Novel Covalent Adaptable Networks (CANs) of Ethylene/1-Octene Copolymers (EOCs) Made by Free-Radical Processing: Comparison of Structure-Property Relationships of EOC CANs with EOC Thermosets

Supporting Information

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Synthesis of BiTEMPS Methacrylate (BTMA) Cross-Linker for Reprocessing Studies Via Extrusion. For reprocessing studies via extrusion, BTMA was synthesized using a modified method. In a nitrogen-filled glove box, TMPM (80.0 g, 355 mmol) was dissolved in 440 mL of pre-dried, degassed tetrahydrofuran (THF). Triethylamine (247.4 mL, 1775 mmol) was added, and the stirring solution was cooled to -35 °C in an acetone/dry ice bath. S_2Cl_2 (14.2 mL, 178 mmol) was dissolved in 40 mL of THF and added dropwise to the cooled solution via syringe pump over 15 min. A yellow suspension formed; this suspension was warmed to room temperature and left to stir for 30 min. After, the suspension was poured into 3 L of DI water and stirred overnight. The resulting precipitate was dissolved in diethyl ether, and two liquid-liquid extractions were performed with brine. The organic layers were combined, dried over $MgSO_4$, and filtered. Solvent was removed under vacuum to give an oil which was mixed with 500 mL of methanol and cooled at -20 °C overnight. After, the recrystallized white solid was dried under vacuum overnight to give BTMA (52.9 g, 55%).

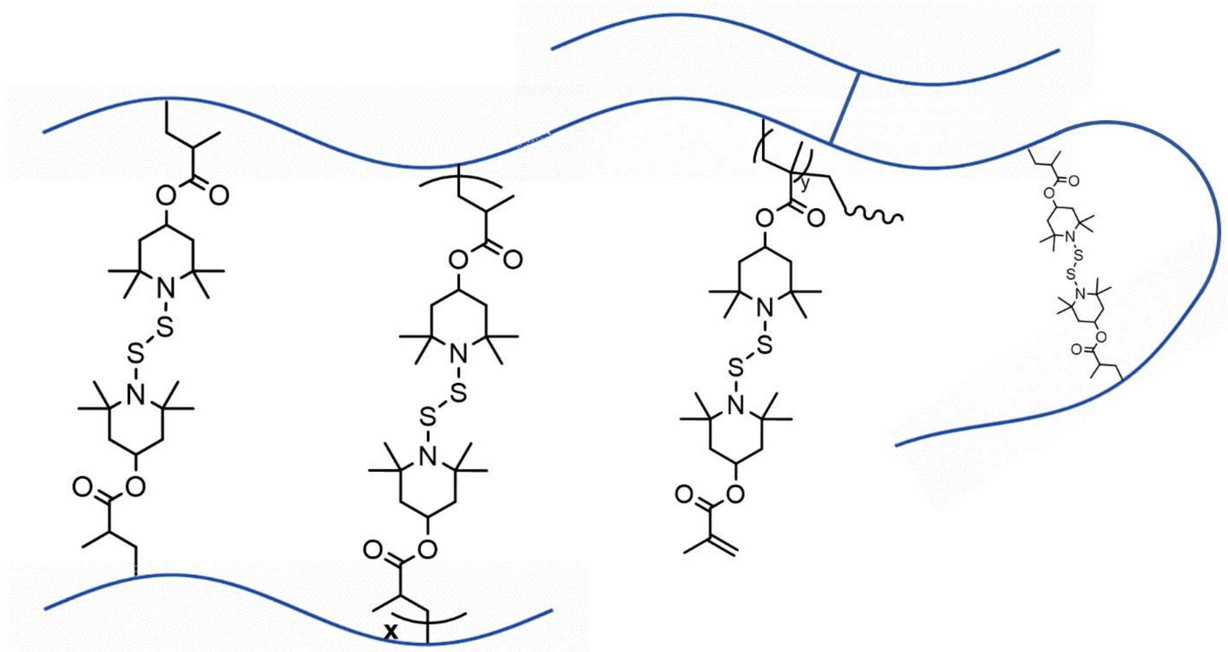

Figure S1. Possible chemistries during the preparation of EOC CANs, including single cross-links, cross-links of a run of multiple BTMA units, dangling BTMA units or runs, intra-chain loops, and permanent crosslinks.

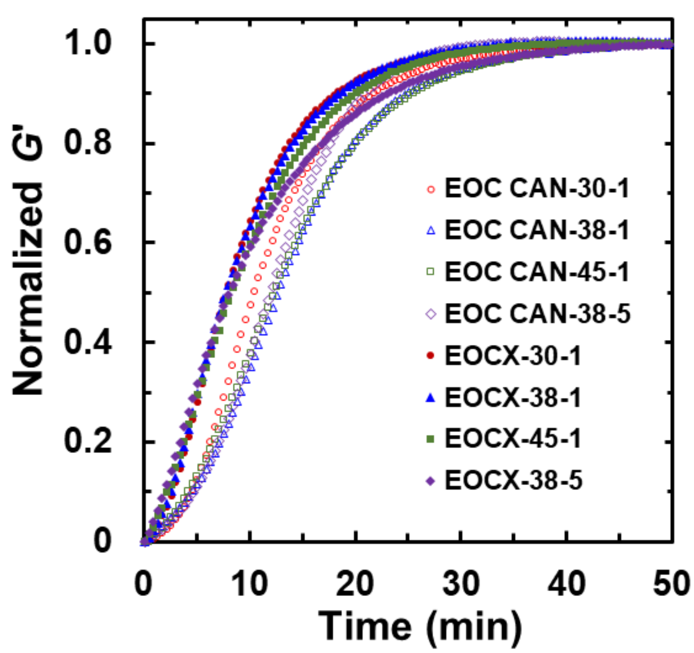

Figure S2. Normalized shear storage modulus (*G*') as a function of curing time at 180 °C obtained by small-amplitude oscillatory shear experiment with 1.0 Hz frequency and 0.1% strain (normalization is done relative to final *G'* value during curing).

