Q20). The mass and nanoparticle volume fraction of each sample were determined using a Mettler Toledo UMX2 Ultra-Microbalance. All samples were prepared and stored in an air-free environment, but were exposed to air for brief periods when using the above instruments.

Bi Precursor Synthesis: Bi[N(SiMe₃)₂]₃ was used as the Bi precursor during nanoparticle synthesis. We made this precursor by a metathesis reaction between BiCl₃ and Li[N(SiMe₃)₂].^[1] The synthesis was carried out under air-free conditions. In a typical synthesis, 1.17 g of Li[N(SiMe₃)₂] was dissolved in 20 mL diethyl ether, and cooled to 0 °C. 1.05 g BiCl₃ dissolved in a mixture of 20 mL diethyl ether and 5 mL tetrahydrofuran (THF) was then slowly added and stirred for 2 hours. The mixture was filtered through a PTFE filter (pore size 200 nm), dried under vacuum for 1 hour, and then redissolved in 10 mL of pentane. The solution was then filtered and evaporated under vacuum for 1 hour. The resulting Bi[N(SiMe₃)₂]₃ was a yellow powder and stored in a nitrogen-filled glovebox for future use.

Bi Nanoparticle Synthesis: The colloidal Bi NPs were synthesized following the procedure of Yarema et al.^[2] In a typical synthesis, 20 g of hexadecylamine (HDA) was degassed and heated to 130 °C. Approximately 100 μL of 1M Li(Et₃BH) dissolved in THF was then injected into the HDA followed by a injection of 0.14 g Bi[N(SiMe₃)₂]₃ and 0.17 g Li[N(SiMe₃)₂] co-dissolved in 2 mL toluene. The time between injections was typically 15 s and the nanocrystal growth time was 15 s at the injection temperature. The reaction mixture was then rapidly cooled to room temperature by a water bath. This reaction results in Bi NPs with HDA ligands on their surface. To improve colloidal stability, the HDA ligands were then switched with oleic acid (OA) by adding 200 μL oleic acid to the Bi NP dispersion and vortexing for 1 minute. Size variation was achieved by varying the reaction temperature and the amount of Li(Et₃BH) during the synthesis. Lower injection temperatures and larger quantities of Li(Et₃BH) result in smaller NP diameters. The Bi NPs were isolated from the reaction mixture by precipitating with ethanol three times. The colloidal NPs were then stored in a common nonpolar solvent (toluene or hexane). The TEM samples were prepared by drop-casting from dilute nanocrystal dispersions onto a copper TEM grid. The sizes of Bi NPs were determined by statistical analysis of TEM images containing ~ 200 - 400 Bi NPs using ImageJ. The diameter uncertainties indicated in this work represent the standard deviation of the NP diameters.

Nanocomposite Formation: The nanocomposite was synthesized by a three-step approach. First, the Bi NPs were synthesized as described above. The NPs were then further cleaned by additional ethanol precipitations and then dissolved in THF. The PI resin was dissolved in THF in a separate container by stirring for 30 minutes. An appropriate amount of Bi NP solution was then added and the combined solution stirred for an additional 3 hours.

* Author to whom correspondence should be addressed. Electronic mail: rywang@asu.edu

The nanocomposite was made by dropping the combined solution into an aluminum DSC pan and evaporating the solvent at 50 °C for 1 hour. The composite was then heated on a hot plate for 1 hour at 300 °C prior to DSC. Without this last step, the NP melting temperature during the first thermal cycle was elevated, presumably due to the strong interactions between the NP core and oleic acid ligands. For TEM, samples were prepared by drop-casting from dilute nanocomposite dispersions onto a SiN_x window.

Volume fraction Determination: The volume fractions of the nanocomposites were determined by measuring the Bi concentration and PI resin concentration separately in their respective solutions. The concentration of PI resin was measured by drop-casting a sample with 100 μL of PI resin solution, letting the solvent evaporate, and then measuring the mass with a microbalance (readability 0.1 μg). The concentration of the PI resin was typically ~ 5 mg/mL. The Bi concentration in the NP dispersion cannot be determined by simply measuring the mass of a drop-casted sample from the NP dispersion. This approach would measure the combined mass of the Bi NP core and the attached surface ligands. Since only the Bi is the phase change component, it is important to get a true measure of the Bi concentration, which we did using a DSC method. The DSC sample was prepared by drop-casting 200 μL of the NP dispersion into a DSC pan. This sample was then heated to 300 °C and held isothermally for 1 hour before a standard ramp test from 0 °C to 300 °C at a rate of 10 °C/min. Due to the absence of PI resin, the Bi NPs melted and coalesced during the isothermal step. In the following ramp test, a melting peak was observed at the bulk Bi melting temperature (~ 271 °C). The Bi mass was then calculated by dividing the integral of the melting peak by the enthalpy of fusion for bulk bismuth (51.9 J/g). The Bi concentration in a typical NP dispersion was ~ 2 – 3 mg/mL. The composite's NP volume fraction was then calculated by using the polymer and Bi content in the sample. We note that this calculation method slightly overestimate the Bi volume fraction because it neglects volume contributions from the NP surface ligands.

