Supplementary Information (SI) for Nanoscale.

Supplementary information

Controlling nanoparticle aggregation via gel point shift in the in situ photochemical synthesis of plasmonic epoxy-based nanocomposites

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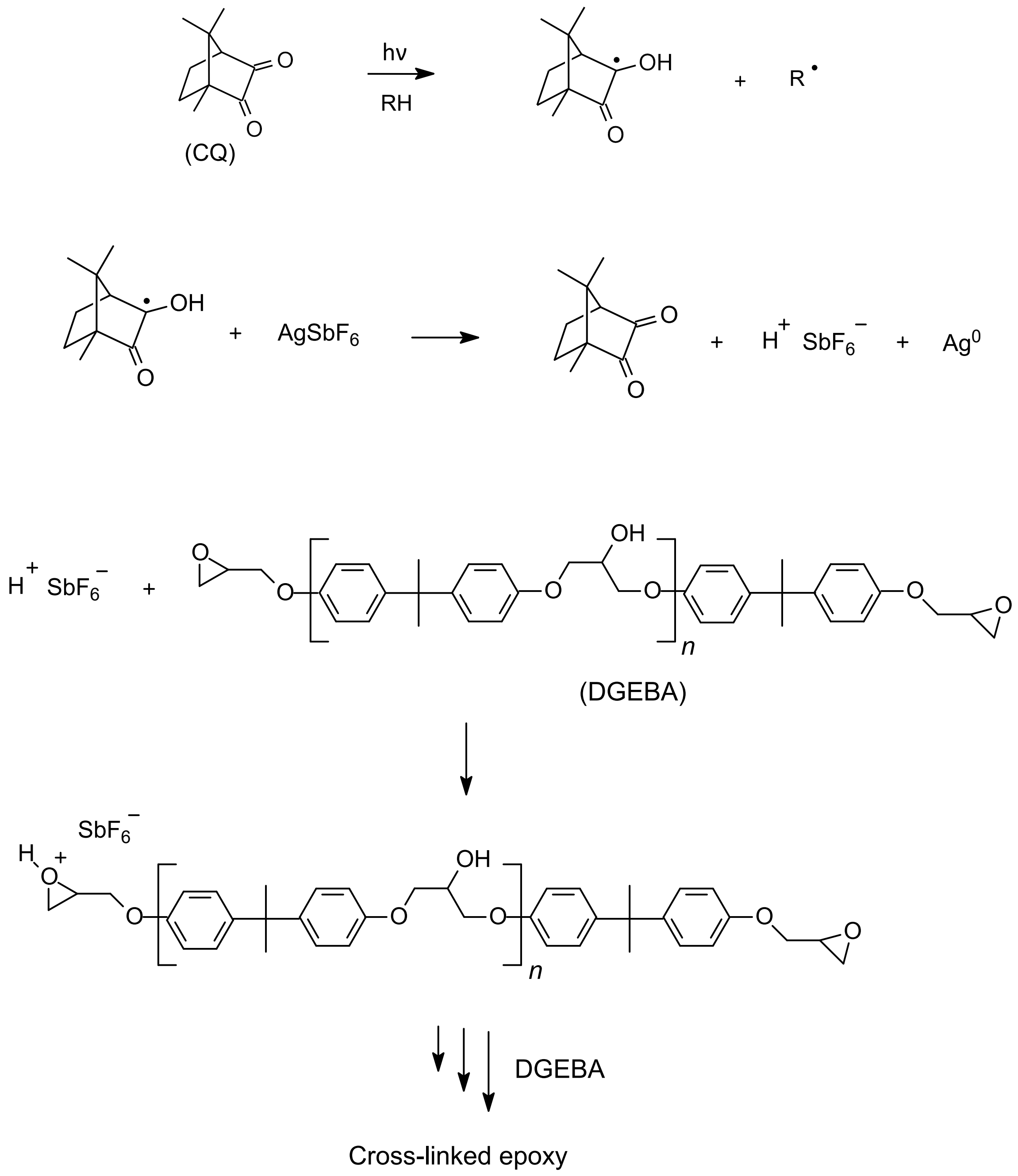

Scheme S1. Proposed mechanism for the in situ photochemical synthesis of silver/epoxy nanocomposites through simultaneous processes of visible-light-induced electron transfer and cationic polymerization.