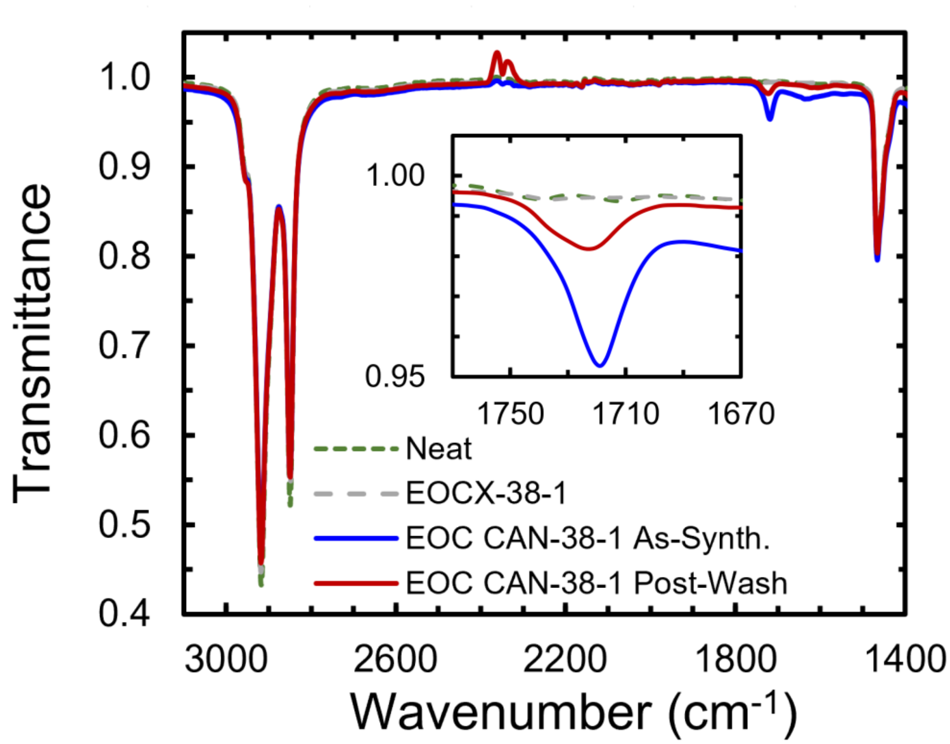

Figure S3. FTIR spectra of neat EOC-38-1, 1st-molded EOCX-38-1, and 1st-molded EOC CAN-38-1 before and after washing in boiling xylene via Soxhlet extraction. The carbonyl stretch at ~1720 cm^{-1} indicates that BTMA was grafted to EOC backbones during reactive processing.

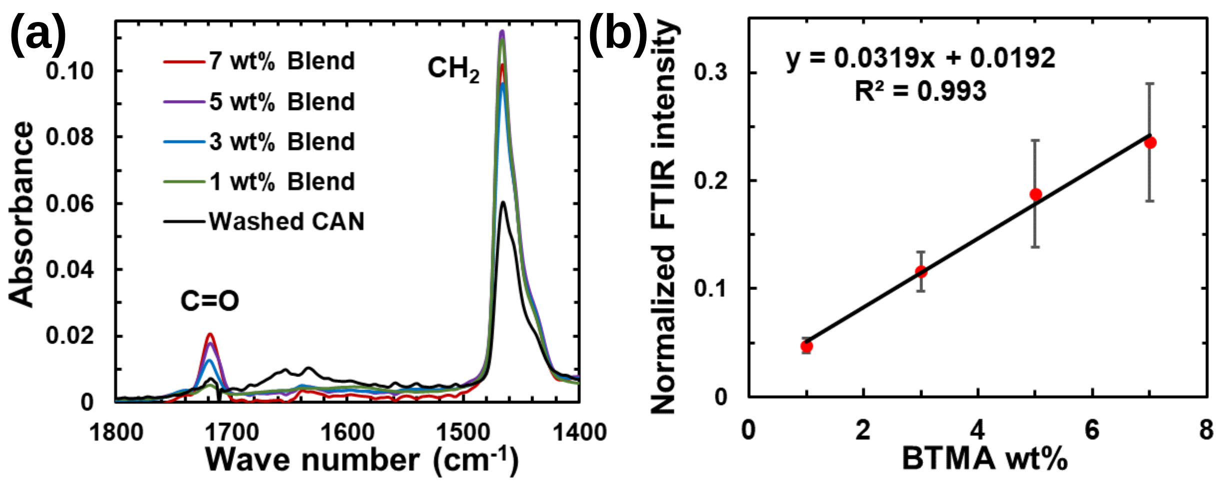

Figure S4. (a) FTIR spectra of blends of EOC-30-1 with varying amounts of BTMA and washed EOC CAN-30-1. (b) FTIR calibration curve: intensity of BTMA C=O (1720 cm^{-1}) normalized by C−H (1470 cm^{-1}) as a function of BTMA wt% in blends of EOC-30-1 with varying amounts of BTMA.

