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Supporting Information

Effects of Dynamic Covalent Bonds Multiplicity on Performance of Vitrimeric Elastomers

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Figure S1. 1 H NMR (a), 13 C NMR (b) and FTIR (c) spectra of VPGA.



Figure S2. ¹H NMR spectrum and the signals assignment of GR.



Figure S3. FTIR spectra of the uncured and cured GR and VGR samples.



Figure S4. ¹H NMR spectrum and the signal assignment of VGR.



Figure S5. ¹H NMR spectrum of GR.



Figure S6. ¹H NMR spectrum of VGR.



Figure S7. Cross-linking kinetics of elastomeric vitrimers with single DCBs at 180 °C.



Figure S8. (a) Cross-linking kinetics of blank GR and VGR compounds at 180 °C. (b) Photos of the swelling behaviors of the resultant GR and VGR samples in toluene.



Figure S9. Photos of the samples swollen in toluene for 3 days.



Figure S10. Comparison of cross-link densities (V_e) and swelling ratios of elastomeric vitrimers with single DCBs.



Figure S11. Representative stress-strain curves of elastomeric vitrimers with single DCBs.



Figure S12. Temperature dependence of Tan δ of elastomeric vitrimers with single DCBs.



Figure S13. Fitting stress relaxation curves of β (a), S2 (b), Sch (c), $\beta/S2$ (d), β/Sch (e), S2/Sch (f) and $\beta/S2/Sch$ (g) samples at different temperatures with 1% strain. (h) Temperature dependence of τ^* of all the elastomeric samples. The activation energy was calculated by fitting τ^* with Arrhenius equation.



Figure S14. Normalized stress relaxation curves of GR sample cured by DDM without the

addition of TBD at 180 °C.



Figure S15. Creep curves of all the elastomeric vitrimers under a nominal stress of 0.15 MPa at

180 °C.



Figure S16. (a) Stress-strain curves of the original and recycled β /S2/Sch samples after various recycling cycles. (b) Recovery ratios of mechanical performance for recycled β /S2/Sch samples after various recycling cycles.



Figure S17. FTIR spectra of the original and recycled β /S2/Sch samples after various recycling

cycles.



Figure S18. Isothermal TGA curve of all samples at 210 °C for 3 h.



Figure S19. Stress-strain curves (a) and FTIR spectra (b) of the original and recycled $\beta/S2/Sch$ samples. The recycled sample were prepared by hot pressing 1h after grinding the sample maintained at 210 °C for 3 h.

	Electrolyte solution				Activator solution		Emulsifier solution
Ingredients	Potassium hydroxide	Phosphoric acid	EDTA	TAMOL	Fe-EDTA	SFS	Rosin soap
Content/g	0.40	0.23	0.03	0.13	0.02	0.04	4.60
		Monomers			Deoxidant	Initiator	molecular weight regulator
Ingredients	Deionized water	Styrene	Butadiene	GMA	SHS	РМН	TDDM
Content/g	190	40	60	3	0.04	0.06	0.20

Table S1. The recipe of synthesis of GR

Table S2. Formulations for all the elastomeric samples^a

Samples	ß	<i>S2</i>	Sch	β/S2	ß/Sch	S2/Sch	β/S2/Sch
GR (phr)	100	100	_	100			_
VGR (phr)			100		100	100	100
DDM (phr)	2		2		2		
DDD (phr)		2.5		2.5		2.5	2.5
DMI (phr)	1.4	1.4	_	1.4	_	_	—
TBD (phr)	0.6			0.6	0.6		0.6

^aphr: per hundred parts of rubber.

Table S3. Compositions and molecular weights of the GR.

Sample	Com	mposition (wt%)		Mn	Mw	Mz	PDI
	Butadiene	Styrene	GMA	(g/mol)	(g/mol)	(g/mol)	
GR	23.6	72.35	4.05	47149	183699	354825	3.896

Samples	TC90 (min)	ML (dN·m)	MH (dN∙m)	$\Delta M (dN \cdot m)$
β	66.05	1.12	20.82	19.70
<i>S2</i>	74.55	1.23	21.23	20.00
Sch	288.35	1.17	19.13	17.96
β/S2	29.72	1.19	20.45	19.26
ß/Sch	146.85	1.34	17.67	16.33
S2/Sch	340.40	1.22	20.14	18.92
β/S2/Sch	162.68	1.20	19.94	18.74

Table S4. Vulcanization parameters for all the elastomeric vitrimers

Table S5. Mechanical properties, cross-link density and T_g of all the samples.

