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Supporting Information

Large-Area Patterning of the Tackiness of a Nanocomposite Adhesive by Sintering of Nanoparticles under IR Radiation

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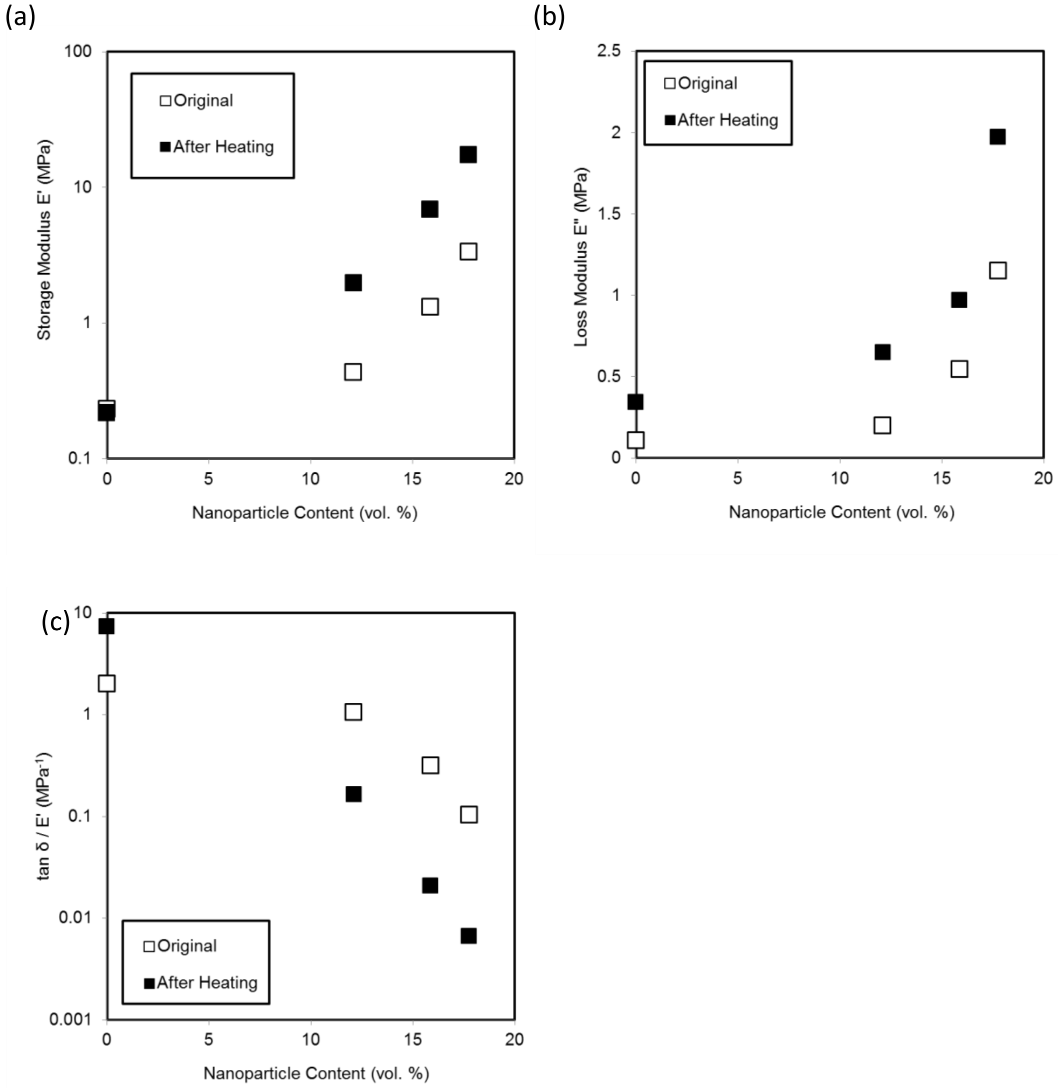

Figure S1. Values for the dynamic mechanical properties of the nanocomposite PSA, with various nanopoarticle contents, before and after heating in a convection oven at 140 °C for 30 minutes. (a) Storage modulus, (b) loss modulus, and (c) tan δ/ E’, obtained by DMA at 1 Hz and at a temperature of 22 °C.

