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Conductive Vitrimer Nanocomposites Enable Advanced and Recyclable Thermo-sensitive Materials

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Experimental details

Materials

Vanillin, epichlorohydrin (purity ≥99.9 %), tetrabutyl ammonium bromide, jeffamined230 (D230), jeffamined400 (D400), and $Zn(Ac)_2$ were bought from Aladdin Reagent, China. Ethanol, sodium hydroxide were supplied by Sinopharm Chemical Reagent Co., Ltd., China. Carbon black (**CB**) 101 with particle size around 95 nm was obtained from Evonik Degussa, Germany. Bisphenol A epoxy resin (DER331, epoxide equivalent 182～192 g/eq) was supplied by DOW Chemical Company, USA. Pripol 1040 was provided by Uniqema. It is a mixture of derivatives of C18 fatty acids containing about 23 wt.% dimers and 77 wt.% trimers. 3-Aminopropyltriethoxysilane (KH550) was bought from Hongjia Chemical Co., Ltd., China. All the chemicals or materials were used as received.

Preparation of M-230 and M-400

The preparation routes of M-230 and M-400 are shown in Fig. 1a and Fig. S1. Except for the different curing agents, the preparation route of M-230 and M-400 was the same. Take the preparation of M-230 as an example, vanillin-based epoxy monomer 3-methoxy-4-(oxiran-2-ylmethoxy) benzaldehyde (MB) was synthesized from vanillin and epichlorohydrin according to our previous work.[1] MB (5 g, 0.024 mol) and D230 (4.15g, 0.018 mol) were mixed together and heated at 105 ℃ until MB was completely melted, then it was poured into a poly (tetrafluoroethylene) mold and cured at 100 °C for 2 h (Remove bubbles in the first 30 min) and post-cured at 150 ℃ for 2 h and 170 ℃ for 2 h to get M-230 film with thickness of approximately 300 μm. With the same method, DER331 was cured with D230 (or D400) (the molar ratio of N–H to epoxy group was 1:1) to achieve D-230 (or D-400) (Fig. S2).

Preparation of D-P 5% and D-P 0.1%

D-P 5% and D-P 0.1% were prepared through two steps according to the reported method with some modification (Fig. S3).[2] For the first step, 10 g of Pripol 1040 (296 g/mol $_{COOH}$) and the catalyst $Zn(Ac)_2$ at different concentrations of 0.1 mol% (for D-P 0.1%) and 5 mol% (for D-P 5%) to the COOH groups were placed in a 50-mL round-bottom flask at 80 °C. Then the mixture was gradually increased from 80 °C to 180 °C under vacuum. Evolution of acetic acid demonstrated that the fatty acids replaced the acetates as ligands of Zn^{2+}. When no gas was observed and catalyst particles were fully solubilized (around 3 h), the modified Pripol 1040 was obtained. 5 g of DER331 and 7.92 g of modified Pripol 1040 (molar ratio between -COOH and epoxy is 1:1.2) were mixed together and heated to 130 °C until the mixture is homogeneous. Then the mixture was poured into a poly (tetrafluoroethylene) mold and cured at 130 °C for 2 h (remove bubbles in the first 10 min) and post-cured at 150 ℃ for 2 h and 170 ℃ for 2h to get D-P 5% or D-P 0.1% film with thickness of approximately 300 μm.

Surface modification of CB

Prior to use, the surface of CB was firstly modified by using 1% weight ratio of silane coupling agent (KH550) to improve the compatibility and dispersion in the vitrimer matrices. KH550 was hydrolyzed in ethanol/water (v:v, 4:1) mixed solvent by magnetic stirring for 30 min, and CB was evenly dispersed in ethanol via sonication for 30 min. Then the hydrolyzed KH550 and dispersed CB were mixed together via 3000 rpm mechanical stirring for 5 h to enable the coupling agent to evenly cover the CB surface. After vaporizing the solvent, the silane coupling agent was further reacted with CB at 100 ℃ in a vacuum oven for 1 h and then CB was filtered by the distilled water and then dried in a vacuum oven for 5 h.

Preparation of nanocomposites

The preparation routes of M-230-CB, M-400-CB, D-230-CB, D-400-CB, D-P-CB 5% and D-P-CB 0.1% are shown in Fig. S1, Fig. S2 and Fig. S3. Except for the different polymer matrices, the preparation routes of all samples are the same. Take the preparation of M-230-CB as an example, the pre-cured vitrimer was obtained by mixing the MB (2 g, 0.0096 mol) and D230 (1.66 g, 0.0064 mol) together and heating at 105 ℃ until MB was completely melted. Pre-cured vitrimer and CB (20 wt.% of pre-cured vitrimer) were mixed together distributed in 20 mL of ethanol via sonication with 600 W power for 30 min. Then the mixture was put on a 70 ℃ heating plate and mechanically stirred with 3000 rpm until the viscosity increased. Subsequently the mixture was placed in a tetrafluoroethylene mold and vaporizing solvent at 70 ℃ in a vacuum oven for 1 h. Finally, M-230-CB film with thickness of approximately 300 μm was obtained via hot pressing at 120 ℃ for 1 h and post-cured at 150 ℃ and 170 ºC for 2 h, respectively.

Stress relaxation

Stress relaxation measurements on M-230, M-230-CB, M-400-CB, D-P-CB 5% samples were conducted on a rotational rheometer HR-3 (TA instruments, America) with different temperatures by applying a constant shear strain of 1%. The axial force is controlled at around 1N. The relaxation time τ* was calculated as time required for the initial modulus to decrease to 1/e. τ* s followed the Arrhenius law with temperature (eq. S1) as follows:[3]

Equation S1:

$$\tau^*(T) = \tau_0\, exp\,(E_a/RT)$$

where, τ_0 is the characteristic relaxation time at infinite temperature, T is the experimental temperature, E_a is the activation energy of the bond exchange process, and R is the universal gas constant. The topology freezing temperature (T_v) is usually considered as the temperature at which the viscosity becomes higher than 10^{12} Pa s.[4,5] Here, T_v is considered the temperature at which the relaxation time, τ*, is 10^6 s.[4]

Reprocessing recycle

A plate vulcanizer was used to carry out the reprocess recycling test for three cycles. The M-230-CB film was cut into small pieces and placed between two steel sheets covered with two tetrafluoroethylene films and hot pressed at 150 °C under a pressure of 10 MPa for 30 min. After cooling to room temperature, recycled films were obtained. The FTIR spectra and PTC effect before and after three cycles reprocessing were tested.

