

Electronic supplementary information (ESI) for

An effective approach of preparation of epoxy vitrimers through in situ formation of dynamic and permanent linkages in one-pot curing reaction

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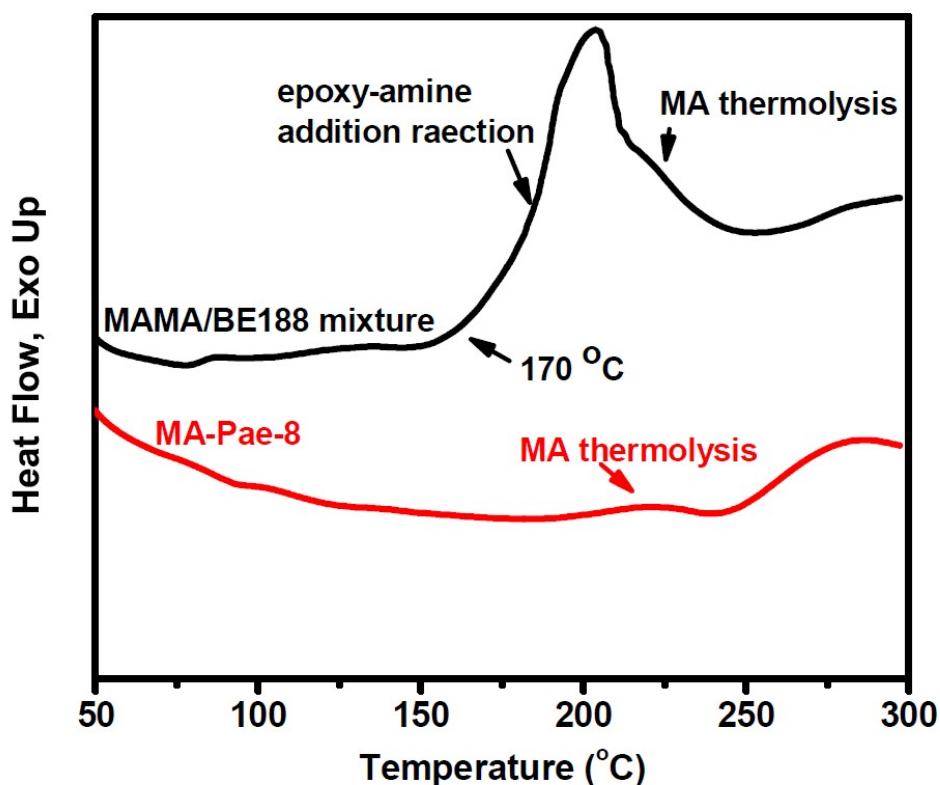


Figure S1. DSC thermograms of the MAMA/BE188 mixture and MA-Pae-8. The exothermic peaks are assigned to amine/epoxy addition reaction and MA thermolysis reaction. The disappearance of the signal of amine/epoxy addition reaction in MA-Pae-8 thermogram indicated the synthesis of MA-Pae-8 was majorly performed with the amine/epoxy addition reaction.