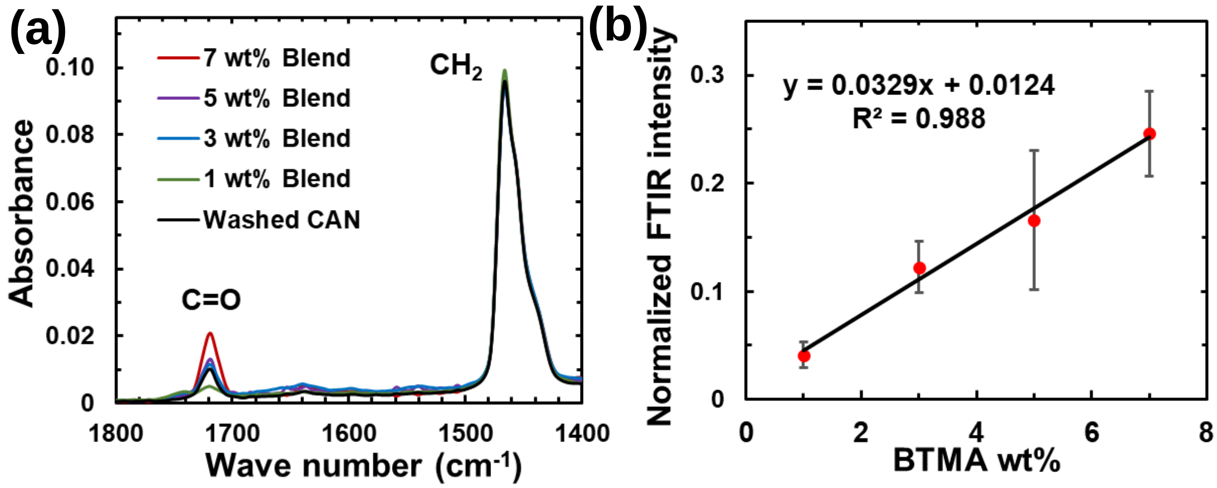

Figure S5. (a) FTIR spectra of blends of EOC-38-1 with varying amounts of BTMA and washed EOC CAN-38-1. (b) FTIR calibration curve: intensity of BTMA C=O (1720 cm^{-1}) normalized by C−H (1470 cm^{-1}) as a function of BTMA wt% in blends of EOC-38-1 with varying amounts of BTMA.

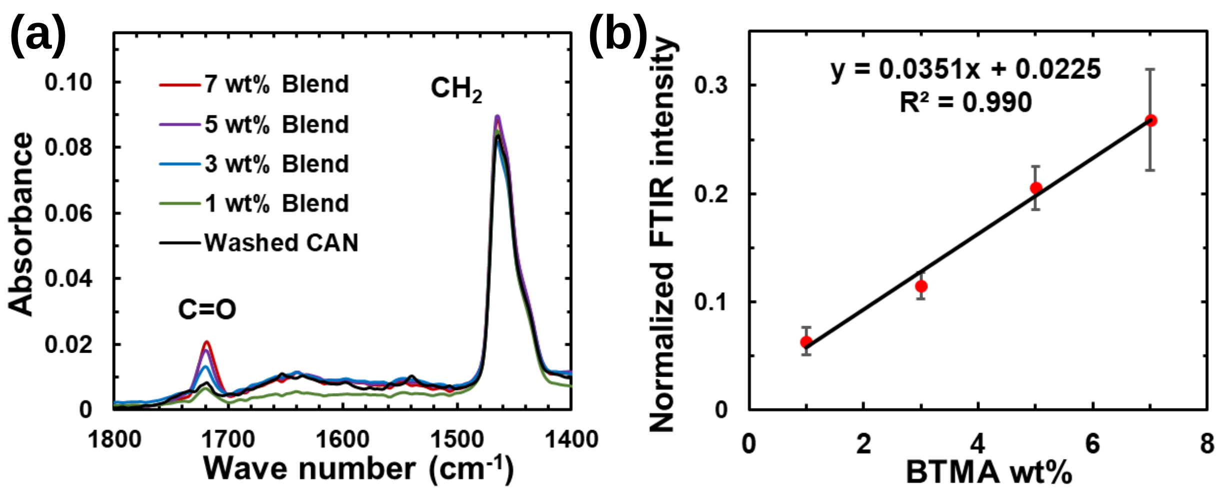

Figure S6. (a) FTIR spectra of blends of EOC-45-1 with varying amounts of BTMA and washed EOC CAN-45-1. (b) FTIR calibration curve: intensity of BTMA C=O (1720 cm^{-1}) normalized by C−H (1470 cm^{-1}) as a function of BTMA wt% in blends of EOC-45-1 with varying amounts of BTMA.

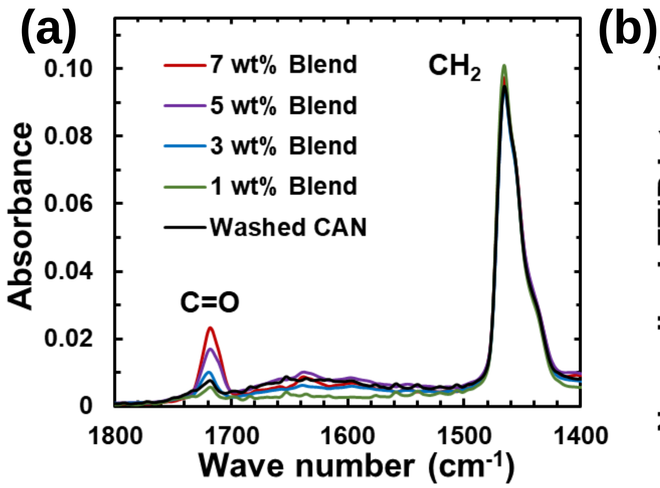

Figure S7. (a) FTIR spectra of blends of EOC-38-5 with varying amounts of BTMA and washed EOC CAN-38-5. (b) FTIR calibration curve: intensity of BTMA C=O (1720 cm^{-1}) normalized by C−H (1470 cm^{-1}) as a function of BTMA wt% in blends of EOC-38-5 with varying amounts of BTMA.

