

Supporting information

**High performance, self-adhesive and recyclable dynamic crosslinked
waste rubber particle blends toward upcycling of waste rubber**

Lingmin Kong, Rui Wu, Junqi Zhang, Shaoqi Huang, Zhengtian Xie* and Jinrong Wu*

State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China.

*Corresponding author: E-mail: wujinrong@scu.edu.cn; zt-xie@scu.edu.cn.

Content

Materials	3
Preparation of XWRP	3
Preparation of XWRP-O	3
Preparation of XWRP-W	3
Preparation of XVR	4
Preparation of XWRP/ENR blends	4
Characterization	5
Supplementary Figures	8
Supplementary Tables	10

Materials

Epoxidized natural rubber(ENR) with an epoxidization degree of 50% and Isoprene rubber(IR) were supplied by the Agricultural Products Processing Research Institute, Chinese Academy of Tropical Agricultural Science, China. Waste rubber particles (WRP, mesh size is 120 mesh) were supplied by Sichuan Chuanhuan Technology Co., Ltd. Carbon black(N330) was bought from Carbot Co., Ltd. Sebacic acid(99%), acrylic acid(AA,99%), benzoyl peroxide(75%), $K_2S_2O_8$ (99%), zinc acetate($Zn(Ac)_2$, 98%) and 1, 2-dimethyl-imidazole (DMI, 99%), were purchased from Adamas reagent Co., Ltd. AA were uninhibited via column chromatography before use.

Preparation of XWRP

Firstly, 20 mL of a 5%wt BPO toluene solution was added to 20 g of WRP under mechanical stirring for 5 minutes. Afterward, the WRP was swelled overnight in a cold chamber (-4°C). Next, the swelled WRP and 250 mL of an 8%wt AA aqueous solution were added to a 500 mL three-neck bottle equipped with mechanical stirring. The mixture was bubbled with an argon atmosphere for 30 minutes. Then, the mixture was heated to 80°C and stirred at a rate of 500 rpm for 6 hours. After the reaction, the resulting slurry was filtered, and the cake was dispersed again in 1 L of deionized water for washing and filtering three times. Finally, the filter cake was dried at 40°C for 48 hours to obtain XWRP.

Preparation of XWRP-O

Control sample XWRP-O was prepared in toluene with an initiator of BPO. WRP (20g), AA (20g), and BPO (1g) were dispersed in 250 ml of toluene. The mixture was added into a 500ml three-neck bottle and bubbled with an argon atmosphere for 30 minutes. Then, the mixture was heated to 80°C and stirred at a rate of 500 rpm for 6 hours. After filtering and washing, the filter cake was dried at 40°C for 48 hours to obtain XWRP-O.

Preparation of XWRP-W

Control sample XWRP-W was prepared in water with an initiator of $K_2S_2O_8$. WRP (20g), AA (20g), and $K_2S_2O_8$ (1g) were dispersed in 250ml of DI water. The mixture

was added into a 500ml three-neck bottle and bubbled with an argon atmosphere for 30 minutes. Then, the mixture was heated to 80°C and stirred at a rate of 500 rpm for 6 hours. After filtering and washing, the filter cake was dried at 40°C for 48 hours to obtain XWRP-W.

Preparation of XVR

Vulcanized rubber film without filler was prepared first. IR was first plasticized five times with a two-roll opening roller. Then, stearic acid, zinc oxide, antioxidant 4010, sulfur, and accelerator CZ were added and mixed. The compound was hot pressed at 143°C for 15 minutes using a plate vulcanizing machine to prepare a 1mm thin vulcanized rubber film (VR). The ingredients list is shown in Table S1.

