Supplementary information

Tough tetrazine-functionalized styrene–butadiene rubber with self-adhesion through zinc-nitrogen coordination

Kyohei Kotani,*[a,b] Katsuhiko Tsunoda[a] and Hideyuki Otsuka*[b]

[a] Sustainable and Advanced Materials Division, Bridgestone Corporation, 3-1-1, Ogawahigashi-cho, Kodaira-shi, Tokyo 187-8531, Japan

[b] Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

*Corresponding authors: Kyohei Kotani (Email: kyohei.kotani@bridgestone.com), Hideyuki Otsuka (Email: otsuka@mac.titech.ac.jp)

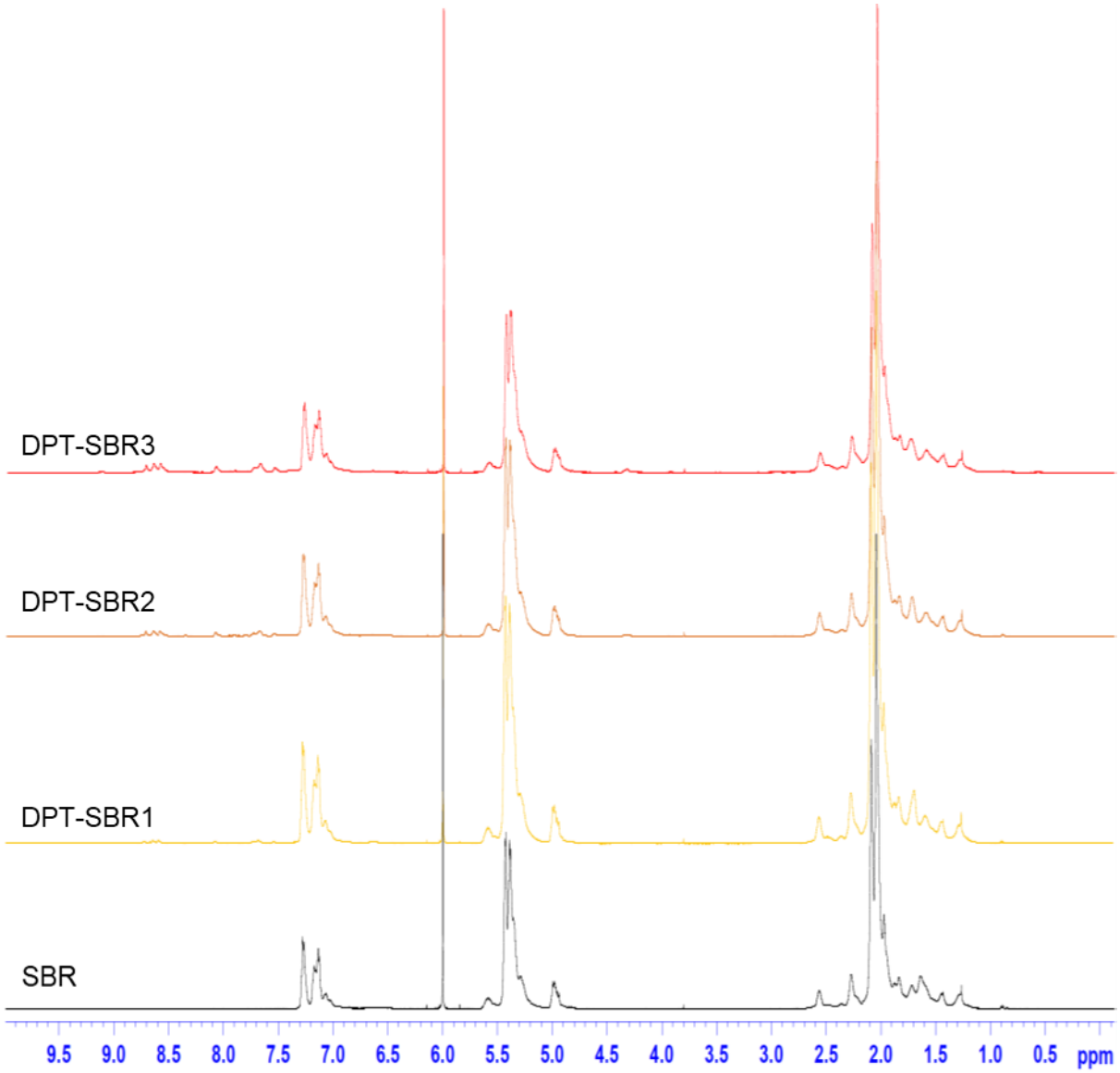

Fig. S1 ^{1}H NMR spectra of SBR (black line), DPT-SBR-1 (yellow line), DPT-SBR2 (orange line) and DPT-SBR3 (red line) ($CDCl_3$, 600 MHz).

The ratios of styrene, butadiene, butadiene 1,4 unit, butadiene 1,2 unit, and DPT unit were calculated by the following equations respectively. Here, *I (A)*, *I (B)*, *I (C)*, and *I (D)* represent the integral ratio of δ 8.81–7.46 ppm (aromatic 8H of DPT unit), 7.45–6.40 ppm (aromatic 5H of styrene unit), 5,70–5.05 ppm (1H of butadiene 1,2 unit and 2H of butadiene 1,4 unit), and 5.05-4.70 ppm (2H of butadiene 1,2 unit), respectively.

$$Styrene\ unit\ (mol\%) = \frac{I\,(B)/5}{I(D)/2+(I(C)-I\,(D)/2)/2+I(B)/5+I(A)/8} \times 100\ (mol\%) \quad \text{(S1)}$$

$$Butadiene\ unit\ (mol\%) = \frac{I\,(D)/2+(I(C)-I(D)/2)/2}{I(D)/2+(I(C)-I\,(D)/2)/2+I(B)/5+I(A)/8} \times 100\ (mol\%) \quad \text{(S2)}$$

$$Butadiene\ 1{,}4\ unit\ (mol\%) = \frac{I\ (D)}{I(D)+I(C)-I(D)/2} \times Butadiene\ unit\ (mol\%) \quad \text{(S3)}$$

$$Butadiene\ 1{,}2\ unit\ (mol\%) = \frac{I(C)-I(D)/2}{I(D)+I(C)-I(D)/2} \times Butadiene\ unit\ (mol\%) \quad \text{(S4)}$$

$$DPT\ unit\ (mol\%) = \frac{I\ (A)/8}{I(D)/2+(I(C)-I\ (D)/2)/2+I(B)/5+I(A)/8} \times 100\ (mol\%) \quad \text{(S5)}$$

Modification efficiency is determined by following equation.

$$Modification\ efficiency\ (\%) = \frac{Loading\ DPT\ ratio\ to\ butadiene\ unit}{DPT\ unit} \times 100\ (\%) \quad \text{(S6)}$$

Table S1 Loading DPT ratio to butadiene unit, integral ratio, and modification-efficiency

