Supplementary Information

Nanoparticle-based photothermal heating to drive chemical reactions within a solid: using inhomogeneous polymer degradation to manipulate mechanical properties and segregate carbonaceous by-products products

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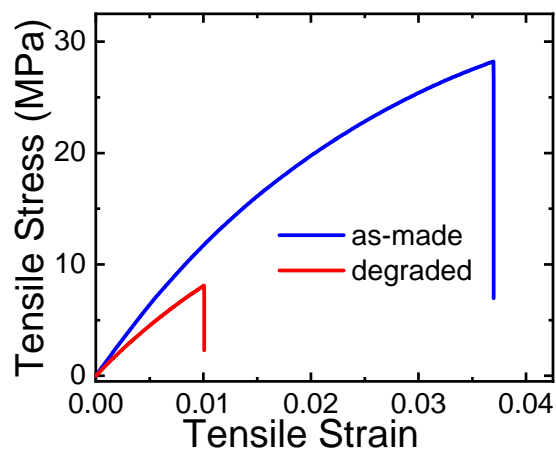[b] Department of Physics, NC State University, Raleigh NC 27695, USA

Figure 1: Characteristic stress-strain curves for as-made (blue line) and highly-degraded (red line) PECA:starch composite samples. The deteriorated sample was conventionally-heated in an oven at 185 °C for 1 hour.

Tensile testing specimens of PECA:starch and PECA:starch:AgNPs composites fabricated as rectangular films (100 mm long x 8 mm wide x 0.5 mm thick) using single column tabletop testing system (Instron 5944) equipped with a 2 kN load cell and Bluehill 3 software for data recording and analysis was utilized. All mechanical tests were conducted at room temperature with a relative humidity of 65% and an extension rate of 0.5 mm/min. The gauge length was fixed at 30 mm to meet the ASTM-D695 standard regarding sample length to width ratio. Paper frames were used to prevent grip point failure. Prototypical stress-strain curves (as shown in Fig. S1) for as-made and highly-degraded composite samples of PECA:starch demonstrate a mostly brittle fracture in both as-made and highly degraded material forms.
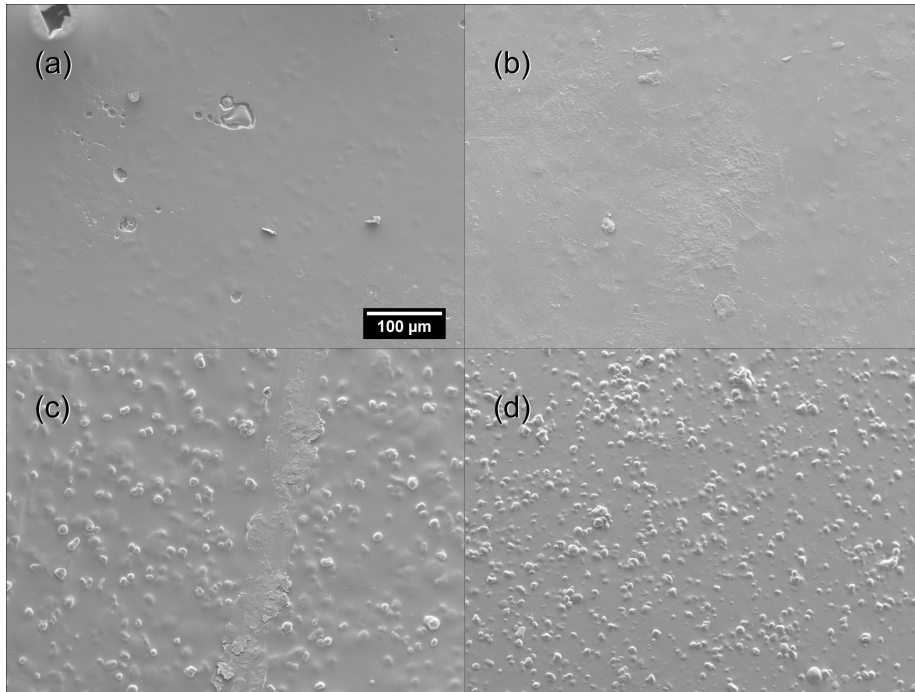
Figure 2: SEM on surface of samples (a) as-made, and after 1 hour treatment at (b) 140 °C, (c) 180 °C, and (d) 200 °C. As PECA mass is removed from the surface, starch granules are revealed.

