Supplementary Information:

Carbon Nanotube Enhanced Dynamic Polymeric Materials Through Macromolecular Engineering

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EXPERIMENTAL PROCEDURES

Materials

All reagents were obtained from commercial suppliers and used as received unless otherwise specified. Azobisisobutyronitrile (98%, AIBN) was obtained from MilliporeSigma. Fufuryl alcohol (97%) was obtained from MilliporeSigma. Methacrylic acid (99.5%, MA) was obtained from ACROS Organics. Paradimethylaminopyridine (99%, DMAP) was obtained from ACROS Organics. 1-Ethyl-3-(3- dimethylaminopropyl)carbodiimide (98%, EDC) was obtained from Carbosynth. Multiwalled carbon nanotubes (98%, CNTs) were obtained from MilliporeSigma. Ethyl acrylate (99%, EA) was obtained from TCI. Ethyleneglycol dimethacrylate (98%, EGDMA) was obtained from MilliporeSigma. Glycidyl methacrylate (97%, GMA) was obtained from TCI. 1,1′-(methylenedi-4,1-phenyl-ene bismaleimide (95%, BMI) was obtained from MilliporeSigma. N,N'-dimethylethylenediamine (98%) was obtained from TCI. Hydrochloric acid (12 M, HCl) was obtained from Fisher Scientific. Sodium hydroxide pellets

(97%, NaOH) was obtained from RICCA. Ammonium chloride (98%) was obtained from Alfa Aesar. 2- (Propionicacid)yldodecyl trithiocarbonate (PADTC) was synthesized as outlined in the literature.[1]

Furfuryl Methacrylate (FMA) Monomer Synthesis

Furfuryl Methacrylate (FMA) is a monomer synthesized and used as a starting material in this Raft polymerization. Furfural Alcohol (12g) and DMAP (8.95 g, .0306 mol) were placed in a 50 mL round bottom flask with magnetic stir bar. Dichloromethane (DCM) (150 ml) and methacrylic acid (12.6 g) were added into the round bottom flaks. The reaction mixture was cooled to 0 C in an ice bath and EDC (44 g) was added. The solution was allowed to warm at room temperature and stirred for 24 hours at room temperature. After the reaction, the DCM phase was washed with) 0.2M hydrochloric acid (5x150 ml), followed by 1 wash with saturated brine (150 ml), 1 washes with 0.5 M NaOH (4x150 ml), 1 wash with water (140 ml), one wash with saturated ammonium chloride (140 ml), and finally one wash with saturated brine solution (140 ml). The solvent was removed by vacuum, yielding the product. The FMA product agreed with literature,[2] with peaks giving 7.42 (s, 1H), 6.42 (d, J = 3.2 Hz, 1H), 6.40 – 6.33 (m, J = 3.1, 1.9 Hz, 1H), 6.13 (s, 1H), 5.57 (s, 1H), 5.13 (s, 2H), 1.94 (s, 3H).

Synthesis of Polymers by RAFT Polymerization

The four groups of polymeric materials being synthesized in this research project include a branched system with 7% FMA (Poly(EA$_{100}$-FMA$_7$)-Br), 4.5% FMA (Poly(EA$_{100}$-FMA$_{4.5}$)-Br), a linear system (Poly(EA$_{100}$-FMA$_7$)-Lin), and a control system with 7% GMA (Poly(EA$_{100}$-GMA$_7$)-Lin). Each of the polymers are prepared in a similar manner. Each material was polymerized using RAFT polymerization. Each material had ca. 100 units of ethyl acrylate as the

backbone forming monomer with different amounts of dynamic Diels-Alder crosslinkers from FMA and static EGDMA crosslinkers/branching points.

Synthesis of Poly(EA$_{100}$-FMA$_7$)-Br

On a 10 gram scale of EA (0.010 mol), FMA (0.97 g, 0.006 mol), PADTC (0.292g, 0.0008 mol), AIBN (0.0273 g, 0.0002 mol), EDGMA (0.165 g, 0.0008 mol), and toluene (16.93 g) were placed in a 50 mL round bottom flask equipped with a stir bar, and capped with a rubber septum. The reaction mixture was put in an ice bath and stirred for 20 minutes while deoxygenating under nitrogen gas. The solution was then placed in an oil bath at 60°C and stirred for 10 hours. The polymer was recovered after precipitating in hexanes and left in a vacuum oven overnight. Poly(EA$_{100}$-FMA$_7$)-Br was confirmed by 1H-NMR with 86% conversion.

Synthesis of Poly(EA$_{100}$-FMA$_{4.5}$)-Br

On a 10 gram scale of EA (0.010 mol), FMA (00.62 g, 0.004 mol), PADTC (0.292g, 0.0008 mol), AIBN (0.0273 g, 0.0002 mol), EDGMA (0.165 g, 0.0008 mol), and toluene (16.93 g) were placed in a 50 mL round bottom flask equipped with a stir bar, and capped with a rubber septum. The reaction mixture was put in an ice bath and stirred for 20 minutes while deoxygenating under nitrogen gas. The solution was then placed in an oil bath to at 60°C and stirred for 10 hours. The polymer was recovered after precipitating in hexanes and left in a vacuum oven overnight. Poly(EA$_{100}$-FMA$_{4.5}$)-Br was confirmed by 1H-NMR with 86% conversion.

Synthesis of Poly(EA$_{100}$-FMA$_7$)-Lin

On a 10 gram scale of EA (0.010 mol), FMA (0.97 g, 0.006 mol), PADTC (0.292g, 0.0008 mol), AIBN (0.0273 g, 0.0002 mol), and toluene (16.93 g) were placed in a 50 mL round bottom flask with a stir and capped with a rubber septum. The reaction mixture was placed in an ice bath and stirred for 20 minutes while deoxygenating under nitrogen gas. The solution was then placed in

an oil bath to at 60°C and stirred for 10 hours. The polymer was recovered after precipitating in hexanes and left in a vacuum oven overnight. Poly(EA_{100}-FMA_7)-Lin was confirmed by 1H-NMR with 74% conversion.