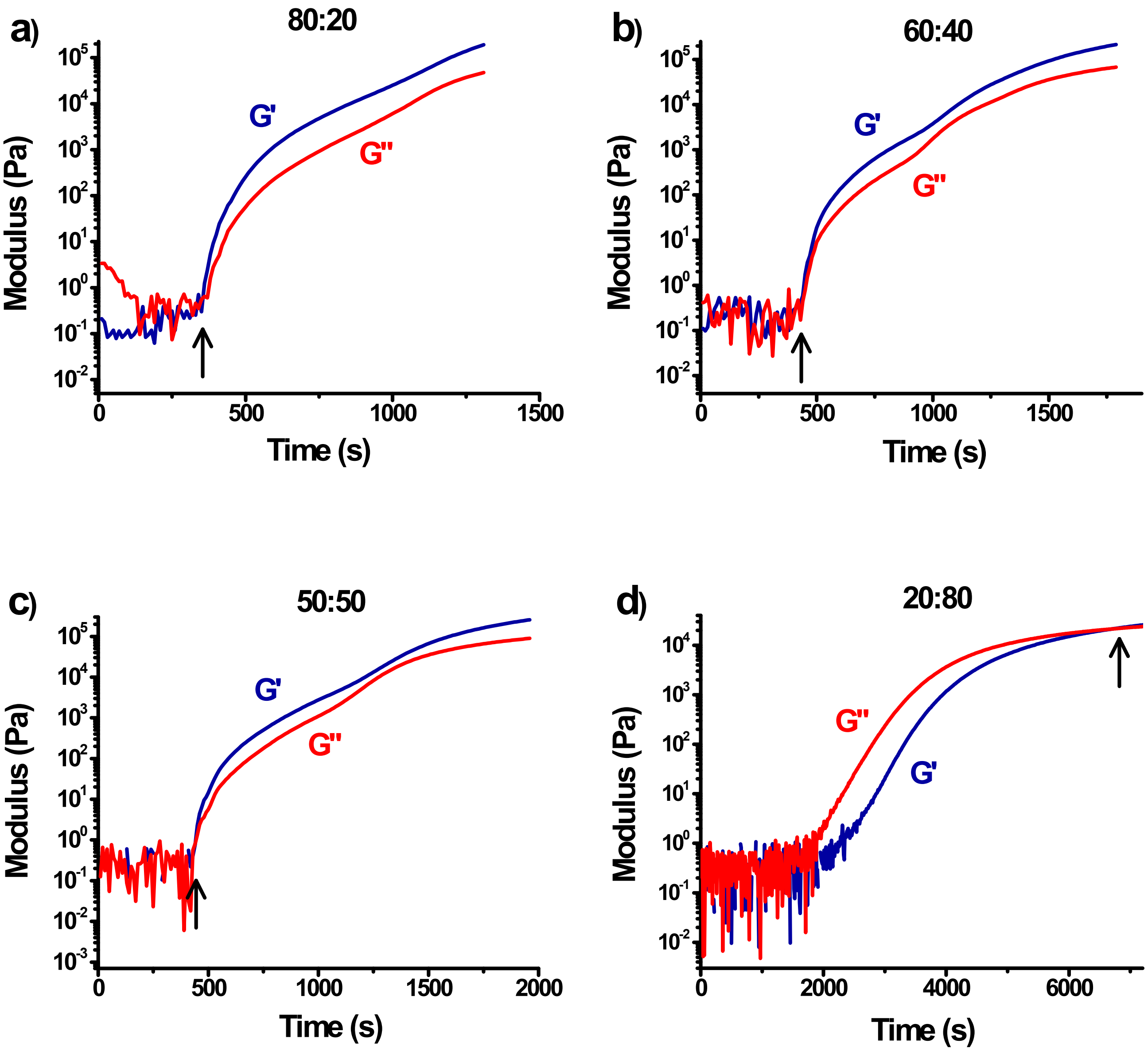

Figure S1. Evolution of the storage (*G'*) and loss (*G''*) moduli during the cationic ring-opening polymerization at 140 ºC of blends with different DGEBA:PGE weight ratios: (a) 80:20; (b) 60:40; (c) 50:50 and (d) 20:80.