Chemical recycle

M-230-CB film with dimension of 10 mm × 10 mm × 0.3 mm was degraded in 5 mL of 0.05 M HCl ethanol/H_2O (8/2, v/v) solution at room temperature for 5 h. The degraded solution was processed via sonication with 600 W power for 30 min and then put on a 70 ºC heating plate and mechanically stirred with 3000 rpm until the viscosity increased, subsequently placed in a tetrafluoroethylene mold and put in a vacuum oven at 70 ºC for 1 h to vaporize solvent, and a pre-recycled M-230-CB was gotten. Then a recycled M-230-CB film was obtained via putting the pre-recycled M-230-CB in 0.05 M NaOH aqueous solution at room temperature for 5 h and in deionized water for 5 h, and then evaporating water at 80 °C for 2 h and being post-cured at 150 °C for 1 h. The FTIR spectra and PTC effect before and after three cycles of chemical recycle were tested.

Characterization

Fourier transform infrared (FTIR) measurements were performed on a Micro-FTIR machine Cary620 (Agilent, America), the infrared spectrum of the samples is measured directly with a diamond probe. The morphology of the samples was observed by scanning electron microscopy (SEM, Thermo scientific Verios G4 UC, America) and transmission electron microscopy (TEM, JEOL2100, Japan). For SEM, the samples were fractured in liquid nitrogen and the fractured surface was sputtered with gold before SEM observation. For TEM, the samples were cut to 70 nm thickness. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere on a DSC214 differential scanning calorimeter (NETZSCH, Germany). Samples (8-10 mg) were heated from -30 to 200 °C at a heating rate of 10 °C min^{-1} and held at 200 °C for 5 min to eliminate thermal history, and then they were cooled to -30 °C at a cooling rate of 10 °C min^{-1} followed by being heated again to 200 °C at a rate of 10 °C min^{-1}. The T_g was obtained from the second heating curve. Tensile tests were carried out on a Z1.0 tensile machine (Zwick, Germany). Testing samples were cut into dog-bone shapes and tested at a cross-head speed of 2 mm min^{-1}. Thermogravimetric analysis (TGA) was carried using a Mettler-Toledo TGA/DSC1 thermogravimetric analyzer (METTLER TOLEDO, Switzerland) with approximately 5 mg samples heated from 50 to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Dilatometry test was performed on a thermomechanical analyzer TMAF3 (NETZSCH, Germany). Rectangular samples (5 cm × 5mm × 0.3mm) were measured while applying a heating rate of 5 °C min^{-1} from 25 to 220 °C with a weak elongational stress of 0.01 MPa applied to avoid buckling. The room-temperature electrical conductivity was measured by the four-point probe method with a ST-2258C multifunction digital four-probe tester (Suzhou Jingge Electronic Co., Ltd., China). The PTC effect of various composites was tested using the two-terminal method by heating and cooling samples at a heating and cooling rate of 5 °C min^{-1} on a temperature-controlled plate, and a digital multimeter UT533 (Uni-Trend, China) was connected to the samples. The two sides of the samples were painted uniformly by one thin silver paste as an electrode to reduce the contact resistance and then were dried in the oven for 1 h.

Supplemental Figures and Tables

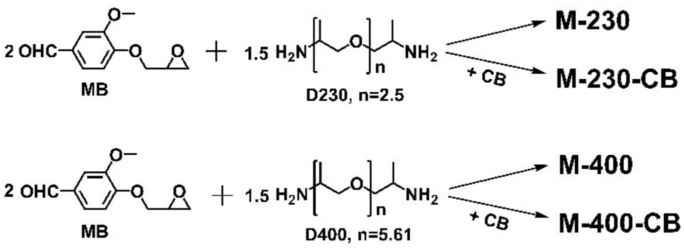

Fig. S1 Synthetic routes of M-230, M-400, M-230-CB, and M-400-CB.

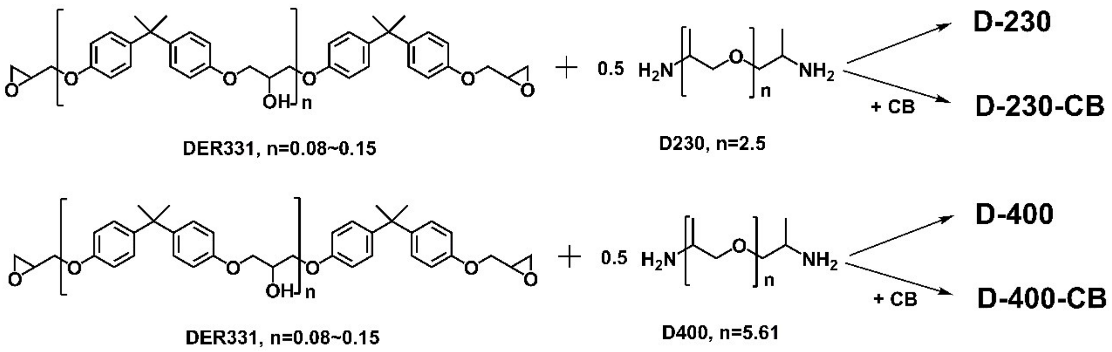

Fig. S2 Synthetic routes of D-230, D-400, D-230-CB, and D-400-CB.