Synthesis of Poly(EA_{100}-GMA_7)-Lin

On a 10 gram scale of EA (0.010 mol), GMA (0.92 g, 0.006 mol), PADTC (0.292g, 0.0008 mol), AIBN (0.0273 g, 0.0002 mol), and toluene (16.72 g) were placed in a 50 mL round bottom flask equipped with a stir bar, and capped with a rubber septum. The reaction mixture was put in an ice bath and stirred for 15 minutes while deoxygenating under nitrogen gas. The solution was then placed in an oil bath to at 60° C and stirred for 16 hours. Poly(EA_{100}-GMA_7)-Lin was confirmed by ^{1}H-NMR with 95% conversion. The polymer was recovered after precipitating in hexanes and left in a vacuum oven overnight.

Crosslinking of FMA Materials by post-polymerization Diels-Alder Chemistry

Each precursor polymer was combined with 1.5 polymer weight amount of dioxane. This crosslinking synthesis was performed by dissolving polymer in dioxane with 0.9, 0.45, 0.2, or 0 weight percent of CNTs in respect to polymer weight were added for the 7% branched polymer system. For the 4.5% FMA branched system, 7% FMA Linear system, and 7% GMA control system, only 0.9 or 0 weight percent of CNTs in respect to polymer weight were added to each reaction flask. The flask was then placed in an ultrasonic bath for three hours until all of the CNTs were dispersed evenly in the polymer matrix. After the CNT dispersion, an addition of ½ mole equivalent of 1,1′-(methylenedi- 4,1-phenyl-ene bismaleimide (BMI) was dissolved in 0.5 weight amount of dioxane based off the polymer weight. The reaction contents were then transferred into a Teflon mold and covered with a

glass cover for 24 hours at 50 °C.

Crosslinking of GMA materials by post-polymerization epoxide ring opening

N,N'-dimethylethylenediamine (0.2568 g, 2.91 mmol) and dioxane (14.64 g) were added to the polymer to facilitate crosslinking. If CNTs are used, Multiwall carbon nanotubes (0.0923 g) were added prior to the ring opening reaction. The resulting mixture was sonicated for 3 hours to attain homogeneity, then the polymer was set to mold for 24 hours at 50 °C.

ANALYTICAL METHODS

^{1}H-Nuclear Magnetic Resonance (NMR) calculation of monomer conversion

Each NMR experiment was performed on a Bruker 300 or 500 MHz spectrometer nuclear magnetic resonance (^{1}H-NMR) using CDCl3 as the solvent at 298 K.

Determination of Monomer Conversion by ^{1}H-NMR

Monomer conversion was determined by NMR by integrating the sum of polymerized and unpolymerized ethyl acrylate (4.4-4.0 ppm) against the vinyl protons at 6.5, 6.1 and 5.8 ppm. Consumption of FMA was found to be near quantitative in each case by NMR.

^{1}H-NMR determination of the Mn of the primary polymer chain

The number average molecular weight (Mn) for the primary chain in the polymer was calculated using Bruker 300 or 500 MHz spectrometer hydrogen nuclear magnetic resonance (1H-NMR) of the isolated polymer material in CDCl$_3$. The resulting NMR gave peaks representative of the different constituents of the polymer, estimated to be representative of the average polymer chain. By using the known equivalences and the molecular weights of the reagents, the Mn was calculated as the sum of the peak integration multiplied by the molecular weight for each reagent. After precipitation of the polymers, the NMR gives a triplet at 3.4 ppm. That is from the CH$_2$ of the CTA at the sulfur and is integrated to 2 ppm. The 5 ppm region is the amount of

remaining FMA from the ester in the furan group. At 4.1 ppm, the CH_2 in EA is found. 6.4 ppm is the aromatic in FMA.

Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was performed on an Agilent 1260 Gel Permeation Chromatography System (GPC) equipped with an autosampler, an Agilent 1260 isocratic pump, Agilent 1 guard and 2 Mixed-B columns, degasser, and an Agilent 1260 refractive detector and a Agilent MDS Viscometer. The sample injection volume was 100 µL and the eluent, tetrahydrofuran, had a flow rate of 1 mL/min at 30 °C. This system was calibrated using poly(methyl methacrylate) (PMMA) solutions with molecular weights ranging from 617,000 to 1,010. Molecular weights reported are based on universal calibration relative to the PMMA standards. Each sample was filtered before injection through a 200 nm filter.

Fourier transform infrared (FTIR) spectroscopy

A Bruker IFS 66/S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF_2 beam splitter, and a liquid nitrogen cooled InSb detector was used for all FTIR spectroscopy.

CNTs TEM Imaging

Aqueous suspension of commercial multi walled CNTs were dispersed on freshly prepared nitrocellulose substrate and carbon coated 300mesh copper grids. Samples were imaged at 120 keV with a JEOL 1200 EX II.

Scanning Electron Microscopy

Samples were trimmed and mounted on edge with conductive adhesive to reveal internal organization. Samples were imaged in a Zeiss Supra-35 FEG VP with secondary electron imaging at 1 or 2Kv.

Tensile Test

An Instron 3344 universal testing system equipped with a 100 N load cell was used at room temperature for all tensile tests. The elongation of the materials was increased at rate of 1 mm s-1. The experiment was performed until failure. Each material was subjected to at least 3 replicates.

Self-Healing Procedure

After the crosslinking synthesis, some of the dog-bone shaped materials undergo self-healing procedures. Those materials were first sliced in half with a razor. The two separate ends of that material were then pressed backed together at the sliced area using mild pressure from fingers. Afterwards all of the materials, both cut and uncut were placed into an oven at 75 °C for 24 hours to expose the materials to equivalent thermal history. Samples were then subjected to tensile tests.

Differential scanning calorimetry (DSC)

Glass transition temperatures and were measured using differential scanning calorimetry (DSC), and performed on a TA Instruments Q20 system with a heat cool heat cycle ranging from -40 °C to 160 °C. The heating rate was 10 °C per minute with data collected only from second heating cycle.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a TA instruments Q500. The experiments were performed using heating rate of 10 °C/min 500 °C a under nitrogen with a flow rate of 40 mL/min.

Dynamic mechanical analysis (DMA)-Frequency Sweep Methods

Frequency sweep dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 system equipped with a film tension clamp using an isothermal temperature/ frequency sweep test. Temperature was set to 30 °C with one minute of equilibration time prior to the experiment. Data was collected five points per decade with a strain of 0.3%, a preload force of 0.01 N.

Dynamic Mechanical Analysis (DMA) -Temperature Sweep Methods

Temperature sweep dynamic mechanical analysis (DMA) were performed on a TA Instruments Q800 system equipped with a film tension clamp using a temperature ramp/ frequency sweep test. The frequency was held constant at 1.0 Hz and the temperature ranged from 30 °C to 150 °C at a rate of 5 °C/minute. The test had one minute of equilibration time at 30 °C prior to the temperature ramp. The experiment was performed with a strain of 0.3%, a preload force of 0.01 N.

