Supporting Information

Self-Constructed Tree-Shape High Thermal Conductivity Nanosilver Networks in Epoxy

Kamyar Pashayi,[ǂ] *Hafez Raeisi Fard,*[†] *Fengyuan Lai,*[‡] *Sushumna Iruvanti,*[§] *Joel Plawsky,*[§]
Theodorian Borca-Tasciuc[†,*]

[ǂ] School of Science, Engineering, and Technology, Pennsylvania State University, Middletown, PA 17057-4846, USA

[†] Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

[‡] Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

[§] IBM Systems & Technology Group, Hopewell Junction, NY 12533, USA

[§] Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

I. Effect of PVP coating on particles dispersion

In order to study effect of PVP coating on particles behavior in epoxy matrix, uncoated 35 nm silver particles were purchased and the Raman Spectroscopy and dispersion behavior of that in epoxy matrix are compared with those of coated 20 nm particles. Raman Spectroscopy of silver particles reveals existence of silver oxide and confirms presence of PVP coating on the surface of 35 nm and 20 nm particles, respectively (see Figure S1).

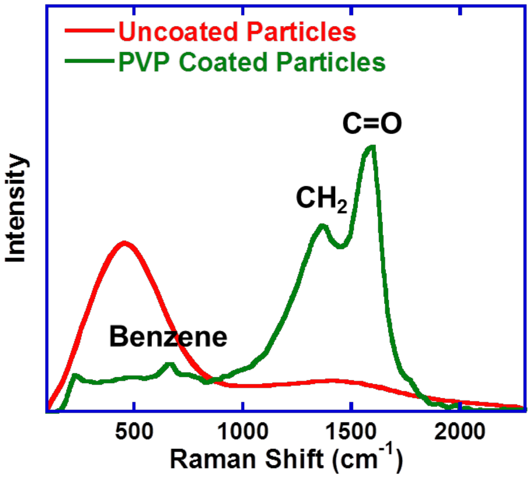

Figure S1. *Raman spectroscopy of PVP coated 20 nm and uncoated 35 nm silver nanoparticles.*

The peak at 456 cm^{-1} in is attributed to existence of silver oxide layer on the surface of 35 nm particles. Additionally, the peaks at 1584 cm^{-1}, 1354 cm^{-1}, and 665 cm^{-1} are assigned to CH_2 and C=O stretching and benzene ring modes in a PVP chain.

Respectively, figures S2a & b show TEM and SEM images of uncoated 35 nm in dry form and after sonication in epoxy for 60 minutes. These images display that uncoated particles form clusters during synthesis, storage or shipping and sonication of particles in epoxy did not help for particles dispersion.

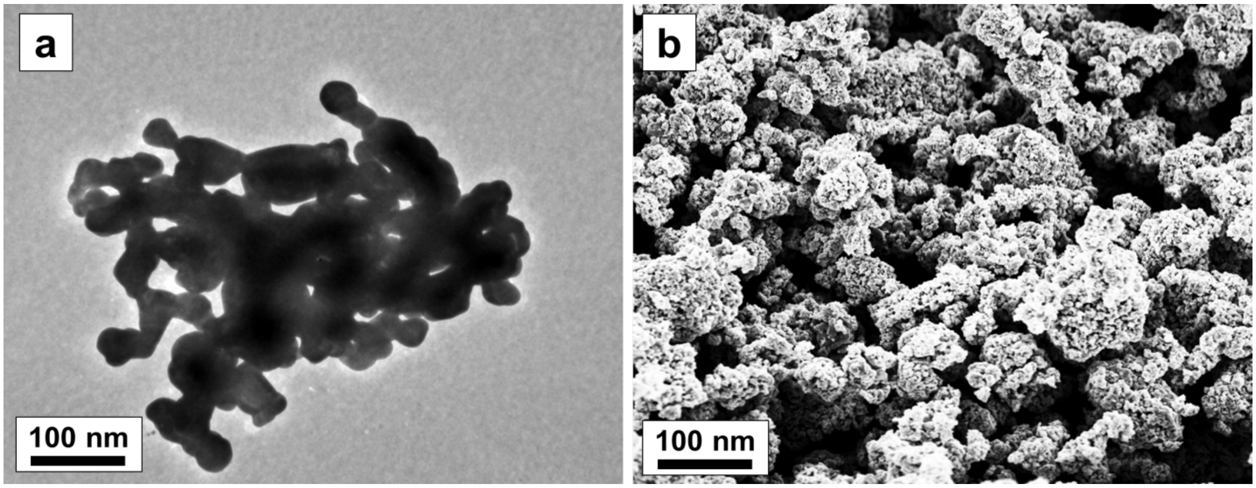

Figure S2. *(a) TEM image of dry 35 nm silver cluster and (b) agglomerated/aggregated 35 nm particles in epoxy matrix.*

Aggregation and low-wettability of uncoated 35 nm particles mixed with epoxy can be attributed to the presence of silver oxide layer on the surface of particles. This emphasizes the crucial role of PVP as a dispersing agent in 20 nm silver particles.

