

Supporting Information

Electrically and Thermally Conductive Underwater Acoustically Absorptive Graphene/Rubber Nanocomposites for Multifunctional Applications

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Materials and Methods:

Materials:

The styrene butadiene rubber latex (SBR) (solid content: 48%) was provided by Hunan Xianghu Chemical Trade Co., Ltd (China). Graphene sheets were prepared by the liquid phase stripping method. Other curing agents used here were of analytical grade purity.

Preparation of graphene via liquid phase stripping method:

The solution consisting of 5 wt% graphite power in N-methyl pyrrolidone (NMP) suffers ultrasound treatment for 8 h. NMP was selected as a solvent because its surface energy (40.7 mN/m) is close to that of graphene (54.8 mN/m), which can act as stabilizing agents to exfoliate graphene sheets against reaggregation during exfoliation. From the view point of thermodynamics, the small difference of surface energy would decrease their mixing enthalpy and thus enable the direct exfoliation of graphite without the use of surfactant. Then, the obtained dispersion was

centrifuged for four times at 5000 rpm to remove the large numbers of macroscopic aggregates of graphite.

Preparation of graphene/SBR nanocomposites via spray drying method:

The preparation graphene aqueous solution (4.5 wt%) was dispersed into SBR latex by stirring violently for 6 hours. The aqueous suspension containing crosslinked agent sulfur and other additives were added into the SBR latex followed with vigorous stirring to obtain a mixed latex suspension with about 10% solid content. Other additives include zinc oxide, stearic acid and dibenzothiazole disulfide used as vulcanization accelerator, which can shorten the curing time, reduce the curing temperature and improve rubber properties. The experimental formula for preparation of vulcanized graphene/SBR nanocomposites and neat SBR followed the recipe given in Table S1. With the homemade spraying dryer equipment, the mixture was sprayed and dried at 140 °C with suspensions feeding rate 200 mL/min under N₂. Eventually, graphene/SBR nanocomposites containing vulcanizing reagent was obtained.

These nanocomposites were then compress molded and vulcanized at 150 °C and 20 MPa for 10 minutes, and then cooled under 5 MPa at room temperature for 5 minutes. The obtained graphene/SBR nanocomposites were designated as RG/L-S(X), in which X represents weight ratio of graphene and SBR. For compared, neat SBR without graphene filler was

designated as RL-S.

Table S1. The experimental formula for preparation of vulcanized graphene/SBR nanocomposites.

Content (phr)	RL-S	RG/L-S (1-20)	RG/L-S (1-10)	RG/L-S (1-5)	RG/L-S (1-2)
SBR	100	100	100	100	100
ZnO	5	5	5	5	5
Sulfur	4	4	4	4	4
Stearic acid	1.5	1.5	1.5	1.5	1.5
Dibenzothiazole disulfide(DM)	3	3	3	3	3
Graphene (GN)	0	5	10	20	50

phr: parts per hundred rubber

Characterization:

X-ray diffraction (XRD) equipped with graphite monochromatized Cu K α radiation (D/MAX-rA, Japan) to analyze the powder diffraction patterns. Fourier transform infrared (FT-IR) spectroscopy was conducted on a model TENSOR-27 FTIR spectrometer from Bruker. Raman spectra were performed with a Lab RAM HR800 from JY Horiba. The thickness of graphene nanosheet was characterization by atom force microscopy (AFM, Veeco, USA). The sample morphology and structure were characterized by Scanning electron microscope (SEM, modelSU8000, Hitachi, Japan). Thermogravimetric analysis (TGA) was measured using a Q5000 analyzer (manufacturer?) from 30 to 700 °C under N₂ at a heating rate of 20 °C min⁻¹. The electrical properties of the samples were measured