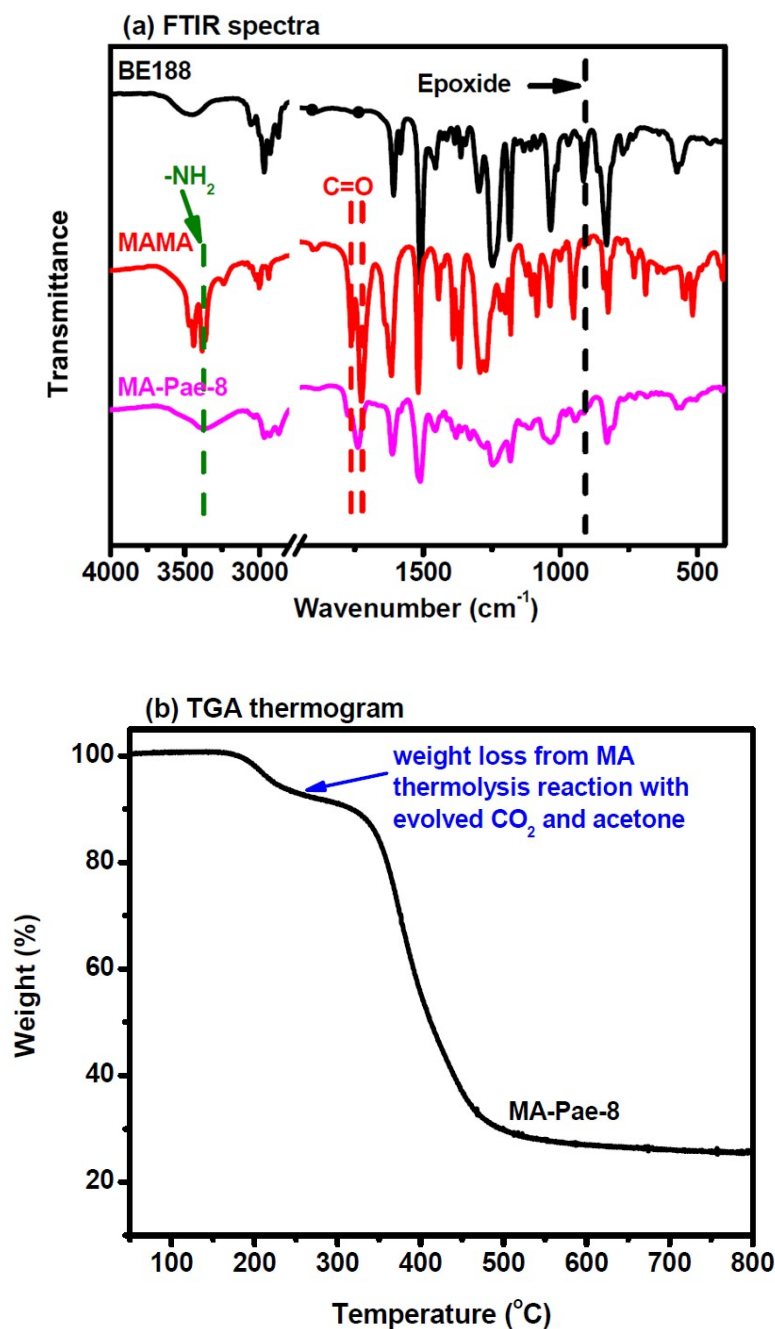


Figure S2. (a) FTIR spectra of MA-Pae-8. Compared to the raw materials, MA-Pae-8 did not exhibit the absorption peaks of amine and epoxy groups, indicating the 2 groups involved in the reactions for preparation of Ma-Pae-8. The absorptions of C=O groups found with MAMA was still observed with MA-Pae-8, supporting to it possessed MA groups. (b) TGA thermogram of MA-Pae-8. The weight loss at about 200-250 °C corresponded to the MA thermolysis with involves of CO₂ and acetone byproducts.