We should add that, before SEM imaging of nanocomposites, a thin layer of epoxy is selectively removed using a selective wet etching process with methylene chloride and samples were sputter coated with ~1 nm of platinum.

II. Curing time of nanocomposites for curing time vs κ measurements

Curing times of samples used for curing temperature-κ experiment are provided in table S1.

Table S1. *Curing time and density of samples prepared at different curing temperatures.*

T_{curing}(ºC)	t_{curing} (h)	Density (g.cm^{-3})
20	168	3.52
40	48	3.56
80	10	3.89
120	4	4.07
150	1	4.45
180	1	4.33

III. Effect of processing time and temperature on nanocomposite agglomeration

Optical microscopy was utilized to study the effects of annealing time and temperature on particle agglomeration of 20 vol% silver-epoxy nanocomposite. The change in diameter of the darker area (which contains silver particles) was visually observed and captured.

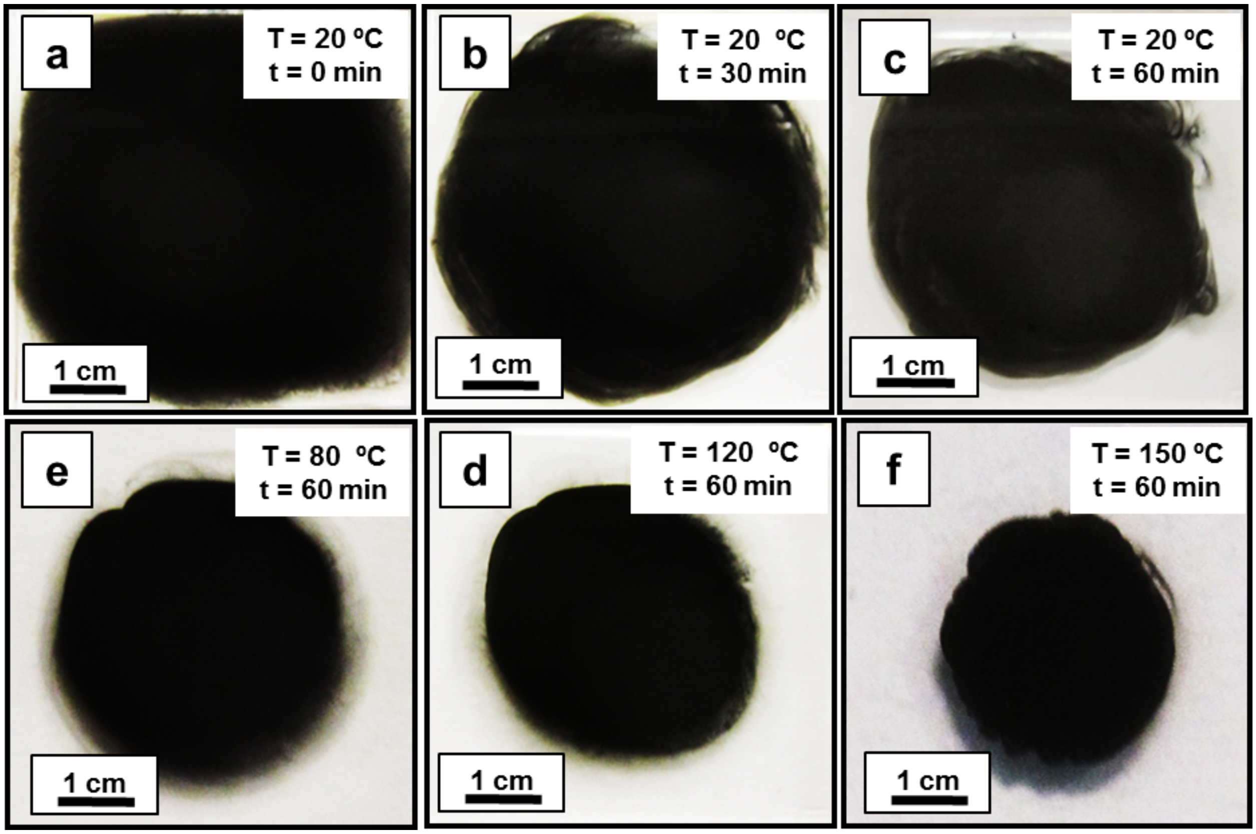

Figure S3. *Optical microscopy images of 20 vol% silver-epoxy nanocomposite as a result of processing time and temperature.*