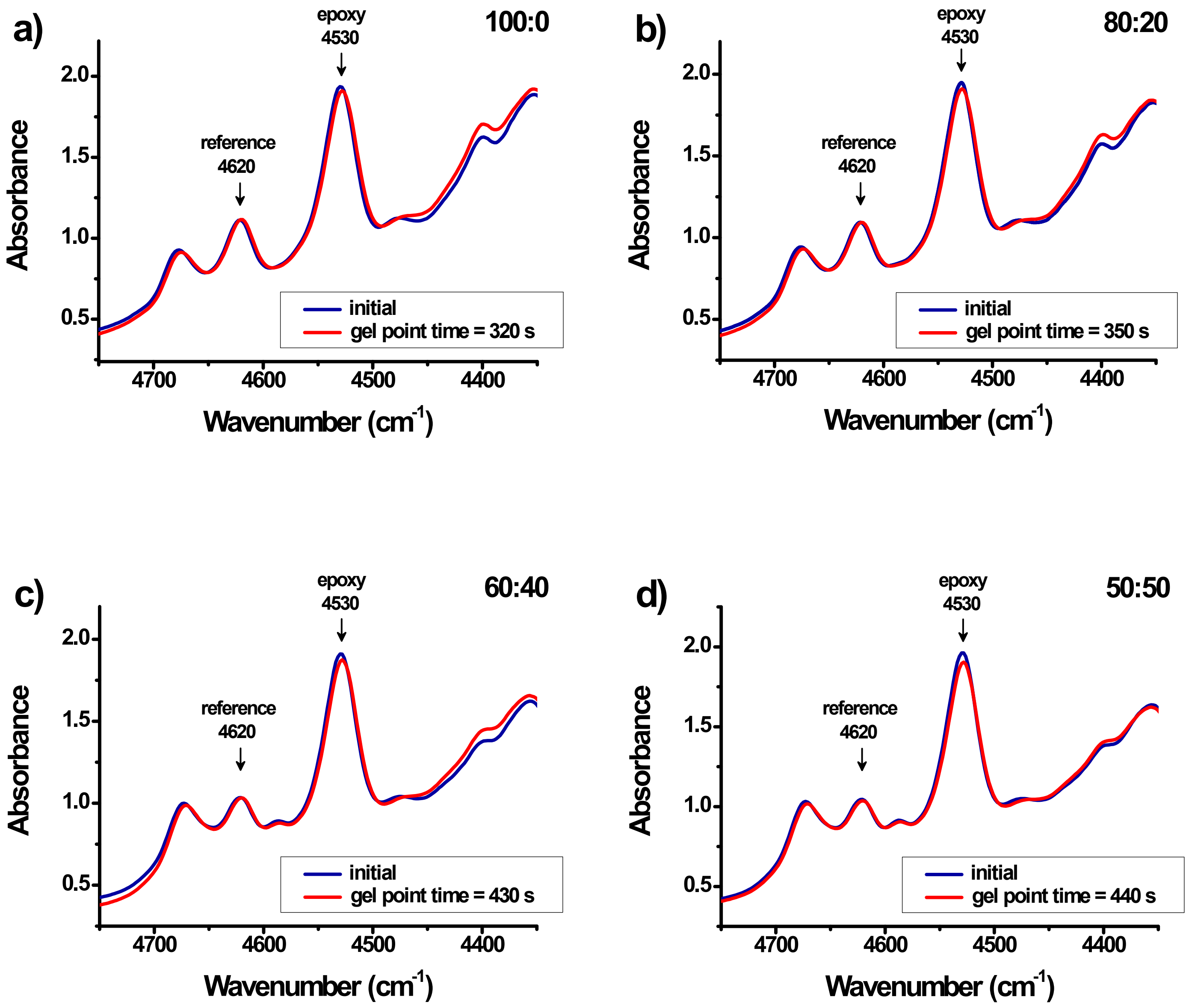

Figure S2. FTIR spectra recorded at the onset of the polymerization reaction at 140 °C and at the gel point for blends with different DGEBA:PGE weight ratios ratios: (a) 100:0; (b) 80:20; (c) 60:40; and (d) 50:50.