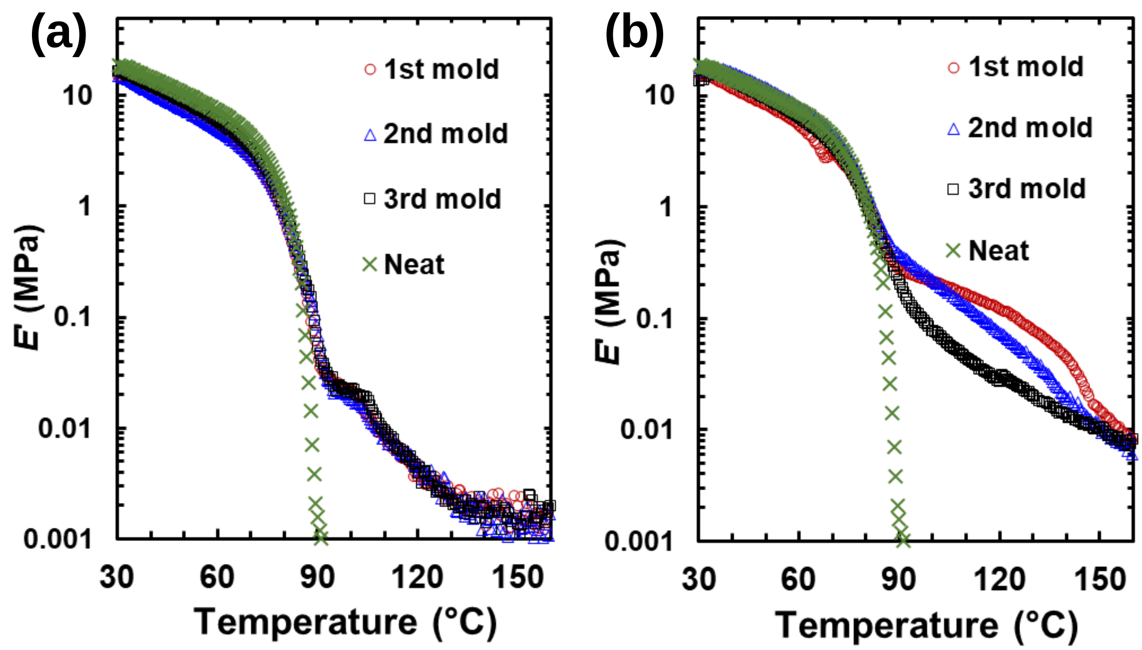

Figure S8. Tensile storage modulus (*E*') as a function of temperature and molding of (a) EOC CAN-31-30 with 5 wt% BTMA and 1 wt% DCP and (b) EOC CAN-31-30 with 10 wt% BTMA and 2 wt% DCP alongside neat EOC-31-30.

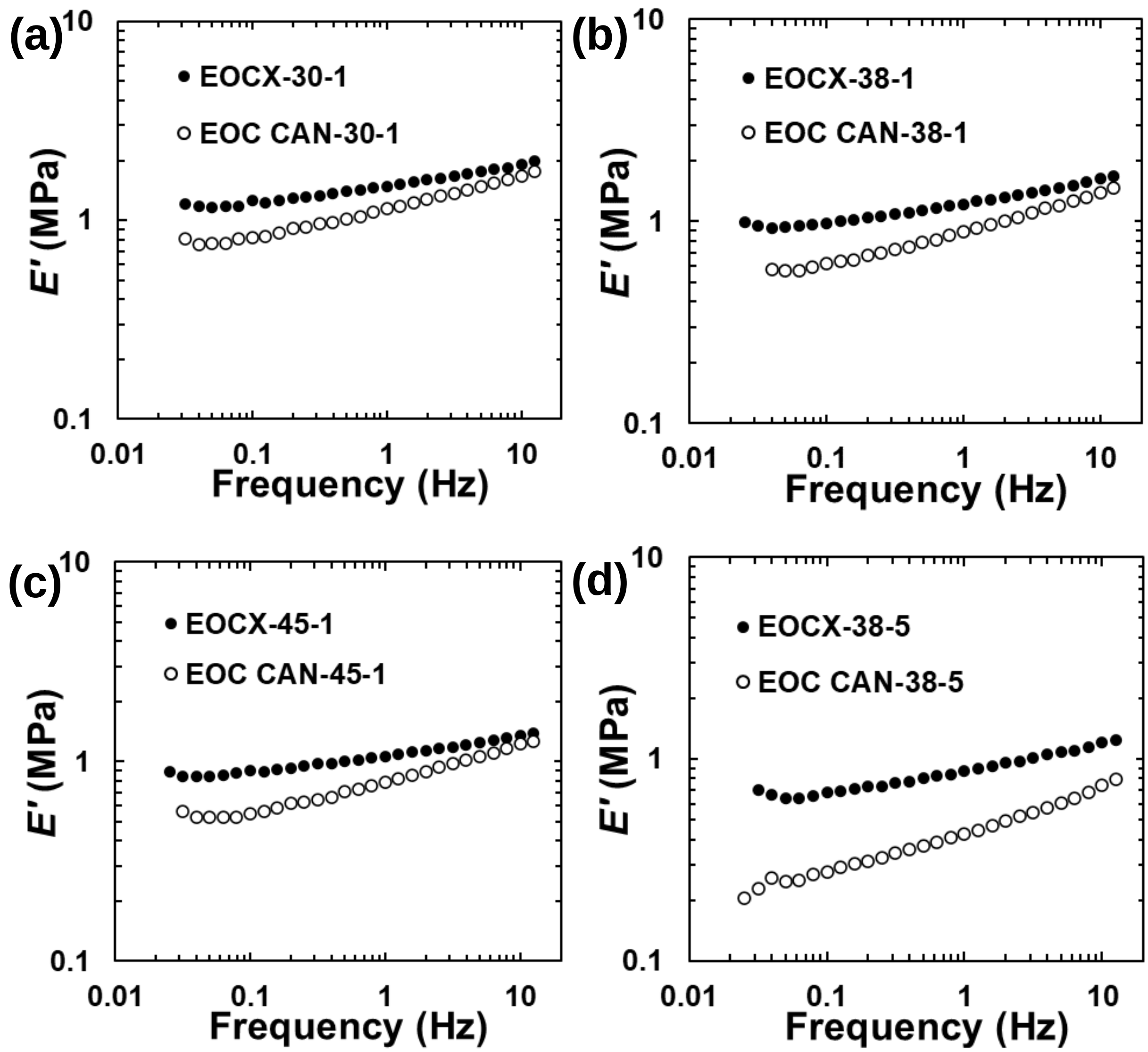

Figure S9. Storage modulus (*E'*) at 100 °C as a function of frequency for EOCXs (filled symbols) and EOC CANs (open symbols) made from (a) EOC-30-1, (b) EOC-38-1, (c) EOC-45-1, and (d) EOC-38-5.

