

Electronic Supporting Information

Utilizing composite recyclate as reinforcement in inverse-vulcanised polymers

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Materials

All chemicals, reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used as received. Dialead™ (K223HM, 200 µm av. length) pitch-based milled carbon fiber (mCF) was sourced from Mitsubishi Chemical Corporation (Japan).

Rheology

The rheological properties of the sample were measured using a Discovery HR-1 hybrid rheometer (TA Instruments, New Castle, United States) equipped with the Environmental Test Chamber and 25.0 mm diameter aluminium parallel plate geometry. Prior to testing, samples were carefully loaded onto the lower plate at room temperature. Inertia, bearing friction correction, gap temperature compensation, and rotational mapping calibration were all performed prior to sample test runs. The gap was set to 500 µm with a 5% trim gap. The excess sample was trimmed prior to commencement to ensure proper filling. A temperature ramp was performed from room temperature to 140°C at a heating rate of 2 °C/min and 120 s soak time, using compressed air flow at 10 l min⁻¹. Throughout the test, an oscillatory strain was applied with a constant frequency of 1 Hz and a strain amplitude of 0.1%, which was predetermined to be within the linear viscoelastic region of the material, with data acquisition set to 1 S/s. The complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') were recorded as a function of temperature. Raw data was exported and processed in Origin version 2022 (OriginLab Corporation, Northampton, United States).

Differential Scanning Calorimetry

Differential scanning calorimetry was carried out on a Discovery 250, TA instrument. A sample size of around 3.5mg was used. The furnace was purged with nitrogen at 20mL/min and equilibrated at 0 °C for 5 minutes. A heat-cool-heat cycle was conducted on each sample from 0 °C to 165 °C at a 15 °C/min heating rate. The second heating cycle's heat flow was analysed for the composites' glass transition temperatures using TRIOS software.

Scanning electron microscopy

The scanning electron microscopy (SEM) imaging was performed on Zeiss Supra 55-VP and JEOL 7800F using a SE2 and LED detector, respectively. The electron accelerating voltage (electron high tension) of 5 kV and a working distance of ~8mm was used for imaging. Prior to imaging, composite samples were mounted to an aluminium pin stub using double sided carbon tape. The samples were then coated with a conductive coating (gold) using the Leica ACE500. For composites, the native fractured surface was imaged without polishing, except for the novel composite incorporating recyclate filler, which was polished prior to coating and imaging.

Flexural strength testing

Flexural properties of the composites were measured using an Instron Universal mechanical tester, in accordance with ASTM D2344. Five specimens 4 mm in thickness, 12 mm in width, and 35 mm in length were placed into a 3-point bend fixture with an effective flexural span of 30 mm between the two support pins. A central roller of 10 mm diameter was subsequently used to apply a bending force across the flexural specimen at a displacement-controlled rate of 1 mm/min. Applied compressive load and displacement were subsequently recorded to calculate flexural strength and modulus.

Hardness testing

The hardness properties of the samples were measured using a digital durometer equipped to measure Shore-D hardness (STARR, Model: DSD-D). Prior to testing samples were synthesised as detailed above. To test, the indenter was pressed onto the surface of the specimen till the pressure foot was in close contact to the specimen. The instrument automatically reported the hardness value when a stable measurement was obtained. To attain an average hardness, five sample readings were measured.

Synthesis of Poly(S-*r*-DCPD)

The synthesis of poly(S-*r*-DCPD) was conducted as detailed in previous literature with changes to the polymer curing.^{1, 2} Elemental sulfur (5.0 g, 156.2mmol) and dicyclopentadiene (5.00 g, 37.9 mmol) were placed in a reaction vessel and stirred (300 rpm) at 140 °C for ~2.5 hours. Following this, the obtained pre-polymer was transferred to the appropriate mould and cured at 140 °C for 3 hours followed by 160 °C for 2 hours to obtain the fully crosslinked polymer.

Synthesis of composites (Poly(S-*r*-DCPD)/mCF)

For the synthesis of mCF composites, 10% equivalence of mCF (1.2g) was added to the reaction vessel containing elemental sulfur (5.4 g, 168.69 mmol) and DCPD (5.4 g, 40.85 mmol). The reaction was conducted as detailed above. The prepolymer/mCF mixture was transferred to moulds and cured at 140 °C for 3 hours followed by 160 °C for 2 hours to obtain the fully crosslinked polymer.

Mechanical recycling of pDCPD/mCF composite

The pDCPD/mCF composites were recycled using Bruker Tribolab UMT. The sample was attached to a stationary upper drive using a sample holder. The rotary lower drive was equipped with a metal file programmed to rotate at 80 RPM for 5 minutes with 15 second intervals to avoid heating of the composite. The lower drive was lined using aluminium foil to conveniently collect the composite recycle. After collection, the powder was sieved through a 355 µm sieve to obtain the recycle filler used in composite manufacturing.

