Supporting Information

Thermally-Degradable Thermoset Adhesive Based on a Cellulose Nanocrystals / Epoxy Nanocomposite

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Experimental Section

Materials and Methods

Poly[(phenyl glycidyl ether)-co-formaldehyde] with average M_n ~ 345 g/mol (BisF, Sigma-Aldrich), tetraethylenepentamine (Sigma-Aldrich), and cellulose nanocrystals (CNCs, Alberta-Pacific Forest Industries Inc.) were used as received. BisF/CNC nanocomposites were fabricated using a planetary mixer/deaerator (Kurabo Mazerustar, KK-250S). For better uniformity of mixing, BisF was warmed to 60 ^{o}C to reduce viscosity. The surface of metal specimens was cleaned using soap and gently sanded with a belt sander equipped with a P1000 sanding belt. After sanding, specimens were cleaned using isopropyl alcohol. BisF resin and hardener were mixed with a 5:1 weight ratio, and specimens were prepared using the method described in ASTM standard D1002 ("Standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal)"). The curing process was performed at 100 °C for 1.5 hours for both pristine BisF and BisF/CNC nanocomposites.

Characterization

For shear strength measurement, a universal testing machine (Instron 5966 equipped with a 10 kN load cell) was employed, and the measurements were carried out according to ASTM standard D1002. A minimum of 30 specimens per nanocomposite composition were tested. For thermogravimetric analysis (TA instruments TGA Q50), samples were heated to 800 °C at a rate of 10 °C/min under a nitrogen flow. To dry the CNC-only sample, the temperature was held at 100 °C for 5 minutes before completing the temperature ramp. A Thermo-VG Scientific ESCALab 250 with a monochromatic Al Kα source (1486.6 eV) and a charge compensation gun were employed to perform X-ray photoelectron spectroscopy (XPS). All peak positions were calibrated against the C 1s standard (284.8 eV). Time-of-flight secondary ion mass spectroscopy (ION-TOF SIMS-5) was performed using a Bi^{3+} ion as a primary beam with a charge compensation gun.