Then, the vulcanized rubber film was cut into 1mm×1mm pieces. 20g of VR pieces were immersed in a 20ml 5%wt BPO toluene solution and allowed to swell overnight. The surface of the swelled pieces was carefully cleaned using mirror paper before modification. After swelling, these pieces and 250ml AA aqueous solution (8%wt) were added into a 500ml three-neck bottle, and the mixture was bubbled with argon atmosphere for 30 minutes. The reaction was then carried out at 80°C for 6 hours. After the reaction, the samples were cooled to room temperature, removed, and soaked in deionized water for 6 hours. This procedure was repeated three times to ensure the removal of unreacted small molecules. Finally, the samples were dried at 40°C for 48 hours.

Table. S1 Formulae of VR model

Ingredient	Amount(phr) ^a
IR	100
Stearic acid	2
ZnO	5
Antioxidant 4010 ^b	1
Accelerator CBS ^c	1
Sulfur	2

^aParts by weight per hundred parts rubber. ^b*N*-Cyclohexyl-*N'*-phenyl-*p*-phenylenediamine. ^c*N*-Cyclohexylbenzothiazole-2-sulphonamide

Preparation of XWRP/ENR blends

Firstly, ENR was compounded with crosslinking agent SA and 40phr (parts of per

hundred parts of rubber) carbon black, different amounts of XWRP on a two-roll opening roller. The ratio of the carboxyl group to the epoxy group is 1:30. Then, catalyst DMI and Zn(Ac)₂ were added with the dosage of 25% and 10% of the molar amount of the carboxyl group, respectively. In this context, the sample code of X_x refers to the sample with *x* phr XWRP. The sample without XWRP was named as ENRC

For comparison, the control sample with WRP was prepared as above and named as W_{*x*}, *x* refers to the phr of XWRP.

Characterization

FT-IR spectra were collected using a Thermo Scientific Nicolet iS5 in the range of 4000–400 cm⁻¹ with a 2 cm⁻¹ resolution. Wide angle X-ray diffraction (WAXD) was performed on a Philips X'Pert Graphics & Identify with Ni-filtered CuK α radiation (λ = 0.154 nm) at a generator voltage of 35 kV and a generator current of 25 mA. Angle scanning was performed at a speed of 2.4°/min from 5° to 80°. X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an XSAM800 (Kratos) using a monochromatic Mg Ka X-ray source radiation (hν = 253.6 eV) operated at 12 kV and 15 mA. SEM was performed on FEI Apreo S HiVoc. Thermogravimetric analyses of the modified rubber powder were tested using a TGA2. Thermal Gravimetric Analyzer (Mettler Toledo). The sample was heated from 35°C to 800 °C at the rate of 10 °C /min under a nitrogen atmosphere. The grafting ratio of carboxy groups is attained according to:

$$GR_x = \frac{\text{Residual weight}_{WRP} - \text{Residual weight}_{XWRP}}{Mw_{AA}} \quad (1)$$

Where GR_{*x*} is the grafting ratio of carboxy groups, Mw_{AA} is the molecule weight of AA.

The contact angles of the samples at different times were tested using a DSA25 Contact Angle Meter instrument (Kruss, Berlin, Germany). Each sample was tested three times, and the average value was taken as the result. Curing properties were examined by Gotech RPA8000 at 180°C. After pre-heating the discs of ODR to a temperature of 180°C, 5g of the samples was inserted between the two discs and the torque was monitored as a function of time. The gel content of blends was characterized

by the Soxhlet extraction method. The sample (around 0.1 g) was wrapped with filter paper. The THF was used as the extraction solution and reflux for 24 h. Later, the samples were dried at 60 °C for 24 h in a vacuum oven. The gel content was calculated by m_1/m_0 , where m_0 is the initial mass and m_1 is the final mass after drying. The swelling ratio was calculated by the equilibrium swelling test. The swelling ratio is defined as w_2/w_1 , where w_1 is the weight of the deswollen rubber and w_2 is the total weight of rubber and solvent in the swollen sample. Based on the Flory-Rehner equation, the crosslinking density of each sample can be determined:

$$-\left[\ln(1 - v_r) + v_r + \chi v_r^2\right] = V_0 n (v_r^{1/3} - v_r/2) \quad (2)$$