Synthesis of composites using recycled filler (Poly(S-*r*-DCPD)/recyclate filler)

For the synthesis of composites using recycle filler, 5.3% and 10.7% equivalence of recycle fillers was added to the reaction vessel containing elemental sulfur (5.4 g, 168.69 mmol) and DCPD (5.4 g, 40.85 mmol). The reaction was conducted as detailed above. The prepolymer/mCF mixture was transferred to moulds using a ~2-4 mL of chloroform. The mixture was degassed using a high vacuum set-up equipped with a solvent trap cold using liquid nitrogen. The degassed prepolymer/filler mixture was then cured at 140 °C for 3 hours followed by 160 °C for 2 hours to obtain the fully crosslinked polymer.

Recycling of composite material via hot-pressing

The fractured composite was crushed using a mortar and pestle to obtain a composite powder. The powder was loaded to silicon moulds and placed between two metal plates. The plates were moved to the hot-press heated to 160 °C. The powder was pressed using 1T force for 24 hours. After pressing the plates were removed from the hot-pressed and allowed to cool to room temperature before collecting the recycled specimens.

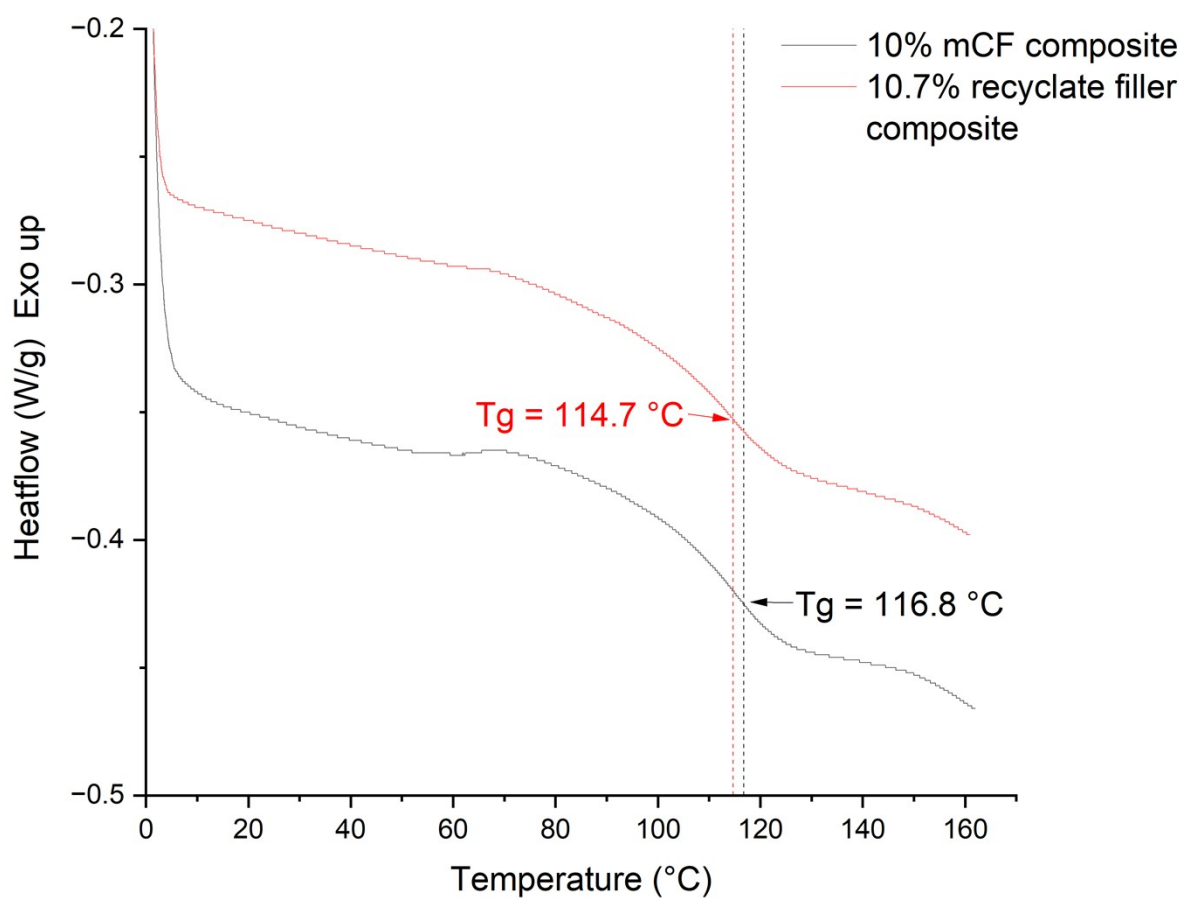
Glass transition (T_g) analysis using differential Scanning Calorimetry

Figure 1. Differential scanning calorimetric analysis of composites reinforced with 10% neat milled carbon fibers (black) and 10.7% recycled filler (red).