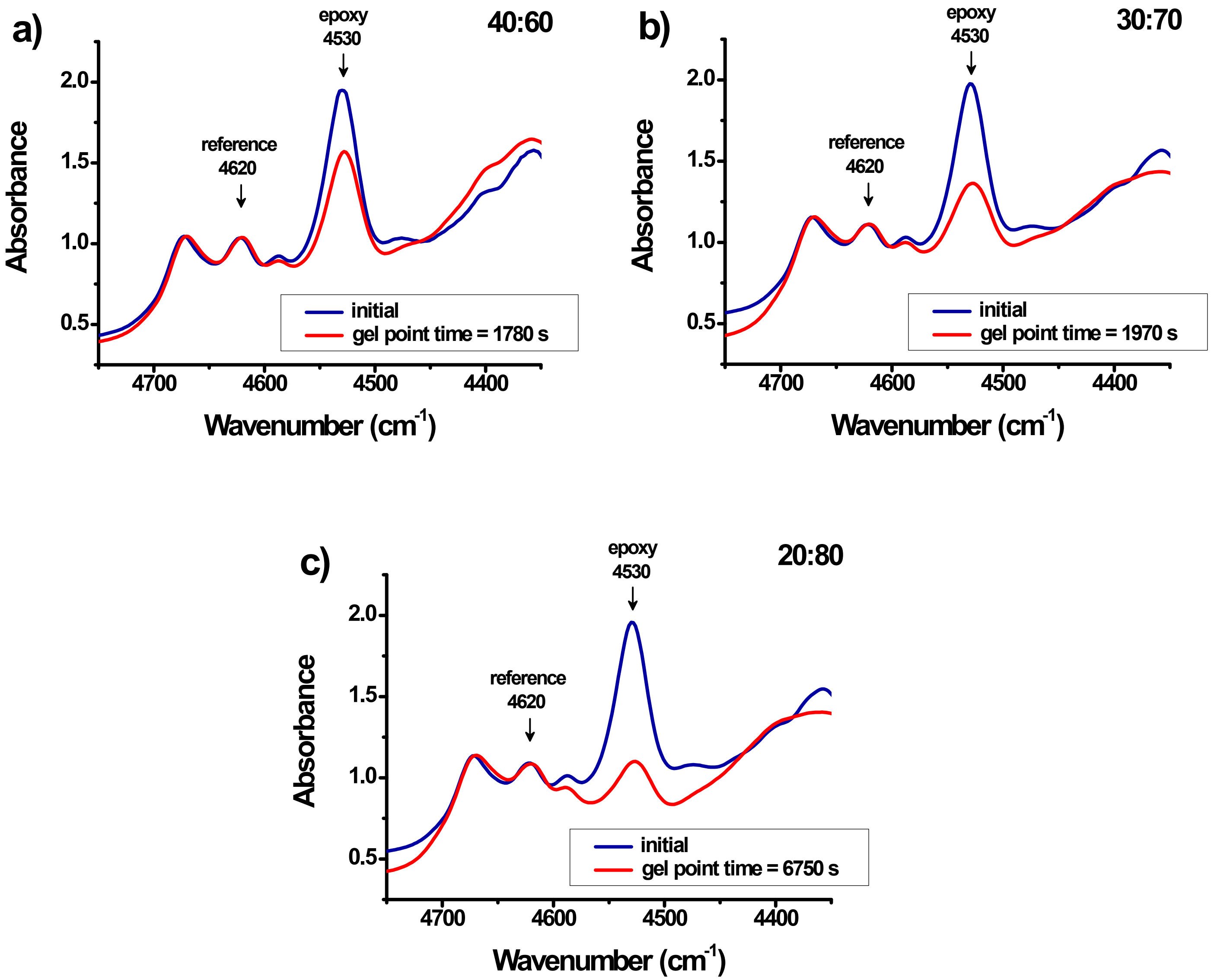

Figure S3. FTIR spectra recorded at the onset of the polymerization reaction at 140 °C and at the gel point for blends with different DGEBA:PGE weight ratios ratios: (a) 40:60; (b) 30:70; and (d) 20:80.

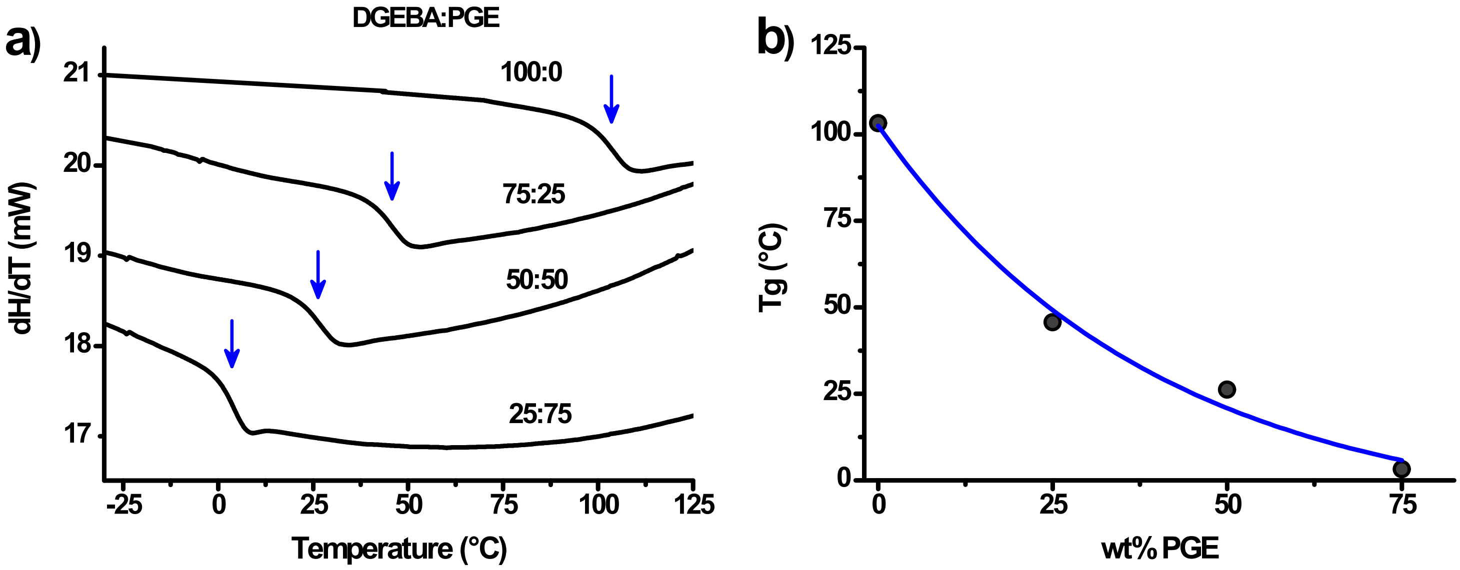

Figure S4. (a) Second heating DSC scans of silver/epoxy nanocomposites prepared with different DGEBA:PGE ratios. The blue arrow on each curve indicates the glass transition temperature (T_g) of the epoxy matrix, defined as the midpoint of the transition. (b) Variation of T_g as a function of PGE content. DSC measurements were performed using a PerkinElmer Pyris 1 calorimeter under a dry nitrogen atmosphere. Samples (~10 mg) were first heated from 20 °C to 150 °C (first heating scan), then cooled to −50 °C (cooling scan), and finally heated again from −50 °C to 150 °C (second heating scan). A heating/cooling rate of 10 °C/min was used for all scans.