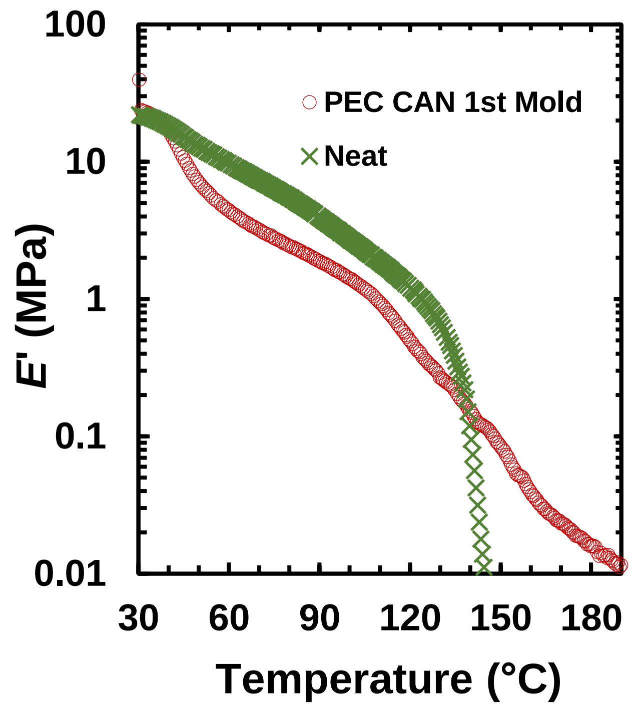

Figure S10. Tensile storage modulus (*E*') as a function of temperature for neat PEC as well as its failed cross-linking attempt (PEC CAN 1st Mold).

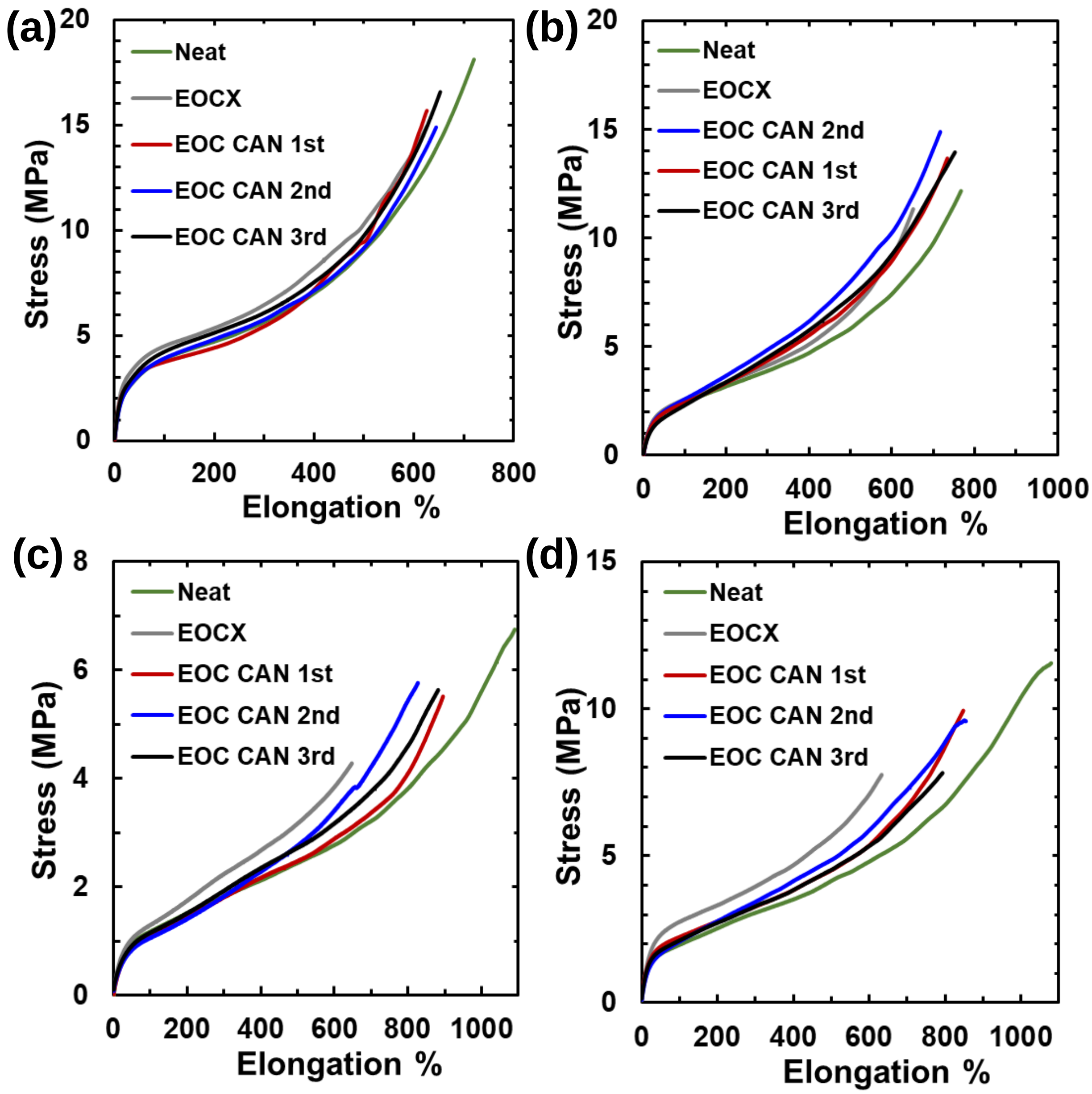

Figure S11. Room-temperature stress-elongation curves of EOCXs and EOC CANs made from (a) EOC-30-1, (b) EOC-38-1, (c) EOC-45-1, and (d) EOC-38-5 with their corresponding neat counterparts.

