Supporting Information

Polyethylene (PE) Vitrimer by Cross-linking Two Mass-produced Ethylene-based Polymers through One-step Reactive Blending

Xuanwei Zhang[a], Siyu Guo[a], Xiaopei Li[b], Yongjie Zhang*[a]

[a] School of Textile and Material Engineering, Dalian Polytechnic University, Dalian 116034, China

[b] Instrumental Analysis Centre, Dalian Polytechnic University, Dalian 116034, China

*Corresponding Author: Yongjie Zhang (yjzhang@dlpu.edu.cn)

Table S1 Gel fraction and ester conversion of PE vitrimers

Sample	EVA (g)	TMS-PE (g)	TT-01 (g)	Gel fraction (wt%)	Conversion (%, C=O)
Si60	25.00	15.00	0.30	37.7	13.9
Si90	21.05	18.95	0.38	51.2	19.2
Si120	18.18	21.82	0.44	60.9	27.6

Table S2 Thermal properties of raw materials and PE vitrimers

Sample	$T_{c,\,EVA}$ [a] (°C)	$T_{c,\,TMS\text{-}PE}$ [b] (°C)	$\Delta H_{c,\,EVA}$ [a] (J/g)	$\Delta H_{c,\,TMS\text{-}PE}$ [b] (J/g)
EVA	52.45	\	28.48	\
TMS-PE	\	114.25	\	55.85
Si60	54.57	100.51	25.90	52.35
Si90	50.31	100.69	24.47	52.51
Si120	45.34	100.11	18.03	50.88

[a] Normalized to EVA for PE vitrimers

[b] Normalized to TMS-PE for PE vitrimers

Table S3 Storage modulus and molecular weight between cross-links of self-cross-linked TMS-PE and PE vitrimers

Sample	$E^{'}$ (MPa) [a]	M_c (g/mol) [b]
self-cross-linked TMS-PE	0.68	13185
Si60	0.33	27759
Si90	0.68	13471
Si120	0.97	9444

[a] E' represents the storage modulus at 407 K; [b] M_c represents the molecular weight between cross-links, according to Equation S2 (vide infra).

Table S4 Mechanical properties of ethylene-based commodity polymers

Sample	Manufacturer	Designation	Elongation at break [a] (%)	Tensile strength [b] (MPa)
LDPE	Dow Chemical	1000	390	12
	Total Energies	1022FH24	350	12
	Nexus Resin	1017	300	9
	Nexus Resin	818	400	10
	Sinopec Yanshan Petrochemical	1I50A	320	8
LLDPE	Sinopec Zhongyuan Petrochemical	DFDC-7050	500	8
	Sinopec Yangzi Petrochemical	DFDA-7042	750	8
	Shanghai Secco Petrochemical	LL0220KJ	600	10
	Shanghai Secco	LL0209KJ	620	10

	Petrochemical			
	SABIC	M200024	450	12
EVA	Dow Chemical	40L	930	7.3
	Jiangsu Sierbang Petrochemical	UE2825	1610	9.0
	Arkema	2803	930	18.5
	Dupont	460	540	10.4
	BASF-YPC	V5100J	750	22.5

Data collected according to the China Plastic Online website and the China Material Properties Query website