where v_r is the volume fraction of the rubber in the swollen mass, V_0 is the molar volume of the solvent (106.2 cm³ for toluene), n is the number of active network chain segments per unit of volume (crosslinking density), and χ is the Florye-Huggins polymer-solvent interaction. The value of χ for ENR in toluene is 0.341. The value of v_r is attained according to:

$$v_r = \frac{w_1(1 - \varphi - \alpha)/\rho_2}{w_1(1 - \varphi - \alpha)/\rho_2 + (w_2 - w_1\varphi f - w_1(1 - \varphi))/\rho_1} \quad (3)$$

where ρ_1 and ρ_2 are the densities of the solvent and the rubber, respectively. φ is the weight fraction of WRP or XWRP in blends. α is the weight fraction of carbon black. w_1 is the weight of the deswollen rubber and w_2 is the total weight of rubber and solvent in the swollen sample. f is the swelling ratio of WRP and XWRP, 3.16 and 2.26 respectively.

Dynamic mechanical tests, dilatometry experiments, stress relaxation experiments and cyclic strain recovery tests were performed on a DMA Q850 (TA instruments). Dynamic mechanical tests were performed at a frequency of 1 Hz from -100 °C to 120 °C by using a tensile mode at an oscillation amplitude of 20 μ m. The heating rate was 3 °C /min. The dimensions of the rectangle sample strips were 20×4×1 mm. Dilatometry experiments were conducted by measuring the length of the sample when it was heated from -50 to 250 °C at 3 °C/min, and a weak stress of 10 kPa was applied to avoid buckling. Stress relaxation experiments were also conducted on the DMA

machine with 0.3% constant applied, and balanced for half an hour to exclude the influence of thermal expansion. For cyclic strain recovery tests, the stress applied on the sample was alternated between 0.1 MPa for 20 min and 0 MPa for 5 min in each cycle. Mechanical properties and adhesive properties were performed on a universal testing machine (Instron 5967) at room temperature with a cross-head speed of 500 mm min⁻¹. The specimen was a dumbbell shaped thin strip with dimensions of 25×4×1 mm. At least three specimens have been tested, and the average data were adopted. To measure adhesion strength and debonding energy, lap-shear tests were performed on a universal testing machine (model 5967) with a load cell of a maximum of 5000N and meanwhile the force and the extension were recorded. The free ends of the substrates were attached to flexible copper wire, to which the machine grips were attached. The bonding objects used in this work were designed as plates, the size is 100 mm × 25 mm × 2 mm, and the area of the lap part is 25 mm × 12.5 mm. Adhesive strength is defined as the ratio of the maximum force of the adhesive joint in the lap shear test and the overlap area, calculated by the formula:

$$Adhesive\ strength = \frac{F_{max}}{WL} \quad (4)$$

where F_{max} is the maximum force in the lap shear process till failure, N; WL is the area of the initial overlap of two objects, mm².

Debonding energy is attained according to:

$$Debonding\ energy = \frac{\int F dx}{WL} \quad (5)$$

where $\int F dx$ is defined as the integral of the force vs. displacement graph, or energy of adhesion (J). WL is the measured overlap area of the adhesive joint (mm²).