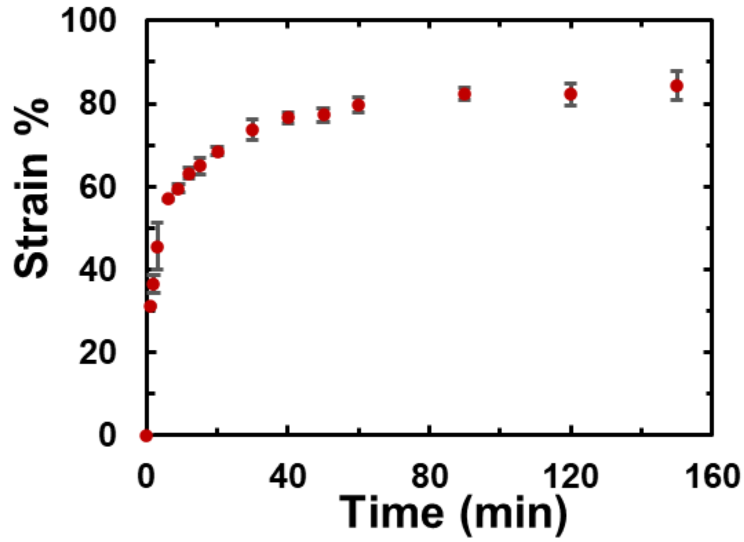

Figure S12. Strain as a function of time for EOC CAN-45-1 at 50 °C under a tensile load of 0.33 MPa.

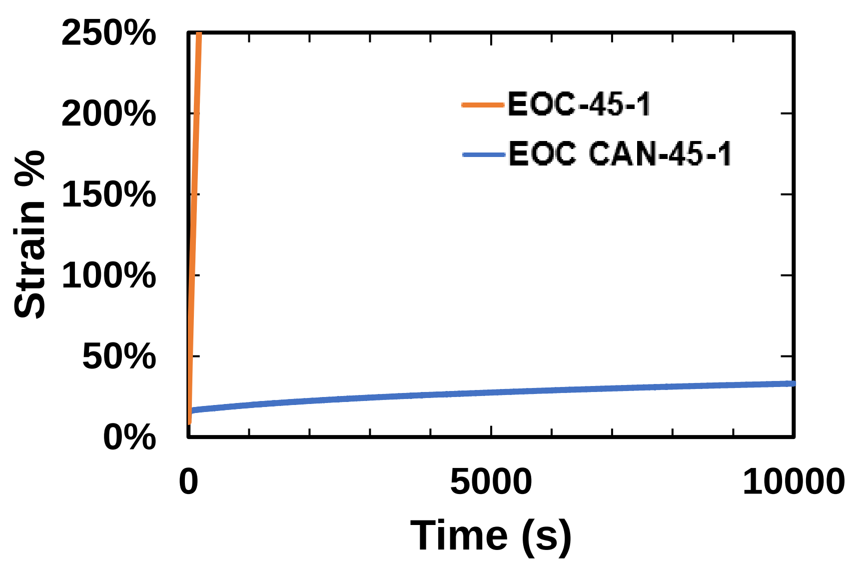

Figure S13. Strain as a function of time for EOC-45-1 and EOC CAN-45-1 at 90 °C under a shear load of 3.0 kPa.