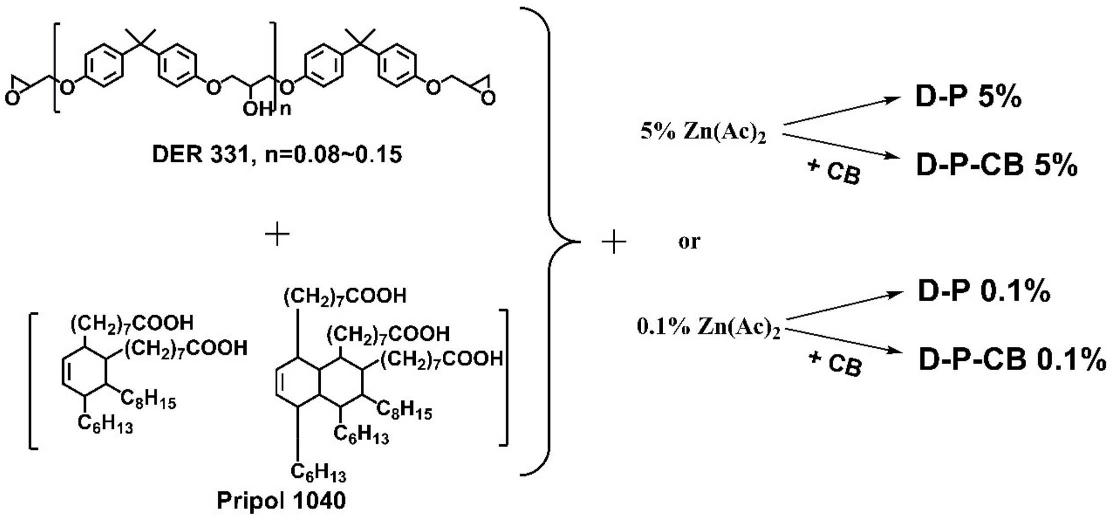

Fig. S3 Synthetic routes of D-P 5%, D-P 0.1%, D-P-CB 5%, and D-P-CB 0.1%.

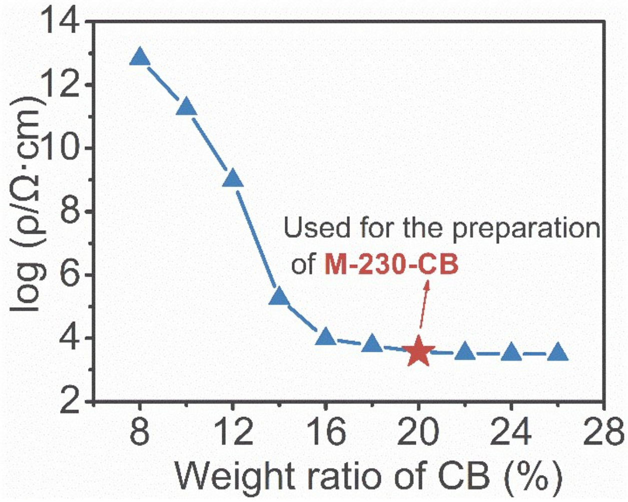

Fig. S4 The percolation curves of M-230/CB composites with different CB loading.

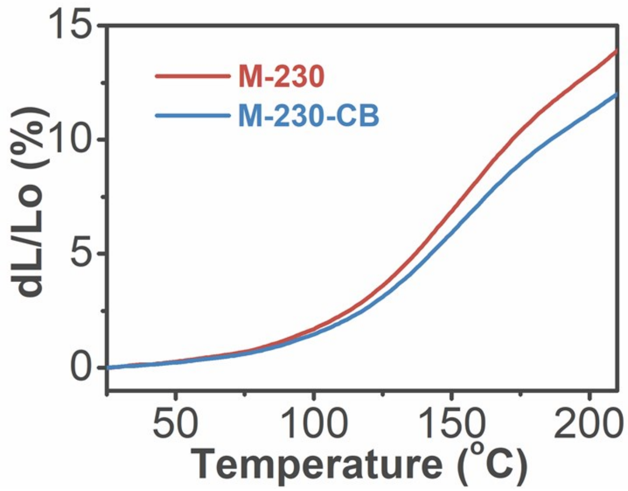

Fig. S5 Dilatometry test of M-230 and M-230-CB from 25 to 210 °C at a heating rate of 5°C min^{-1}.