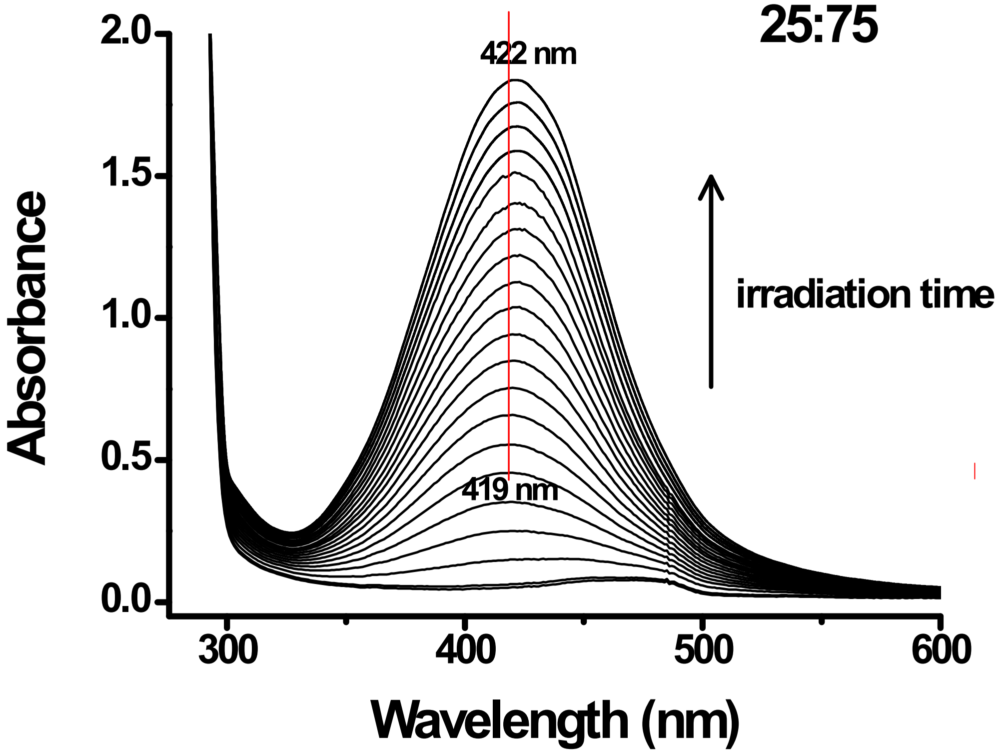

Figure S5. Evolution of the plasmon band of silver NPs during irradiation at room temperature for the sample formulated with a 25:75 DGEBA/PGE ratio. These UV–Vis spectra correspond to those in Figure 5b, where the saturated traces (indicated in red in that figure) were omitted and the absorbance scale was expanded. The red vertical line is included as a visual guide to highlight the small but systematic red-shift of ≈3 nm observed between 300 s and 1200 s of irradiation.