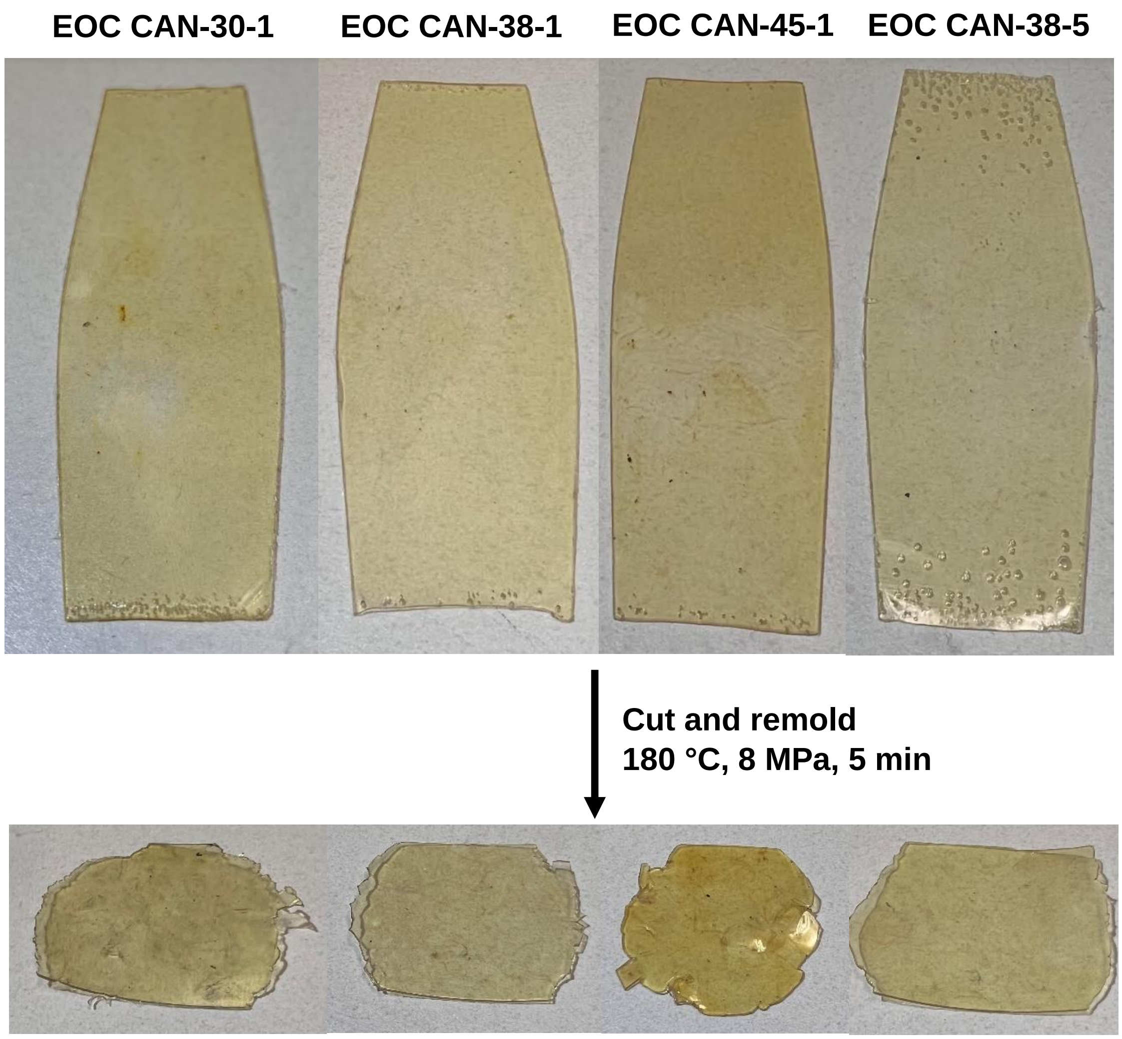

Figure S14. Reprocessing of 1st-molded EOC CANs (top) by cutting and compression-molding (180 °C, 8 MPa, 5 min) pieces into healed films as the 2nd-mold samples (bottom). Another reprocessing step to prepare the 3rd-molded samples was performed in a similar manner.

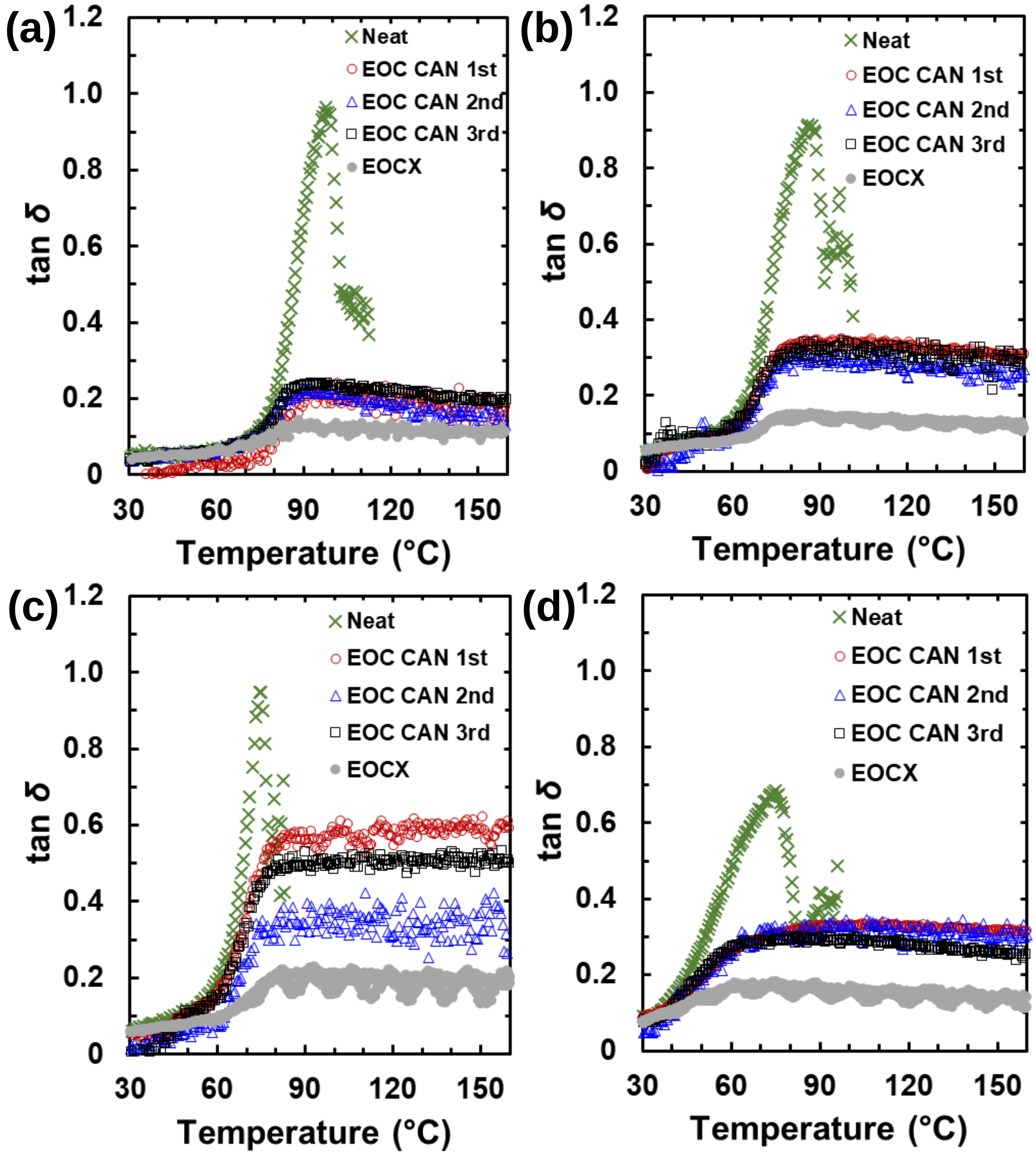

Figure S15. Tan δ as a function of temperature and molding of EOC CANs made from (a) EOC-30-1, (b) EOC-38-1, (c) EOC-45-1, and (d) EOC-38-5 with their corresponding EOCXs and neat counterparts.

Figure S16. Extrusion of EOC CAN-38-1 at 200 °C. Note the surface defects from melt fracture.

Table S1. Thermal properties by DSC of neat EOCs, EOCXs, EOC CANs, and PEC as a function of molding step.

