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Supplementary Information

Enhancing electrical conductivity of rubber composites by constructing interconnected network of self-assembled graphene with latex mixing

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Experimental

Chemicals: The natural rubber latex (solid content: 60 wt%) was provided by Chengdu Fangzheng Co., Ltd (China). Flake Graphite (~75 μm) was obtained from Qingdao Tianhe Graphite Co., Ltd (China). Potassium permanganate ($KMnO_4$) was obtained from Chongqing Boyi Chemical Reagent Co., Ltd (China). Concentrated sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were all analytical-grade and obtained from Sichuan Xilong Chemical Co., Ltd (China). Hydrazine hydrate was purchased from Chendu Kelong Chemical Reagent Company (China). Hydrogen peroxide (30%) was provided by Tianjin Zhiyuan Chemical Reagent Co., Ltd (China). Other reagents including vulcanization agent sulfur, zinc oxide, accelerator N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and 2-mercaptobenzothiazole (MBT), antioxidant (4010NA), and stearic acid are all commercially available.

Preparation of the crosslinked GE/NR composites via a self-assembly in latex

The preparation of GO and GE was described in our recent work and the yield of GE is about 40% from GO.[1] For the vulcanized GE/NR composites, the preparation method is following: the dried GO powder at a concentration of 3.125 mg mL^{-1} was added into the aqueous solution by sonication (KQ-250DE, 40 KHz, Kunshan Ultrasonic Instrument CO., Ltd, China) at 40 ^{o}C for 1 h. Then NR latex was dispersed into the GO solution by sonication for 1 h to obtain the light brown GO/NR latex. Hydrazine hydrate was added into the GO/NR latex and the mixture was subjected to an *in-situ* reduction reaction under ultrasonic irradiation for 2 h to obtain the black GE/NR latex. GO/hydrazine hydrate ratio is 1.25:5 (g/mL). And the aqueous suspension containing crosslinked agent sulfur and other additives were dispersed into the GE/NR latex and then the mixed latex was coagulated. The concentration of sulfur and vulcanization auxiliary aqueous suspension is 3.825 mg mL^{-1}. The vulcanized GE/NR composites experimental formula is given in Table S1. After filtering, the solid mixture was dried in an oven at 65 °C for 4 h. These composites were compressively molded and vulcanized at a temperature of 150 °C and a pressure of 10 MPa for 5 min and then were cooled under a pressure of 5 MPa at room temperature for 3 min. The obtained GE/NR composites were designated as NRLGES-Y, in which Y represents GE content. For example, NRLGES-0.5 represents the vulcanized GE/NR composites with 0.5 phr GE (0.45 vol% GE), which were prepared by self-assembly in latex.

For a comparative purpose, the above GE/NR composites were further mixed by the twin-roll at the room temperature for 5 min. Then, these composites were compressively molded and vulcanized following the same procedures of the above NRLGES. The obtained GE/NR composites after the twin-roll mixing were designated as NRLGES-TR-Y.

Preparation of the uncrosslinked GE/NR composites via a self assembly in latex

For the unvulcanized GE/NR composites, the preparation process and formula were the same as that for NRLGES except that the sulfur and the vulcanization accelerators MBT and CBS were not added. The obtained uncrosslinked GE/NR composites without the twin-roll mixing were designated as NRLGE-Y. The obtained uncrosslinked GE/NR composites, after the twin-roll mixing, were designated as NRLGE-TR-Y.

Preparation of GE/NR composites via conventional methods

GE/NR composites were prepared by direct twin-roll or Haake (Thermo Haake Rheomix 600 Banbury mixer) mixing of GE power and rubber without using the latex mixing process. The obtained samples, which were mixed at room temperature for 10 min, were designated as NRGE-TR-Y and NRGE-HM-Y, respectively. The compression molding parameters are the same as above

Characterization

Transmission electron microscopy (TEM): TEM was performed using a FEI Tecnai G^2 F20 S-TWIN transmission electron microscope, operating at an accelerating voltage of 200 kV. The suspension of a concentration of 0.02 mg/ml GE was prepared by ultrasound for 30 min and water was used as the dispersion medium. For NR latex containing GE samples, the latex after dilution for 15 times was directly dropped on a copper grid for observation. For GE/NR composite samples, the composite was cryo-microtomed using a Leica EM UC6 equipment to get the ultrathin cryo-sections of 70-80 nm thickness, which were collected and directly supported on a copper grid for observation.