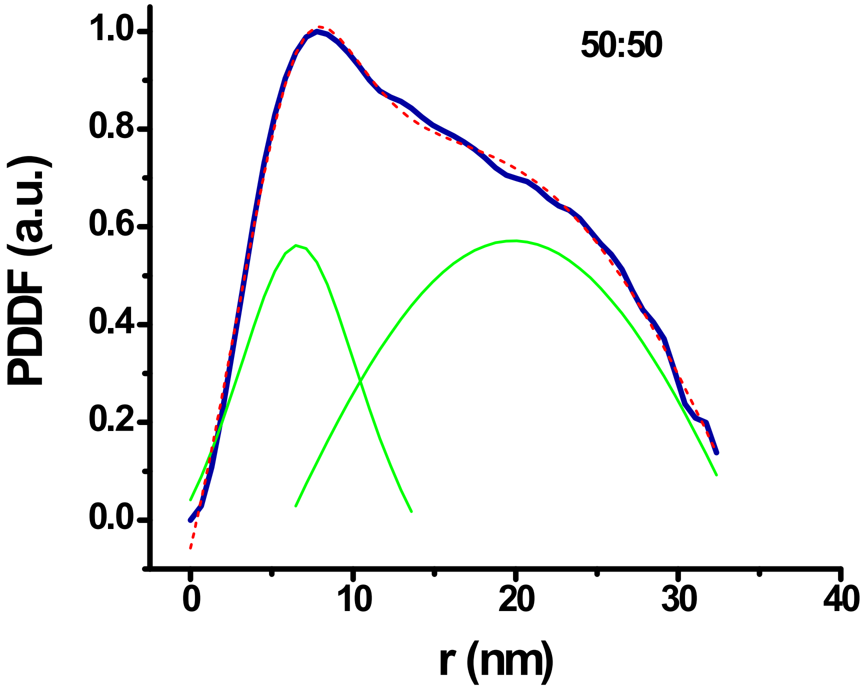

Figure S6. Deconvolution of the Pair-Distance Distribution Function (PDDF) for the silver/epoxy nanocomposite with a 50:50 DGEBA/PGE ratio. Blue curve: experimental PDDF; green curves: individual components from the deconvolution; red dashed curve: reconstructed PDDF obtained by summing the deconvoluted components.

