Tuning the mechanical and dynamic properties of imine bond crosslinked elastomeric vitrimers by manipulating the crosslinking degree

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Equilibrium swelling tests.[1-3]

Equilibrium swelling experiments were conducted by immersing samples in toluene at room temperature for 72 h. After swelling, the solvent was wiped off quickly from sample surface using filter paper, and the samples were immediately weighed and then dried in a vacuum oven at 60 °C until constant weight. Three specimens were measured for each sample.

The swelling ratio is defined as $\frac{(m_1 - m_2)}{m_2}$, and sol fraction is determined as $\frac{(m_0 - m_2)}{m_0}$.

The volume fraction of rubber matrix in the swollen sample, V_r, was calculated by the following equation:

$$V_r = \frac{(m_2 - m_0\varphi)/\rho_r}{(m_2 - m_0)/\rho_r + (m_1 - m_2)/\rho_s}$$

where m_0 is the sample mass before swelling, m_1 and m_2 are the weights of the swollen and deswollen sample, respectively; φ is the weight fraction of the insoluble components; ρ_r and ρ_s are the densities of the rubber and solvent, respectively.

The elastically active network chain density can be calculated by the well-known Flory-Rehner equation:

$$V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - 2V_r/f)}$$

where χ is the Flory-Huggins polymer-solvent interaction parameter (0.23 for PB and toluene), V_s is the molar volume of the solvent (106.5 $cm^3 \cdot mol^{-1}$ for toluene), and f is the functionality of interlinkage (here is 6 in this work).

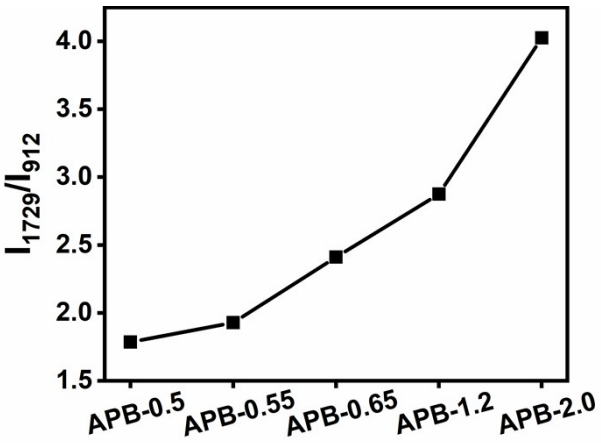

Fig. S1 Normalized peak value of aldehyde groups at 1729 cm^{-1} of APB by using the absorption peaks of 1,2-vinyl at 912 cm^{-1} as an internal reference.

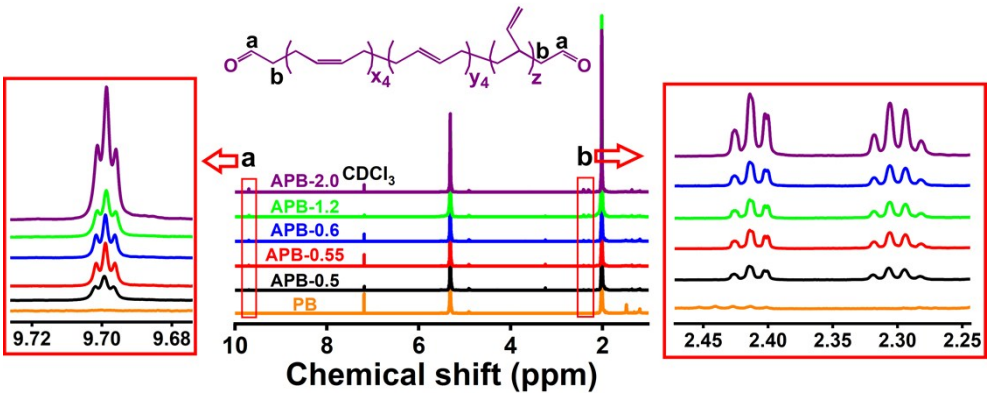

Fig. S2 ^{1}H NMR spectra of PB and APB with the aldehyde related peaks highlighted.

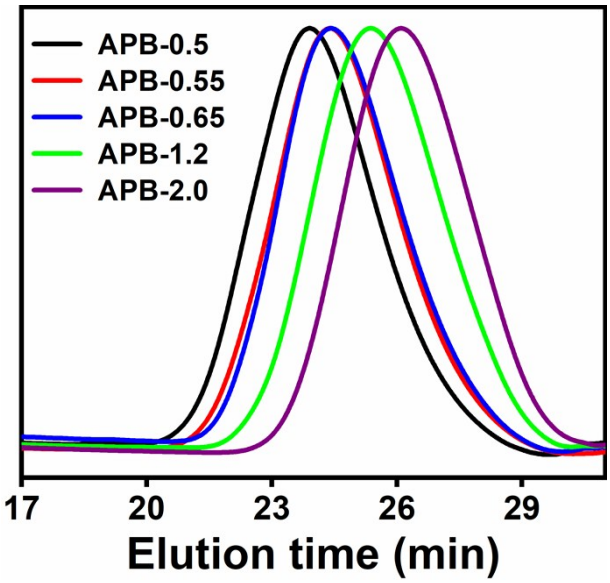

Fig. S3 GPC traces of APB.