Polymer	Loading DPT ratio to butadiene unit (mol%)	*I (A)*	*I (B)*	*I (C)*	*I (D)*	Modification efficiency (%)
SBR	0	0	5.00	11.4	10.8	0
DPT-SBR1	1.0	0.353	5.00	11.0	10.5	75.4
DPT-SBR2	2.0	0.690	5.00	10.6	10.1	76.4
DPT-SBR3	4.0	1.30	5.00	9.92	9.43	75.8

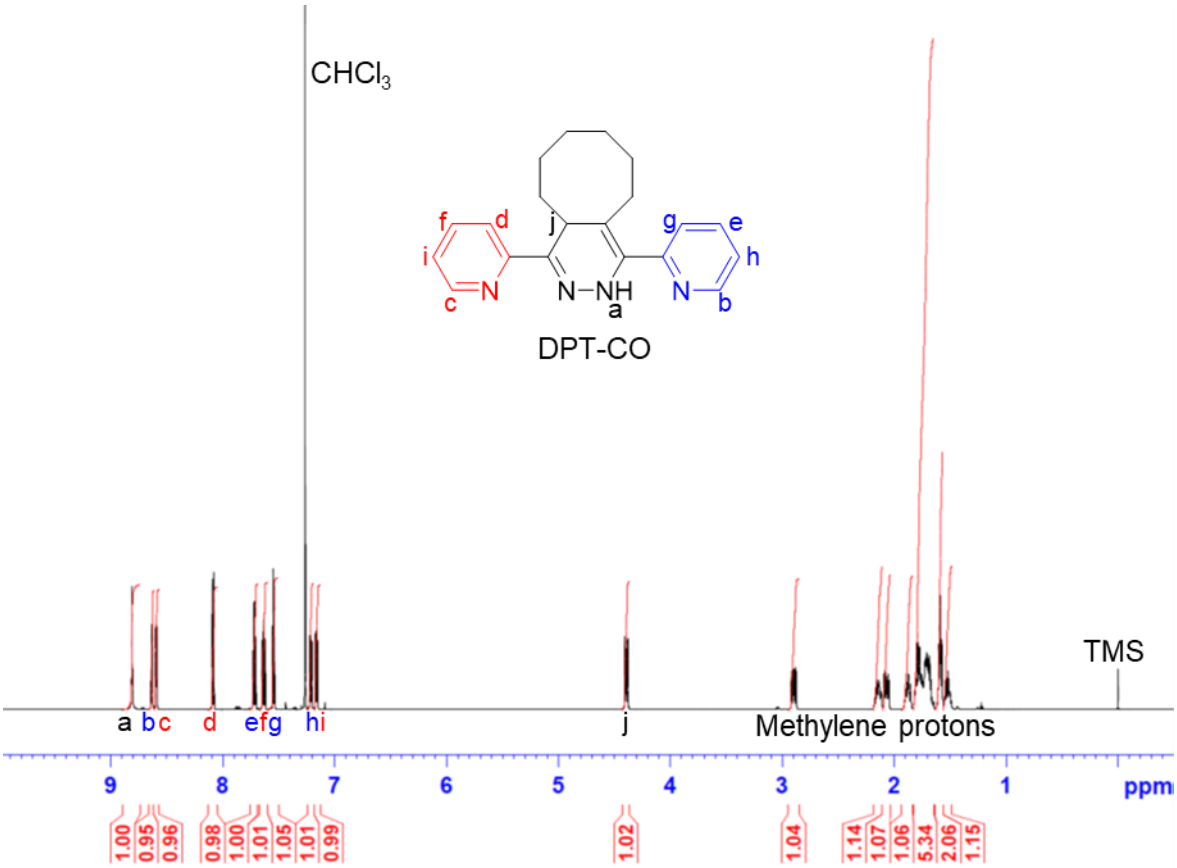

Fig. S2 ^{1}H NMR spectrum of DPT-CO ($CDCl_3$, 600 MHz).