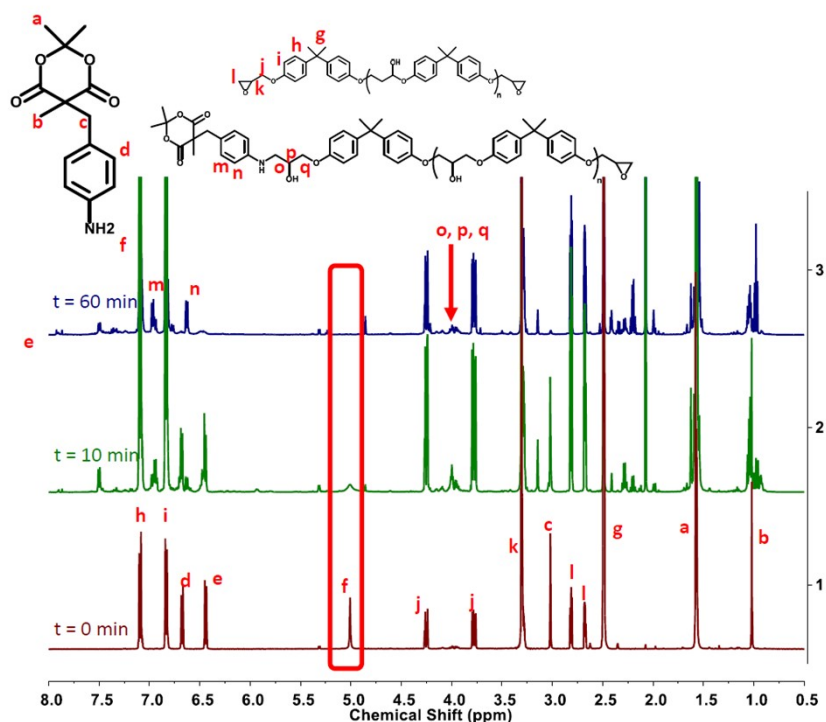


Figure S3. ^1H NMR spectra of MAMA/BE188 mixture at 180 °C at different reaction time, for tracing the reaction between MAMA and BE188. Due to the poor solubility of the reaction product in the solvent (DMSO-d_6), the spectra majorly showed the disappearance of the chemical groups (amine and epoxy) consumed in the reaction.

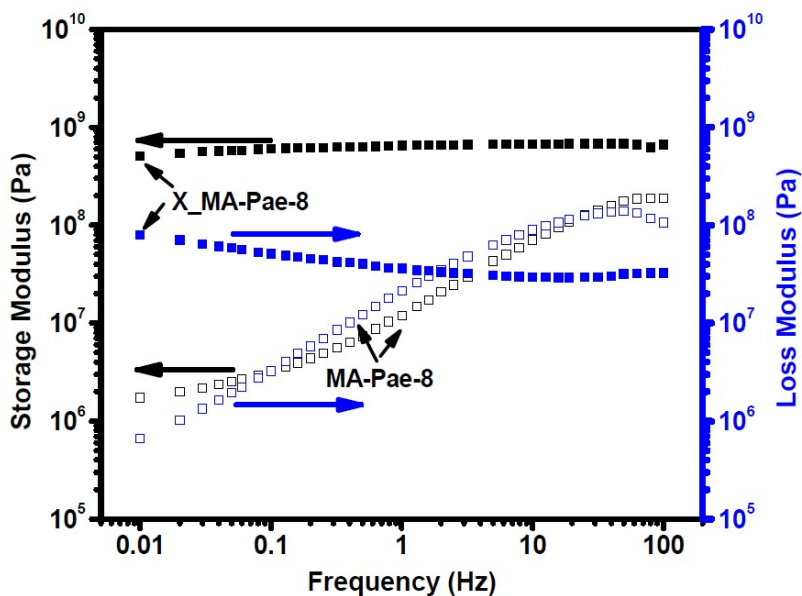


Figure S4. Storage modulus and loss modulus of MA-Pae-8 and its crosslinked analogue (X_MA-Pae-8) recorded at 100 °C and various frequencies. The crosslinked structure of X_MA-Pae-8 was supported with its frequency-independent modulus in

the test.