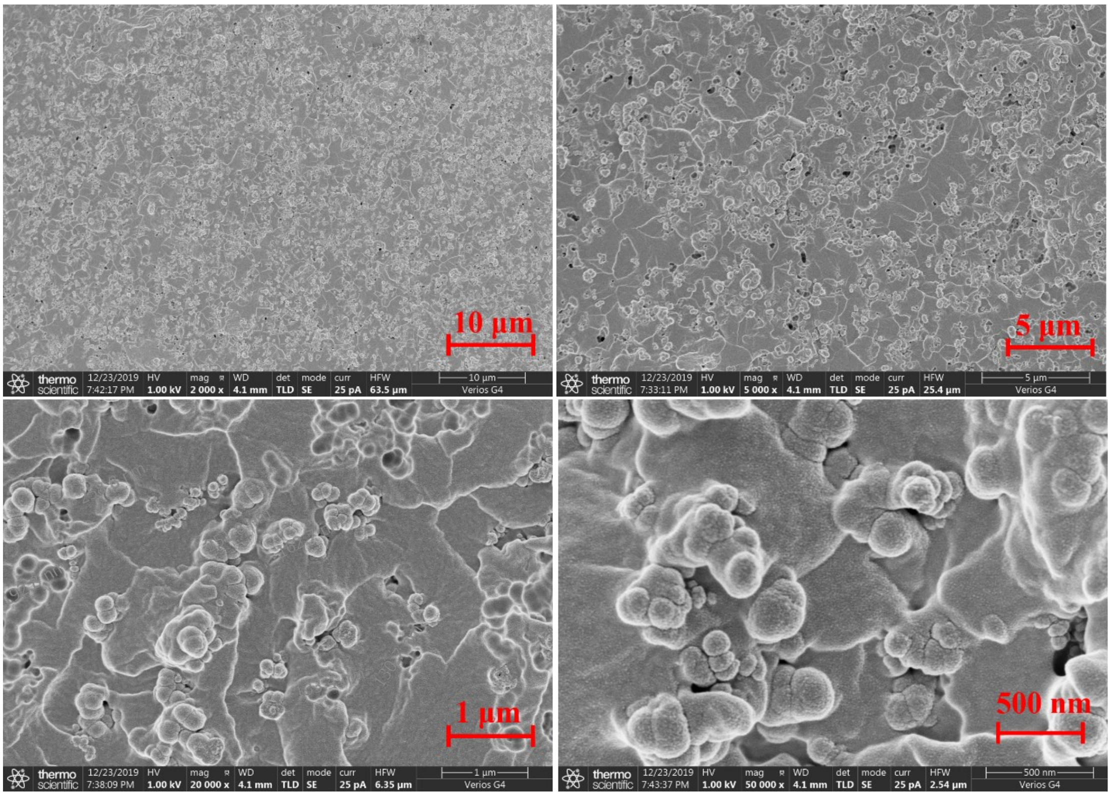

Fig. S6 SEM images of the cross-section surface of M-230-CB with different magnification.

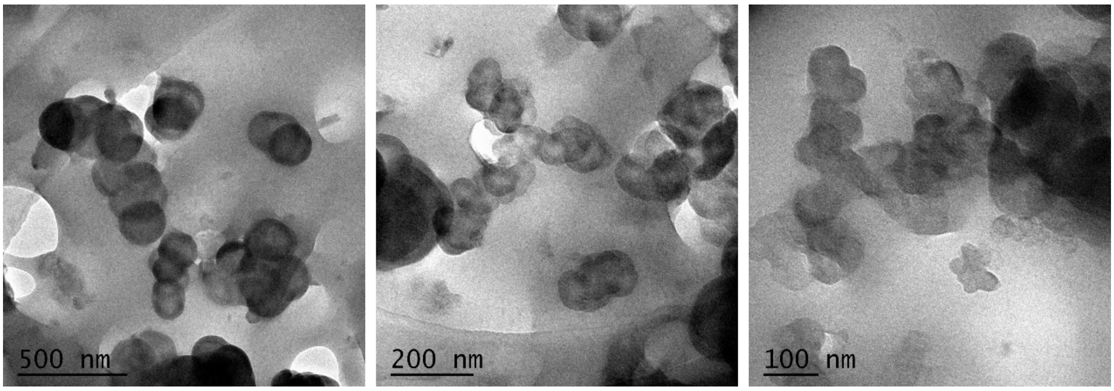

Fig. S7 TEM images of M-230-CB with different magnification.

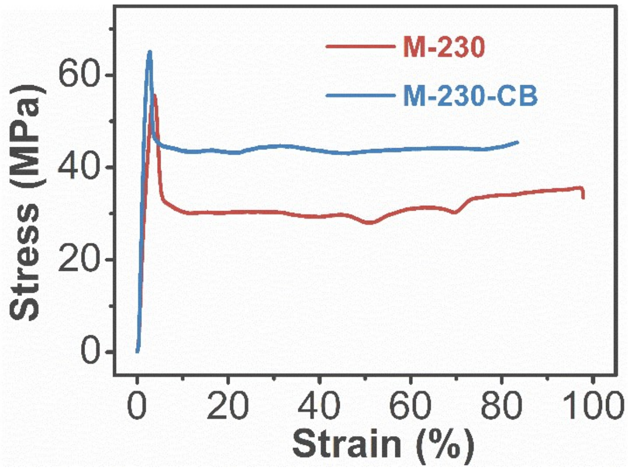

Fig. S8 Representative tensile stress−strain curves of M-230 and M-230-CB.

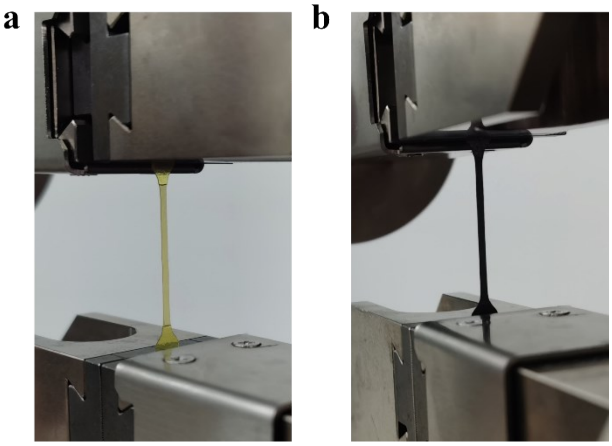

Fig. S9 Photos of the narrow neck formation of a) M-230 and b) M-230-CB during tensile test.

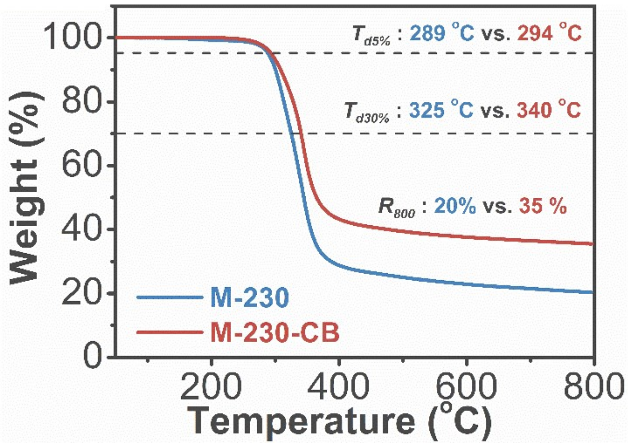

Fig. S10 TGA curves and data of M-230 and M-230-CB under N_2 atmosphere from 50 to 800 °C.