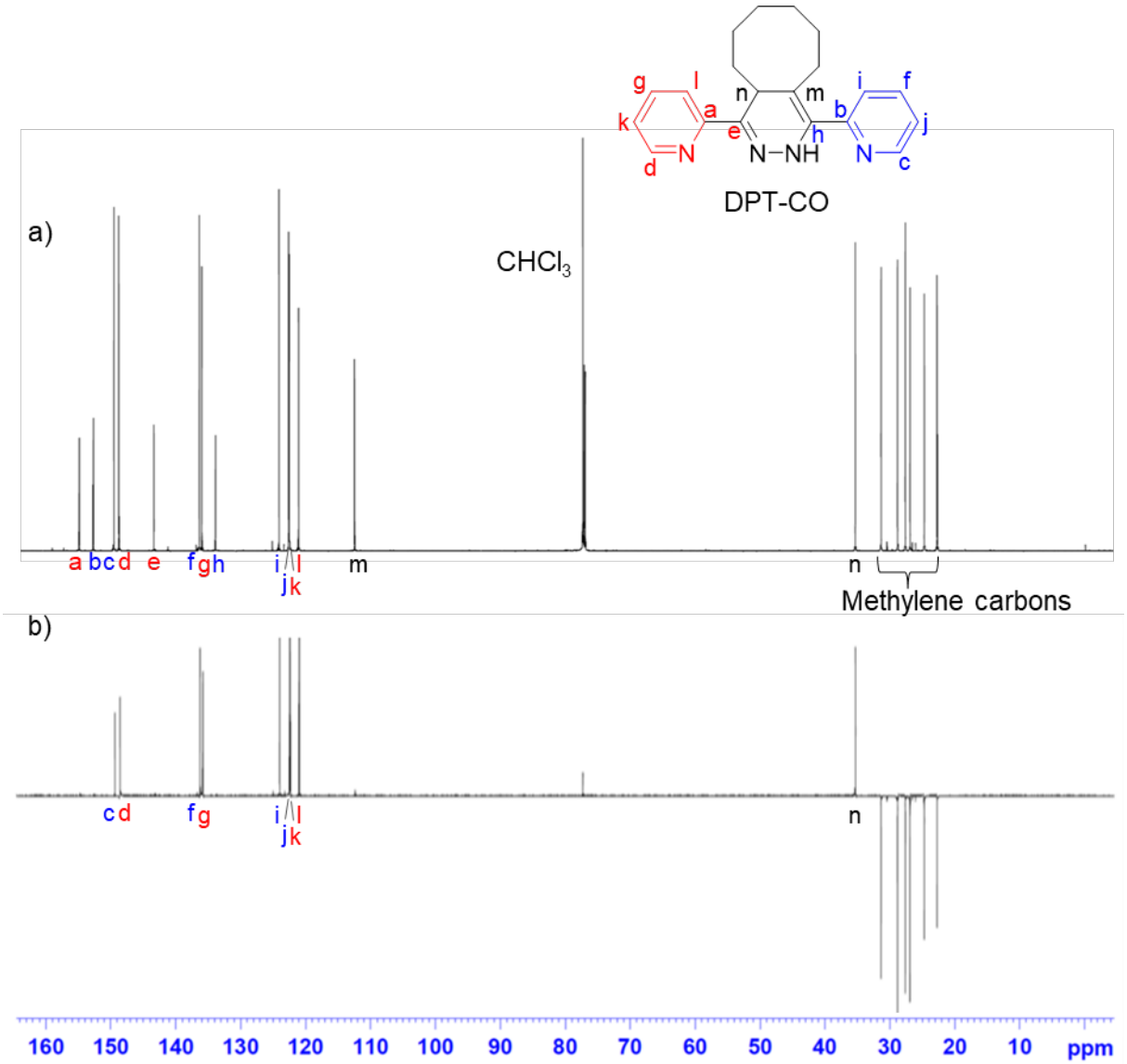

Fig. S3 a) ^{13}C NMR spectrum of DPT-CO and b) DEPT-135 NMR spectrum of DPT-CO ($CDCl_3$, 150 MHz).

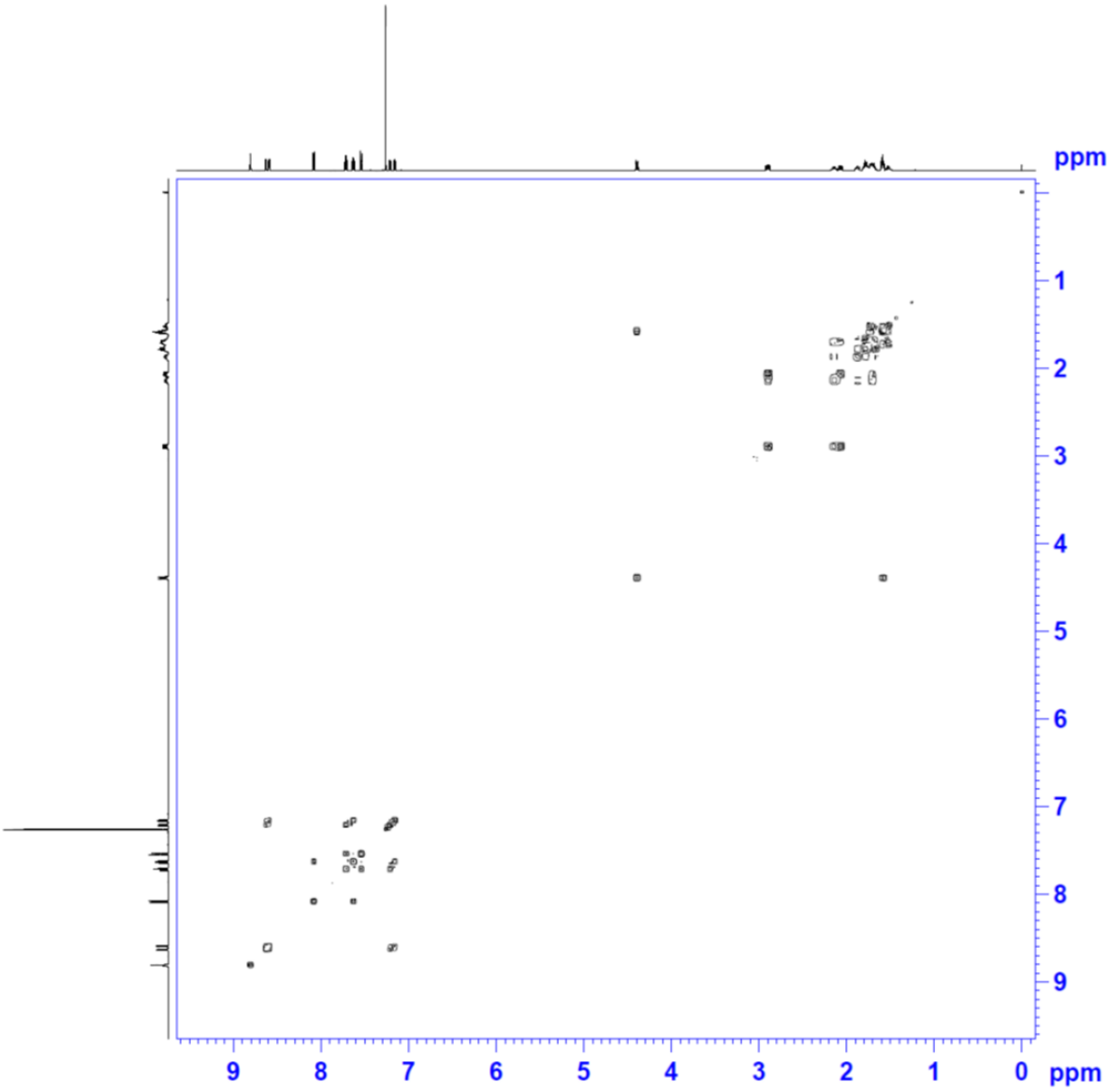

Fig. S4 COSY NMR spectrum of DPT-CO ($CDCl_3$, 600 MHz).