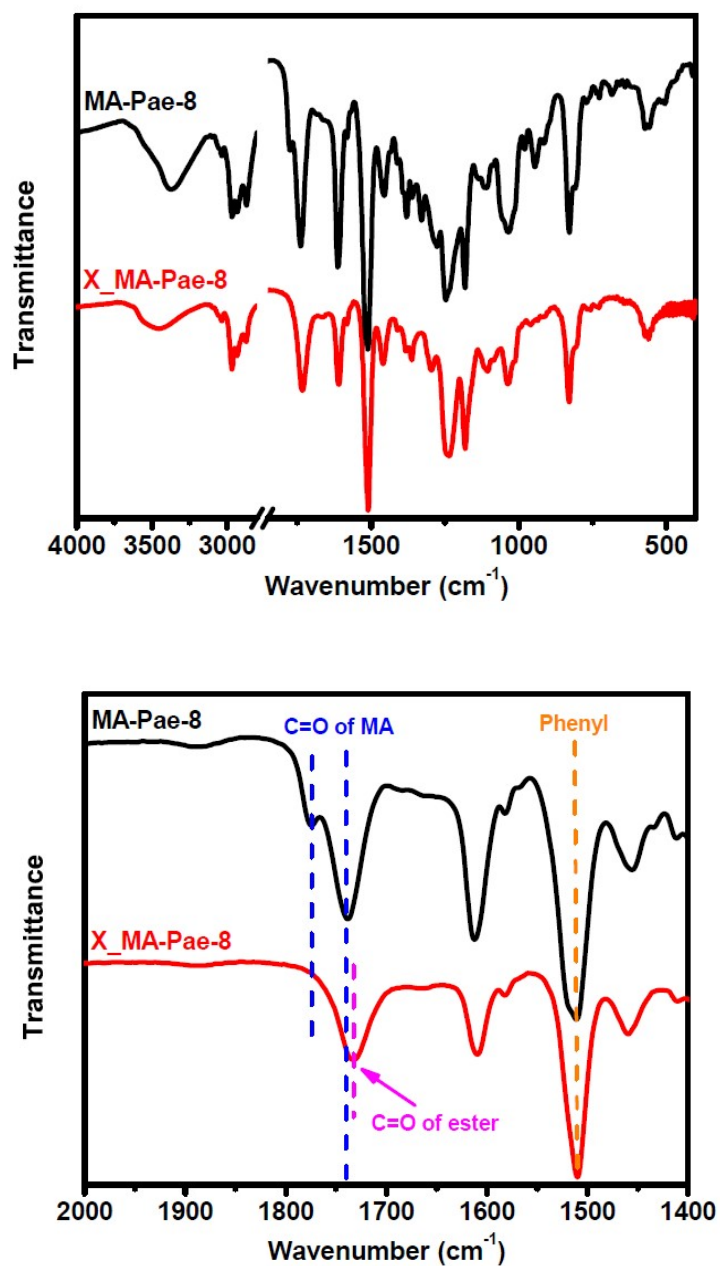


Figure S5. FTIR spectra of MA-Pae-8 and the corresponding thermally crosslinked X_MA-Pae-8. The conversion of MA to ester groups through ketene/-OH addition reaction is characterized with the disappearance of MA absorption at 1738 and 1775 cm^{-1} and the appearance of ester linkages at 1733 cm^{-1} . With the absorption of phenyl group at 1510 cm^{-1} as an internal standard, the conversion of MA to ester groups in the curing reaction is calculated to be above 95 %.