IV. Viscosity versus time for pure epoxy and 20 vol% silver-epoxy nanocomposite

The viscosity-time curve was obtained for pure epoxy and 20 vol% silver-epoxy nanocomposite at 100ºC. Particle agglomeration increased the viscosity of nanocomposites ~ 52 fold after 60 minutes and ~ 153 fold after 90 minutes at 100ºC. The viscosity of pure epoxy is constant after 90 minutes at 100ºC.

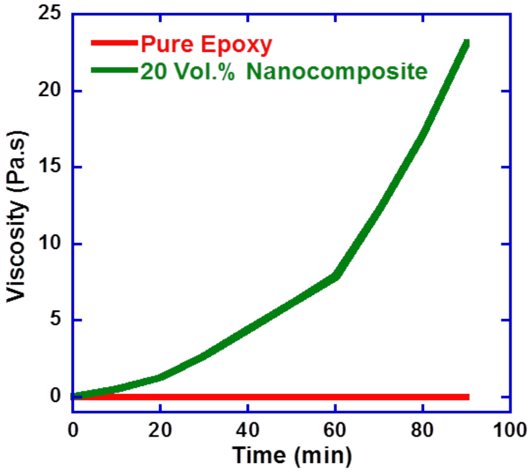

Figure S4. *Viscosity versus time for pure epoxy and 20 vol% silver-epoxy nanocomposite at 100°C.*

V. Theoretical determination of the agglomeration time

We can develop a simple expression for the time required for an effective particle agglomeration. The agglomeration time is calculated by balancing Van der Waals forces against the drag force. Van der Waals forces are given by the equation:

$$F_{vdw} = \frac{Ar_p}{12x^3} \qquad (1)$$

where A is a constant equal to 10^{-21} J, r_p is the particle radius, and x is the distance between two particles. The drag force is expressed by the equation:

$$F_{drag} = 6\pi r_p \mu \frac{dx}{dt} \qquad (2)$$

The parameter μ is the viscosity of the slurry and t is time.[1] Substituting Eq. 1 for Eq. 2 gives the following result:

$$\frac{dx}{dt} - \frac{A}{72\pi\mu x^3} = 0 \qquad (3)$$

Therefore $x(t)$ is related to t by the expression

$$x(t) = \left[x_0^4 - (\frac{A}{18\pi\mu})t \right]^{1/4} \qquad (4)$$

x(t) is obtained from Eqs. 3 by integrating from x with respect to t. Assuming that the particles are identical in size (20 nm), μ=5 N.s/m^2, x_0=10 μm, and x(t)=0 resulted in t=60 minutes.

VI. Differential scanning calorimetry (DSC) for pure PVP

The DSC curve of pure PVP in Figure S5 illustrated a melting peak at 145 ºC with an onset temperature around 75 ºC.

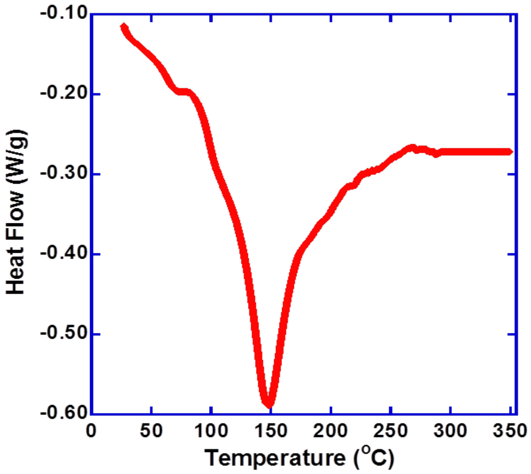

Figure S5. *DSC* of pure PVP with a melting peak at 145 ºC.

REFERENCE

---

(1) Petrucci R. H.; Herring F. G.; Madura J. D.; Bissonnette C. *General Chemistry: Principles and Modern Applications* **2007**, 10th edition, Upper Saddle River, NJ: Prentice Hall.