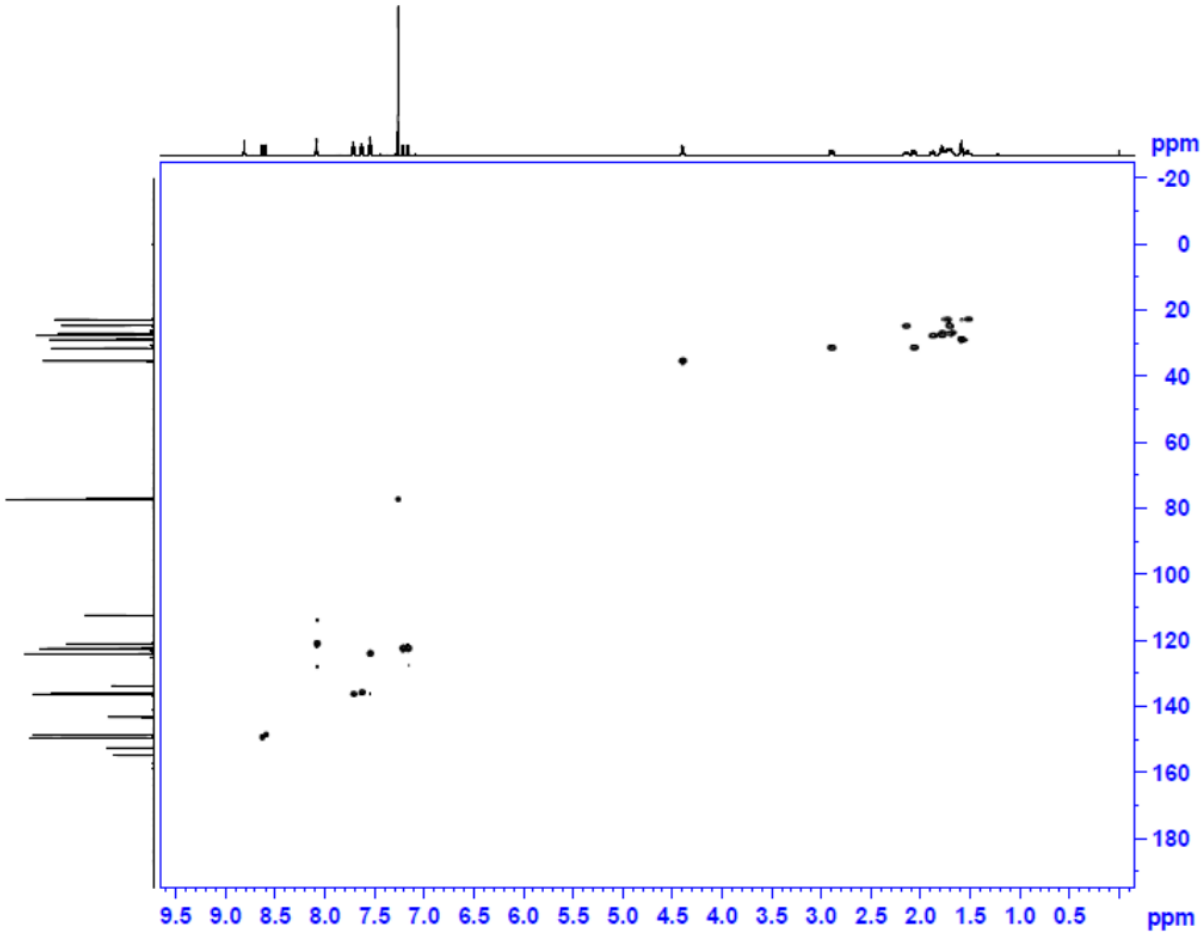

Fig. S5 HSQC NMR spectrum of DPT-CO ($CDCl_3$, 600/150 MHz).

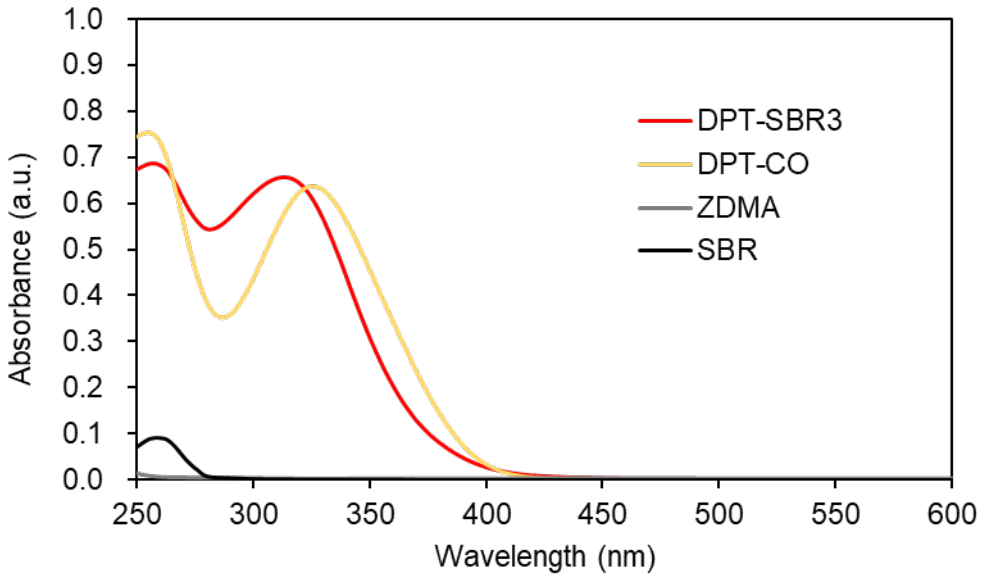

Fig. S6 UV-vis spectra of SBR, ZDMA, CO-DPT and DPT-SBR3.

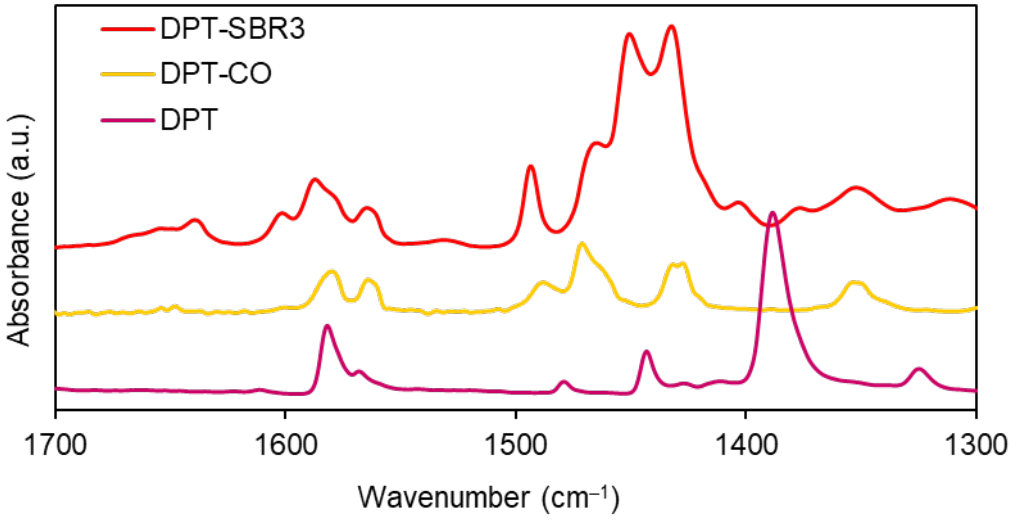

Fig. S7 ATR FT-IR spectra of DPT, DPT-CO and DPT-SBR3.

Preparation of DPT-CO/ZDMA complexes and high-resolution mass spectra (HRMS) study

A round-bottom flask was charged with DPT-CO (27.0 mg, 84.9 μmol) and MeOH (1.0 mL). Subsequently, ZDMA (10.0 mg, 42.5 μmol) was added to the solution at room temperature, which resulted in an immediate color change from pale yellow to orange, indicating that the complexation had reached completion. The resulting solution was further diluted with MeOH and used for HRMS analysis without any purification. As a result, A complex consisting of a Zn^{2+} ion coordinated to two DPT-CO ligands and one methacrylate anion was observed when the molar ratio of ZDMA to DPT-CO was 0.5 (**Fig. S8**). Considering the result of HRMS and UV-vis measurement (Fig. 6 in the article), the bound DPT units in the SBRs are strongly expected to coordinate to Zn^{2+} ions and act as cross-linking points.