Samples	Tensile strength	Elongation at break	Young's modulus	Cross-link density	<i>T_g</i> (°C)
	(MPa)	(%)	(MPa)	(10 ⁻⁴ ·mol/cm ³)	
β	2.1±0.1	130.5±10.5	3.6±0.06	$1.7{\pm}0.01$	-16.2
<i>S2</i>	2.2±0.2	143.3 ± 7.5	3.5±0.10	1.7 ± 0.02	-14.5
Sch	2.5±0.3	152.7±14.7	3.5 ± 0.08	1.5 ± 0.01	-13.6
β/S2	2.2±0.3	156.9±19.6	3.5 ± 0.05	1.5 ± 0.05	-15.3
β/Sch	2.7±0.2	176.6±4.5	3.6 ± 0.05	1.7 ± 0.06	-13.8
S2/Sch	2.5±0.1	161.4 ± 4.2	3.5 ± 0.03	1.5 ± 0.03	-11.2
β/S2/Sch	2.7±0.2	161.0±8.2	3.6±0.04	1.6±0.03	-13.0

Table S6. τ^* , E_a and their synergy coefficients of all the elastomeric vitrimers^a

Samples	$ au^{*}$	R (<i>τ</i> *)	Ea	R² of linear fit	
	(min)		(kJ/mol)	for Ea	
β	201.2 ± 4.2	/	72.8 ± 2.2	0.97	
Sch	129.9 ± 2.76	/	58.1 ± 1.1	0.99	
<i>S2</i>	114.2 ± 3.2	/	51.2 ± 2.0	0.98	
β/Sch	96.9 ± 1.1	0.41 ± 0.01	53.7 ± 1.0	0.99	
$\beta/S2$	73.5 ± 2.4	0.57 ± 0.02	49.9 ± 1.8	0.96	
S2/Sch	43.5 ± 1.8	0.65 ± 0.02	51.6 ± 1.8	0.99	
β /S2/Sch	21.7 ± 1.0	0.86 ± 0.01	51.1 ± 0.7	0.98	
^a R (τ *): Synergetic coefficient of τ *.					

Exchange units	Ea (kJ /mol)	Ref.
Turnaratouification	55~150	[1-4]
Transesterification -	73±2	This work
Incine matchesis	49~86	[5-7]
Imine metatnesis	58±1	This work
D'aultida analaraa	43~127	[8-11]
Disuinde exchange -	51±2	This work

Table S7. Comparison of the activation energies (*Ea*) of different DCBs.

Calculations

Determination of synergy coefficients R

The relaxation time (τ') of hypothesized vitrimers are calculated by the following equations:

$$\tau' = x\tau^*(\beta) + y\tau^*(S2) + z\tau^*(Sch) \tag{1}$$

Where $\tau^*(\beta)$, $\tau^*(S2)$ and $\tau^*(Sch)$ are the τ^* of β , S2 and Sch samples at 180 °C, respectively. Accordingly, the synergy coefficients of the relaxation time ($R(\tau)$) of elastomeric vitrimers with different DCBs multiplicity are calculated:

$$R(\tau) = \frac{\tau' - \tau'}{\tau'}$$
(2)

Where τ^* are the measured characteristic relaxation time of elastomeric vitrimers with different DCBs multiplicity at 180 °C.

Taking a set of stress relaxation test results of $\beta/S2/Sch$ sample with triple DCBs as an example, the proportions of beta-hydroxyl ester, disulfide and Schiff base in its hypothesized vitrimer are 2/5, 1/5 and 2/5, respectively. Accordingly, τ' of the hypothesized vitrimer and $R(\tau)$ of $\beta/S2/Sch$ sample can be calculated as follows.

$$\tau'(\beta/S2/Sch) = \frac{2}{5}\tau^*(\beta) + \frac{1}{5}\tau^*(S2) + \frac{2}{5}\tau^*(Sch) = \frac{2}{5}\times201.2 + \frac{1}{5}\times118.6 + \frac{2}{5}\times126.6 = 154.8 \text{ (min)}$$
$$R(\tau(\beta/S2/Sch)) = \frac{\tau'(\beta/S2/Sch) - \tau^*(\beta/S2/Sch)}{\tau'(\beta/S2/Sch)} = \frac{154.8 - 20.8}{154.8} = 0.87$$

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