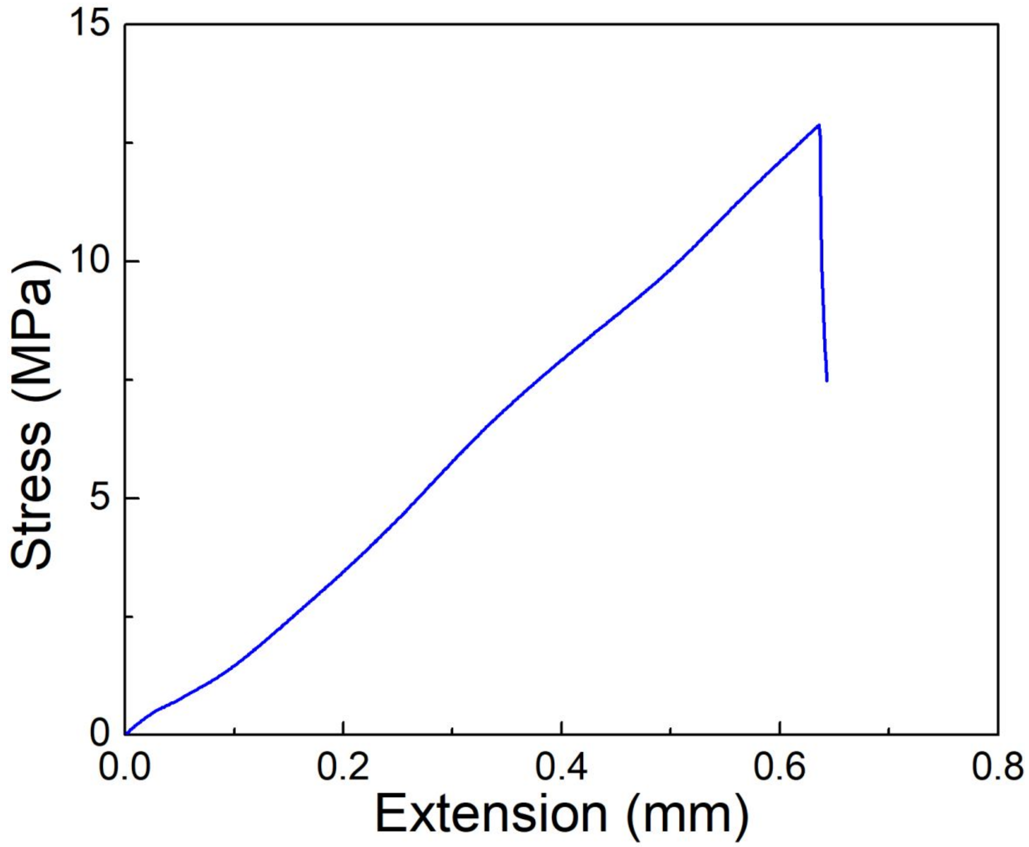

Figure S1. Typical stress-strain plot for as-cured BisF. The abrupt change near 0.6 mm extension corresponds to failure of the adhesive.

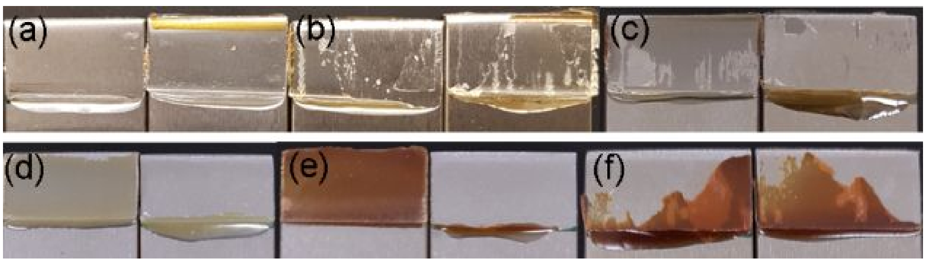

Figure S2. Photographs of metal specimens with adhesive residue following shear testing. The specimens were adhesively bonded with BisF (top, a-c) and BisF/CNC nanocomposites with 30 wt% CNC concentration (bottom, d-f). No thermal treatment was performed in (a, d). Thermal treatments were performed (b, e) at 180 °C and (c, f) at 200 °C.