Electrical conductivity: The conductivity of all samples were measured by a two-point measurement with a picoameter (Keithley 2400) for R $\leq 2\times10^8$ Ω or using a (Keithley 6487) for R > 2 $\times10^8$ Ω. A rectangle samples strip were cut and were painted using silver paste. The measured volume resistance (Ω), R_v was converted to volume resistivity, ρ_v according to ASTM D4496 and D257 using the formula

$$\rho_v = R_v \frac{A}{t} \tag{1}$$

Where A is effective area of the measuring electrode (m^2) and t is specimen thickness (m).

Tensile tests: The measurement of mechanical properties was conducted on a universal testing machine (Instron 5567, US) at room temperature. For initial modulus tests, the rectangle specimens (1 mm thick, 10 mm wide and 45 mm long) were stretched at a crosshead rate of 100 mm/min. The stress-strain curves were recorded. For tensile strength tests, the dumbbell-shaped specimens were stretched until break at a crosshead rate of 500 mm/min according to a China Standard GB/T 528-1998.

Water vapor permeability (WVP): Water vapor permeability was determined using a MOCON Permatran-W3/31 at 25 ^{o}C and 38 ^{o}C, respectively, and setting the relative humidity at downstream and upstream side of the film respectively to 0% and 50%.

Table S1. The experimental formula for preparation of vulcanized GE/NR composites

Content (phr) [a]	Neat NR	NRLGES-0.5	NRLGES-1	NRLGES-2	NRLGES-4	NRLGES-6
GE	0	0.5	1	2	4	6
NRL	166.7	166.7	166.7	166.7	166.7	166.7
Zinc oxide	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3
Sulfur	2.8	2.8	2.8	2.8	2.8	2.8
Antioxidant (4010NA)	3	3	3	3	3	3
Accelerator MBT	0.1	0.1	0.1	0.1	0.1	0.1
Accelerator CBS	1.4	1.4	1.4	1.4	1.4	1.4
OP emulsifier	2	2	2	2	2	2

[a] parts per hundred parts of rubber

Table S2. The electrical conductivity and mechanical properties of neat NR and GE/NR composites with 1.78 vol% GE content obtained with a self-assembly process in latex (NRLGES) and conventional twin-roll mixing (NRGE-TRS).

Sample	Electrical conductivity (S m^{-1})	Tensile strength (MPa)	Elongation at break (%)
Neat NR	2.6×10^{-8}	17.0	1111
NRGE-TRS-2	1.6×10^{-7}	18.8	600
NRLGES-2	2.8×10^{-2}	23.3	783

Table S3. The percolation threshold φ_c and critical exponent (s) for GE/NR composites

Percolation parameters	φ_c (vol%)	s
NRLGES	0.62	1.01
NRLGES-TR	4.62	1.05
NRLGE	0.90	1.09
NRLGE-TR	4.65	1.01

Table S4. Initial modulus for GE/NR composites prepared by different methods

GE (vol%)		0	0.45	0.90	1.78	3.50	5.15	6.76	8.30
Initial modulus (Mpa)	NRLGES	1.38	3.32	4.56	8.23	18.14	36.78	58.91	62.35
	NRLGES-TR	1.45	1.97	2.51	3.08	4.13	6.77	8.84	20.40
	NRLGE	1.00	1.09	1.17	2.36	3.17	12.45	47.29	61.15
	NRLGR-TR	0.24	0.31	0.42	0.67	1.02	2.03	3.77	5.53

References

1 Y. H. Zhan, J. K. Wu, H. S. Xia, N. Yan, G. X. Fei and G. P. Yuan, *Macromol. Mater. Eng.*, 2011, **296**, 590.