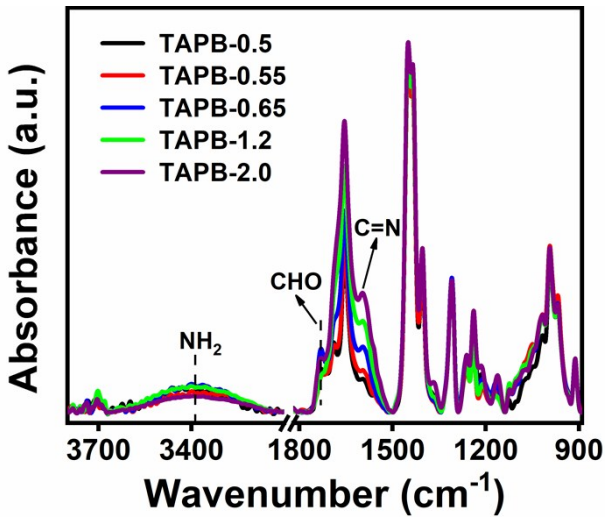

Fig. S4 FTIR spectra of TAPB. All spectra were normalized by using the absorption peaks of 1,2-vinyl as an internal reference.

Table S1. Sol fraction, swelling ratio, crosslinking density, storage modulus (E') at 25 °C and glass transition temperature (Tg) determined by DMA measurement, and average molecular weight between two adjacent crosslinks ($\overline{M}_c$) of TAPB.

Samples	Sol fraction (%)	Swelling ratio (%)	Crosslinking density (10^{-4} mol/cm^3)	E' (MPa)	Tg (°C)	$\overline{M}_c$ (g/mol)
TAPB-0.5	17.8±0.3	892±10	0.50±0.01	0.59	-92	11342
TAPB-0.55	8.3±0.3	595±6	1.04±0.02	1.27	-94	5264
TAPB-0.65	5.9±0.3	471±7	1.56±0.04	1.52	-94	4398
TAPB-1.2	2.8±0.2	336±1	2.78±0.02	2.41	-95	2778

TAPB-2.0	0.8±0.1	253±2	4.50±0.04	3.65	-92	1833

Table S2. Young's modulus, ultimate stress, breaking strain and glass transition temperature of TAPB.

Samples	**Young's modulus (MPa)**	**Ultimate stress (MPa)**	**Breaking strain (%)**
TAPB-0.5	0.24 ± 0.01	0.42 ± 0.04	451 ± 13
TAPB-0.55	0.63 ± 0.01	0.83 ± 0.12	357 ± 20
TAPB-0.65	1.17 ± 0.02	1.08 ± 0.15	207 ± 42
TAPB-1.2	1.99 ± 0.01	1.00 ± 0.01	75 ± 3
TAPB-2.0	3.06 ± 0.03	1.16 ± 0.06	53 ± 5

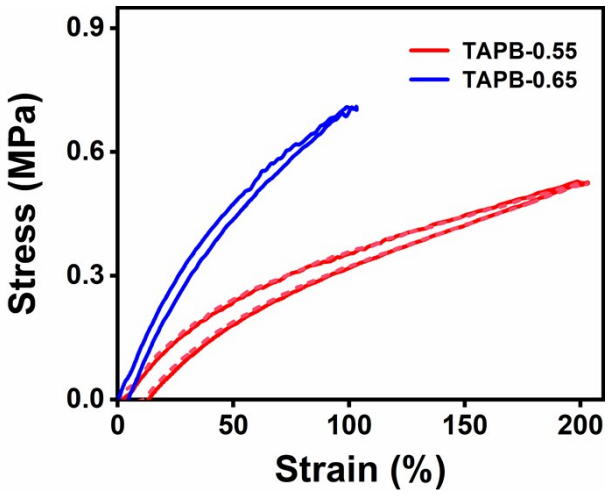

Fig. S5 Loading–unloading cycles of TAPB-0.55 and TAPB-0.65. The dash line is the

second loading–unloading cycle measured by storing the samples at room temperature for 10 min after the first cycle.