Scanning Electron Micrographs

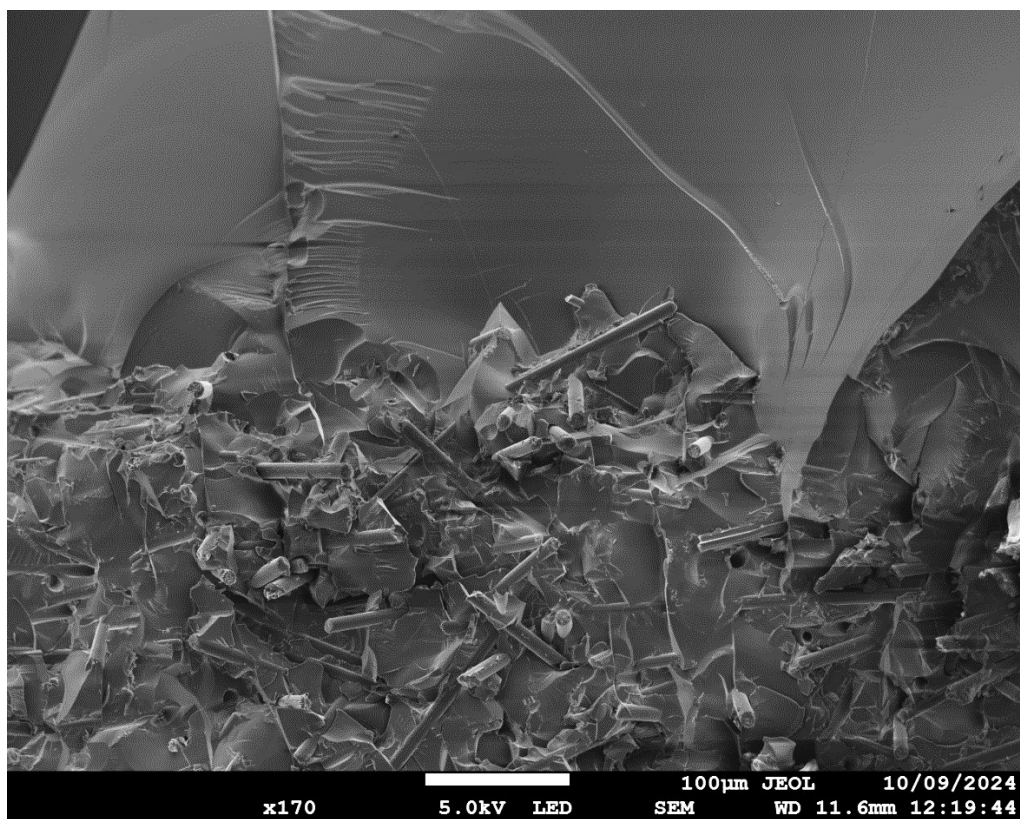


Figure 2. The fracture surface of phase separated composite with mCF settled in the bottom and neat polymer on top.