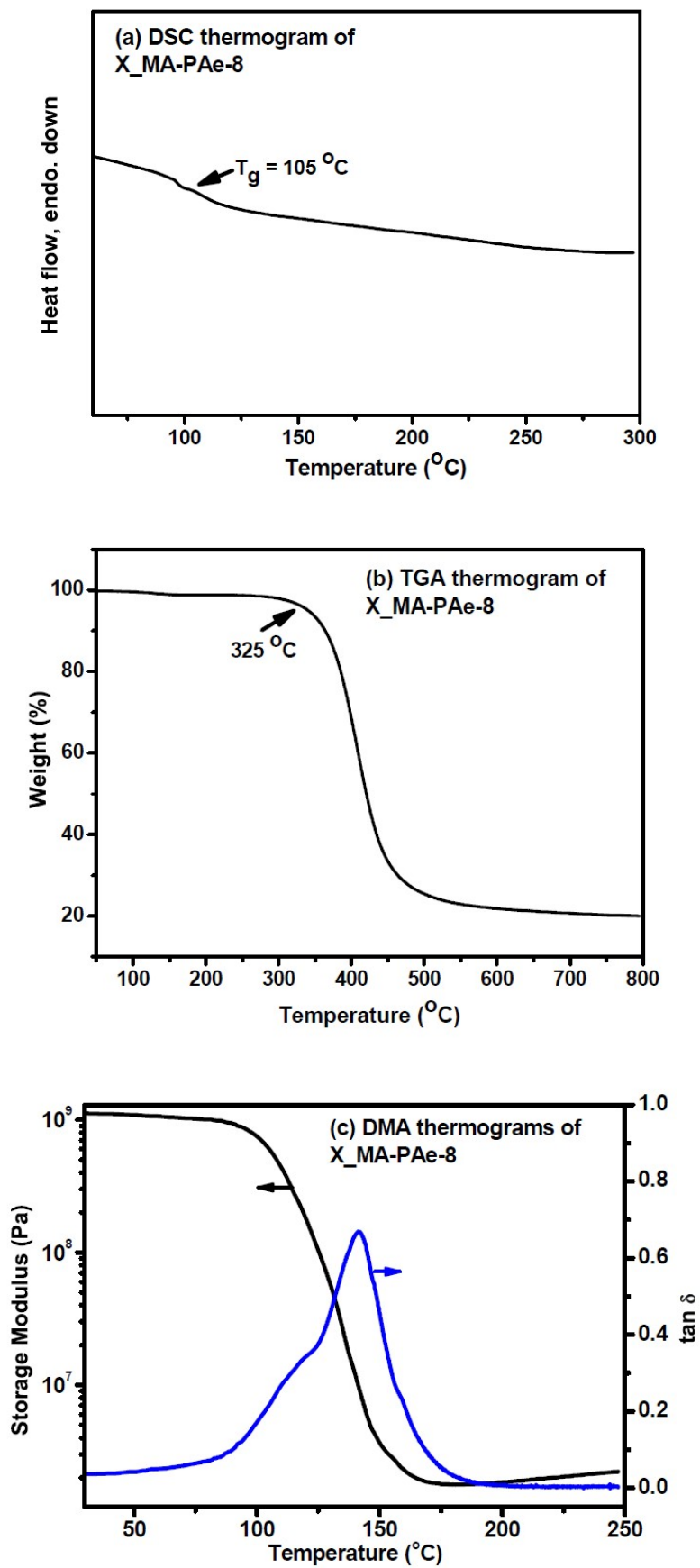


Figure S6. (a) DSC, (b) TGA, and (c) DMA thermograms of X_MA-Pae-8.

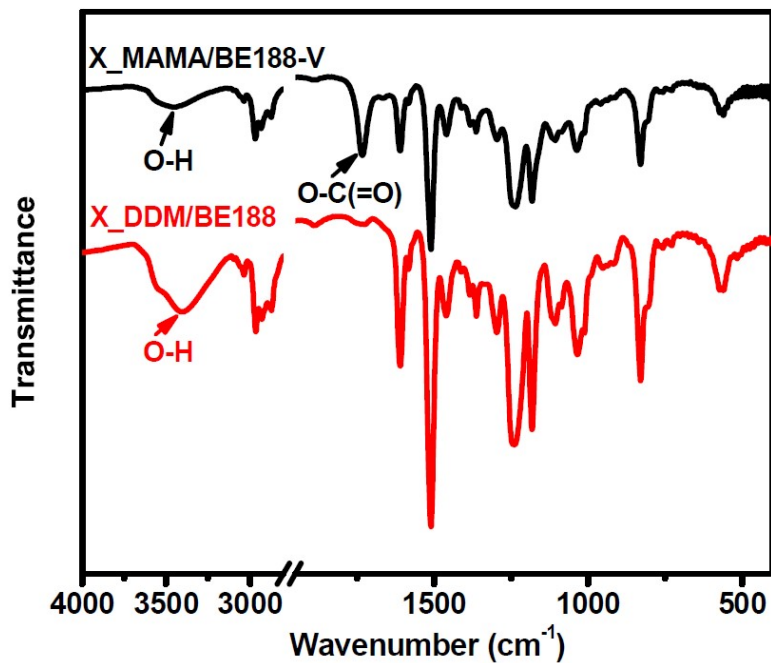


Figure S7. FTIR spectra of crosslinked epoxy resins: X_MAMA/BE188-V and X_DDM/BE188.