Dynamic Mechanical Analysis (DMA) -Creep and Creep Recovery Methods

A TA Instruments Q800 system equipped with a film tension clamp was used for creep and creep recovery experiments. The temperature was held at 30 °C. The test had one minute to equilibrate at 30 °C prior to applying stress. During the creep experiment a stress of 0.05 MPa was applied, with a preload force of 0.01N. The creep time was set for 60 minutes and the recovery time was set for 120 minutes.

Conductivity Methods

The resistance (R) was measured using a Keithely 2450 Source Measure Unit Instrument. The ohmmeter setting was used to determine specimen resistance. A 4-point probe system was used for all samples except poly(EA_{100}-FMA_7)-Br with 0.225 wt % CNTs due to the very low

conductivity of that specimen. The resistivity (ρ) was acquired by dividing the resistance by the length (l) of the material, and multiplying it by its cross sectional area (A).

$$\rho = \frac{R\,A}{l}$$

(S2)

Electrical conductivity (κ) was determined the inverse of the resistivity.

$$\kappa = \rho^{-1}$$

(S2)

Young's Modulus Calculation

An incompressible Ogden hyperelastic constitutive law[3] (eqn (S3)) was used to model the tensile response of the materials.

$$\sigma_{eng} = \frac{2G}{\alpha}\left[\lambda^{\alpha-1} - \lambda^{-1-\left(\frac{\alpha}{2}\right)}\right]$$

(S3)

σ_{eng} is the engineering stress. α is the strain hardening exponent. G is the shear modulus, and λ is the stretch ratio. G and α were found for each sample by fitting eqn (1) to the experimental mechanical data. Eventually, elastic modulus (Y) was found from eqn (S4) assuming an incompressible solid (v=0.5).

$$Y = 2G(1 + v)$$

(S4)

Molecular Dynamics Simulations

To prepare the initial configuration for the MD simulations, multiple polymer chains are placed in a simulation box, which is then compressed during a number of NPT molecular dynamics simulations to reach a desired box volume that is consistent with the polymer density of about 1 g cm−3. The nature of cross-linking that results after this procedure for the MD model setup is consistent with the cross-linking that is observed in the experiments: cross-linkers are randomly

distributed within the polymer network and each cross-linker, at the most, connects two polymer chains together. Additionally, if the desired system includes covalent bonds between the carbon nanotubes and the cross-linkers, 5% of the cross-linker beads will be allowed to form covalent bonds with the carbon nanotube beads, as they interact with the surface beads of the CNTs during the initialization process. Once the suitable configurations are established, in order to evaluate their mechanical behavior, we stretch the simulation domain by defining three different regions along the elongation axis: the bottom part of the simulation domain represents a fixed grip, and the top part the domain is moved with a fixed strain rate. The middle region is the stretching region where we calculate the overall stress based on individual atomic stresses to obtain the stress–strain curves.

Supplementary Data

Table S1: Typical Molecular Weight Data for Polymers determined by SEC using viscometric Universal Calibration.

