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Supplementary Information

Experimental section

Materials. The diglycidyl ether bisphenol A epoxy monomer (EPON 826) and the poly(propylene glycol)bis(2-aminopropyl) ether curing agent (Jeffamine D-230) were purchased from Hexion, and neopentyl glycol diglycidyl ether (NGDE) was obtained from TCI America. Other chemicals were also obtained from commercial sources, including styrene (≥ 99.5%, Sigma-Aldrich), divinylbenzene (DVB, 65%, EM Science), benzoyl peroxide (BPO, 75%, Sigma-Aldrich), sulfuric acid (95–98%, VWR International), sodium hydroxide (≥ 97%, Sigma-Aldrich), methanol (≥ 99.8%, Sigma-Aldrich), and 2-propanol (≥ 99.5%, Sigma-Aldrich). All chemicals were used as received.

Materials Synthesis

Epoxy polymer. Epoxy polymer was obtained by curing a mixture of EPON826 (0.015 mol), NGDE (0.015 mol) and Jeffamine D-230 (0.015 mol) at 100 °C for 1.5 h, and post curing was conducted at 130 °C for another hour. The epoxy polymer was cut into small pieces (roughly 8 mm × 8 mm), rinsed with isopropanol, and blow dried prior to use.

Crosslinked polystyrene (cPS). Crosslinked polystyrene (cPS) samples were prepared via bulk copolymerization of styrene and DVB (2 molar %) with BPO (1 wt%) as the initiator. The polymerization proceeded in a nitrogen environment at 70 °C for 24 hours. After the polymerization, the cPS samples were heated in a vacuum oven at 120 °C for another 2 hours to remove un-reacted styrene monomer. The cPS samples were then demolded, vacuum treated again at 120 °C for another hour, polished using diamond pastes (particle sizes of 6 μm, 3 μm, 0.1 μm), cleaned with isopropanol, and blow dried prior to use.

Sulfonated crosslinked polystyrene (ScPS) and sodium exchanged sulfonated crosslinked polystyrene (SScPS). ScPS was obtained by floating a cPS sample on a concentrated sulfuric acid solution at 90 °C for 30 minutes, followed by thorough rinse with deionized water, blow drying and baking in a 90 °C oven for 1 h.

An ScPS sample was soaked in a dilute sodium hydroxide solution (pH=8.6) for sodium ion exchange. As the ion exchange occurred, the pH value of the solution decreased until a constant pH value of 6.5 was reached at about fifteen minutes, indicating complete ion exchange. Further soaking of this ion exchanged sample into a fresh sodium hydroxide solution (pH=8.6) did not lead to noticeable pH change, confirming that sodium ion exchange was indeed complete under this condition. The SScPS samples used for adhesion bonding experiments were obtained by soaking the ScPS samples in a much more concentrated sodium hydroxide solution (1 M) for a much longer time of 1 hour to ensure complete ion exchange. Afterwards, the samples were rinsed thoroughly with de-ionized water, blow dried, and baked in a 90 °C oven for 1 h.

Caution: After the reaction, sulfuric acid was left at room temperature for at least 4 h. Under constant stirring, the acid was added dropwise into a beaker containing a large

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amount of water. The acid solution was let cool down at room temperature prior to disposal.

Preparation of the model compound mixture. Sodium methanesulfate (0.02 g) and EPON 826 (0.03 g) was dissolved in methanol (approximately 15 mL). The resulting solution was left overnight in a hood to evaporate methanol. The remaining methanol was removed by vacuum (room temperature for 2 hours) before analysis.

Characterization. Contact angle measurement was conducted using a Krüss DSA10L system. The surface roughness was measured using tapping mode atomic force microscope (Dimension 3100, VEECO). The surface chemical composition of samples was analyzed by X-ray photon spectroscopy (XPS, PHI Quantera SXM Scanning X-ray Microprobe, ULVAC-PHI, Inc.) with a 200 µm-diameter X-ray beam. The Raman spectra were taken by excitation with a 10 mW 532 nm source. The samples were placed in the focal plane of the microraman attachment of a Jobin Yvon XY spectrometer (50 X objective). Each spectrum consisted of an average of 20 scans, each with an 8 second integration time.

Adhesive bonding and testing. To develop direct adhesion between the epoxy polymer and a substrate polymer, both polymers were heated in an oven at 80 °C for 10 minutes. As soon as the substrate polymer was taken out of the oven, 50 µL of methanol was dispensed onto its surface and the epoxy polymer was immediately pressed onto the substrate (preload = 8 $N \cdot cm^{-2}$). The adhesive bond was formed after the polymer pair was cooled down at room temperature for 10 minutes (under the preload). The preload was then removed and the adhesion was tested in a tensile mode at a loading rate of 20 $N \cdot s^{-1}$ using a ROMULUS Universal Mechanical Strength Tester (Quad Group Inc.).