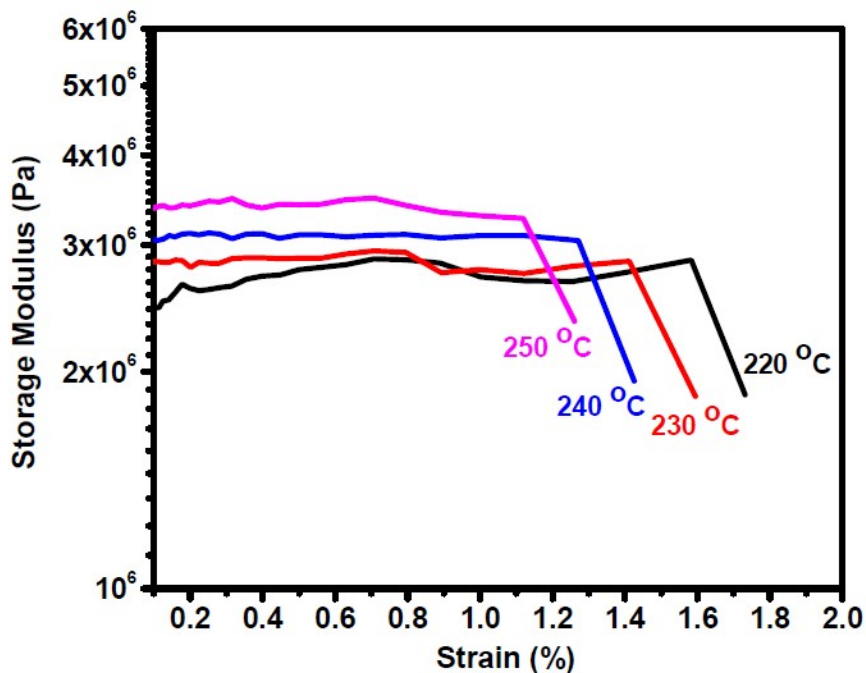


Figure S8. Strain sweep experimental curves recorded on X_MAMA/BE188-V with a constant frequency of 1 Hz at 220 - 250 °C.