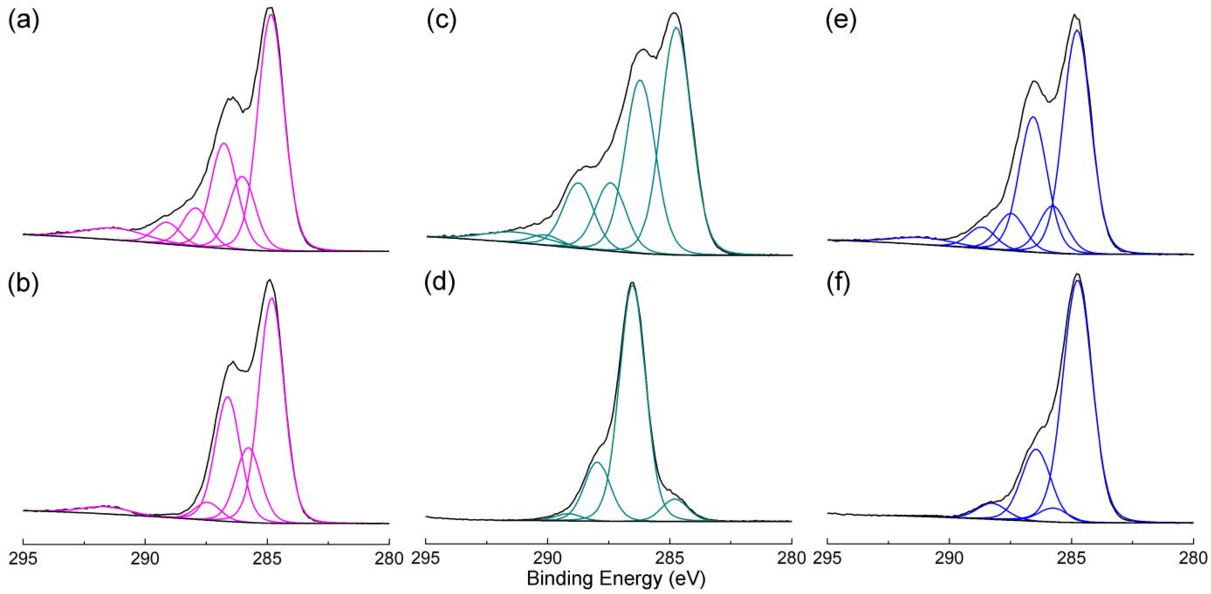

Figure S3. C 1s spectra of thermally-treated (top) and pristine (bottom) BisF (a,b), CNCs (c,d), and BisF/CNC with 30 wt% CNC concentration (e,f).

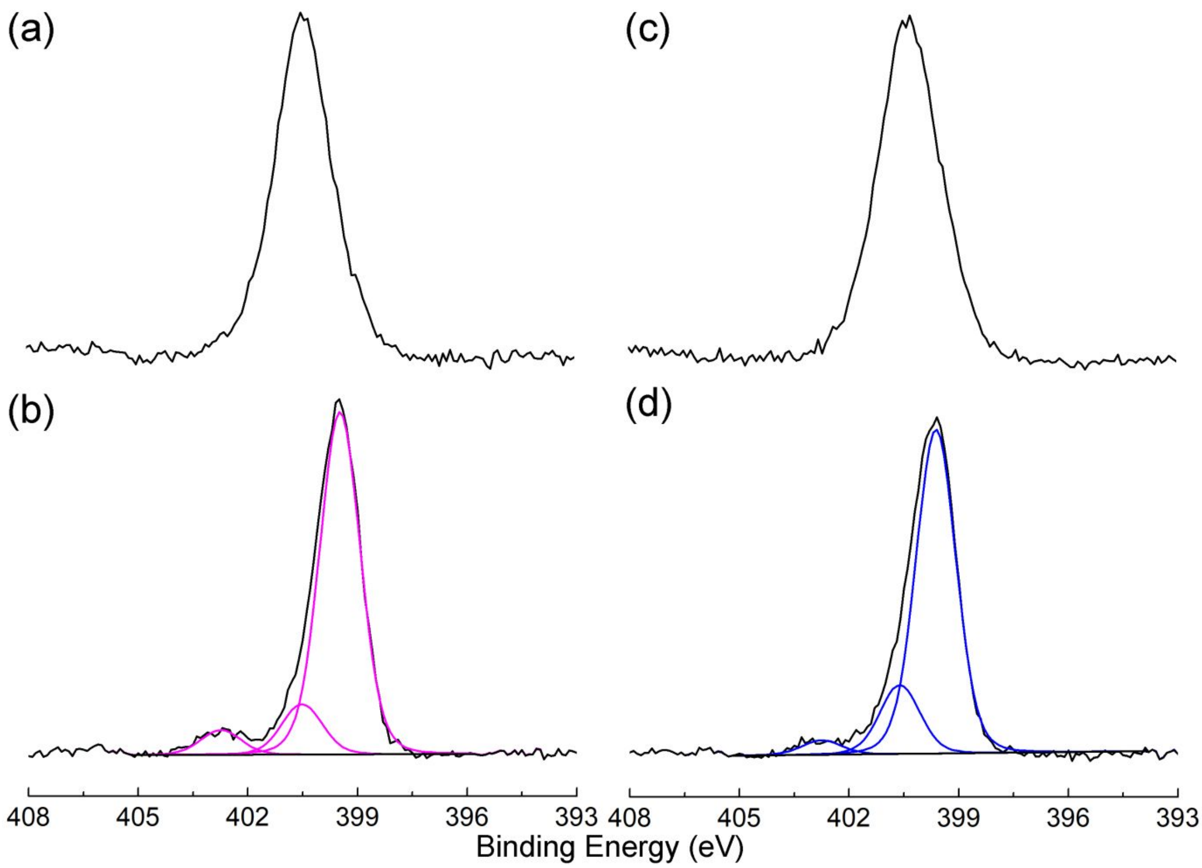

Figure S4. N 1s spectra of thermally-treated (top) and pristine (bottom) BisF (a,b) and BisF/CNC with 30 wt% CNC concentration (c,d).

