Supporting Information

Atomic oxygen resistance vitrimers with high strength, recyclability and thermal stability

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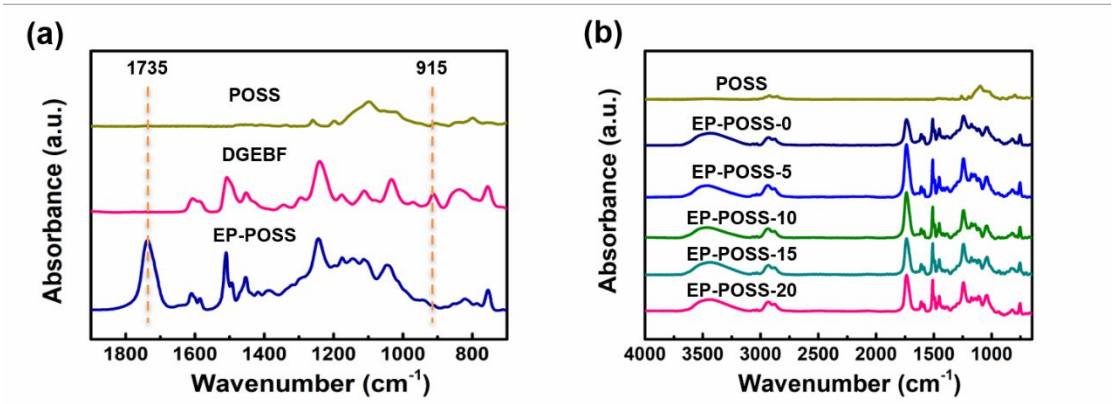

Figure. S1. FTIR spectra of EP-POSS vitrimers. The characteristic peaks at 910cm^{-1}, 1735cm^{-1} and 3459cm^{-1} are belonged to the stretching vibration peak of C-O-C in epoxy groups, the C=O stretching vibration peak in ester bonds and the stretching vibration peak of O-H, respectively.[1,2] In EP-POSS vitrimers, the stretching vibration peak of Si-O-Si (1105 cm^{-1}) becomes stronger gradually from EP-POSS-0 to EP-POSS-20, indicating that the POSS molecules participate in the crosslinking reaction of epoxy resin.

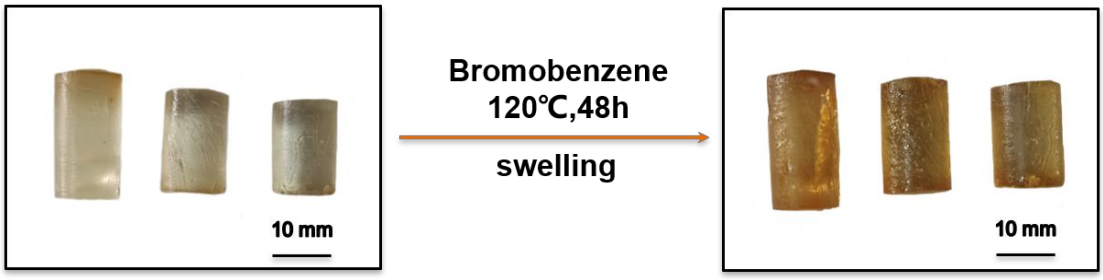

Figure. S2. Photographs of EP-POSS vitrimers before (left) and after (right) swelling experiments. After swelling for 48 h, EP-POSS-0, EP-POSS-10 and EP-POSS-20 were undissolved but swelled in bromobenzene, which indicated all samples had crosslinked network and exchange reactions did not dissociate the molecular chain at high temperature.