Polymer	Conv. (%)	$M_{n\text{-Viscometry}}$	$M_{n\text{-NMR}}$-Primary Chains	M_w/M_n
poly(EA$_{100}$-FMA$_7$)-Lin	73	19000	9600	1.43
poly(EA$_{100}$-GMA$_7$)-Lin	97	16000	9880	1.19
poly(EA$_{100}$-FMA$_7$)-Br	81	28000	14000	1.87
poly(EA$_{100}$-FMA$_{4.5}$)-Br	86	23000	12000	1.68
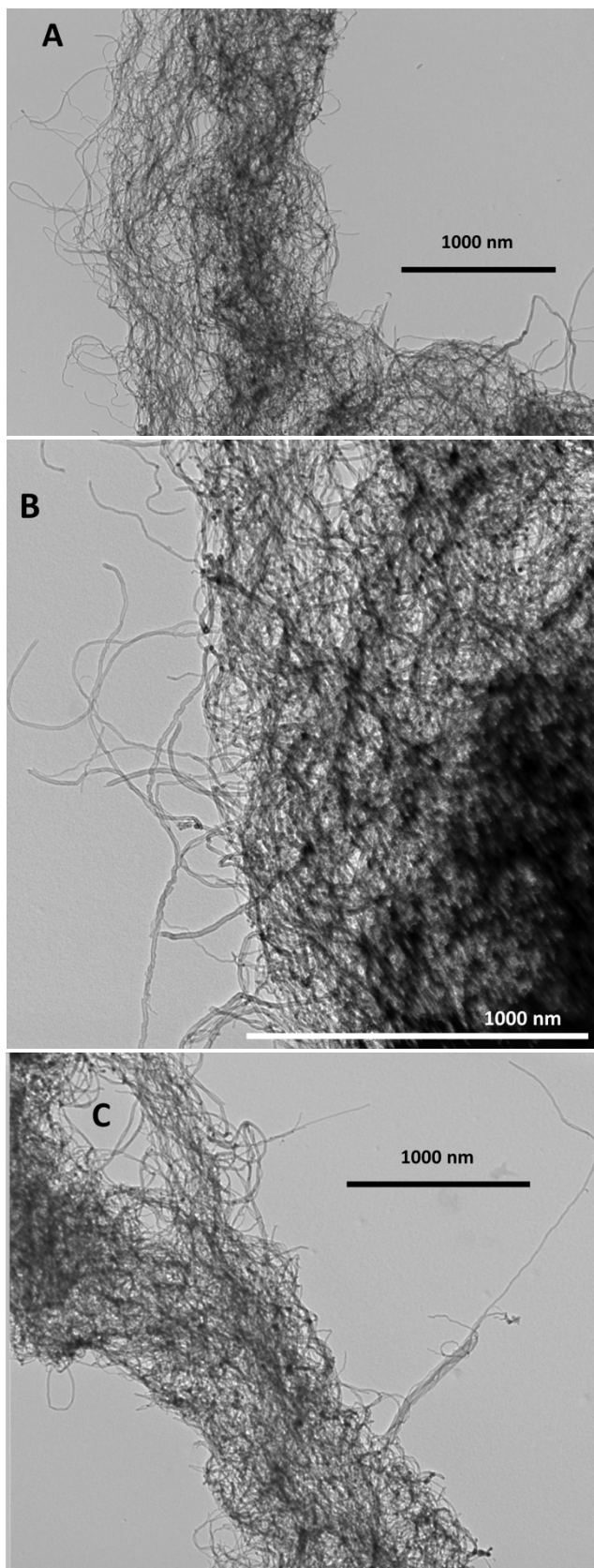
Figure S1: TEM of Carbon Nanotubes. A, B,C give different viewpoints of the grid.
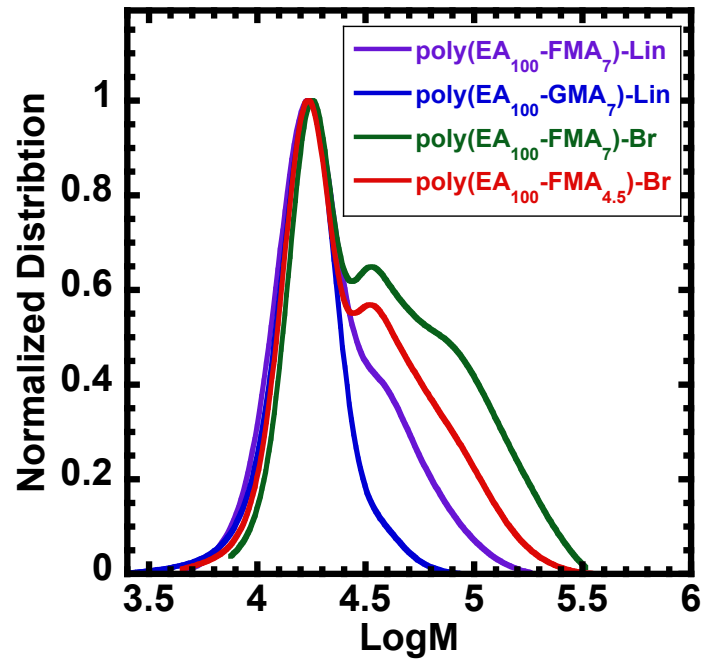
Figure S2: SEC traces of poly(EA$_{100}$-FMA$_7$)-Lin, poly(EA$_{100}$-GMA$_7$)-Lin, poly(EA$_{100}$-FMA$_7$)-Br, poly(EA$_{100}$-FMA$_{4.5}$)-Br.
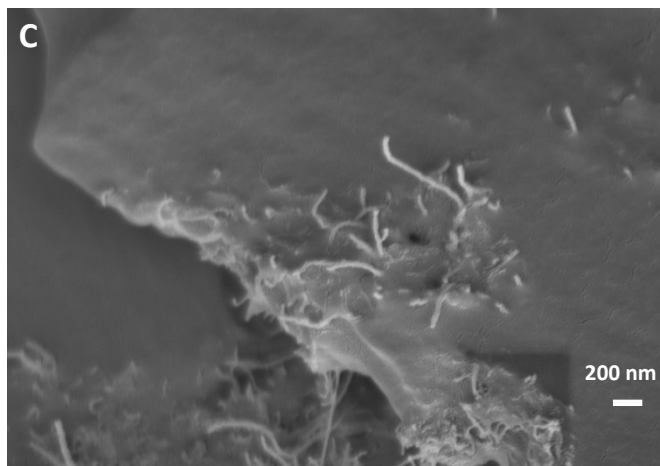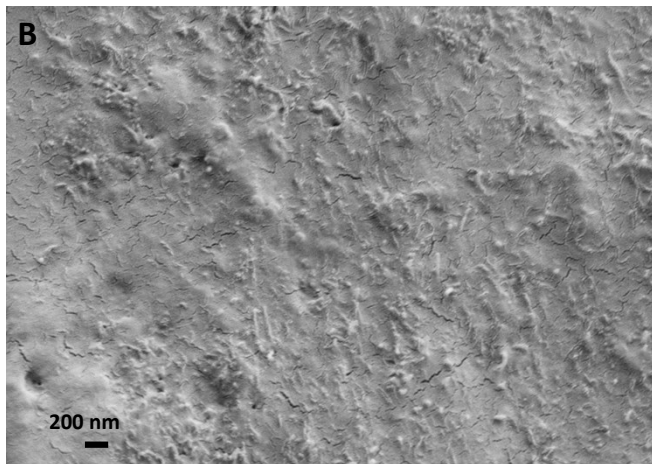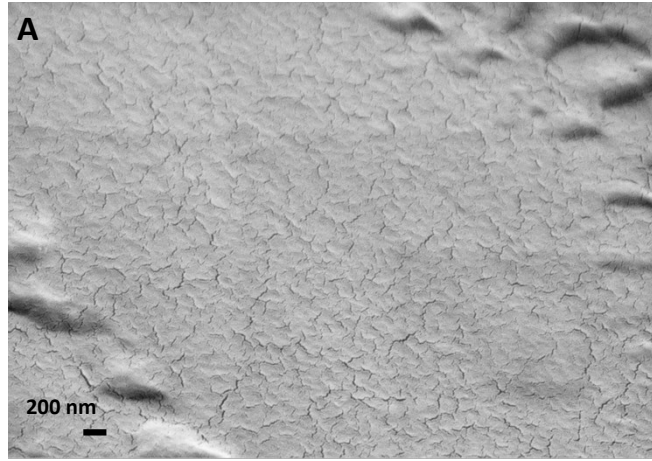
Figure S3: SEM images of poly(EA$_{100}$-FMA$_7$)-Br materials with) 0% and B &C) 0.9 wt% of CNT. B and C give different faces of the CNT based material.
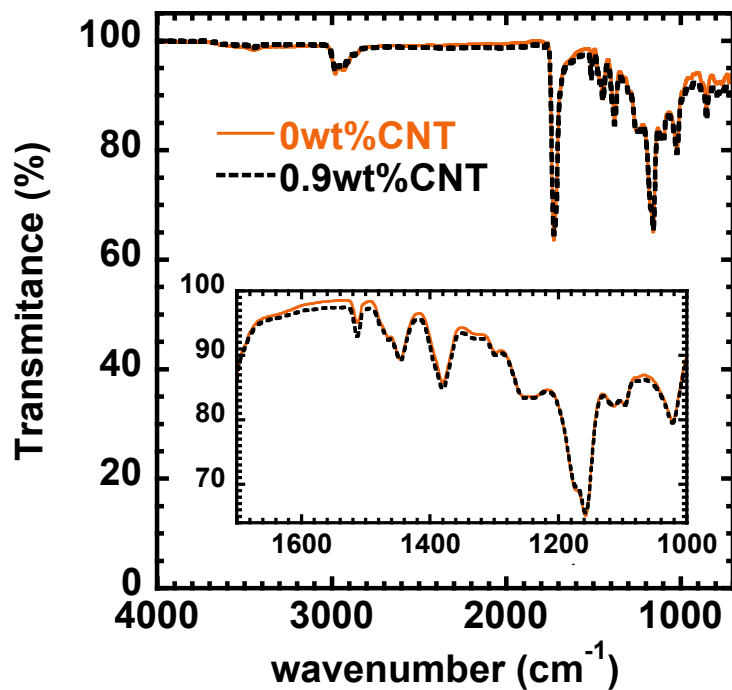
Figure S4: Typical infrared (IR) spectra of the poly(EA$_{100}$-FMA$_7$)-Br materials with 0 wt% and