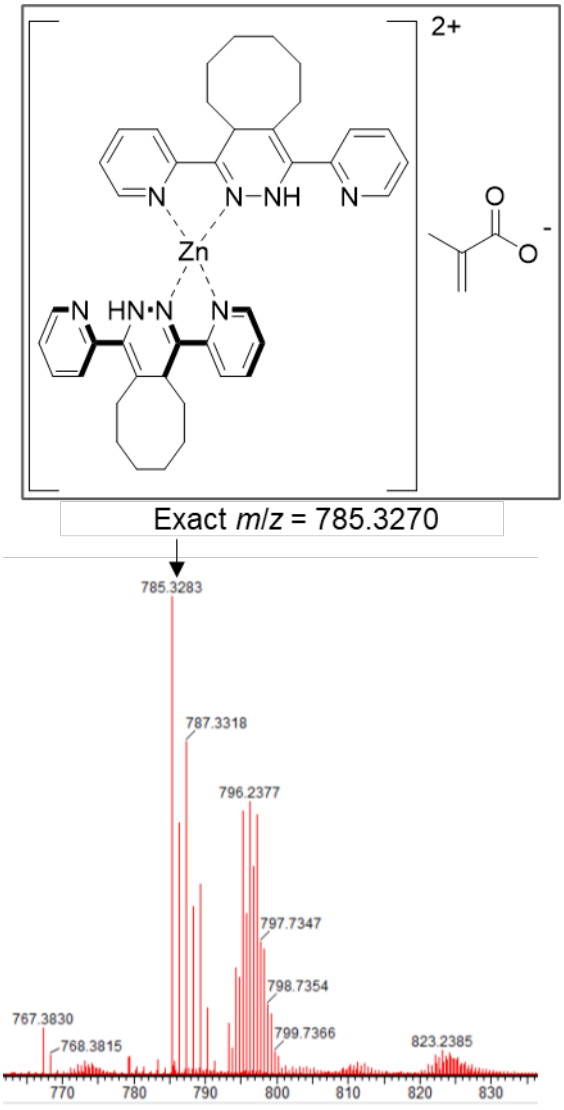

Fig. S8 TOF-MS spectrum of a mixture of DPT-CO and ZDMA (molar ratio ZDMA : DPT-CO = 0.5 : 1) and a plausible structure of the DPT-CO/ZDMA complex.

Table S2 Formulation of prepared cross-linked control samples varying amount of dicumyl peroxide (DCP). The unit of the values (phr) refers to weight fraction of the specified rubber component per 100 units of the base rubber.

Run	1	S1	S2
Sample code	SBR/Z40/DCP	SBR/Z40/DCP–	SBR/Z40/DCP+
SBR	100	100	100
ZDMA	40	40	40
DCP	0.2	0.05	0.4

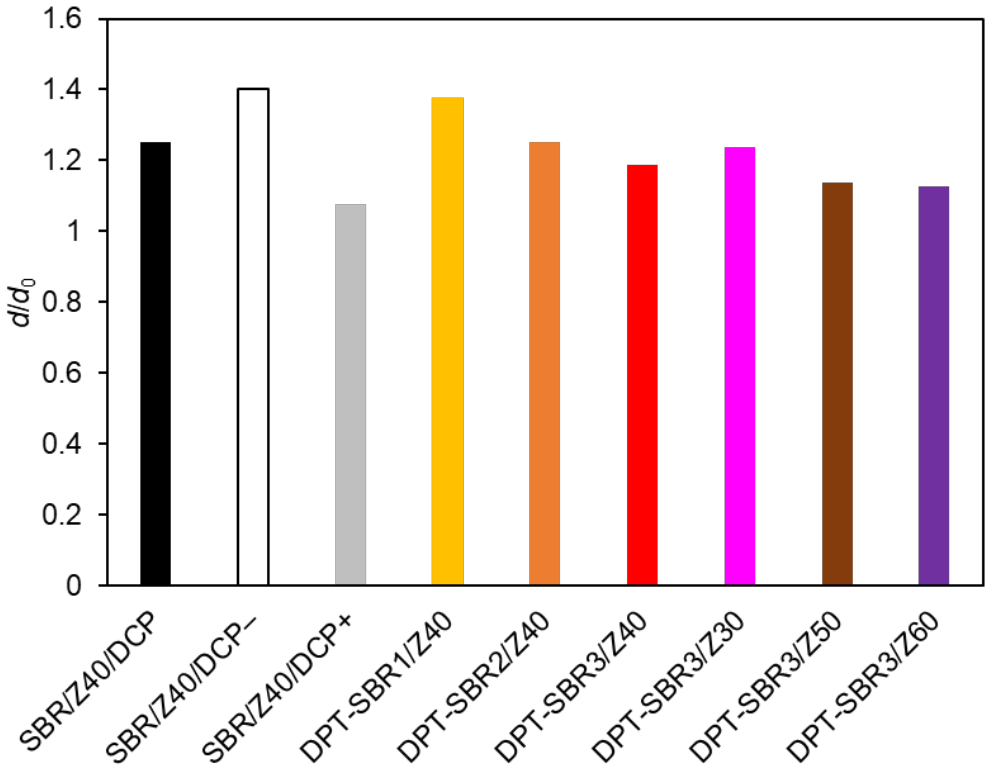

Fig. S9 Swelling degree of each sample after immersion in *n*-heptane for 4 days. Disc-shaped cross-linked specimens of 8.0 mm diameter were immersed in *n*-heptane for 4 days at r.t. and the swelling degree of specimens is defined as the length swelling ratio ($\lambda_s=d/d_0$; d_0 and d represent the diameter of a disc-shaped specimen before and after swelling, respectively).

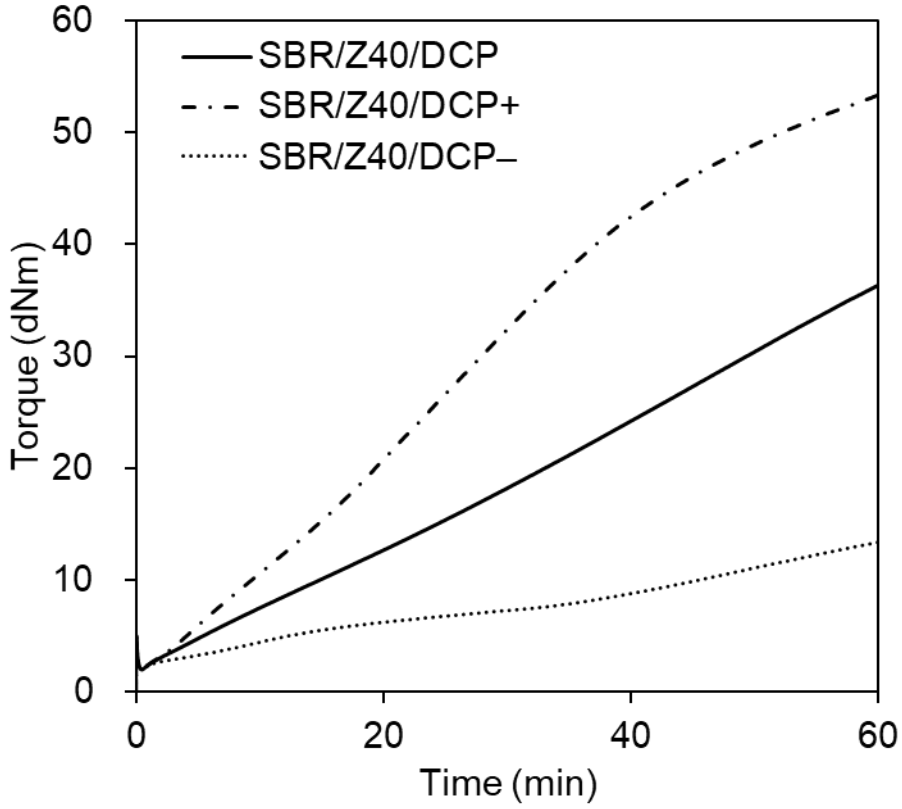

Fig. S10 Elastic torque curves of control samples varying DCP amount measured at 145 °C.