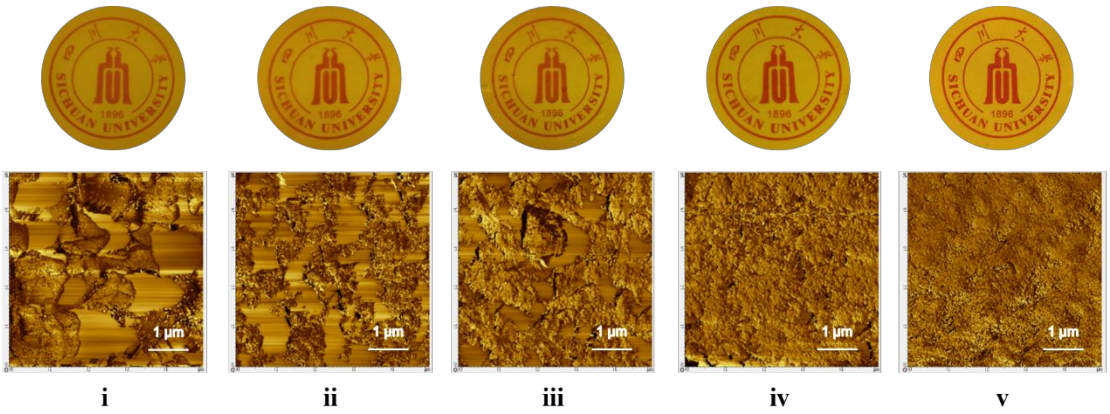

Figure S3. Photographs (top) and AFM images (bottom) of EP-POSS vitrimers after AO tests, mass percentage of POSS is 0 to 20 wt% from Ⅰ to Ⅴ.

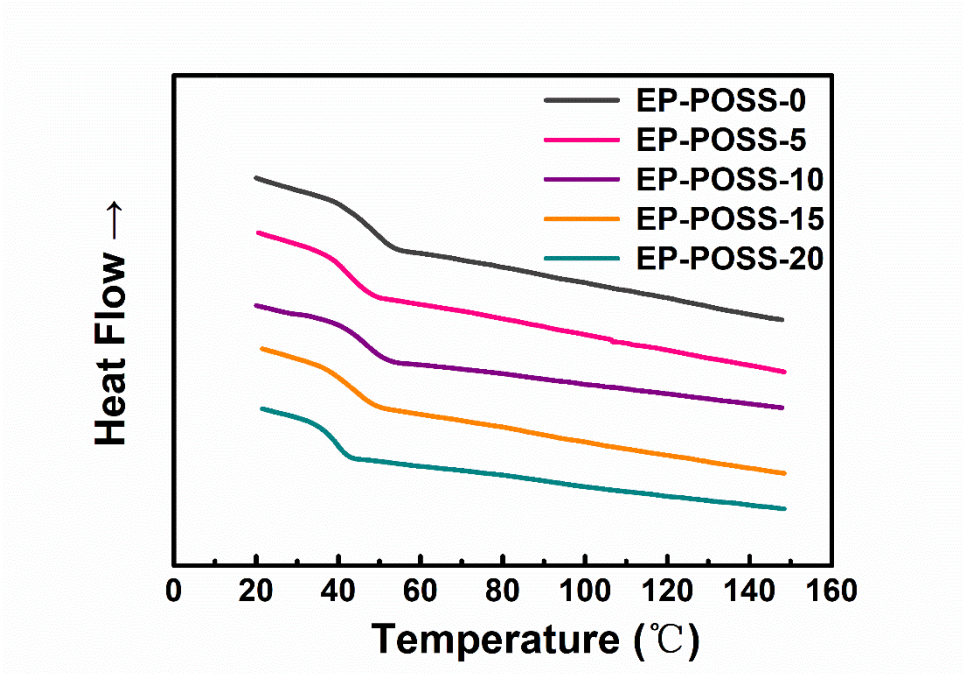

Figure S4. DSC curves of EP-POSS vitrimers.