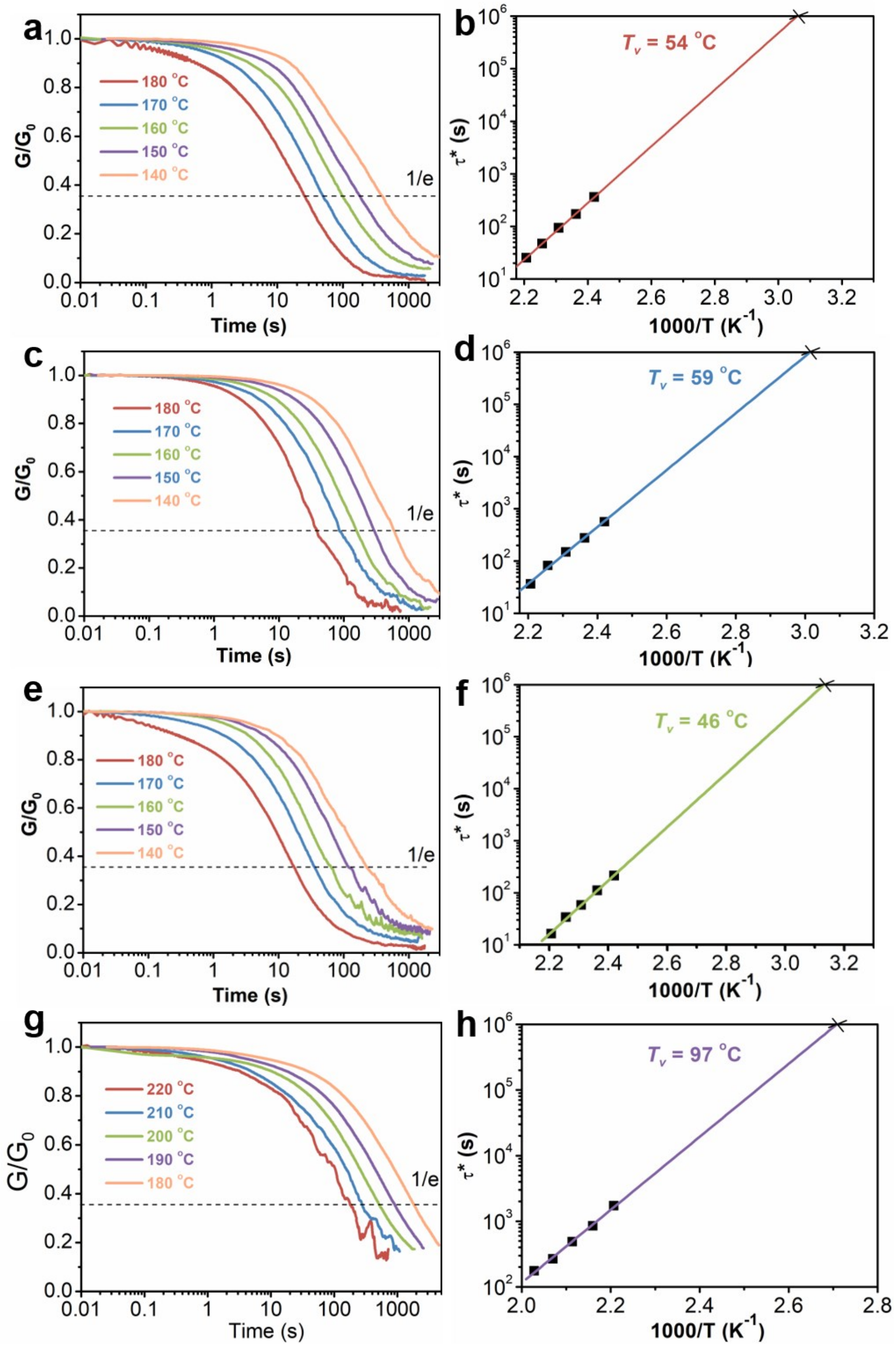

Fig. S11 Normalized stress relaxation curves of a) M-230, c) M-230-CB, e) M-400-CB and g) D-P-CB 5%. Arrhenius analysis of the characteristic relaxation time, τ*, versus 1000/T for b) M-230, d) M-230-CB, f) M-400-CB and h) D-P-CB 5%.

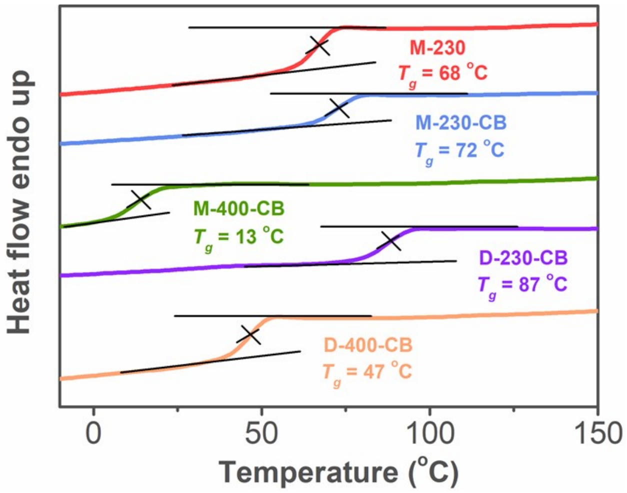

Fig. S12 Non-isothermal DSC curves of different samples.

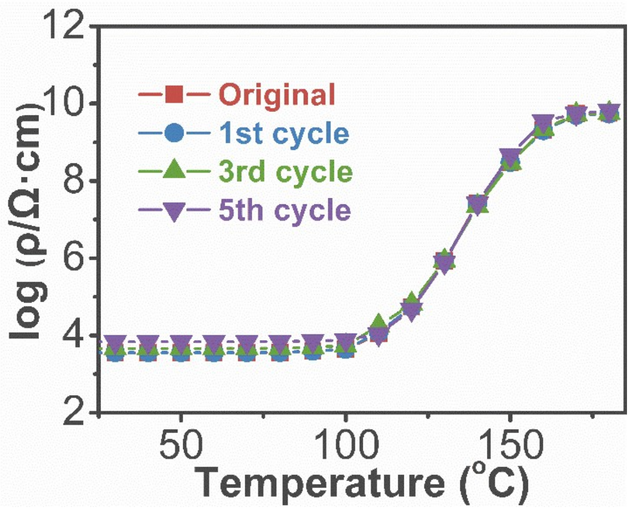

Fig. S13 Temperature-dependent logρ curves for M-230-CB during five heating–cooling cycles from 25 °C to 180 °C with a heating or cooling rate of 5 °C min^{-1}.