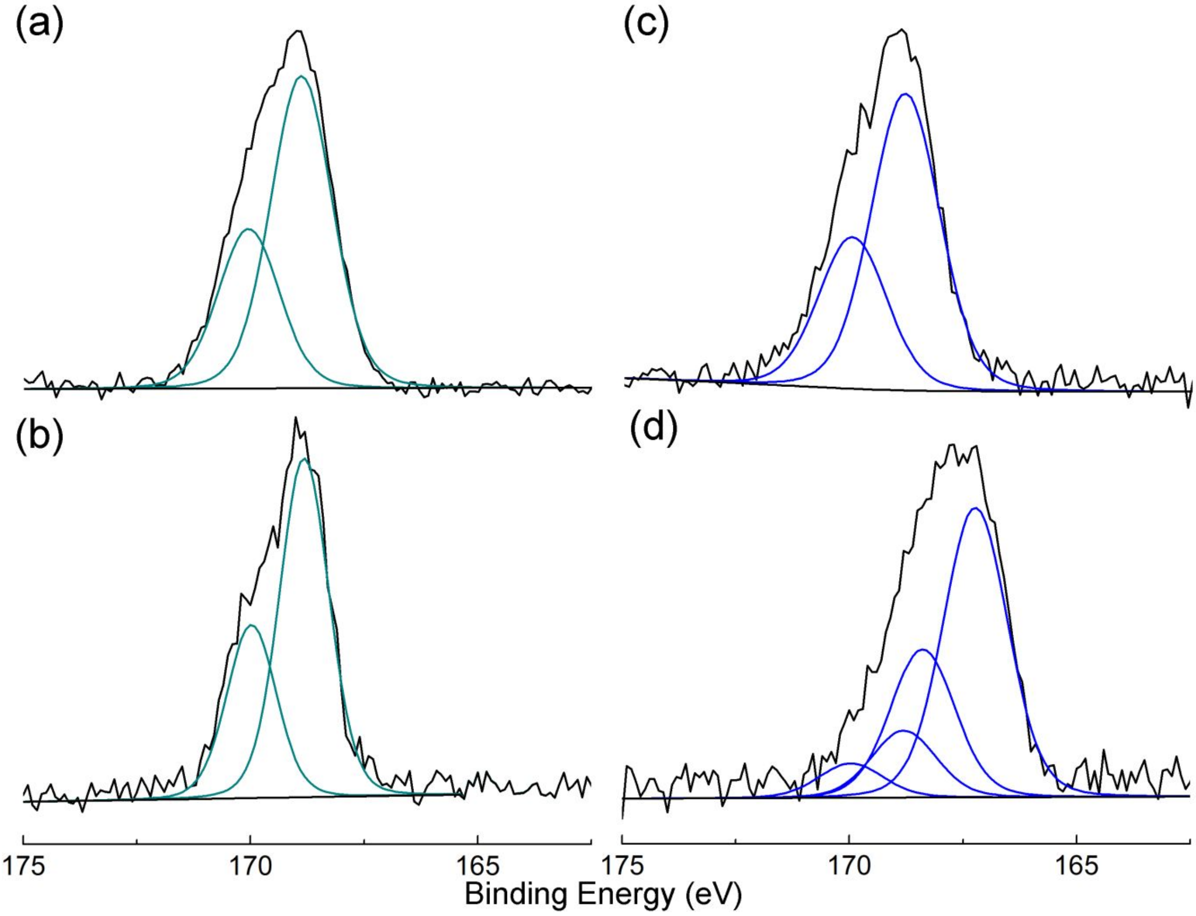

Figure S5. S 2p spectra of thermally-treated (top) and pristine (bottom) CNCs (a,b) and BisF/CNC with 30 wt% CNC concentration (c,d).