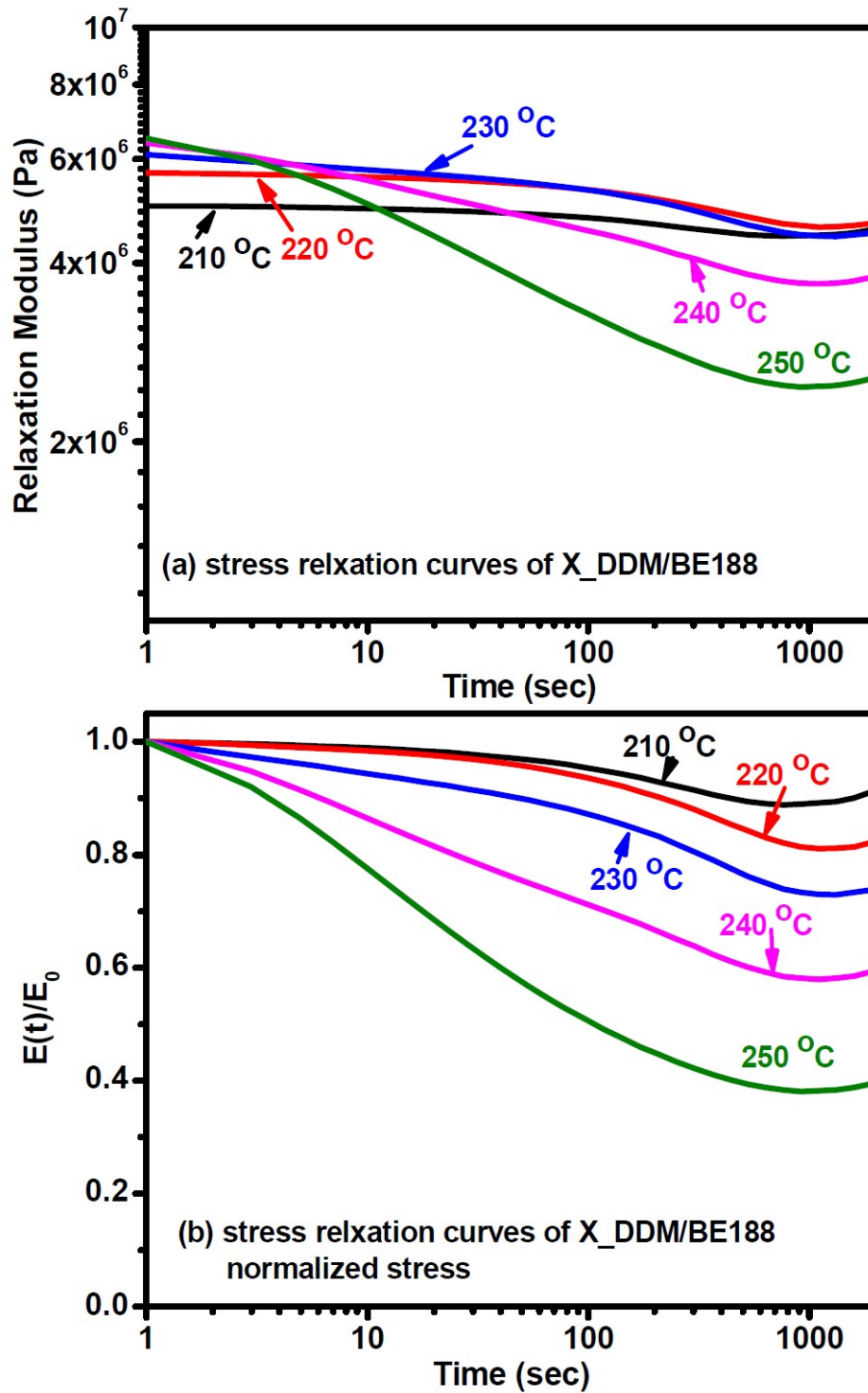


Figure S9. (a) Stress-relaxation tests on X_DDM/BE188 with a constant strain of 1.0 % at 210-250 °C. (b) Plots of the stress relaxation behaviors in term of normalized stress with relaxation time.