0.9 wt% of CNT over the range of 4000 to 700 cm^{-1}. Inset: infrared (IR) spectra of the

poly(EA$_{100}$-FMA$_7$)-Br materials with 0 wt% and 0.9 wt% of CNT over the range of 1700 to 1000

cm^{-1}

Table S2: Proposed fourier transform infrared (FT-IR) spectroscopy peak assignments

based on literature assignments of poly(ethyl acrylate) materials.[4, 5]

Peak (cm^{-1})	Assignment
3300	Carboxylic Acid O-H Stretch
2980	C-H Alkane Stretch
1730	C=O Ester stretch
1520	Cyclic C=C Alkene stretch
1450	Methylene Group C-H Bend
1380	Methyl Group C-H Bend
1250	C-O Asymmetric Stretch
1150	C-O Ester Stretch
1020	C-O-C Stretch
850	C-H Bending
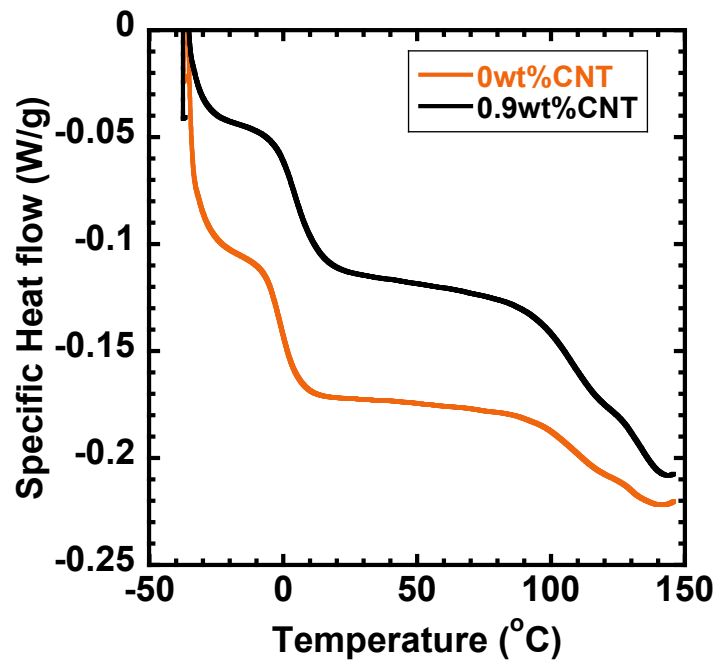
Figure S5: Typical differential scanning calorimetry (DSC) traces of the poly(EA$_{100}$-FMA$_7$)-Br materials with 0 wt% and 0.9 wt% of CNT.