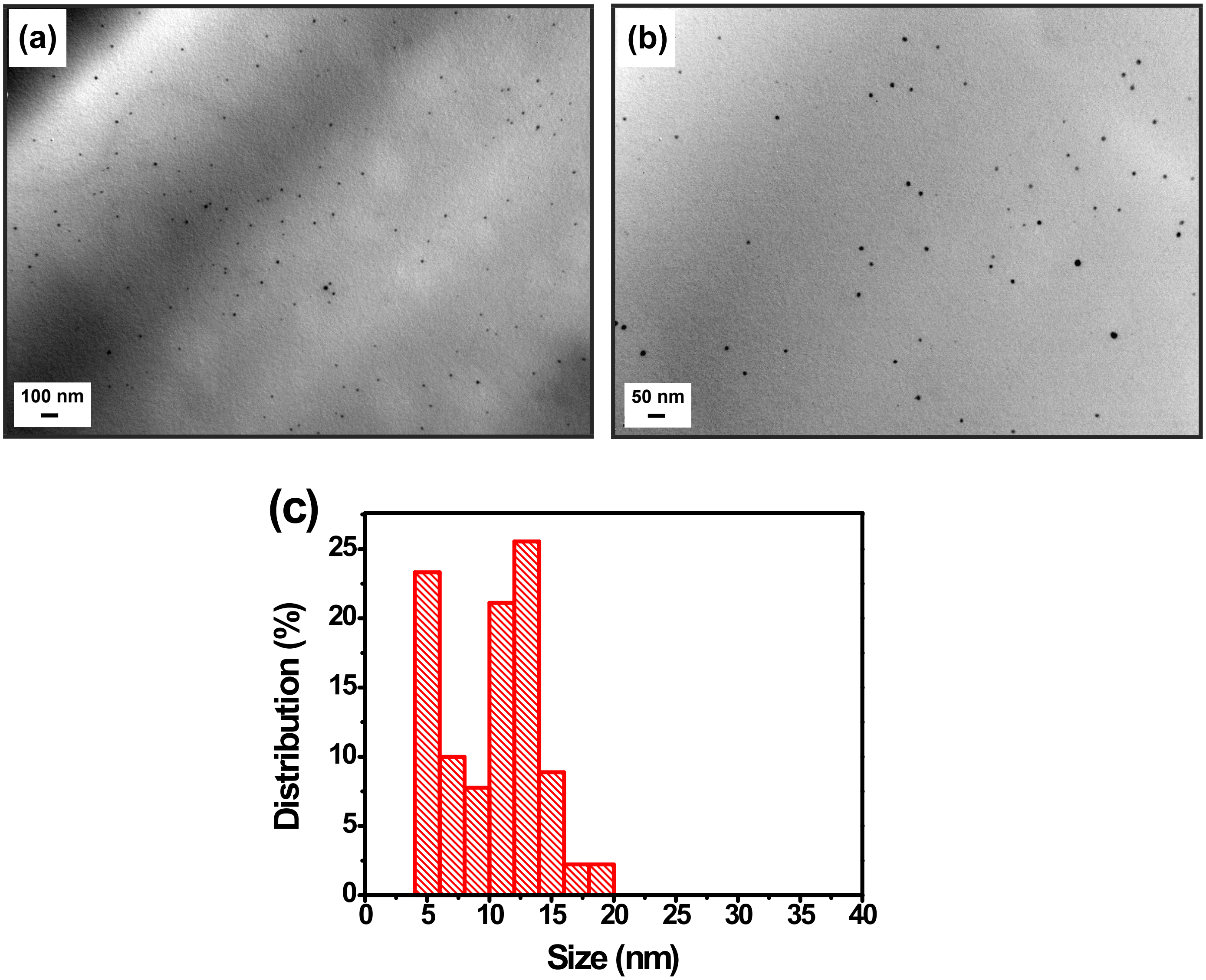

Figure S7. *Top*: TEM images of ultrathin sections from a sample with a 50:50 DGEBA/PGE ratio, shown at (a) lower magnification and (b) higher magnification. *Bottom (c)*: Particle size distribution histogram obtained from TEM image analysis.

Calculation of Pair Distance Distribution Functions (PDDFs)

The pair distance distribution functions (PDDFs) were calculated using the code embedded in SASView 3.1.2. Briefly, the PDDFs were obtained from the experimental scattering curves by applying an Indirect Fourier Transform (IFT) combined with regularization methods to ensure a smooth and physically meaningful PDDF(r) function, as described by D. I. Svergun (*J. Appl. Crystallogr*. 1992, **25**, 495-503). The non-negative regularization parameter (α) acted as a Lagrange multiplier, balancing the smoothness of PDDF(r) with the quality of the fit to the experimental data. The maximum correlation distance (r_{max}) was adjusted to achieve a smooth decay of PDDF(r) to zero at large r values.

Fitting of SAXS data

SAXS data were fitted using the SASfit software package in the *q*-region from 0.08 to 2 nm^{-1}. The models used are implemented into the SASfit package and were used without modification (*Kohlbrecher, J. SASfit: A program for fitting simple structural models to small angle scattering data. https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf*

Data corresponding to the 100:0 sample were modeled assuming a factor form of spherical objects with a log-normal size distribution. Regarding the samples containing PGE, two contributions to the form factor were considered: one corresponding to spherical primary particles and the other to aggregated structures. A log-normal size distribution was assumed for each of these components.

Table S1. Fitting results of SAXS data for silver/epoxy nanocomposites formulated with different DGEBA/PGE ratios.

DGEBA:PGE	Primary particles				Aggregated structures			
	Form factor	Size distribution			Form factor	Size distribution		
	eta	*s*	*p*	*mu*	*eta*	*s*	*p*	*mu*
100:0	0.0166	0.3391	4.0833	4.8245	-	-	-	-
50:50	0.0135	0.3224	5.7240	6.8564	0.0011	0.5139	3.1754	17.0795
40:60	0.0181	0.3757	3.7054	5.1753	0.0041	0.8214	3.7506	22.5986
30:70	0.0180	0.3716	3.6899	4.6166	0.0042	0.7364	3.6974	21.9101
25:75	0.0218	0.2558	4.4112	4.2470	0.0051	0.8864	3.4889	23.9016