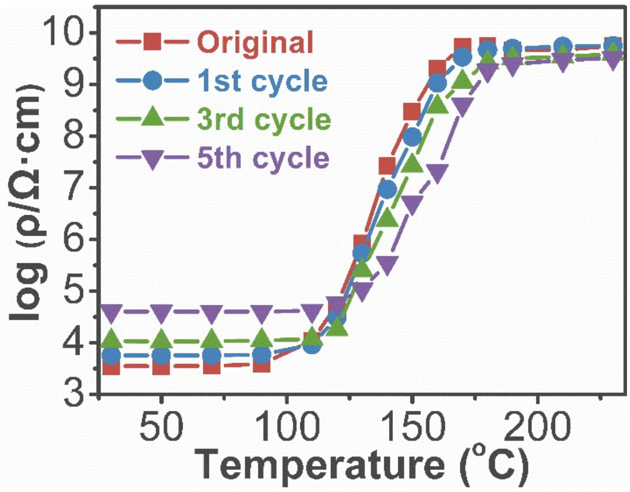

Fig. S14 Temperature-dependent logρ curves for M-230-CB during five heating–cooling cycles from 25 °C to 230 °C with a heating or cooling rate of 5 °C min^{-1}.

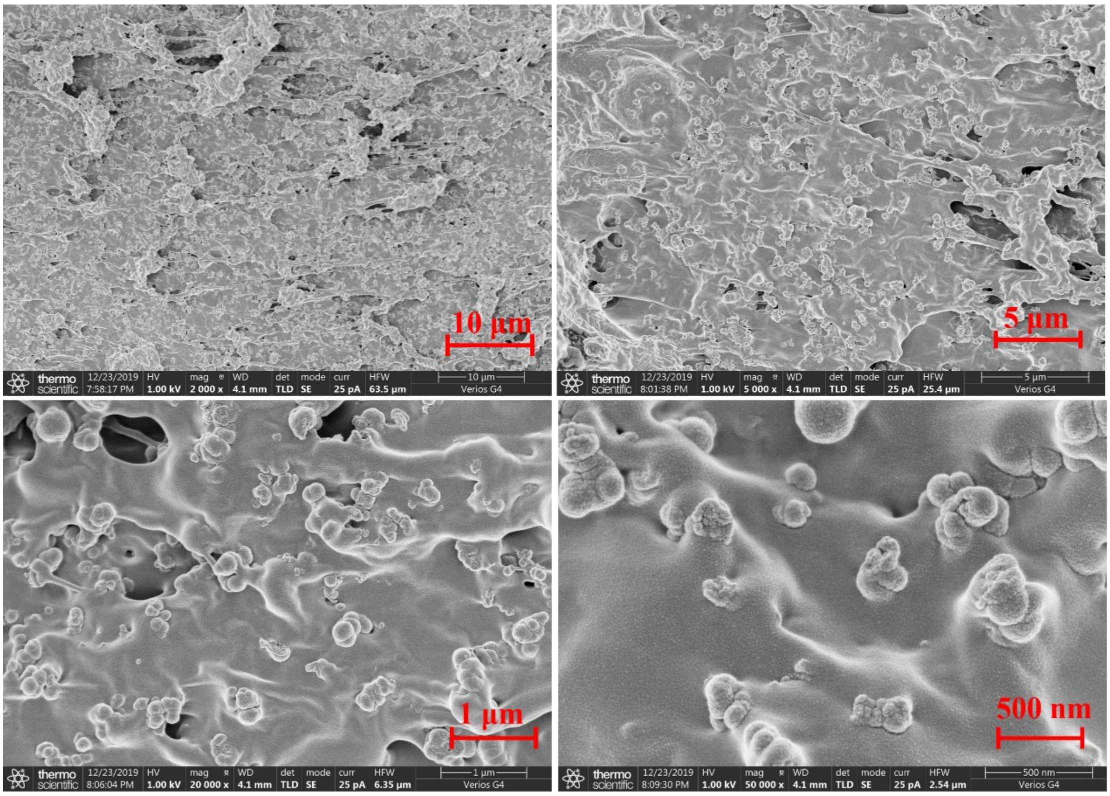

Fig. S15 SEM images of the cross-section surface of M-400-CB with different magnification.

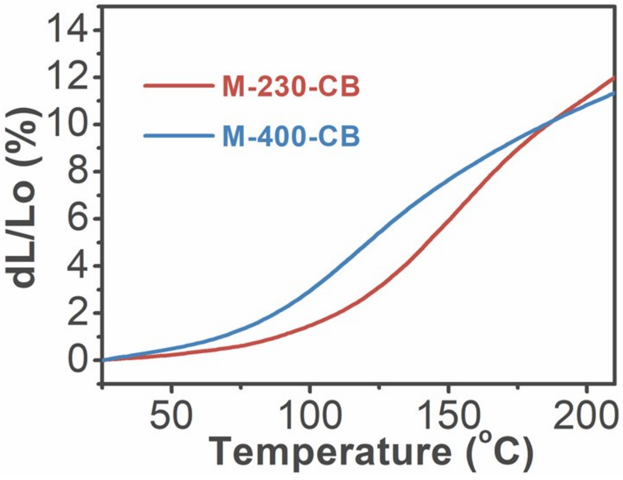

Fig. S16 Dilatometric curves of M-230-CB and M-400-CB.