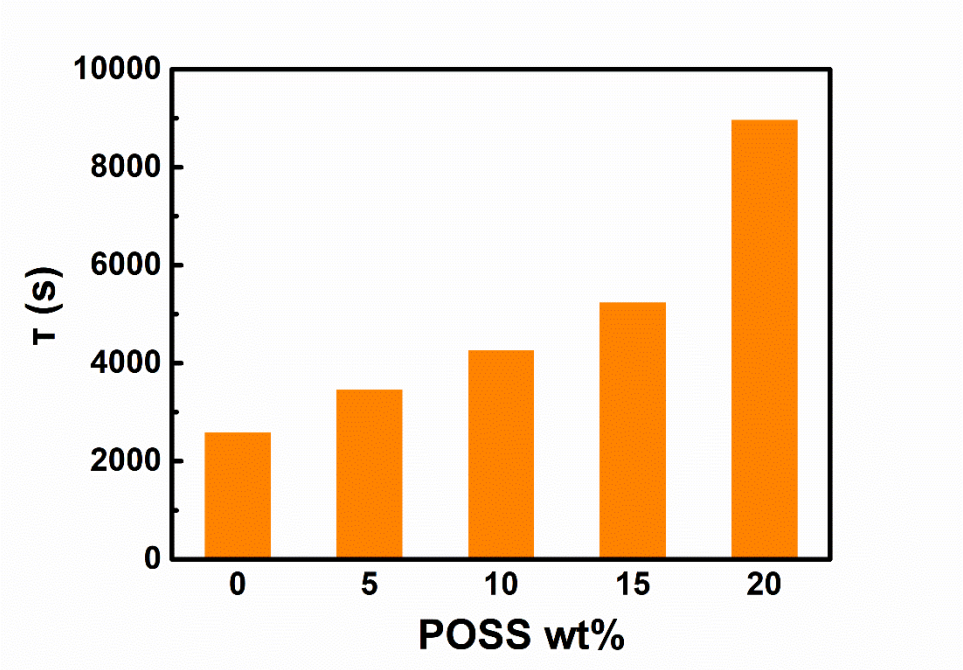

Figure S5. Relaxation times of EP-POSS vitrimers at 200℃.

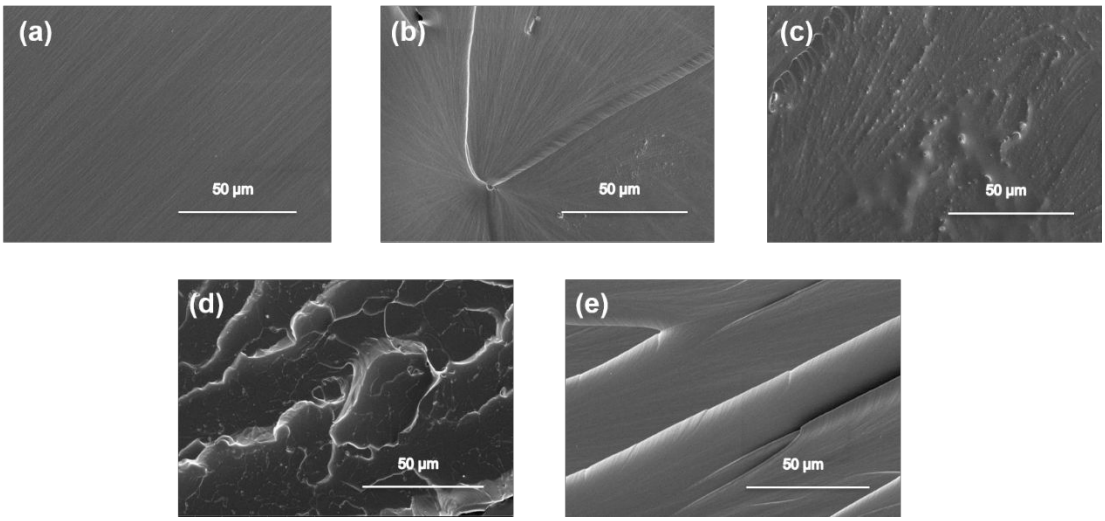

Figure S6. SEM images of fracture surfaces from tensile samples: (a) pure epoxy resin vitrimers, (b) 5 wt% POSS, (c) 10 wt% POSS,(d) 15 wt% POSS, and (e) 20 wt% POSS. Epoxy resin obviously showed brittle fracture due to the highly crosslinked structure, while the fracture surfaces of EP-POSS vitrimers are rougher than that of pure epoxy resin, large amounts of river-liked stripes indicate that the fracture mode of EP-POSS

vitrimers is ductile fracture and POSS has the strengthening and toughening effect on epoxy resin vitrimers.