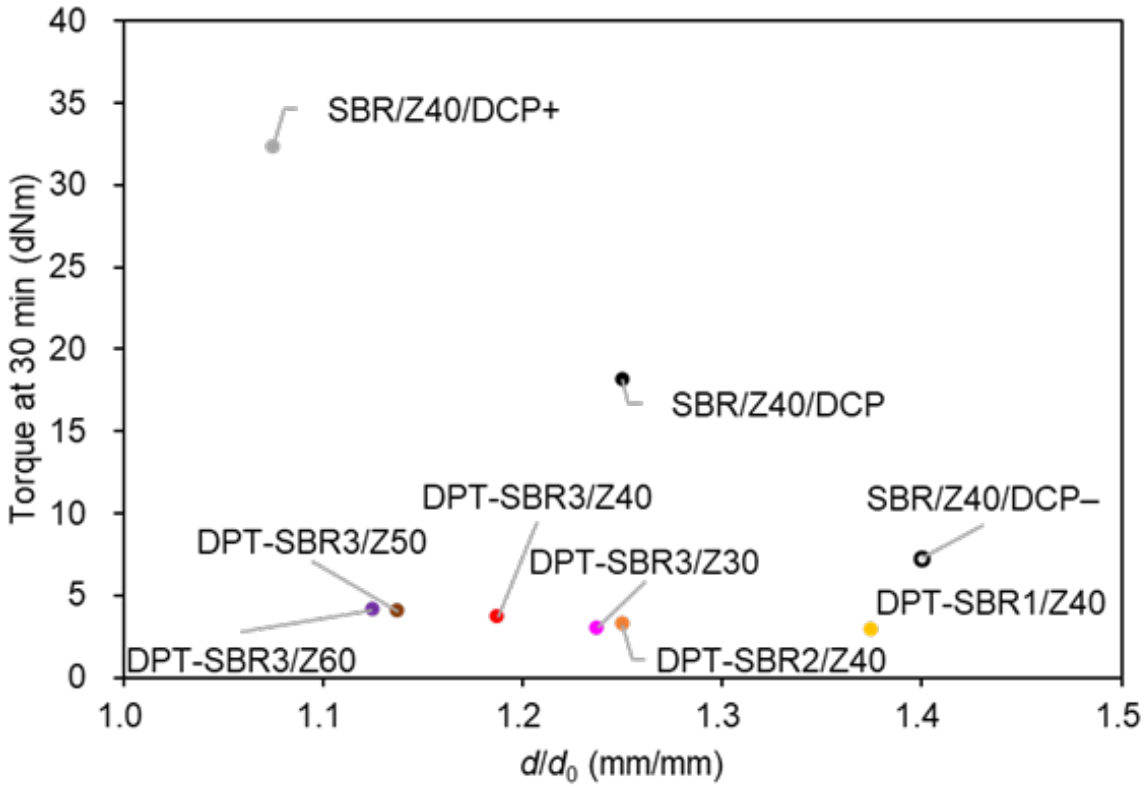

Fig. S11 Relationship between degree of swelling and torque at 30 min on the moving die rheometer.