Table S5 Ester conversion of Si90 before and after reprocessing

Sample	**Conversion (%, C=O)**
Si90	19.2
$Si90_{1st}$	19.4
$Si90_{2nd}$	19.3

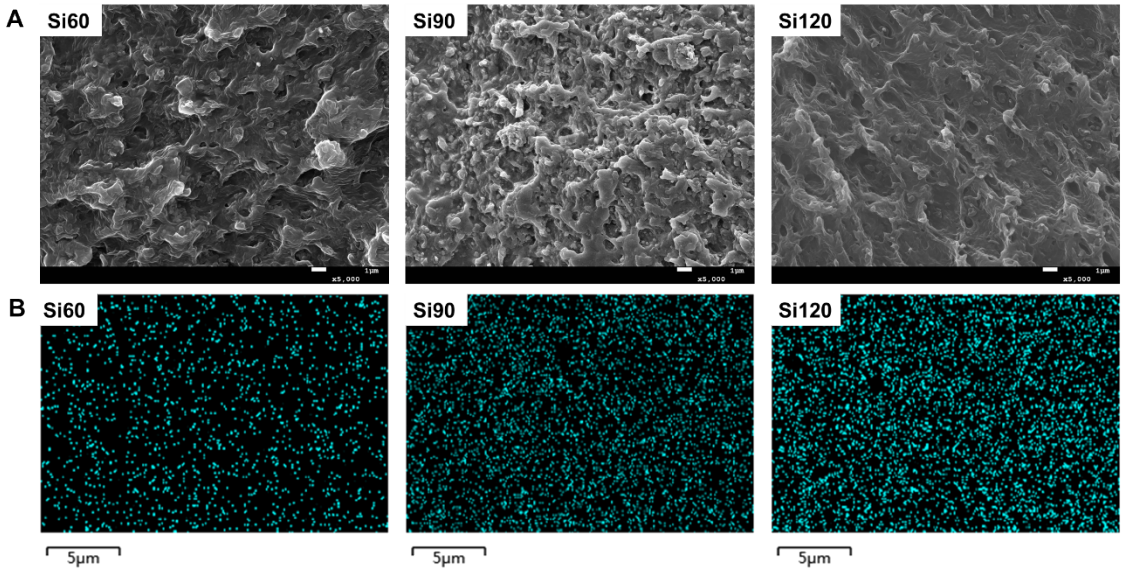

Figure S1 (A) SEM micrographs of PE vitrimers (Scale bar: 1 μm) and (B) silicon element mapping images of PE vitrimers (Scale bar: 5 μm)

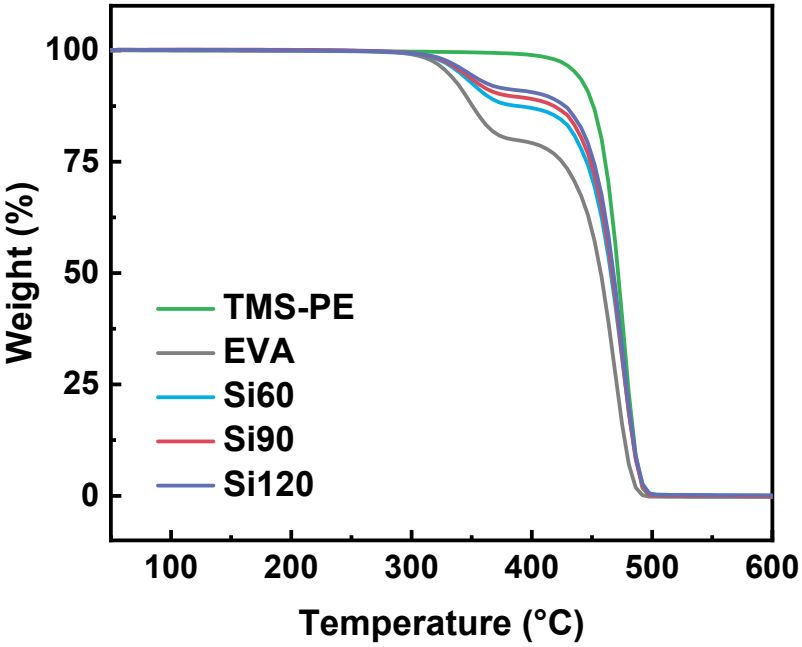

Figure S2 TGA curves of raw materials and PE vitrimers (N_2, 10 °C/min)