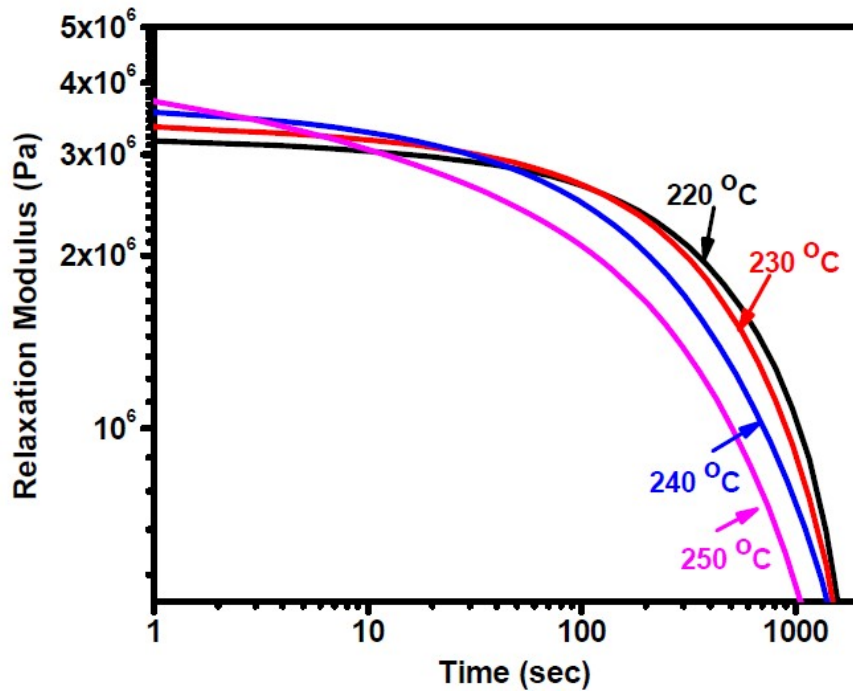


Figure S10. Stress-relaxation tests on X_MAMA/BE188-V with a constant strain of 1.0 % at 220-250 °C.

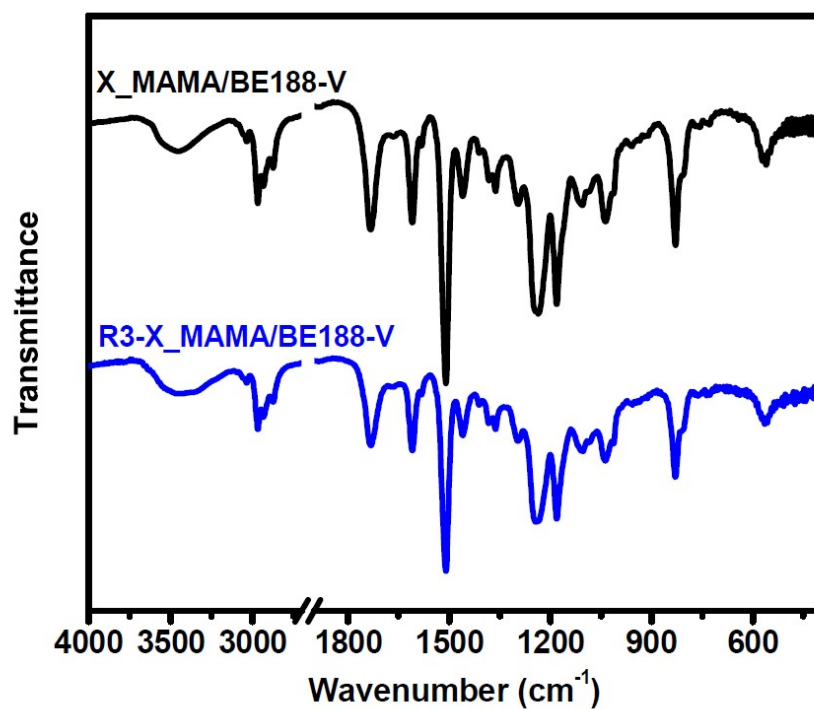


Figure S11. FTIR spectra of X_MAMA/Be188-V and its 3rd-recycled sample (R3_MAMA/BE188-V). The 2 samples did not show obvious and significant differences in the spectra, indicating the recycle and reprocess operation did not bring thermal degradation and chemical changes to X_MAMA/BE188-V.

Table S1. Gel fractions (%) of X_MAMA/BE188-V and the thermally recycled samples. The data recorded on X_DDM/BE188 is included for a comparison.

Sample	Gel fraction (wt%)			
	NMP at 30 °C	NMP at 80 °C	1 N HCl _(aq) at 30 °C	1 N NaOH _(aq) at 30 °C
X_DDM/BE188	95.0	90.3	95.2	91.3
X_MAMA/BE188-V	96.8	93.0	94.2	86.3
R1_MAMA/BE188-V	96.5	92.1	98.1	95.2
R2_MAMA/BE188-V	96.4	92.0	97.8	94.9
R3_MAMA/BE188-V	96.6	92.3	97.9	95.0