directly from the nanocomposites (cylinders with $R=56$ mm, $h=3$ mm) using the four-point technique using Van DerPauw method (Keithley 2400). The thermal conductivities of cylinder samples with $R = 30$ mm, $h = 10$ mm were tested using TPS 2500S from Hot Disk at room temperature. Dynamic mechanical analysis (DMA) by temperature sweep were performed at a constant frequency of 1 Hz, strain 1%, in the temperature range of -30 to 100 °C and a heating rate of 3 °C/min under tensile mode by using a dynamic mechanical analyzer (DMA Q800, TA). The specimen dimensions were $50 \times 5 \times 1$ mm. Mechanical tests were carried out by a single-column static instrument (Instron 5843) equipped with two flat-surface compression stages and a 10 N load cell. Electromagnetic interference shielding (EMI) was measured using a Vector Network Analyzer (Agilent Technologies N5227A, USA). The underwater absorption coefficients were obtained based on the principle of transfer function method at China Ship Academe (the Seventh Academe) under Chinese National Standard GB/T 14369–2011. The sample is cylindrical with the diameter of 120 mm and a height of 25 mm.

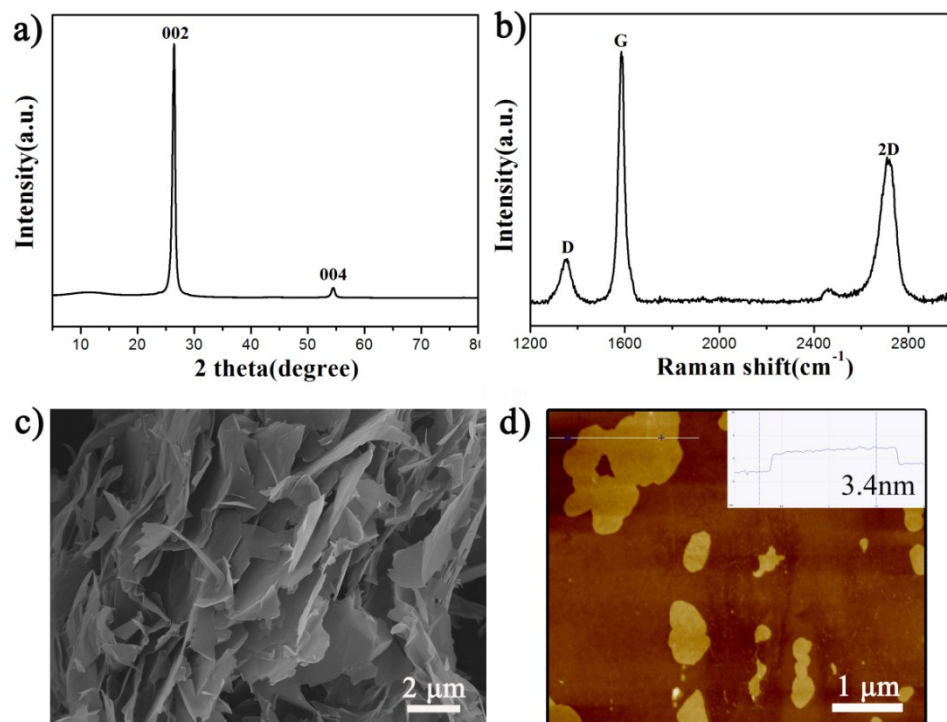


Fig. S1 Pristine graphene characterization; (a) X-ray diffraction patterns, (b) Raman spectra, (c) SEM image and (d) AFM image of the graphene sheets.