Surface morphological images were collected on a variable pressure SEM (Hitachi S3200N) at 2500x magnification (20 kV). Specimens were sputter coated with ~30 nm of gold prior to imaging to reduce charging effects. Fig. S2(a) was representative of the surface of freshly fabricated samples, while (b)-(d) represent the conditions of the free surface after 1 hour degradation at elevated temperatures. As treatment temperature increased, more surface roughness appears, which is taken to be starch granules becoming more exposed as the PECA mass near the surface depolymerizes into ECA and evaporates, leaving behind the starch.
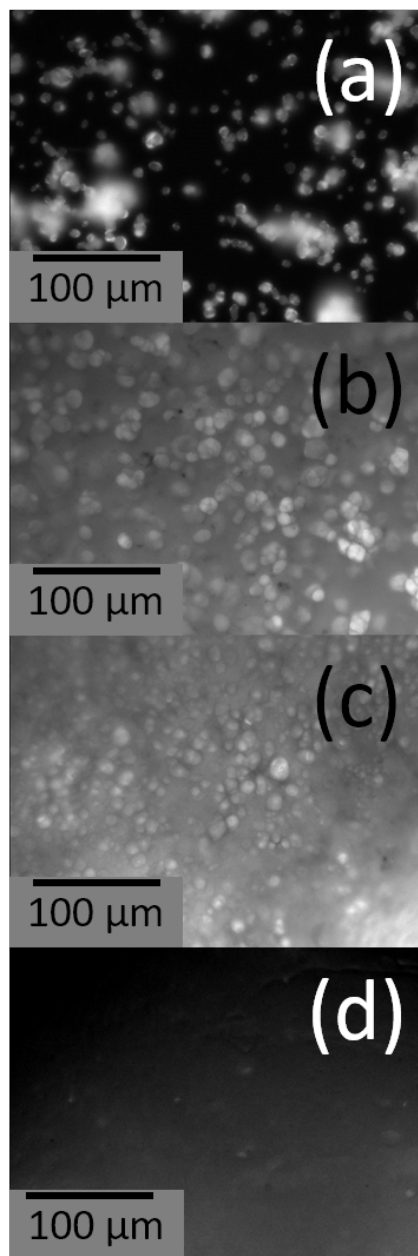
Figure 3: Luminescence images (excitation 350-400 nm, detection 450-500 nm) of starch on a glass microscope slide after treatment in a >200 °C oven (a) and PECA:starch:AgNPs composite samples after 1 hour conventional thermal treatment at either (b) 170 °C, or (c) 215 °C (compare with Fig. 5(e) and (f), respectively). (d) The same image from an as-made PECA:starch:AgNPs sample. All images at $20x$ magnification and have the same scale bar.

Fig. S3(a) is a fluorescence microscopy image from neat starch placed on a glass slide after treatment at high temperatures, where the bright spots are due to starch luminescence and the white smeared regions indicate saturation of the emission detector camera. Figs. S3(b) and (c) are images of PECA:starch:AgNPs sample luminescence after being exposed to either 170 °C or 215 °C for one hour, which can be compared with bright field equivalents shown Figs.5 (e) and (f). Starch granules within the samples are clearly observable and side-by-side comparison of bright field and luminescence images also confirm that most surface structure in Fig. 5 is from starch. For comparison, Fig. S3(d) shows an image from an as-made PECA:starch:AgNPs sample where the starch is non-luminescent.
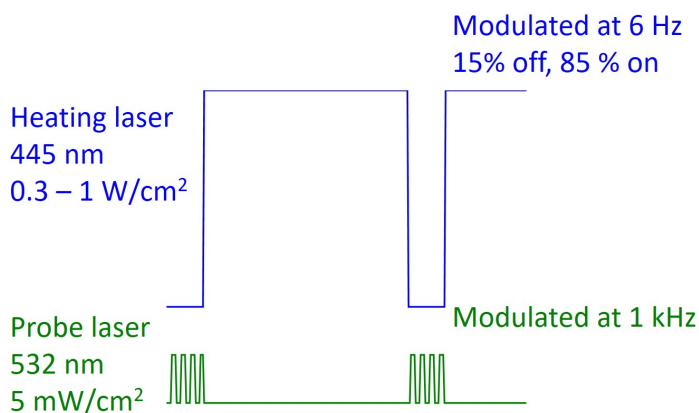

Figure 4: Schematic diagram of light intensity timing curve for the photothermal heating and temperature-measurement light sources. Thermometry measurements are triggered by a pause in the heating laser. In other words, the heating laser is very briefly turned off while a fast fluorescence temperature measurement is completed.

Fig. S4 schematically depicts the timing diagram for the non-contact molecular fluorescence thermometry measurement occurring under near-simultaneous photothermal heating. The high-intensity 445 nm blue laser, which drives the photothermal heating process and is resonant with the LSPR of the silver nanoparticles, is asymmetrically modulated at 6 Hz with an 85% duty cycle. During the brief blue laser interruption, a weak 532 nm green laser amplitude-modulated at 1 kHz excites the Lumogen Orange molecules whose fluorescence is detected and demodulated using a lockin amplifier (SRS 830).
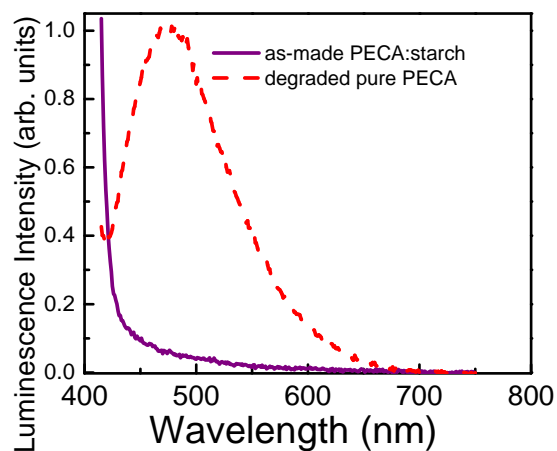
Figure 5: Comparison of emission spectra from as-made PECA:starch (purple line) and degraded PECA (dashed red line) samples. The mass of the pure, degraded PECA and PECA:starch composite samples are matched.

Fig. S5 shows the development of a luminescent degradation by-product in PECA as the material thermally degrades. The as-made sample shows no emission (purple line), only the tail of the spectrometer excitation itself leaking onto the detection pathway. In contrast, the degraded sample (red dashed line) clearly displays a luminescent by-product.