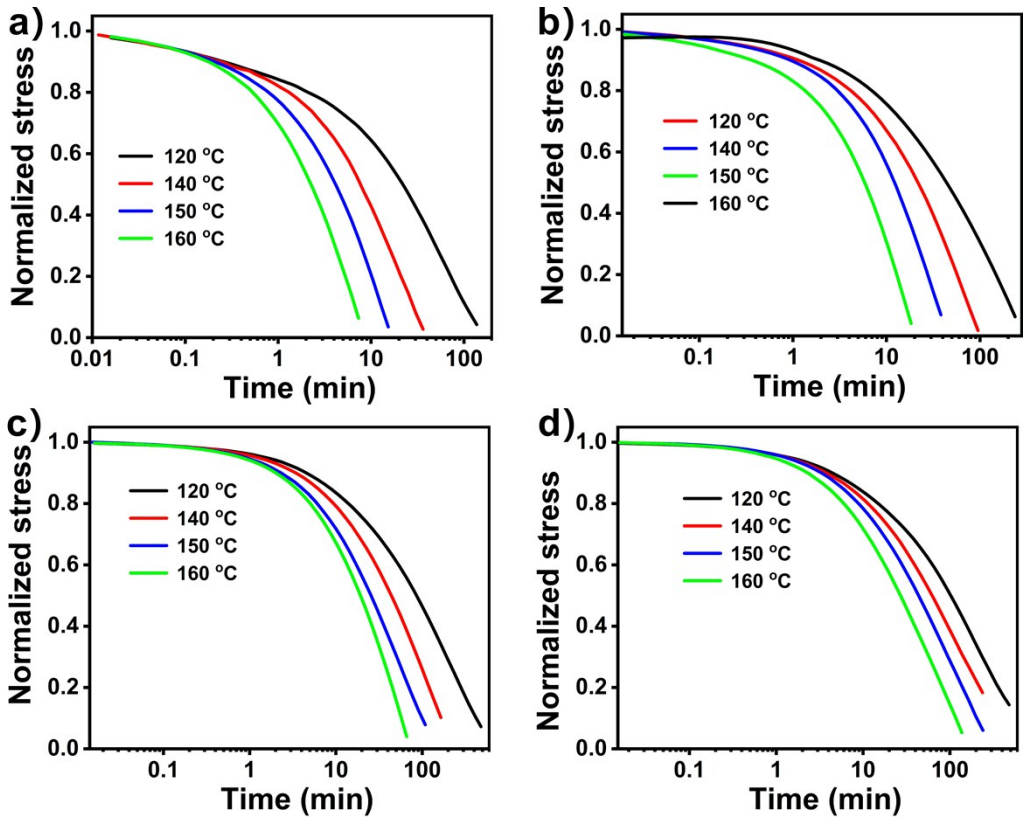

Fig. S6 Normalized stress relaxation of (a) TAPB-0.5, (b) TAPB-0.55, (c) TAPB-1.2 and (d) TAPB-2.0 at different temperatures.

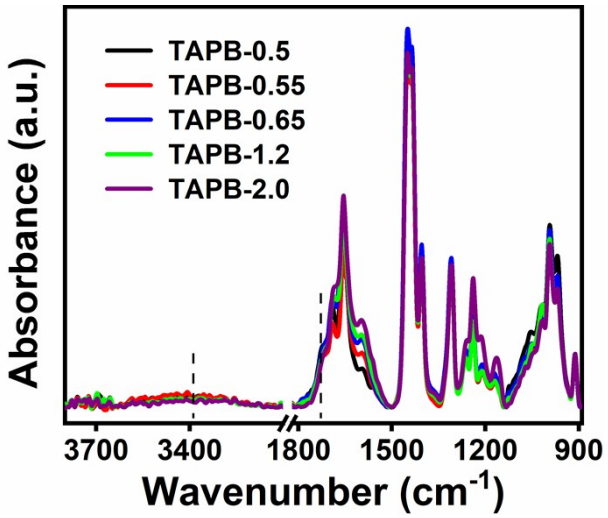

Fig. S7 FTIR spectra of TAPB after being settled at 150 °C for 15 min.