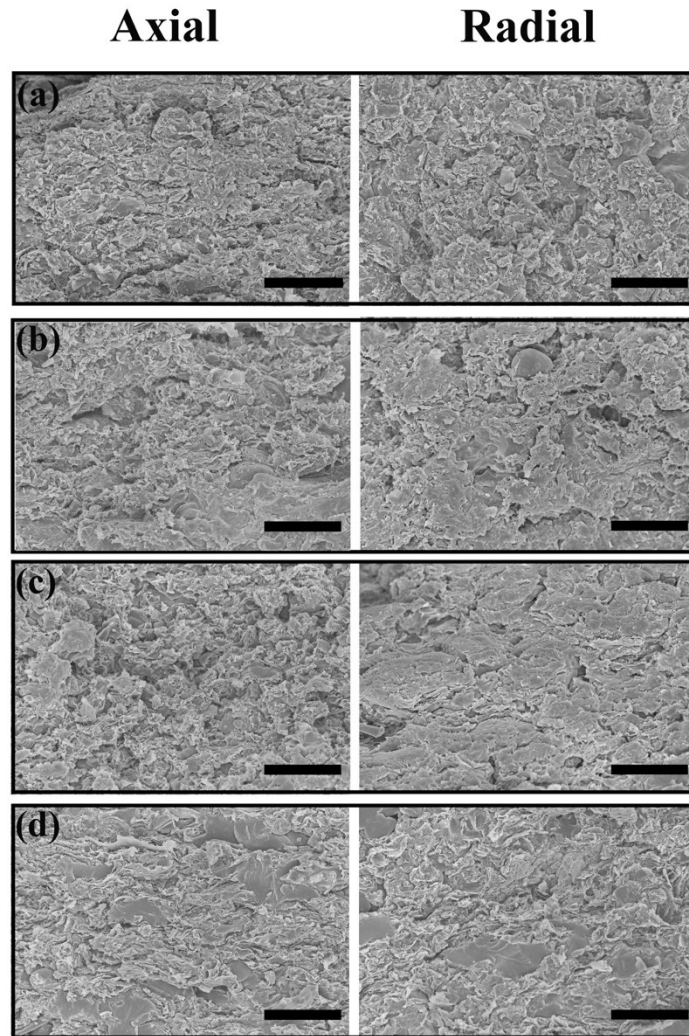


Fig. S2 SEM images (transverse section and longitudinal section) of graphene/SBR nanocomposites with filler content: (a) 1.61 vol%, (b) 3.95 vol%, (c) 8.26 vol% and (d) 15.0 vol%. (the inset scale bar is 100 μm)

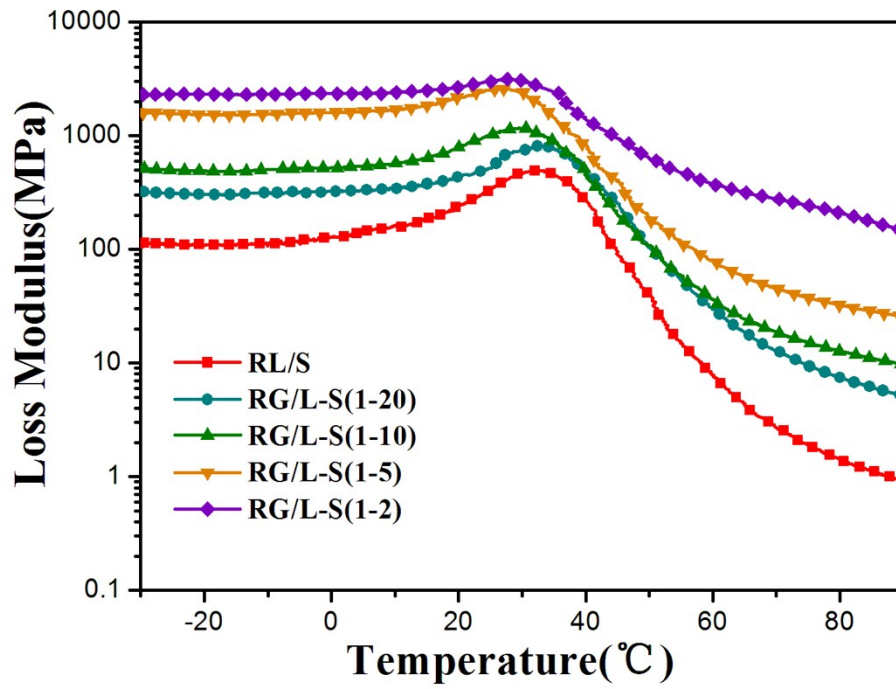


Fig. S3 The loss modulus as a function of temperature for graphene/SBR nanocomposites with different graphene fillers content.