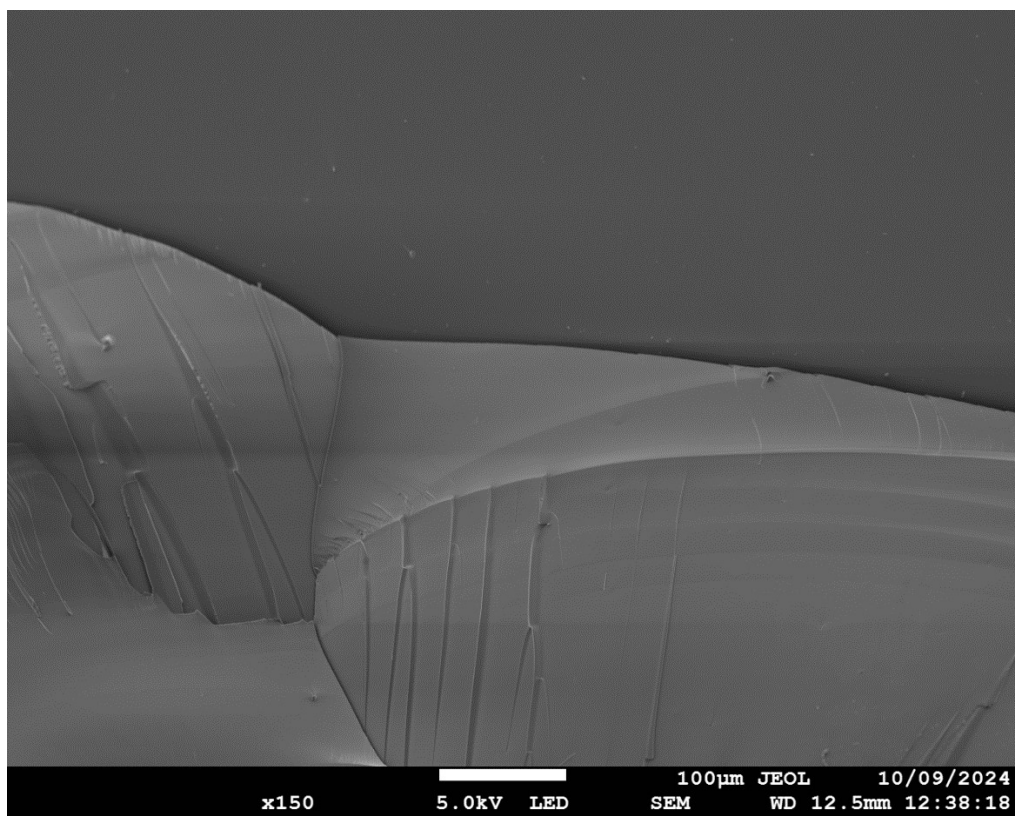


Figure 3. Fracture surface of phase separated composite, polymer layer.

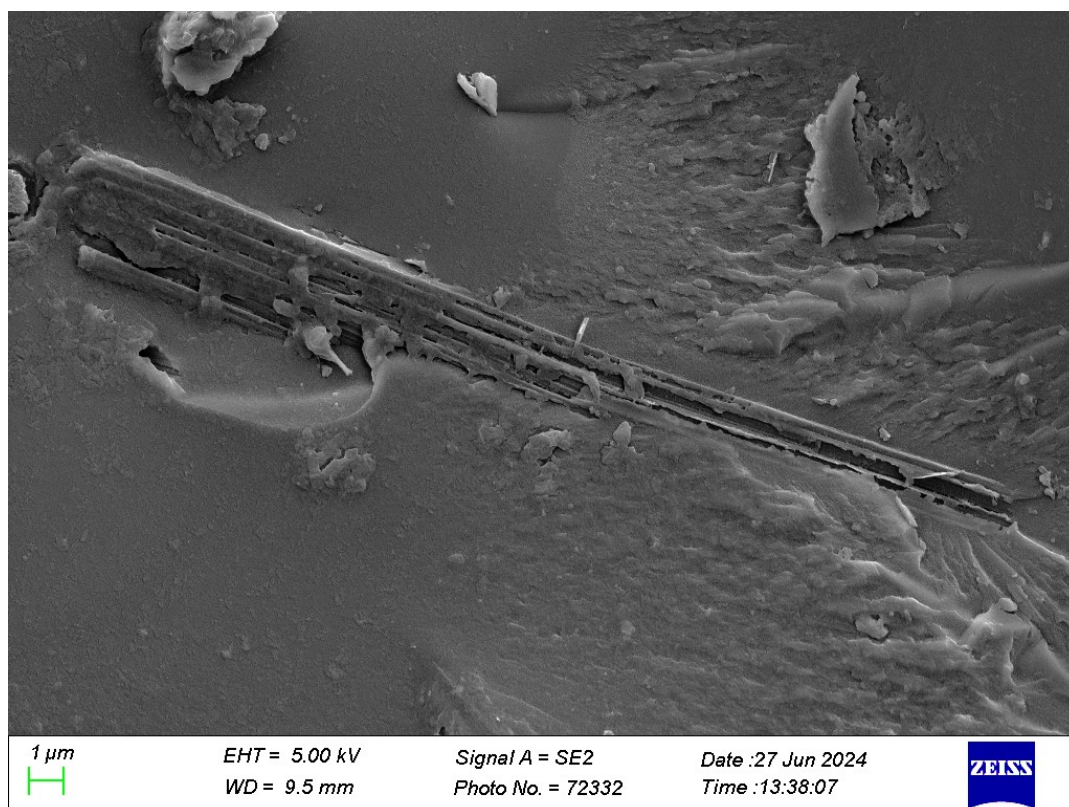


Figure 4. Carbon fibre particulate embedded within recycle-composite (5.3% recycled filler content).

1. Mann, M.; Zhang, B.; Tonkin, S. J.; Gibson, C. T.; Jia, Z.; Hasell, T.; Chalker, J. M., Processes for coating surfaces with a copolymer made from sulfur and dicyclopentadiene. *Polymer Chemistry* **2022**, *13* (10), 1320-1327.
2. Wickramasingha, Y. A.; Simon, Ž.; Hayne, D. J.; Eyckens, D. J.; Dharmasiri, B.; Chalker, J. M.; Henderson, L. C., Adhesives Made from Sulfur Copolymer Composites Reinforced with Recycled Carbon Fiber. *Industrial & Engineering Chemistry Research* **2024**, *63* (28), 12490-12501.