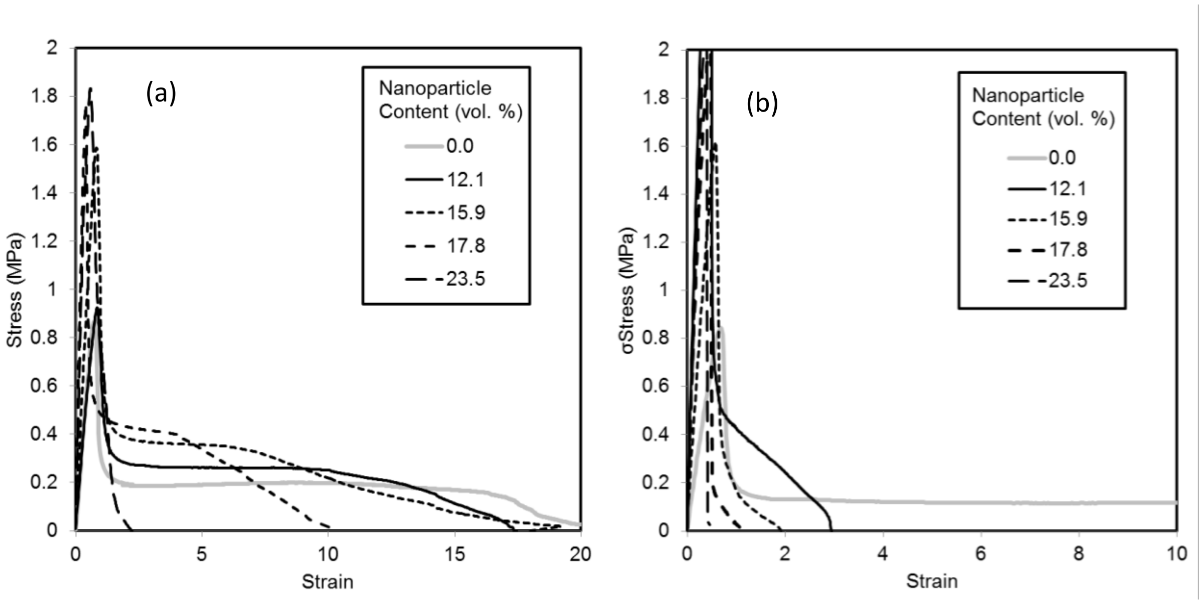

Figure S2. Representative probe-tack curves for nanocomposite adhesives with varying concentrations of hard nanoparticles (vol. %) (a) before IR heating and (b) after IR heating for 30 s.

For the original adhesive in Figure S2c, the stress plateau, which is the region where fibrils are being drawn during debonding, has a value of approximately 0.2 MPa, which is lower than good-performing adhesives.[1-3] The low tack energy can be explained by the elastic modulus being lower than 0.3 MPa, which is the optimum value for a PSA. The sloping tail is indicative of a liquid-like debonding and cohesive failure, which leaves a residue on the probe or second surface, and which is an undesirable trait for a PSA. Hard nanoparticles act as a mobile filler, raising the bulk modulus of the nanocomposite without sacrificing the adhesive properties. In this instance, at the optimal level of nanoparticles of 16 vol. %, the fibrillation plateau rises to 0.5 MPa, without a significant drop in overall plateau length, and has a marked sudden drop upon de-bonding, indicative of an adhesive failure with no residue.

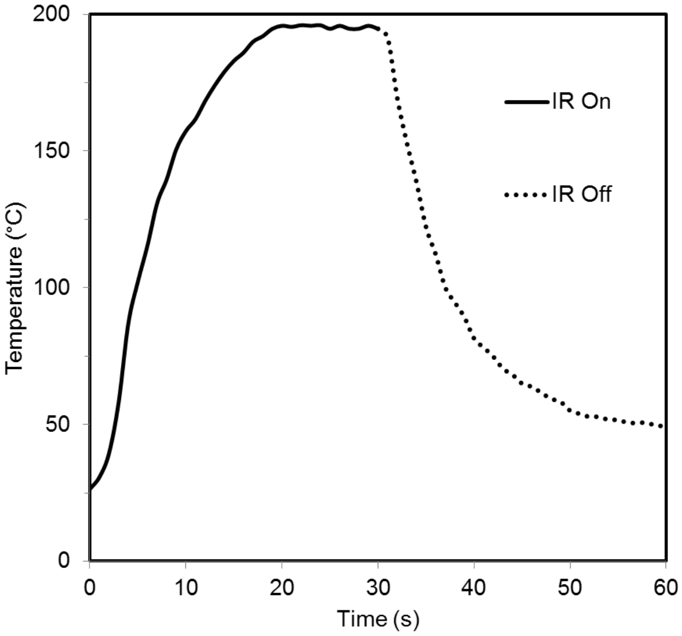

Figure S3. Temperature-time profile of the nanocomposite adhesive when heated by a 4 kW IR emitter that is positioned 3 mm above it. The IR emitter was powered on for 30 s, during which time the adhesive temperature rose from an initial 22 °C to 190 °C. The IR emitter was then switched off, and the adhesive cooled. The temperature was recorded with a thermocouple placed on the film surface, with the temperature logged every 0.1 seconds.