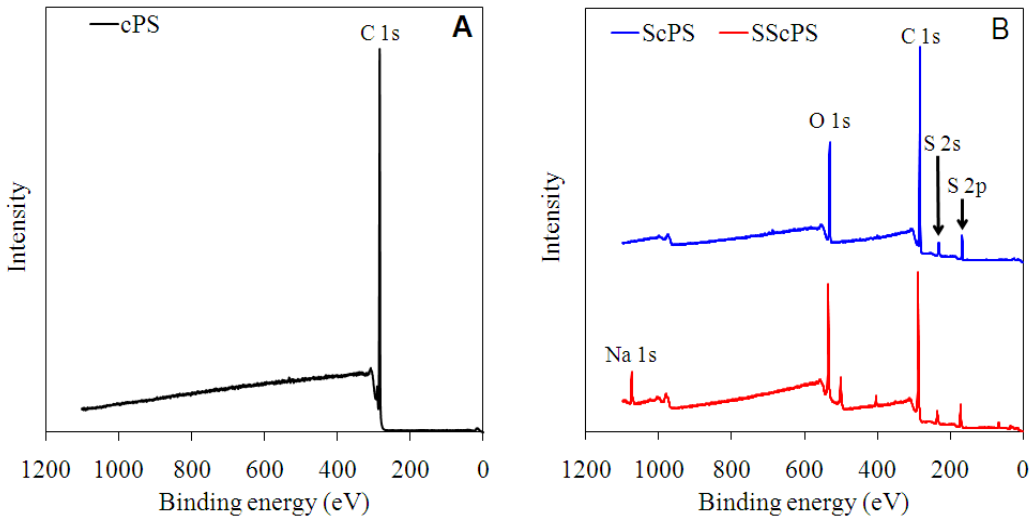

Figure S1. XPS spectra of cPS (A), ScPS(B) and SScPS (B).

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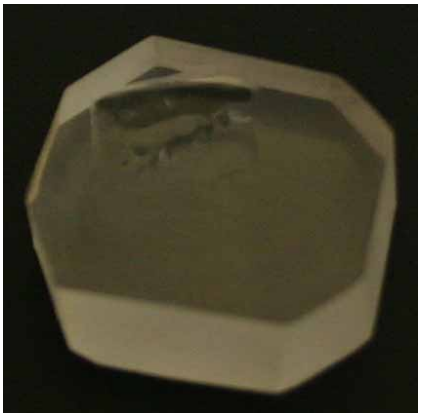

Figure S2. Photo of separated SScPS.

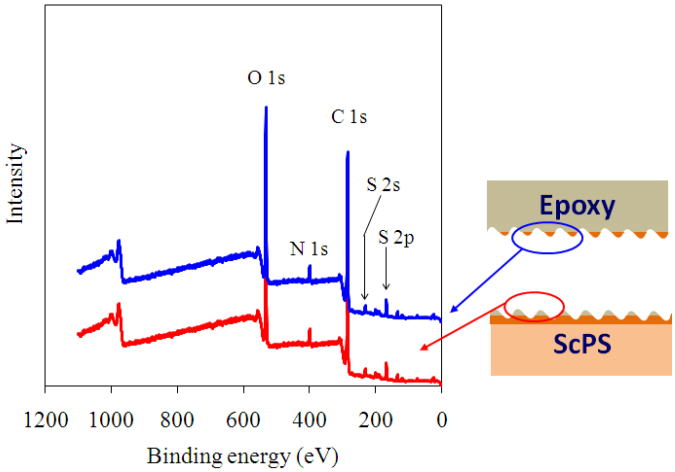

Figure S3. XPS spectra of ScPS and the epoxy polymer after the adhesion test. While the fresh ScPS contains no nitrogen and the fresh epoxy polymer contains no sulfur, the two debonded sample surfaces suggested the transfer of sulfur and nitrogen across the interface, confirming the cohesive adhesion failure between ScPS and the epoxy polymer.

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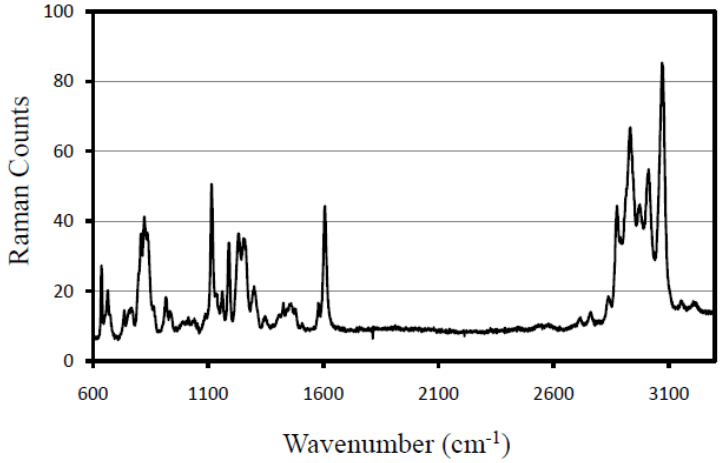

Figure S4. Raman spectrum for EPON 826.

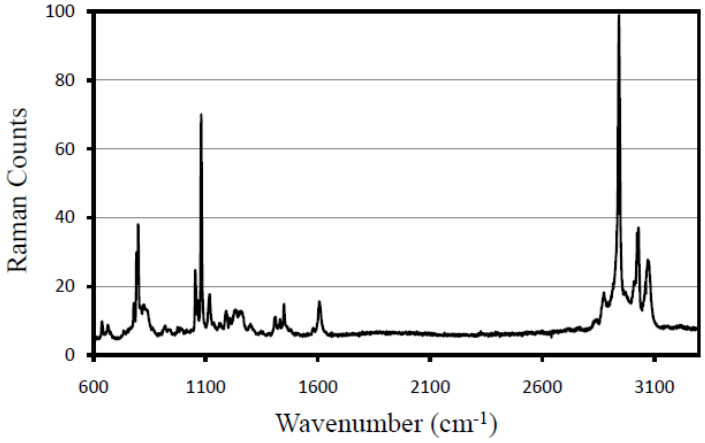

Figure S5. Raman spectrum for the mixture of EPON 826 and sodium methanesulfate.