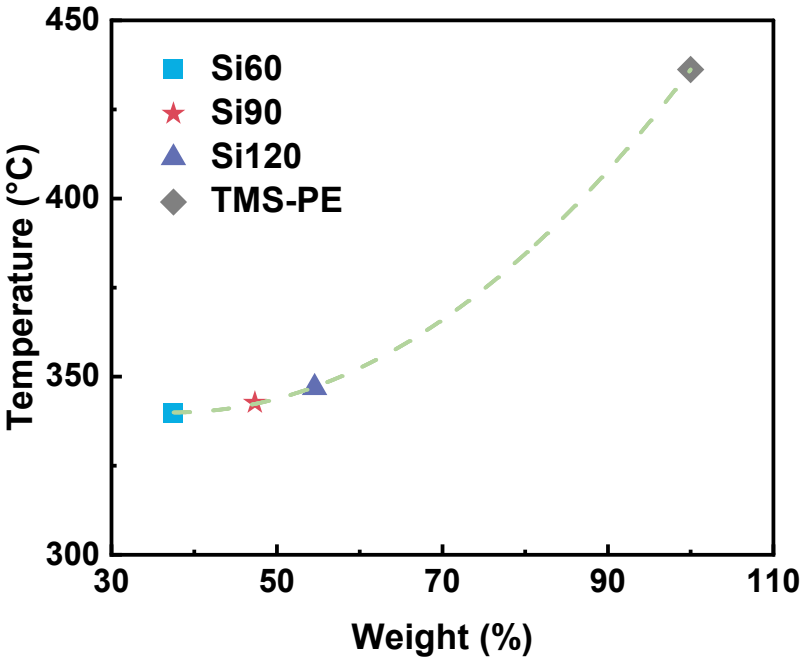

Figure S3 Initial decomposition temperature as a function of TMS-PE content

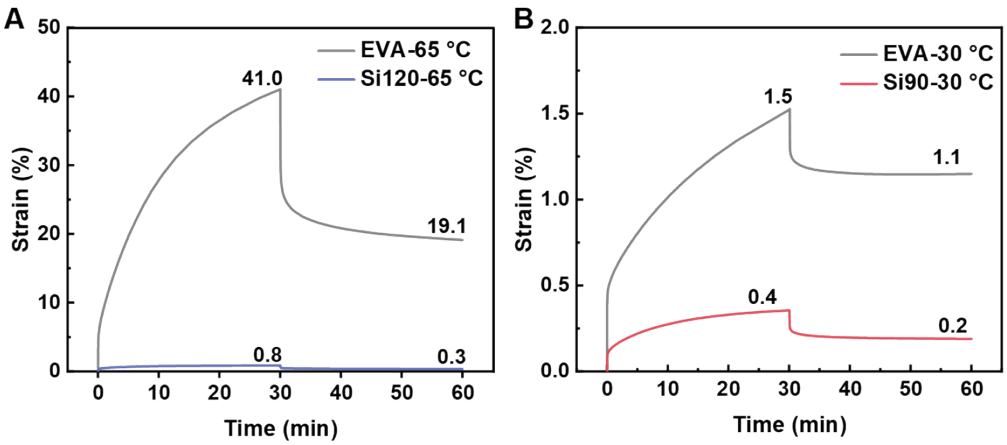

Figure S4 Creep curves of (A) EVA and Si120 measured at 65 °C and (B) EVA and Si90 measured at 30 °C

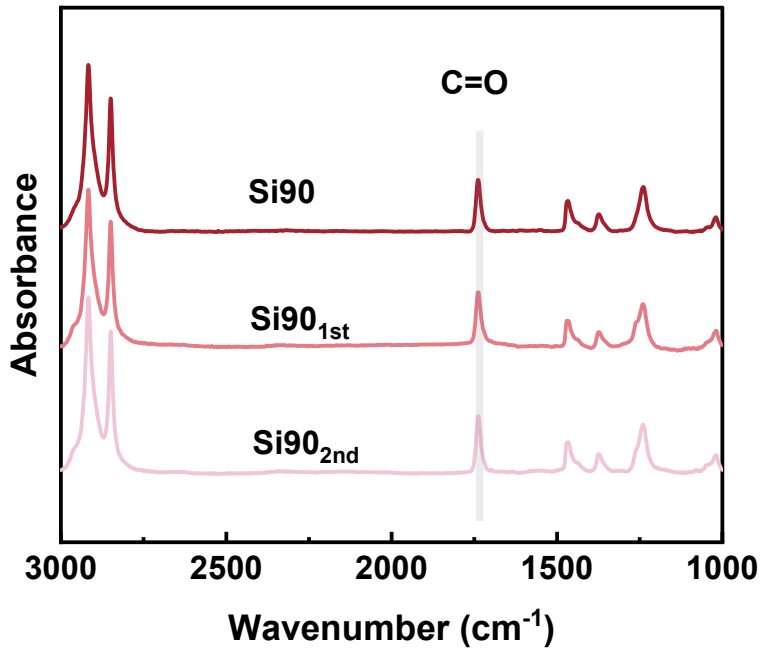

Figure S5 FTIR spectra of Si90 before and after reprocessing cycles

Calculations

Determination of conversions

The calculation process of the ester group conversion for PE vitrimers is as follows.

$$Con.\% = \left[1 - \frac{A_{1740,\,vitrimer}/A_{2920+2850,vitrimer} * EVA\ wt\%}{A_{1740,\ linear}/A_{2920+2850,\ linear}}\right] \times \%$$

(Equation S1)

Where:

$A_{1740,\ vitrimer}$ represents the integrated area of peak at 1740 cm^{-1} for PE vitrimer;

$A_{1740,\ linear}$ represents the integrated area of peak at 1740 cm^{-1} for EVA;

$A_{2920+2850,\ vitrimer}$ represents the integrated area of peaks at 2920 cm^{-1} and 2850 cm^{-1} for PE vitrimer;

$A_{2920+2850,\ linear}$ represents the integrated area of peaks at 2920 cm^{-1} and 2850 cm^{-1} for EVA.

Determination of M_c

The molecular weight between cross-links (M_c) refers to the average molecular weight of the polymer chain segments between two adjacent cross-linking points. Calculation of M_c can be performed using the Equation:

$$M_c = 2(1+\nu)\frac{\rho RT}{\mathrm{E'}} \qquad \text{(Equation S2)}$$

Where:

ν = Poisson's ratio (0.44)

ρ = density (0.94 g/cm^3 or 940 kg/m^3)

R = universal gas constant (8.314 $m^3 \cdot Pa/K \cdot mol$)

T = temperature (407 K)

E' = storage modulus (0.33 MPa at 407 K)

The M_c values for Si60, Si90, and Si120 networks at 407K were calculated to be 27.7,

13.5, and 9.4 kg/mol, respectively.