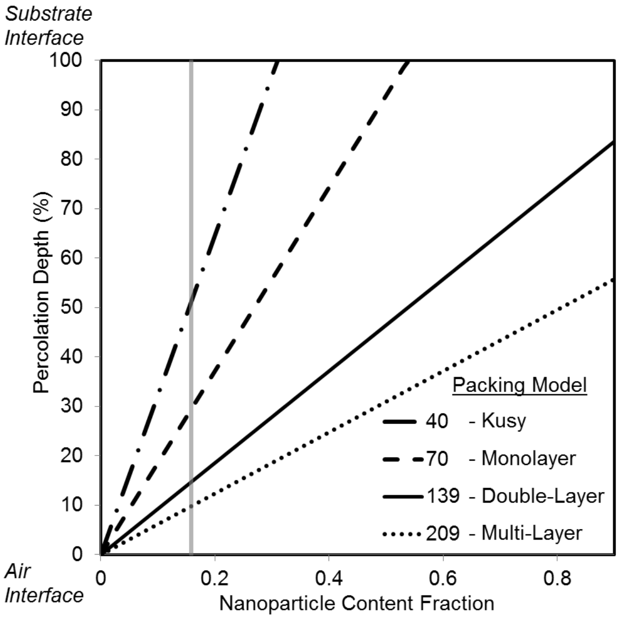

Figure S4. Estimate of the surface layer depth in which the nanoparticles are accumulated. Calculation of the percentage thickness of the nanoparticle surface layer was based on previous formula[4] and assumes different packing arrangements for the nanoparticles around the larger PSA particles. The legend identifies the number of nanoparticles per PSA particle required for the specified type of particle packing. The vertical grey line indicates the optimum nanoparticle concentration of 16 vol. %. The nanoparticle content fraction at 100 % percolation depth indicates the volume of nanoparticles required to create a percolating network for the given packing model.

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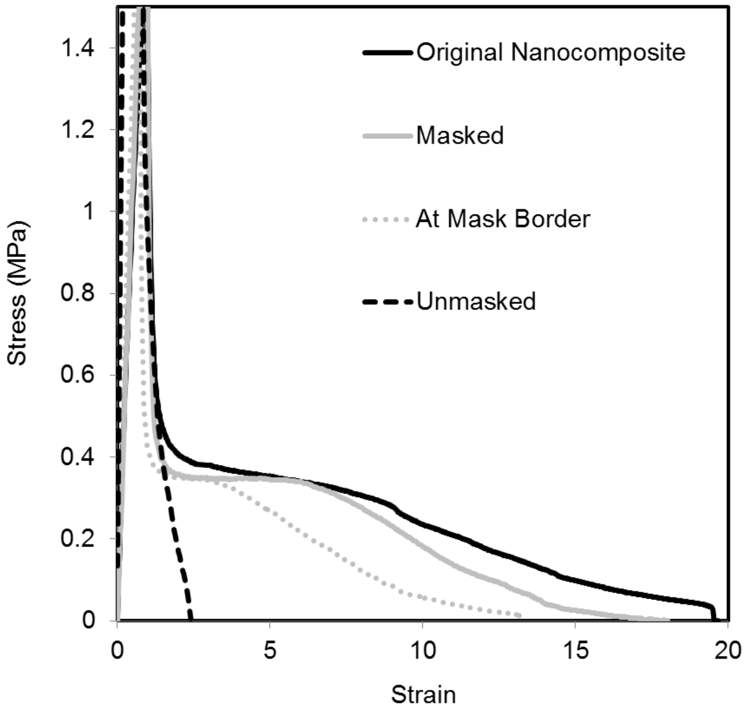

Figure S5. Representative probe-tack curves showing the effects of IR heating under a mask at a height of h = 2 mm above the nanocomposite film surface. Curves are shown before (black solid line) and after (black dashed) IR heating in an unmasked region. Under the masked region (grey solid line) and near the mask border (grey dashed) there are small differences in the probe-tack curves, with the overall adhesion energy (proportional to the area under the curve) dropping near the mask border, indicating IR leakage beneath the mask.