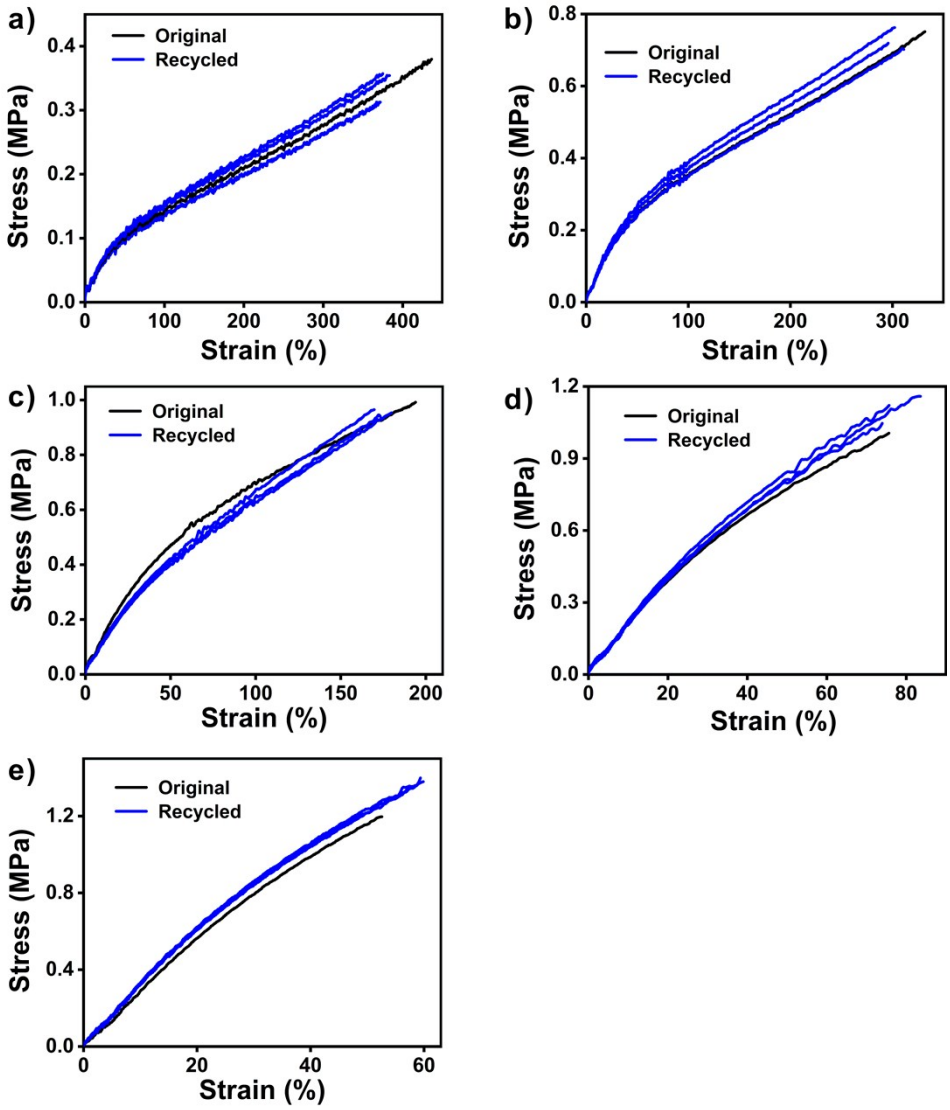

Fig. S8 Stress−strain behavior of original and recycled (a) TAPB-0.5, (b) TAPB-0.55, (c) TAPB-0.65, (d) TAPB-1.2 and (e) TAPB-2.0.

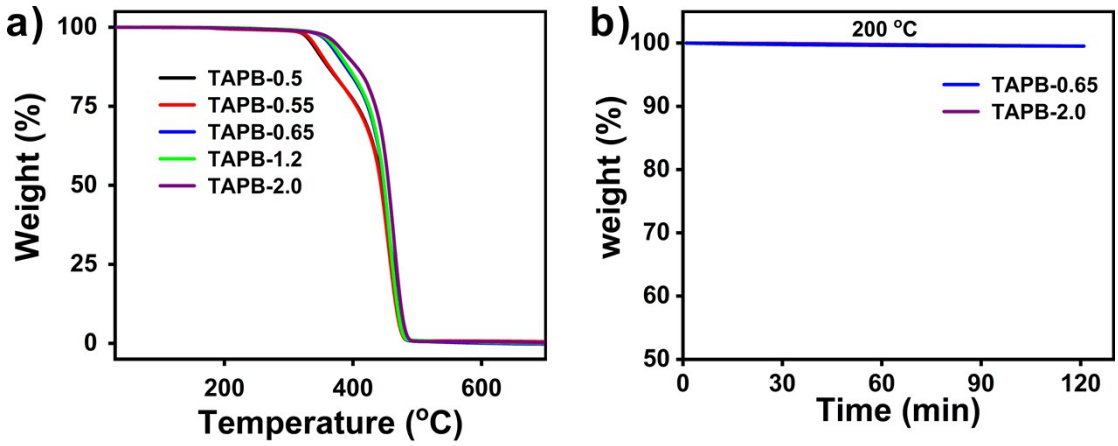

Fig. S9 (a) TGA curves of TAPB. (b) Isothermal TGA curves of TAPB-0.65 and TAPB-2.0 at 200 °C.

References

1. P. J. Flory, *J. Chem. Phys*, 1950, **18**, 108–111.

2. P. J. Flory and J. Rehner Jr, *J. Chem. Phys*, 1943, **11**, 512–520.

3. A. J. Marzocca, A. R. Garraza and M. A. Mansilla, *Polym. Test.*, 2010, **29**, 119–126.