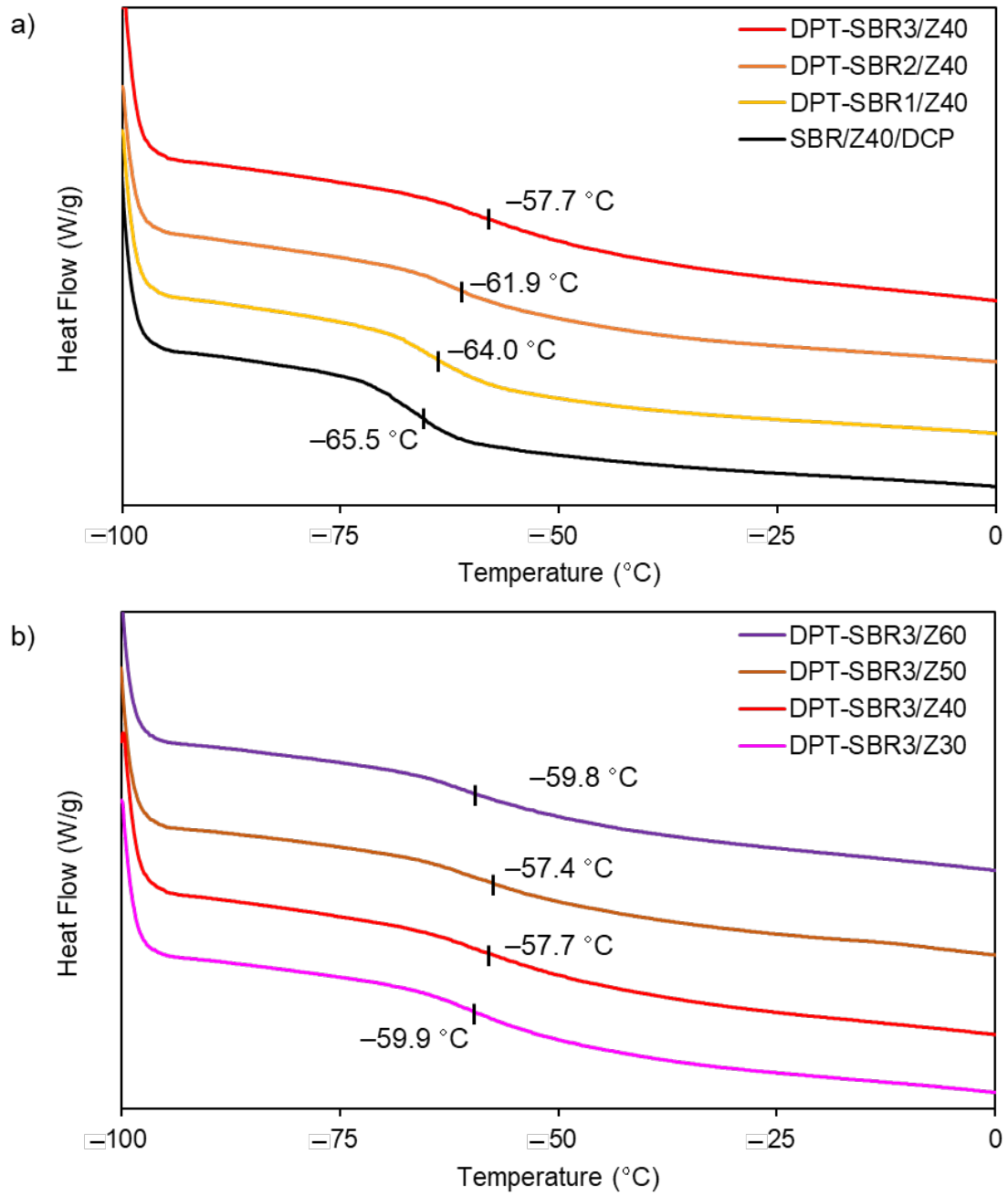

Fig. S12 DSC results for cured rubber samples: a) Effect of the DPT amounts in SBRs and b) effect of the ZDMA amounts.

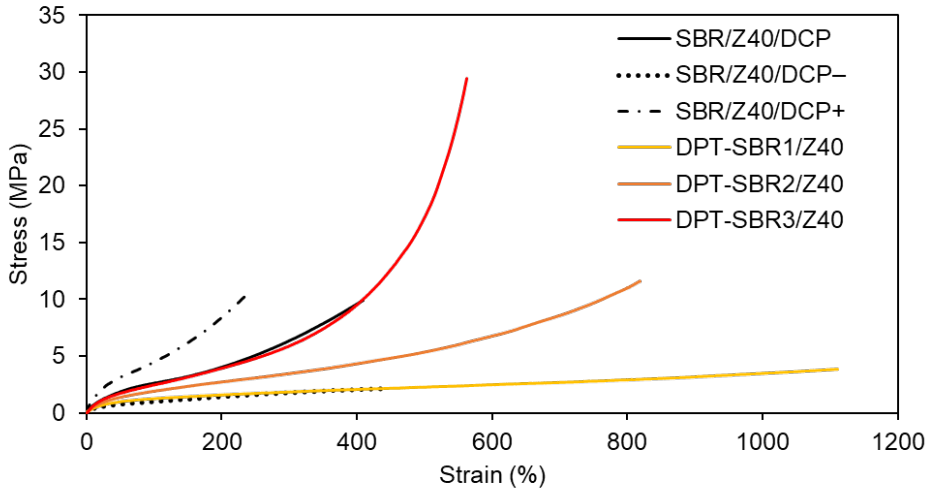

Fig. S13 Engineering stress–strain curves of control samples varying DCP amounts and DPT-SBRs with 40 phr of ZDMA.

Table S3 Moduli and fracture parameters of the cross-linked control samples varying DCP amount shown in Fig. S12. Values in parentheses refer to the standard deviation.

Run/Sample code	Tensile stress at 100% elongation (MPa)	Tensile stress at 300% elongation (MPa)	Elongation at break (E_b) (%)	Tensile strength at break (T_b) (MPa)	Fracture energy (MJ/m^3)
1/SBR/Z40/DCP	2.64 (0.03)	6.44 (0.32)	365 (32)	8.50 (0.98)	14.7 (2.91)
S1/SBR/Z40/DCP–	1.00 (0.02)	1.77 (0.07)	457 (17)	2.15 (0.03)	4.93 (2.25)
S2/SBR/Z40/DCP+	4.36 (0.14)	N.A.	246 (34)	10.4 (1.40)	13.2 (3.05)

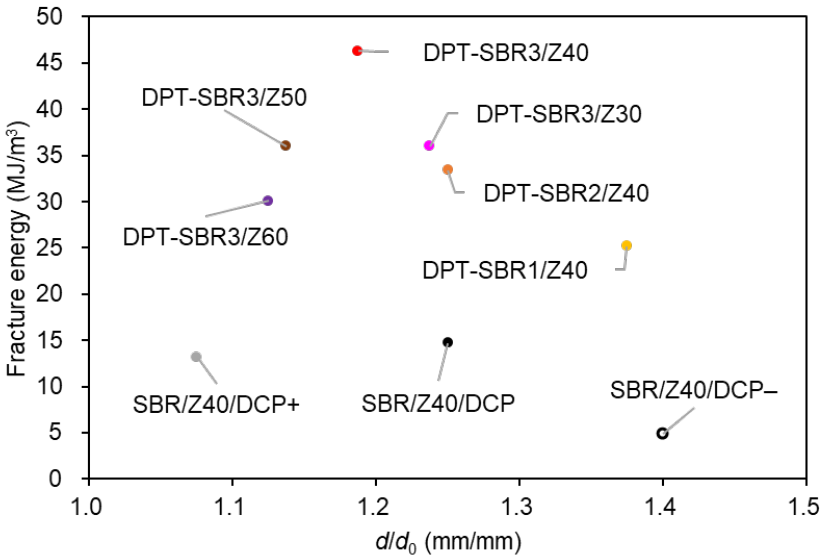

Fig. S14 Relationship between fracture energy and swelling rate using *n*-heptane.

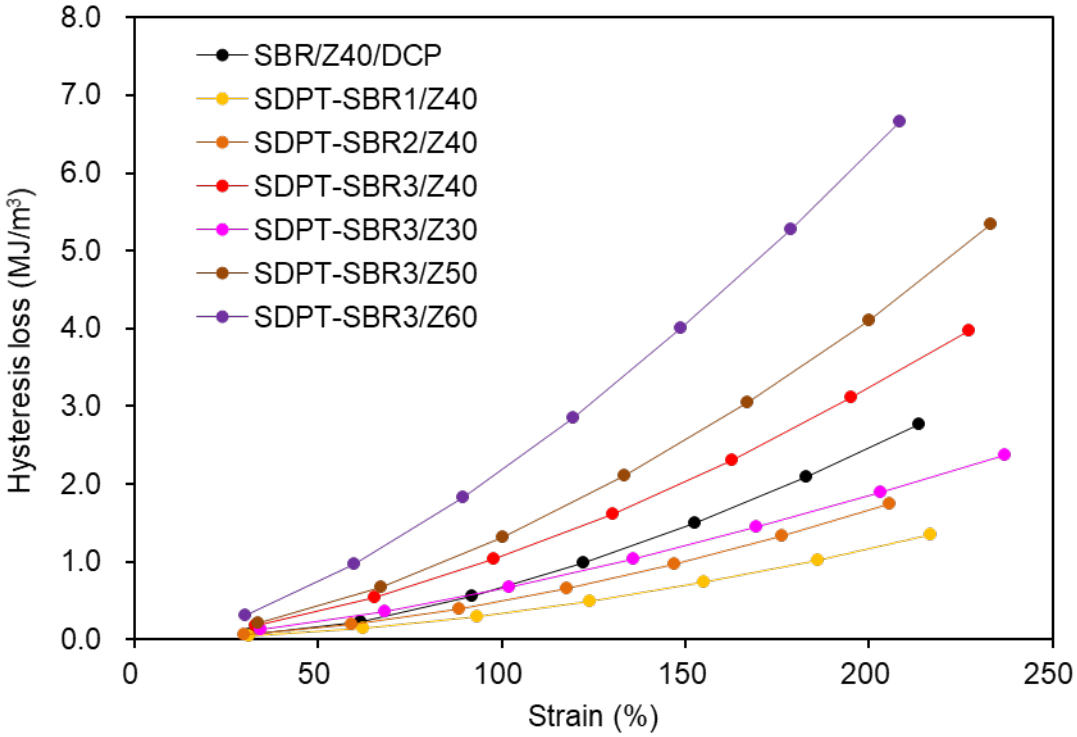

Fig. S15 Strain dependency on hysteresis loss of each sample.