Material	Sample	Mold	$T_{m,peak}$ (°C)	$T_{m,endpoint}$ (°C)	Crystallinity (%)
EOC-30-1	Neat	--	81	98	23
	EOCX-30-1	--	78	95	20
	EOC CAN-30-1	1st	78	95	21
		2nd	78	94	21
		3rd	78	94	20
EOC-38-1	Neat	--	63	85	18
	EOCX-38-1	--	64	80	14
	EOC CAN-38-1	1st	63	83	17
		2nd	62	82	16
		3rd	64	82	17
EOC-45-1	Neat	--	50	67	11
	EOCX-45-1	--	41	64	7
	EOC CAN-45-1	1st	39	62	7
		2nd	40	63	8
		3rd	40	62	8
EOC-38-5	Neat	--	63	85	19
	EOCX-38-5	--	60	81	17
	EOC CAN-38-5	1st	60	85	17
		2nd	61	82	18
		3rd	61	81	17
EOC-31-30	Neat	--	84	96	15
PEC	Neat	--	142	154	14

Table S2. Times in which $G'(t)/G'_0 = 0.95$ (t_{95}) during SAOS curing tests for EOC CANs and EOCXs.

Sample	t_{95} (min)
EOCX-30-1	23
EOCX-38-1	23
EOCX-45-1	27
EOCX-38-5	24
EOC CAN-30-1	27
EOC CAN-38-1	29
EOC CAN-45-1	30
EOC CAN-38-5	24

Table S3. *E*' as a function of temperature and molding step for neat EOCs, EOCXs, and EOC CANs.

Material	Sample	Mold	*E*' (MPa)[a]			
			100 °C	**120 °C**	**140 °C**	**160 °C**
EOC-30-1	Neat	--	0.13	0.0033	0.0011	0.0009
	EOCX-30-1	--	1.4 ± 0.3	1.4 ± 0.2	1.3 ± 0.2	1.54 ± 0.01
	EOC CAN-30-1	1st	1.10 ± 0.09	0.99 ± 0.07	0.90 ± 0.04	0.79 ± 0.04
		2nd	1.14 ± 0.06	1.05 ± 0.03	1.01 ± 0.02	0.95 ± 0.01
		3rd	1.14 ± 0.04	1.03 ± 0.03	0.96 ± 0.05	0.86 ± 0.09
EOC-38-1	Neat	--	0.0092	0.0015	0.0016	0.0014
	EOCX-38-1	--	1.3 ± 0.2	1.3 ± 0.2	1.2 ± 0.1	1.2 ± 0.1
	EOC CAN-38-1	1st	0.76 ± 0.08	0.65 ± 0.04	0.56 ± 0.02	0.48 ± 0.03
		2nd	0.91 ± 0.04	0.76 ± 0.01	0.66 ± 0.02	0.58 ± 0.06
		3rd	0.84 ± 0.04	0.74 ± 0.02	0.65 ± 0.05	0.59 ± 0.05
EOC-45-1	Neat	--	0.0013	0.0013	0.0010	0.0010
	EOCX-45-1	--	0.90	0.81	0.80	0.80
	EOC CAN-45-1	1st	0.69 ± 0.03	0.58 ± 0.03	0.52 ± 0.04	0.44 ± 0.05
		2nd	0.75 ± 0.01	0.63 ± 0.02	0.56 ± 0.02	0.52 ± 0.01
		3rd	0.72 ± 0.07	0.62 ± 0.09	0.57 ± 0.05	0.56 ± 0.01
EOC-38-5	Neat	--	0.0011	0.0011	0.0010	0.0007
	EOCX-38-5	--	0.42 ± 0.03	0.39 ± 0.01	0.37 ± 0.02	0.36 ± 0.04
	EOC CAN-38-5	1st	0.37 ± 0.04	0.29 ± 0.03	0.23 ± 0.03	0.15 ± 0.04
		2nd	0.42 ± 0.04	0.32 ± 0.02	0.23 ± 0.02	0.17 ± 0.03
		3rd	0.45 ± 0.03	0.34 ± 0.03	0.25 ± 0.03	0.18 ± 0.05

[a]Determined by DMA. Error bars represent ± one standard deviation of three or four measurements.

Table S4. Characteristic relaxation times, stretching exponents, average relaxation times, and KWW decay function fits as a function of temperature for EOC CANs.

EOC CAN	*T* (°C)	τ* (s)	β	<τ> (s)	R^2
EOC CAN-30-1	100	208	0.26	3820	0.98
	120	123	0.32	869	0.98
	140	59	0.42	170	0.98
	160	26	0.49	55	0.99
EOC CAN-38-1	100	234	0.28	2960	0.97
	120	132	0.34	716	0.98
	140	63	0.45	160	0.98
	160	27	0.52	49	0.99
EOC CAN-45-1	100	33	0.23	1330	0.98
	120	29	0.30	280	0.98
	140	17	0.39	61	0.98
	160	8	0.54	14	0.99
EOC CAN-38-5	80	34	0.25	730	0.98
	100	30	0.34	160	0.97
	120	14	0.40	48	0.98
	140	7.6	0.55	13	0.98
	160	< 1	--	< 1	--

Table S5. Room-temperature tensile properties of 1st-, 2nd-, and 3rd-molded EOC CANs.

Sample	Mold	Young's modulus (MPa)[a]	Tensile strength (MPa)[a]	Elongation at break (%)[a]
EOC CAN-30-1	1st	21.7 ± 1.1	13.4 ± 2.1	650 ± 70
	2nd	18.6 ± 3.5	14.4 ± 0.7	660 ± 30
	3rd	18.7 ± 3.3	16.7 ± 3.1	670 ± 30
EOC CAN-38-1	1st	7.6 ± 3.5	14.9 ± 1.9	700 ± 110
	2nd	8.5 ± 0.8	12.1 ± 4.0	670 ± 60
	3rd	8.3 ± 0.3	13.0 ± 0.6	710 ± 50
EOC CAN-45-1	1st	3.0 ± 0.1	5.1 ± 1.2	830 ± 120
	2nd	3.0 ± 0.6	5.0 ± 1.3	790 ± 80
	3rd	2.6 ± 0.3	5.4 ± 1.2	850 ± 130
EOC CAN-38-5	1st	7.8 ± 0.9	8.7 ± 1.2	760 ± 80
	2nd	8.4 ± 0.8	7.9 ± 2.4	800 ± 190
	3rd	8.2 ± 1.0	10.8 ± 2.2	910 ± 220

[a]Determined by tensile testing. Error bars represent ± one standard deviation of three measurements.