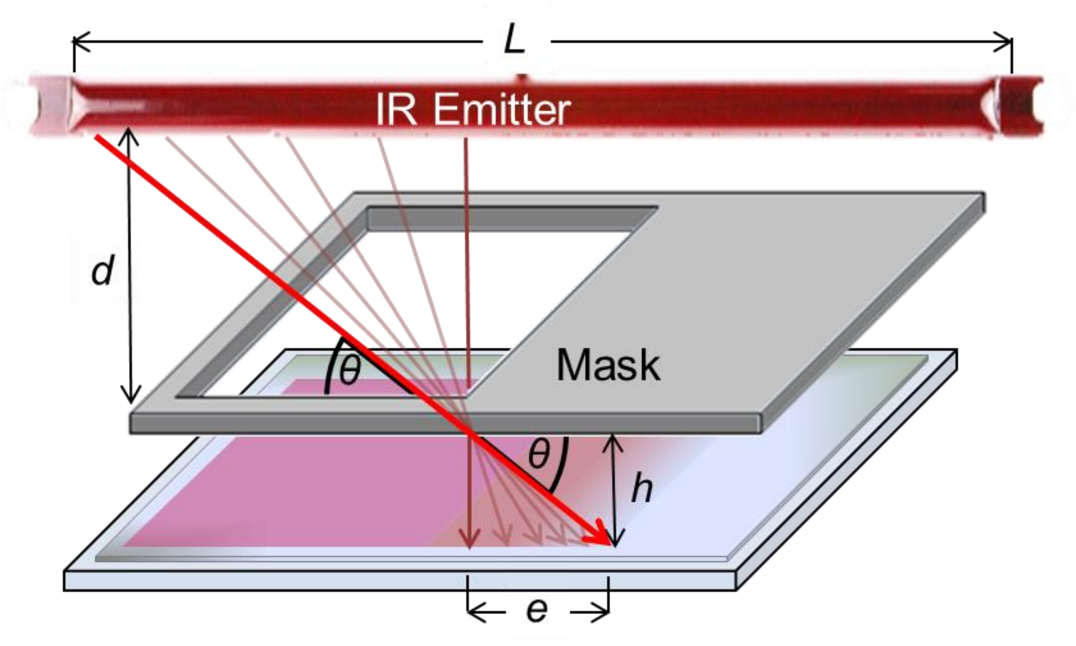

Figure S6. Calculation of stray IR radiation reducing edge resolution of patterns. The figure shows the geometric arrangement of the IR emitter, mask, and PSA (not drawn to scale). The symbols are defined as follows:

L = length of IR emitter = 0.7 m

d = distance between IR emitter and mask = 3 cm = 0.03 m

h = height of mask above PSA = 2 mm = 0.002 m

e = edge effect (distance that IR radiation reaches beyond the edge of the mask)

The IR radiation from the far end of the lamp will strike the mask at an angle-of-incidence of θ. From trigonometry, it can be written that

$$tan\theta = \frac{d}{L/_2}.$$

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IR radiation coming from the far end of the emitter will pass through the mask at an angle θ and strike the adhesive at a distance e from the edge of the mask. Thus, this relation holds:

$$tan\theta = \frac{h}{e}.$$

Substituting for tanθ, we obtain:

$$e = \frac{Lh}{2d}.$$

Thus, for our experiments, where $L = 0.7$ m, $h = 0.002$ m, and $d = 0.03$ m, we find that the distance IR radiation extends beyond the edge of the mask is $e = 0.023$ m or 2.3 cm. This simple calculation can explain why some adhesion is lost under the edge of the mask to distances on the order of 1 cm. If we also consider the radial energy density of the cylindrical IR emitter, assuming it emits equally along its length, we find energy density, E_d varies inversely with radial distance from the emitter, d_r, given by

$$E_d = \frac{P}{2\pi d_r L},$$

where P is the emitted power. It stands to reason that whilst stray radiation at oblique angles from the emitter is able to reach the film surface up to a distance e, it will only do so at large distances. The reduction in energy density as a function of distance from the lamp results in a temperature gradient in this area, with the temperature dropping considerably with increased angle of incidence θ (and thus increased d_r). The gradient in energy density due to oblique radiation leads to a gradient in temperature and therefore a variation in the extent of sintering in areas underneath the mask.

The value of e can be reduced by using a shorter IR emitter or by rotating the emitter by 90 degrees, such that its length runs parallel to the edge of the mask. Additionally, e can be reduced by moving the IR emitter further away (increasing *d*) and by decreasing *h,* as was found in our experiments.

In this derivation, the thickness of the mask is neglected. A mask with a finite thickness would reduce the stray IR radiation. Increasing the mask thickness sufficiently will eliminate stray radiation entirely.

References

(1) Deplace, F.; Carelli, C.; Mariot, S.; Retsos, H.; Chateauminois, A.; K. Ouzineb, K.; Creton, C. Fine Tuning the Adhesive Properties of a Soft Nanostructured Adhesive with Rheological Measurements. *J. Adhes.* **2009**, *85*, 18–54.

(2) Dahlquist, C. A. in *Treatise on Adhesion and Adhesives*; Patrick, R. L., Ed.; Dekker: New York, 1969; Vol. 2, pp. 219-260.

(3) Chang, E. Viscoelastic Properties of Pressure-Sensitive Adhesives. *J. Adhes*. **1997**, *60*, 37–41.

(4) Gurney, R.S.; Dupin, D.; Nunes, J.S.; Ouzineb, K.; Siband, E.; Asua, J. M.; Armes, S. P.; Keddie, J. L. Switching Off the Tackiness of a Nanocomposite Adhesive in 30 s via Infrared Sintering. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5442–5452.