Calorimetry Measurements: The total mass of each DSC sample was kept to approximately 1.2 - 1.3 mg, which corresponds to ~ 0.6 x 10⁻³ cm³ for a composite with 10% NP volume fraction. The DSC measurements were carried out by cyclic heating and cooling between 0 °C and 300 °C at a rate 10 °C/min. During these measurements, a nitrogen atmosphere was maintained using a nitrogen flow rate of 50 mL/min. The DSC data was analyzed using the software provided by TA instruments. To verify the cyclic stability of each sample, all samples were subject to a minimum of 15 melt-freeze cycles.

2. Additional Figures:

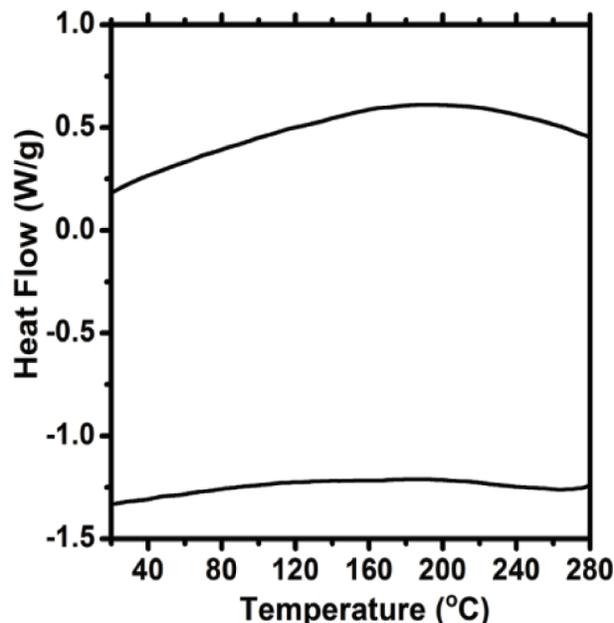


Figure S1. A heating and cooling DSC cycle on pure PI resin.

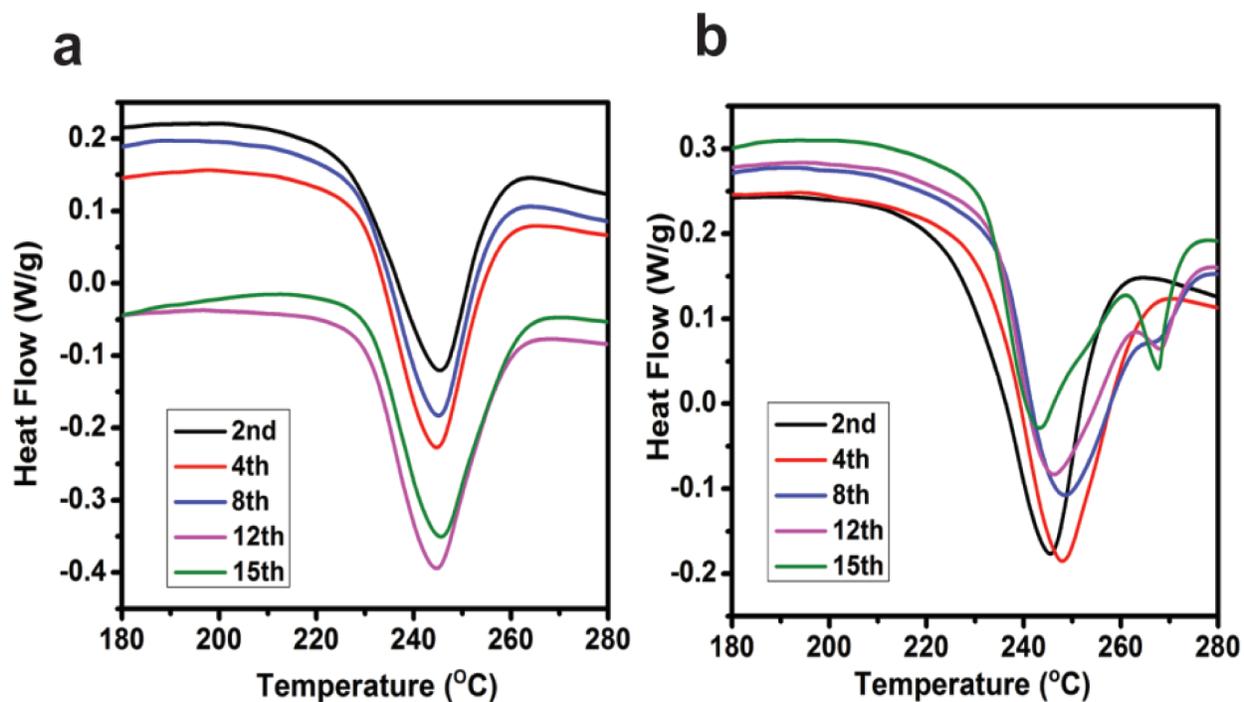


Figure S2. (a) Several representative heating cycles during cyclic DSC measurements on a composite with a 30% Bi volume fraction of NPs. (b) Several representative heating cycles during cyclic DSC measurements on a composite with a 41% Bi volume fraction of the same size NPs.

- [1] C.J.Carmalt, N.A. Compton, R.J.Errington, G.A.Fisher, I.Moenandar, N.C.Norman, K.H.Whitmire, in *Inorganic Syntheses*, ed.A.H. Cowley, Wiley, New York, USA **1997**, Vol. 31, Ch. 1,pp.98.
- [2] M. Yarema, M. V. Kovalenko, G. Hesser, D. V. Talapin, W. Heiss, *J. Am. Chem. Soc.* **2010**, *132*, 15158.