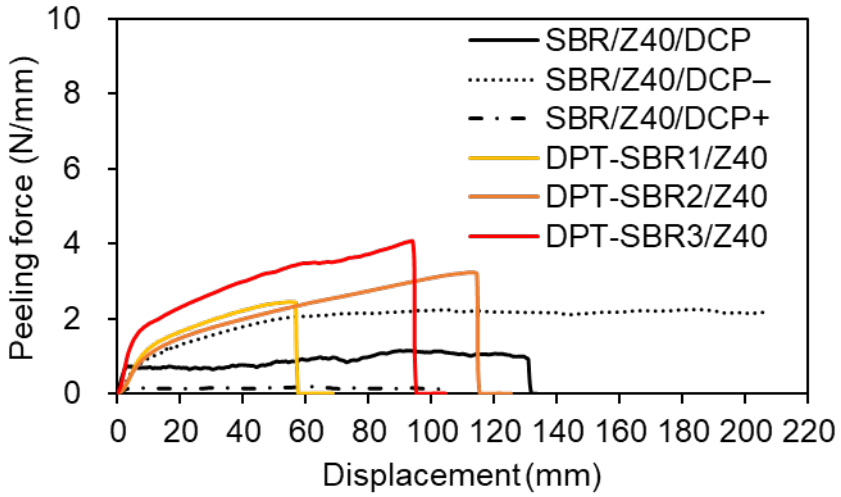

Fig. S16 T-peel tests results of control samples varying DCP amounts and DPT-SBRs with 40 phr of ZDMA.

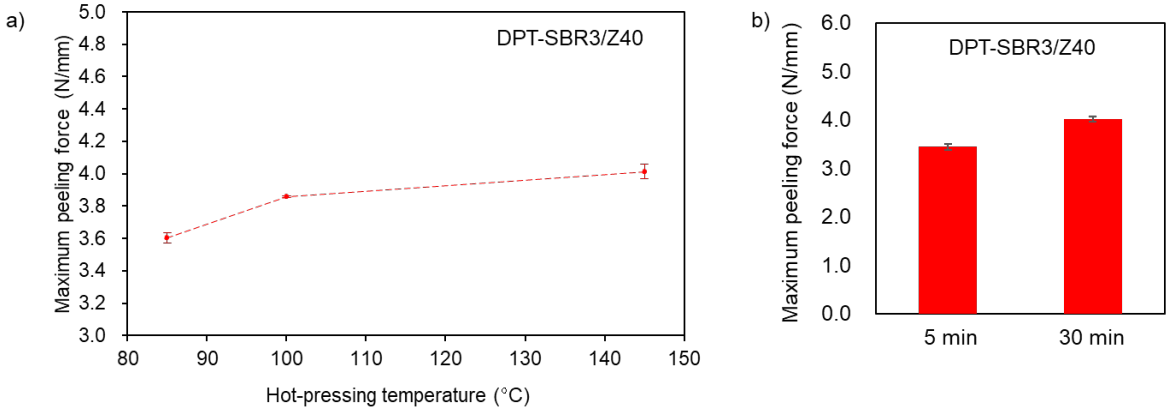

Fig. 17 Relationship between the adhesion strength and hot-pressing condition for DPT-SBR3/Z40: a) Effect of the hot-pressing temperature for 30 min and b) effect of the hot-pressing time at 145 °C.

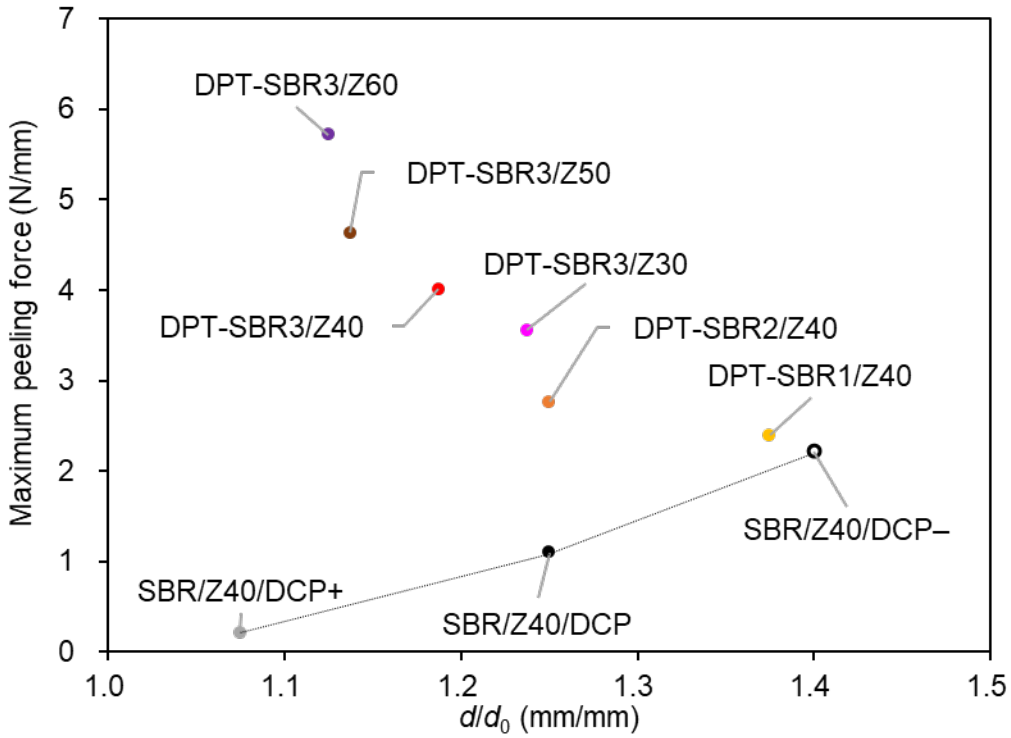

Fig. 18 Relationship between adhesion strength and swelling rate using *n*-heptane.