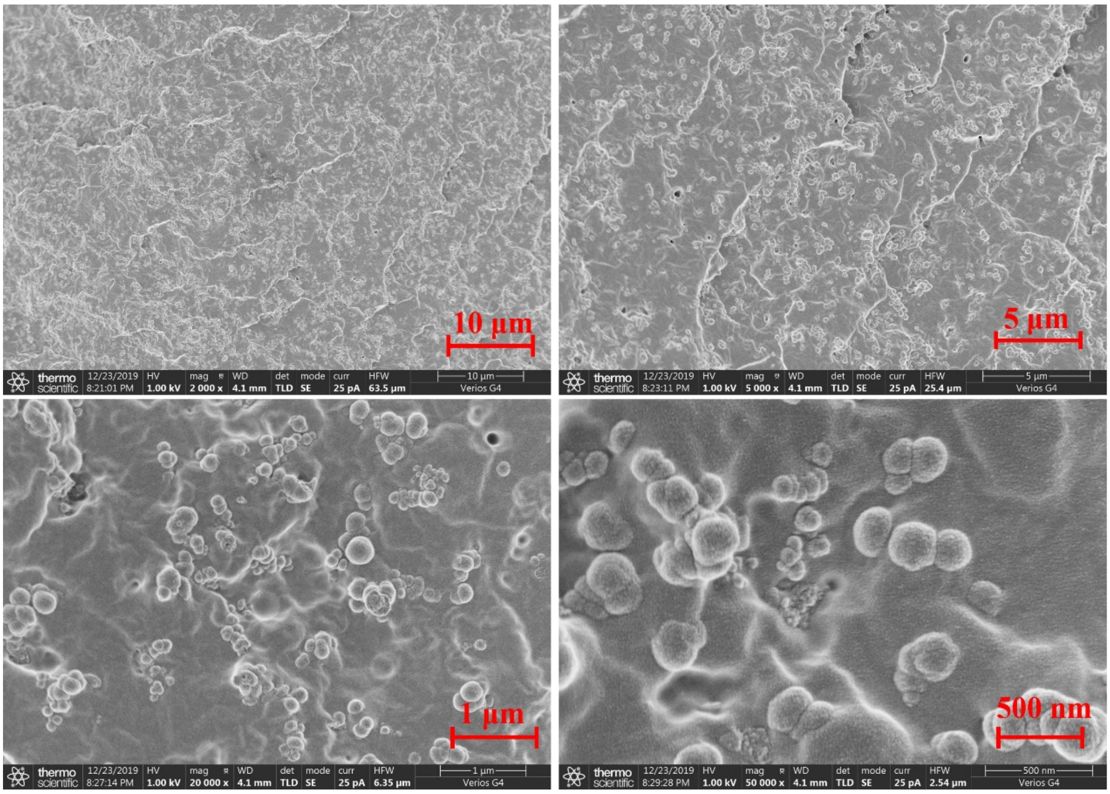

Fig. S17 SEM images of the cross-section surface of D-P-CB 5% with different magnification.

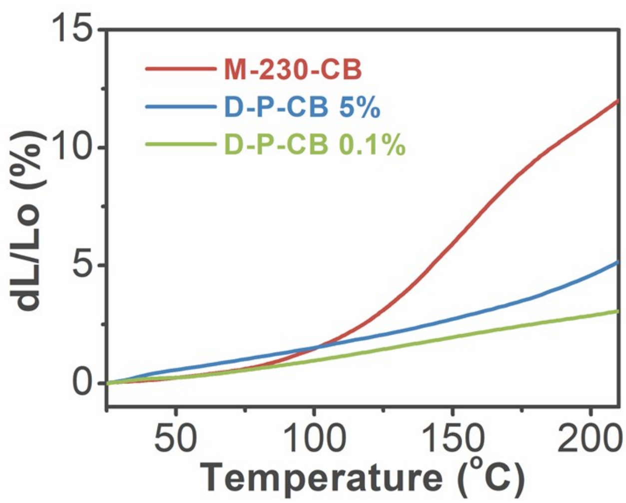

Fig. S18 Dilatometric curves of M-230-CB, D-P-CB 5% and D-P-CB 0.1%.

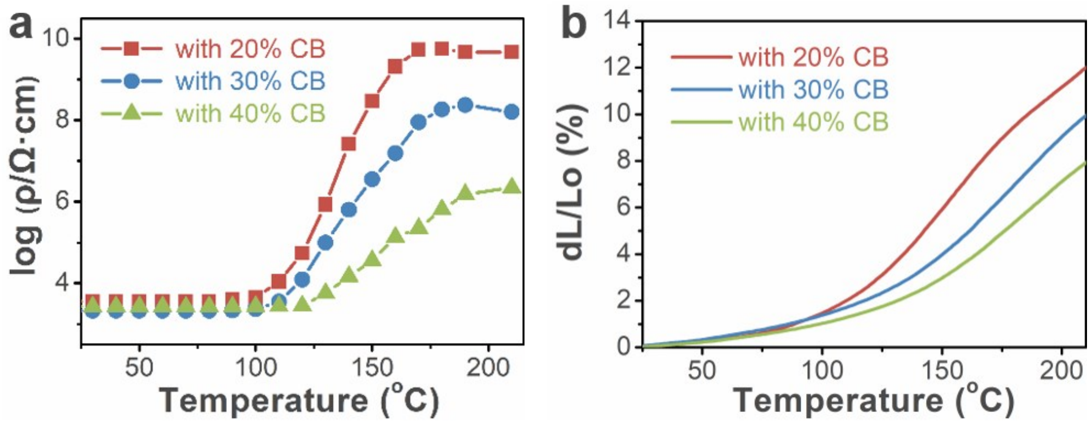

Fig. S19 a) Temperature-dependent logρ curves and b) dilatometric curves for M-230/CB composites with different CB loading from 25 °C to 230 °C with a heating rate of 5 °C min^{-1}

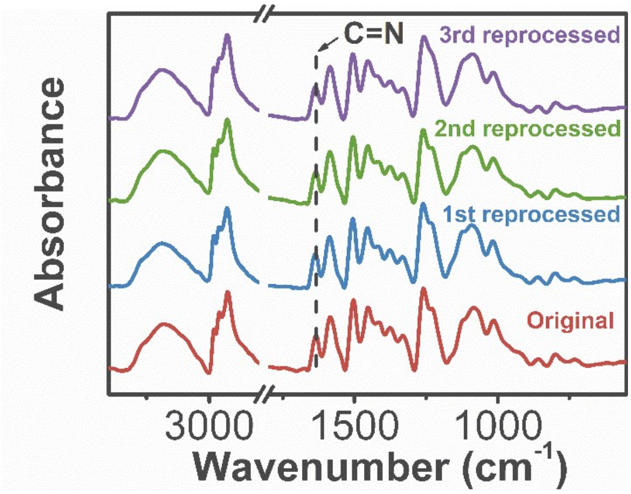

Fig. S20 FTIR spectra of original and reprocessed M-230-CB.