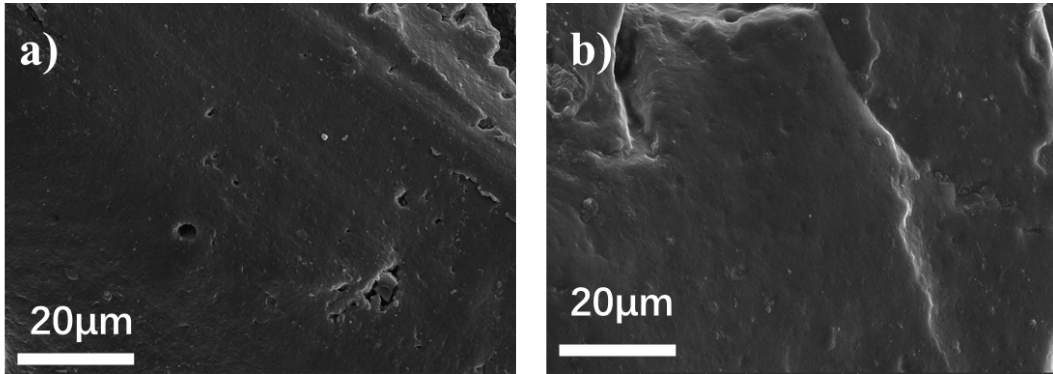


Fig. S1. SEM images of (a)WRP and (b)XWRP.

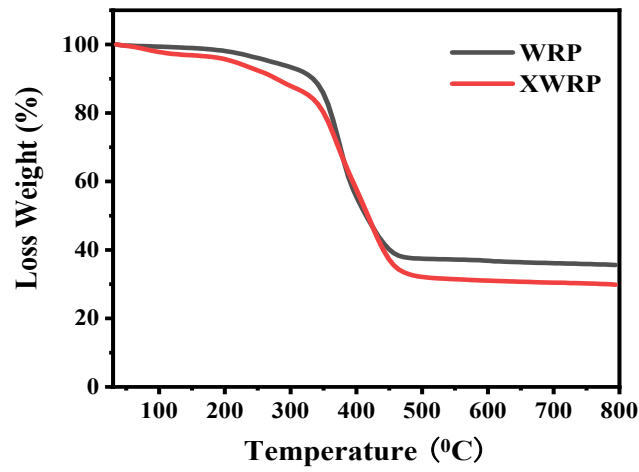


Fig. S2. TGA curves of WRP and XWRP.

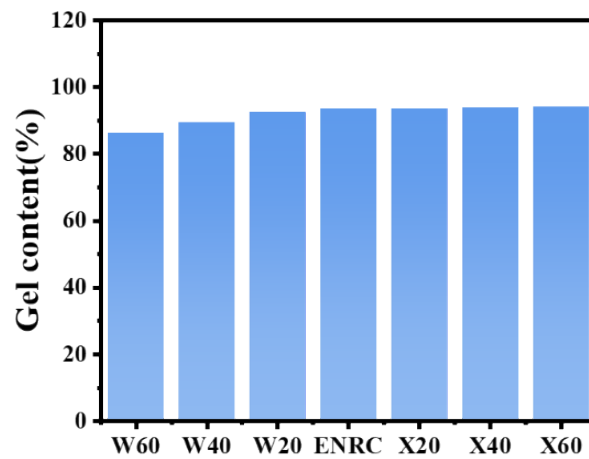


Fig. S3. Gel content of WRP/ENR blends, ENRC and XWRP/ENR blends.

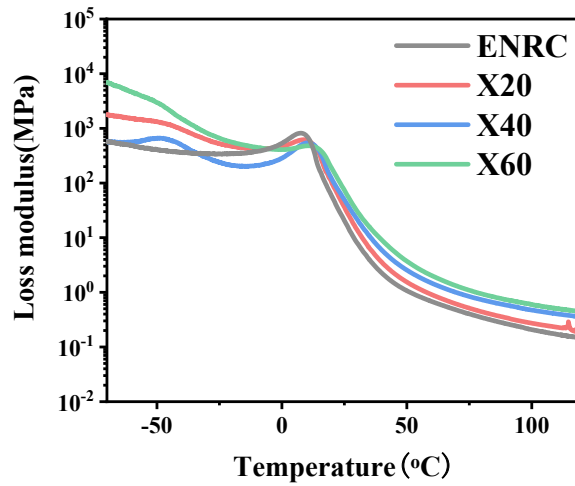


Fig. S4. Loss modulus of ENRC and XWRP/ENR blends.