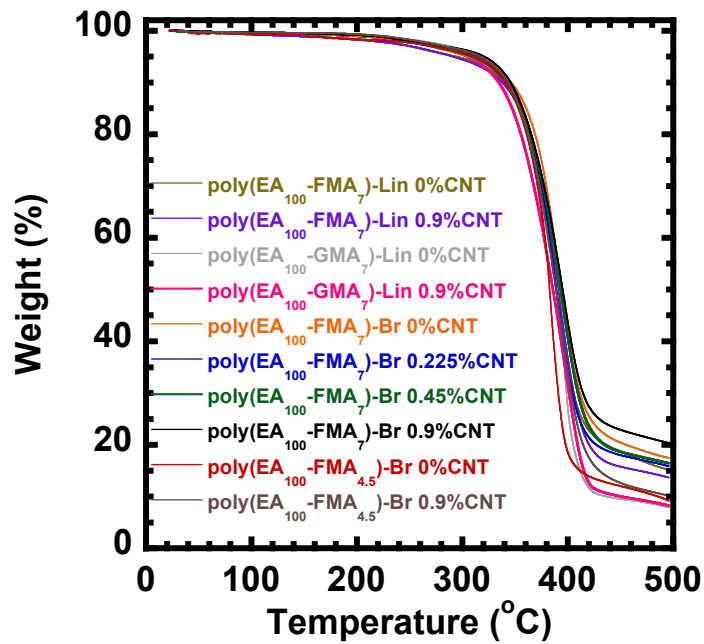
Figure S6: TGA analysis of all materials synthesized.
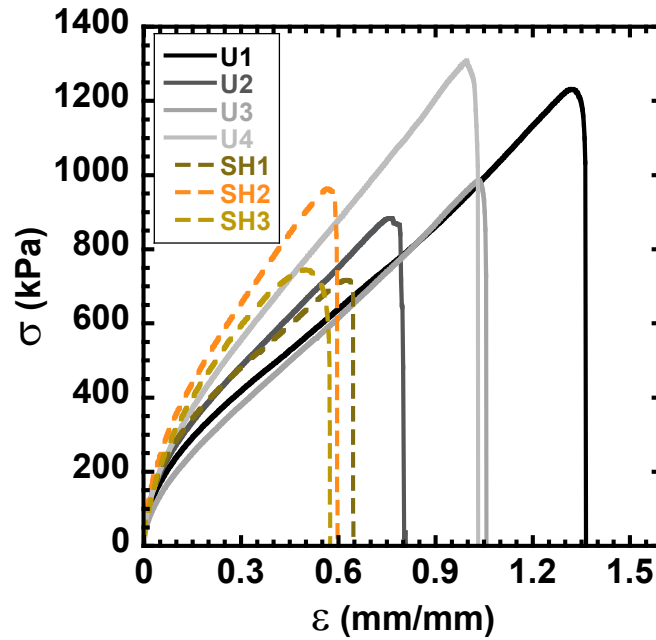
Figure S7: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Lin with 0 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
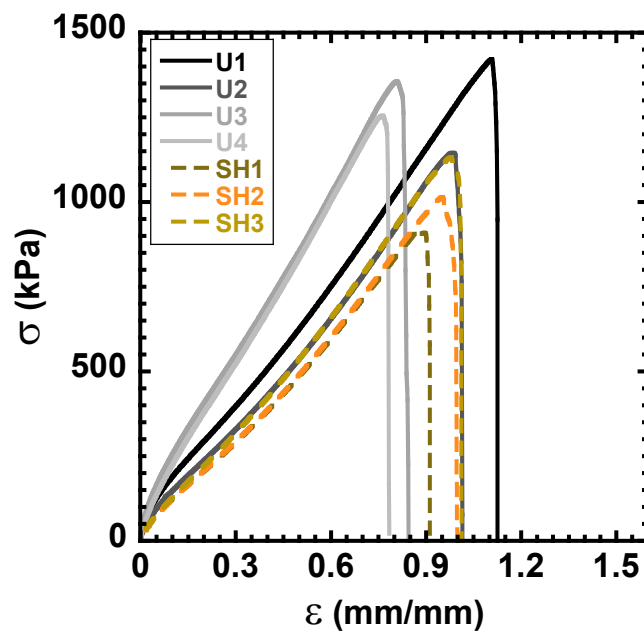
Figure S8: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Lin with 0.9 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
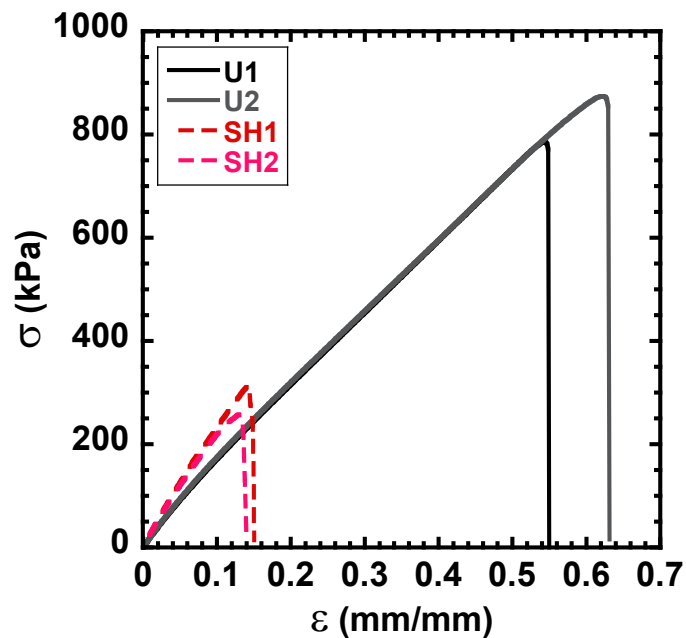
Figure S9: Typical stress (σ) vs strain (ε) curves for poly(EA$_{100}$-GMA$_7$)-Lin with 0 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
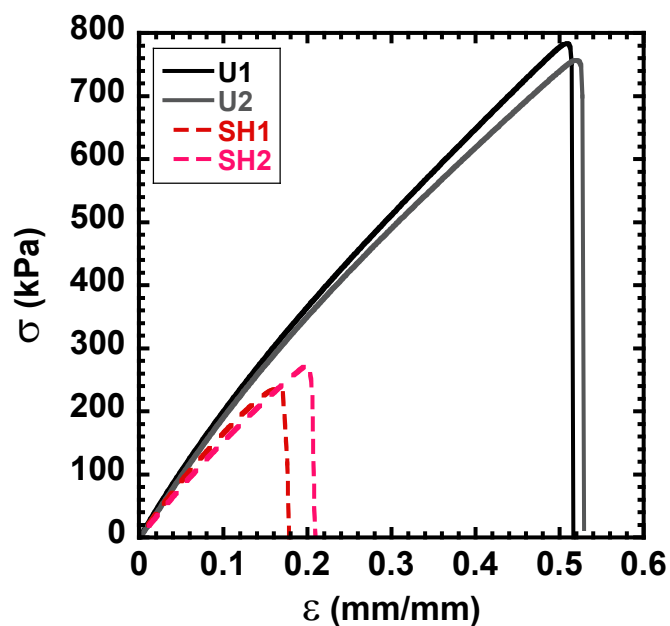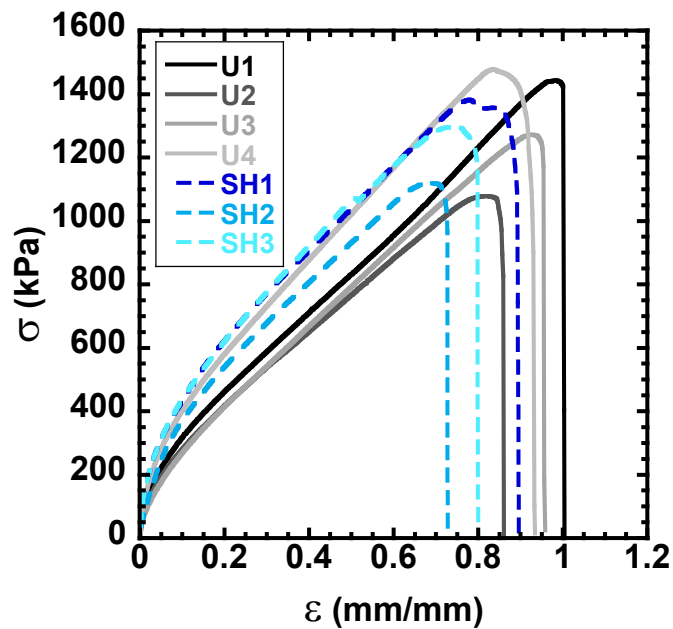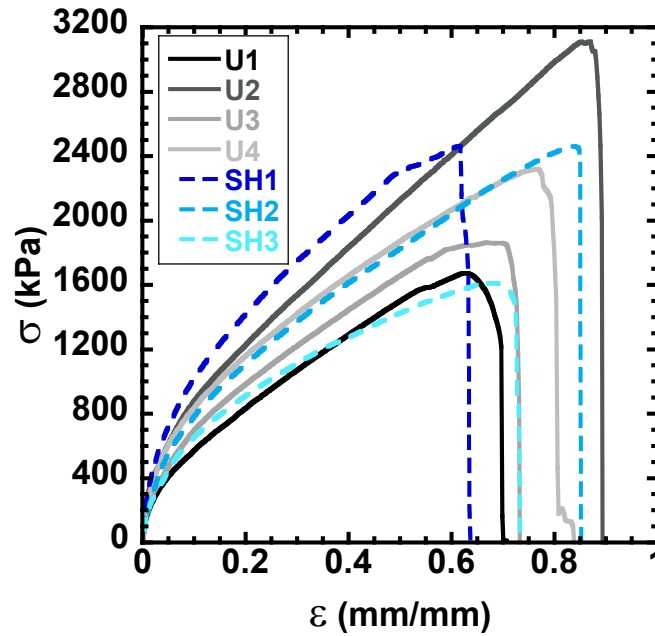