Table S1. Thermal stability properties of epoxy resin with varying POSS contents calculated from TGA curves.

POSS wt%	*T_i (℃)*	*T_{max} (℃)*	*Char yield (%)*
0	318.67	418.33	21.09
5	326.33	418.36	23.55
10	311.0	418.37	25.44
15	314.72	422.63	26.06
20	315.16	422.65	27.16

T_i is the initial decomposition temperature (char yield is 98%), T_{max} is the temperature at the fastest decomposition, and the char yield at 800℃.

Table S2. AO tests results of EP-POSS vitrimers.

POSS wt%	*m_1[a] (g)*	*m_2[b] (g)*	*$\triangle m$[c] (mg/cm^2)*	*Roughness (nm)*	*E_s[d] (×10^{-24}cm^3/O atom)*	*$\triangle d$[e] (×10^{-4} cm)*
0	0.1500	0.1444	0.792	374	3.185	7.581
5	0.1344	0.1315	0.410	156	1.650	3.926
10	0.1904	0.1881	0.325	129	1.308	3.114
15	0.1588	0.1573	0.212	49	0.853	2.031
20	0.1261	0.1252	0.127	26	0.512	1.218

Table S3. Surface atomic concentrations (atom %) determined from XPS before and after exposure to AO fluences.

POSS	*Unexposed Samples*			*AO Exposed Samples*			
wt%	*C 1s*	*O 1s*	*Si 2p*	*C 1s*	*O 1s*	*N 1s*	*Si 2p*
0	79.79	20.21	0	77.16	18.84	4.00	0
5	75.27	19.23	5.50	54.66	28.93	1.97	14.45
10	73.56	20.15	6.29	53.17	30.19	1.58	15.07
15	72.55	19.48	7.97	45.27	34.57	3.18	16.98
20	69.60	20.69	9.71	29.50	40.76	9.69	20.04

Table S4. DMA, DSC results and crosslinking density of EP-POSS vitrimers.

POSS wt%	E_g^a *(MPa)*	E_r^b *(MPa)*	T_g^c *(℃)*	T_g^d *(℃)*	M_c *(kg·mol^{-1})*	V_c *(mol·m^{-3})*
0	2710	4.0	68.7	45.1	2.7	435.1
5	6896	5.8	59.9	41.9	1.8	637.8
10	7415	7.0	62.3	47.9	1.5	764.2
15	12080	7.6	66.1	44.2	1.4	821.2
20	3694	11.4	63.9	42.2	0.9	1248.5

[a] E_g is the glassy storage modulus at 25℃, [b] E_r is the rubbery storage modulus taken 30℃ above T_g, [c] T_g is the glass transition temperature measured by DMA, [d] T_g is the glass transition temperature measured by DSC.

Table S5. Tensile results of EP-POSS vitrimers.

POSS wt%	***Tensile strength (MPa)***	***Elastic modulus (MPa)***	***Elongation at break (%)***	***Fracture toughness (kJ·m^{-3})***
0	77.59±10.23	1746±172	6.91±0.24	39.84±3.16
5	93.86±1.22	2164±260	6.85±0.33	40.03±2.71
10	94.36±0.2	1637±50	8.71±0.52	54.98±4.80
15	92.10±1.5	1994±113	6.80±0.73	41.36±1.04
20	84.52±3.97	1668±151	8.21±0.58	47.18±2.56

SI References

(1) Yang, H.; He, C.; Russell, T. P.; Wang, D. Epoxy-Polyhedral Oligomeric

Silsesquioxanes (POSS) Nanocomposite Vitrimers with High Strength, Toughness, and Efficient Relaxation. *Giant* **2020**, *4*. https://doi.org/10.1016/j.giant.2020.100035.

(2) Liu, H.; Li, J.; Gao, X.; Deng, B.; Huang, G. Double Network Epoxies with Simultaneous High Mechanical Property and Shape Memory Performance. *J. Polym. Res.* **2018**, *25* (2). https://doi.org/10.1007/s10965-017-1427-9.