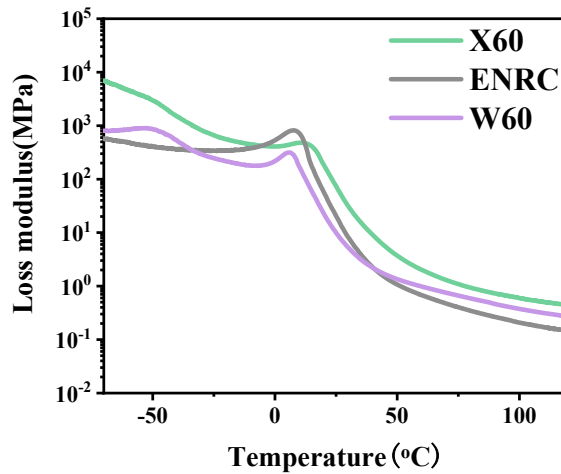


Fig. S5. Loss modulus of X60, ENRC and W60.

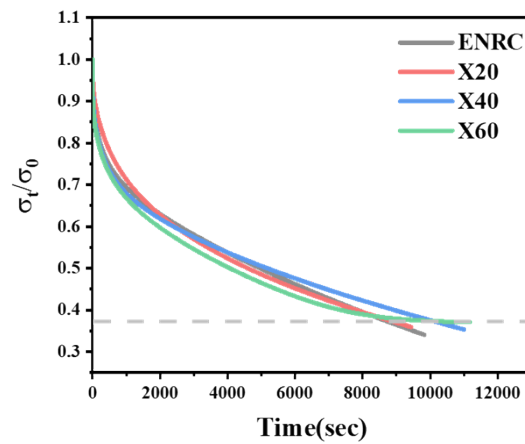


Fig. S6 Normalized stress relaxation of ENRC and XWRP/ENR blends under 180°C.

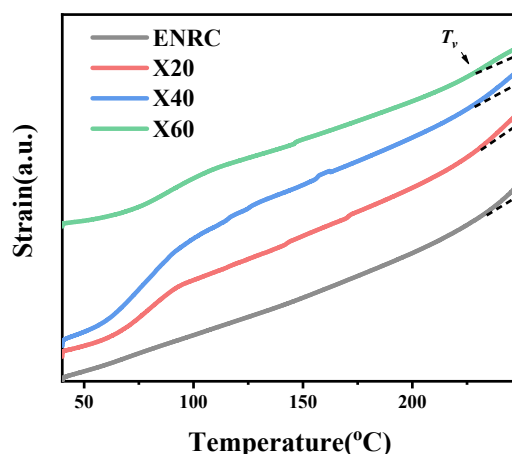


Fig. S7. Dilatometry experiments for ENRC and XWRP/ENR blends samples.

Table. S2. curing parameters of ENRC, XWRP/ENR blends and WRP/ENR blends.

	MH(dN.m)	ML(dN.m)	t ₁₀ (m:s)	t ₉₀ (m:s)
ENRC	10.28	0.08	6:56	40:22
X20	15.31	0.15	4:13	23:46
X40	16.13	0.24	3:26	26:56
X60	17.18	0.48	3:34	26:58
W20	7.87	0.15	9:43	49:02
W40	6.17	0.18	10:49	51:49
W60	5.78	0.29	9:53	52:03

Table.S3. Comparison of adhesion strength among different adhesives.

Adhesives	Adhesion strength (MPa)	Reference	Corresponding letters in Fig. 5c
ESOBV-1	5.67	Ref 34	a
DEP	4.34	Ref 35	b
P1	2.8	Ref 36	c
E1 ₈₆ E3 ₁₄	1.6	Ref 37	d
OTgCS	2.5	Ref 38	e
ATBN-16	7.6	Ref 39	f
PV-1071	6.79	Ref 40	g
ESO/GL Vitrimer	3.42	Ref 41	h
C-PU-PTMEGs	2.45	Ref 42	i
6-HTPB	2.14	Ref 43	j
Se-EP/Oz-L adhesive	6.5	Ref 44	k
PDETAS10-FBA-2	8	Ref 45	l

This Work

11.49

/

/