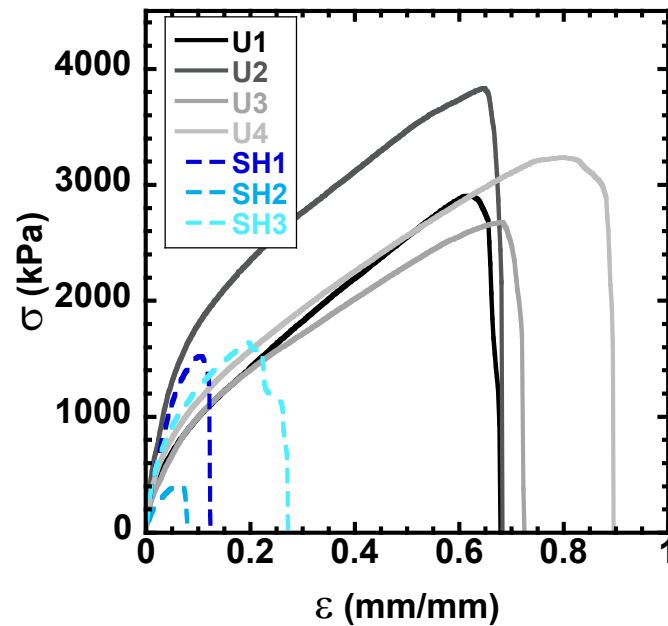Figure S10: Typical stress (σ) vs strain (ε) curves for poly(EA$_{100}$-GMA$_7$)-Lin with 0.9 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
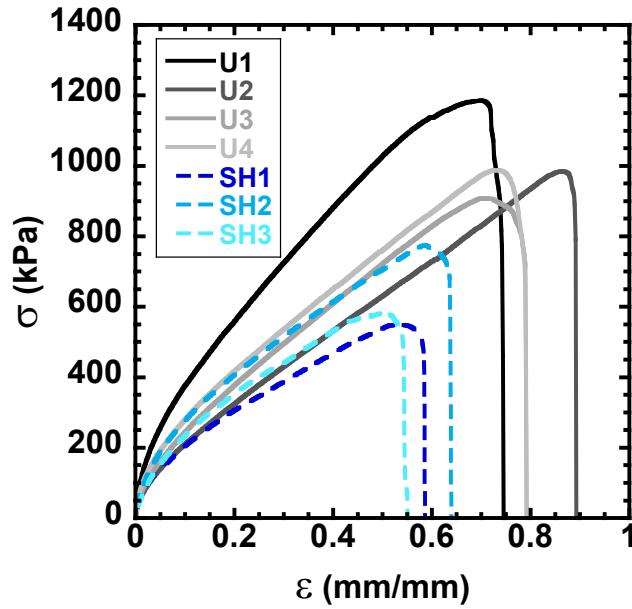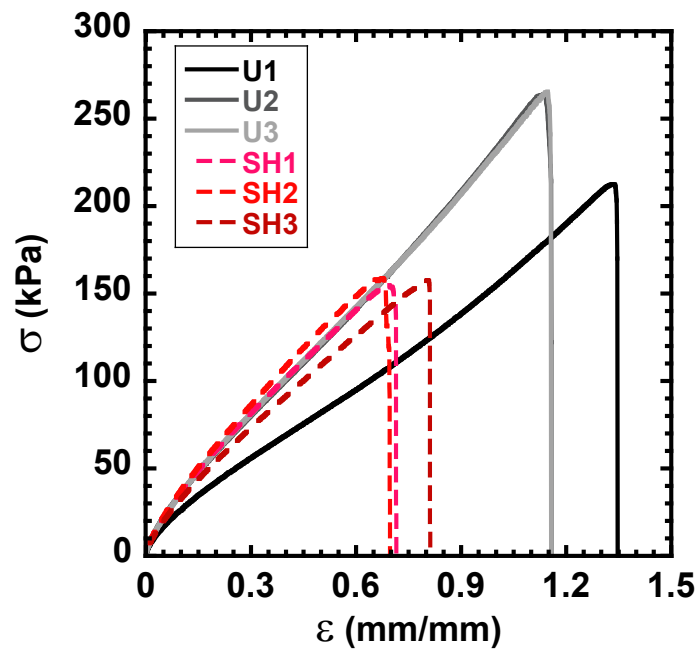
Figure S11: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Br with 0 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.

Figure S12: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Br with 0.225 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.

Figure S13: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Br with 0.45 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.

Figure S14: Typical stress (σ) vs strain (ε) curves for poly(EA_{100}-FMA_7)-Br with 0.9 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.