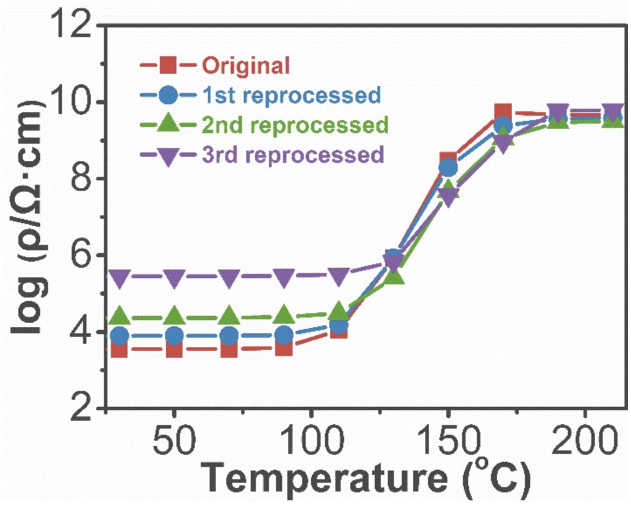

Fig. S21 Temperature-dependent logρ curves for M-230-CB during three reprocessing cycles.

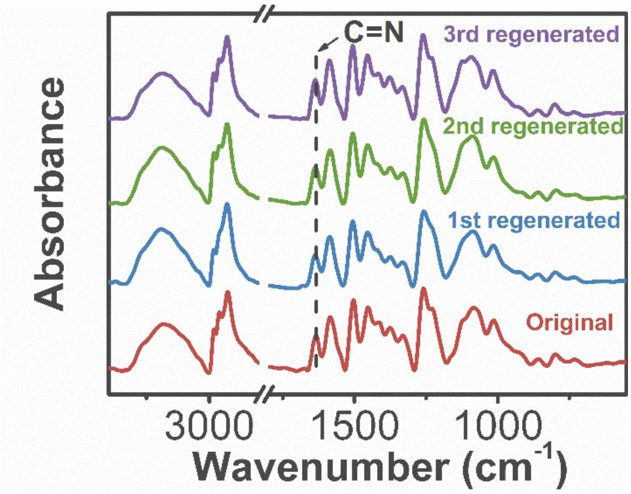

Fig. S22 FTIR spectra of the original and regenerated M-230-CB.

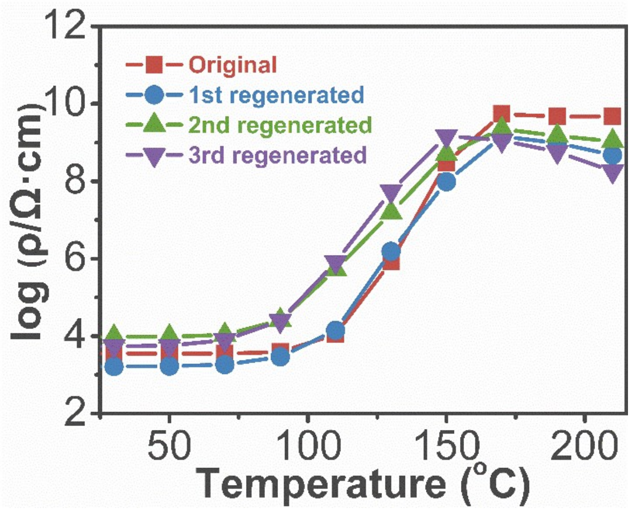

Fig. S23 Temperature-dependent logρ curves for M-230-CB during three chemically recycling cycles.

Table S1 Volume resistivity at room temperature (ρ at RT), T_g, T_v, T_s, and PTC intensity (I_{PTC}) for different samples.

Samples	ρ at RT (Ω·cm)	$T_g{}^a$ (°C)	$T_g{}^b$ (°C)	T_v (°C)	T_s (°C)	I_{PTC}
M-230-CB	3530	72	103	59	112	6.2
M-400-CB	1140	13	-	46	93	5.3
D-P-CB 5%	8330	-	-	97	142	3.5
D-P-CB 0.1%	35100	-	-	-	-	0.6
D-230-CB	2390	47	46	-	49	2.5
D-400-CB	7930	87	87	-	88	2.6

a: obtained from DSC test; b: obtained from dilatometry.

Table S2 Volume resistance at room temperature (*ρ* at RT), and PTC intensity (I_{PTC}) for M-230-CB before and after repeatability test and recyclability test.

Samples	ρ at RT (Ω·cm)	I_{PTC}	Repeat rate or Recovery rate for I_{PTC} (%)
Original	3530	6.2	
1st repeat at 180 °C	3610	6.2	100
2nd repeat at 180 °C	3980	6.1	98.4
3rd repeat at 180 °C	4720	6.1	98.4
4th repeat at 180 °C	5570	6.0	96.8
5th repeat at 180 °C	6830	6.0	96.8
1st repeat at 230 °C	5730	5.9	95.2
2nd repeat at 230 °C	7400	5.7	91.9
3rd repeat at 230 °C	11300	5.5	88.7
4th repeat at 230 °C	28900	5.3	85.5
5th repeat at 230 °C	41000	4.9	79.0
1st reprocessed	7930	5.6	90.3
2nd reprocessed	23200	5.1	82.3
3rd reprocessed	283000	4.3	69.4
1st chemical recycled	1630	5.9	95.2
2nd chemical recycled	9530	5.4	87.1
3rd chemical recycled	5430	5.5	88.7

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