Figure S15: Typical stress (σ) vs strain (ε) curves for poly(EA$_{100}$-FMA$_{4.5}$)-Br with 0 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
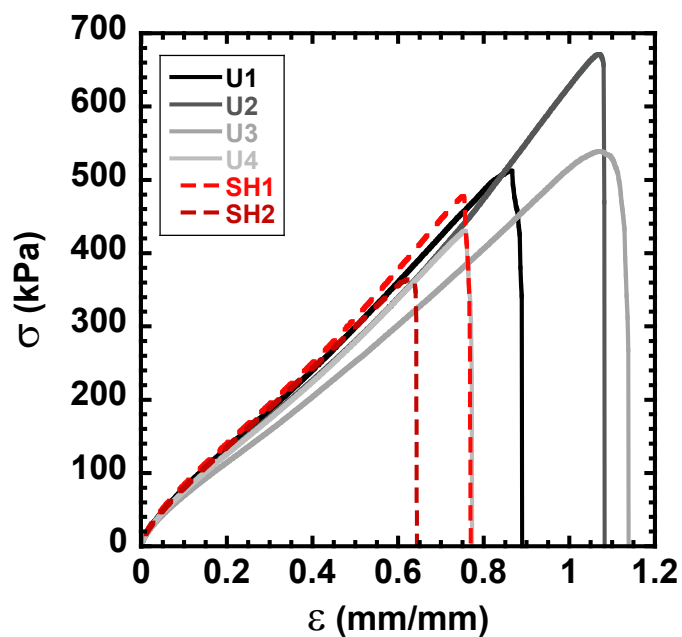

Figure S16: Typical stress (σ) vs strain (ε) curves for poly(EA$_{100}$-FMA$_{4.5}$)-Br with 0.9 wt% CNT materials that were either uncut (U) and 24h self-healed (SH) at 75 °C.
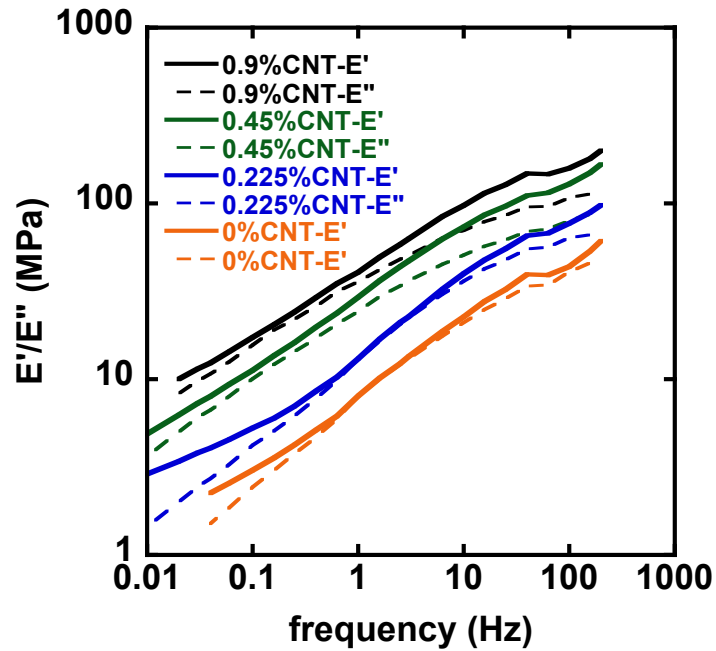
Figure S17: Frequency sweep data for materials of poly(EA$_{100}$-FMA$_7$)-Br with different weight percent loadings of CNT. Experiment was performed with 0.3% applied strain at a temperature of 30 °C.
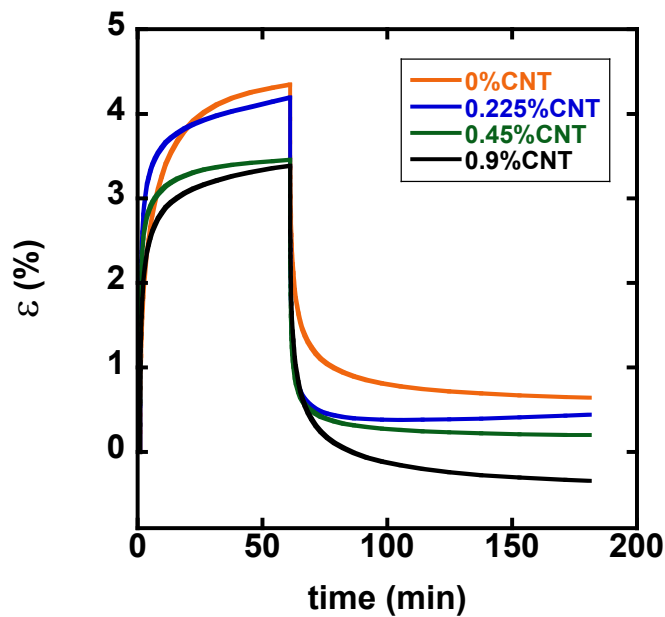

Figure S18: Creep and creep recovery data of poly(EA$_{100}$-FMA$_7$)-Br with different weight percent loadings of CNT. Creep experiment was performed with 50 kPa of applied stress at a
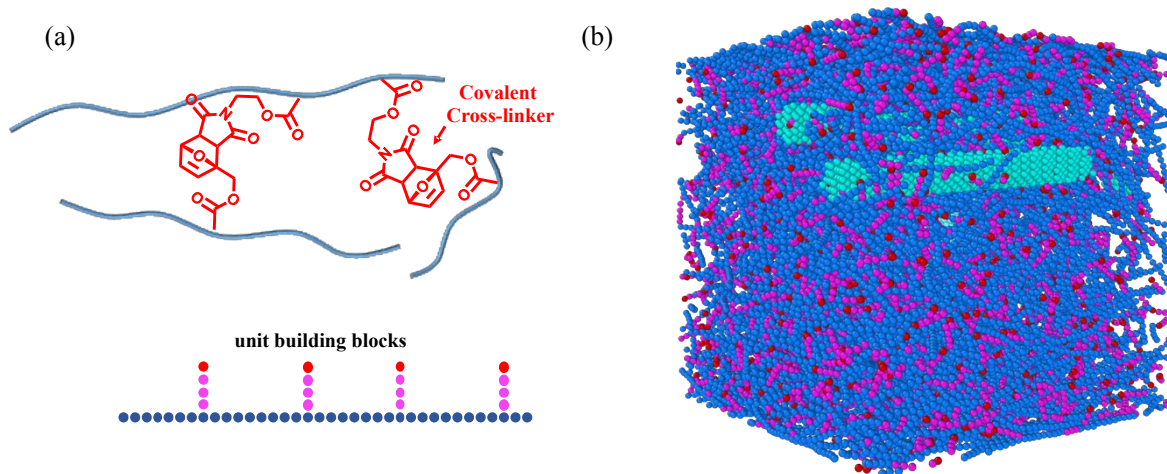
temperature of 30 °C.

Figure S19: (a) Schematic demonstration of the cross-linked polymer network and the covalent cross-linkers within the coarse-grained model. (b) Snapshot of Molecular Dynamics simulation of a system of covalently cross-linked polymer network reinforced with carbon nanotubes. The rigid cylindrical domains shown in cyan color represent carbon nanotubes embedded within the polymer network.

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