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Electronic Supplementary Information

A new approach to construct three dimensional segregated graphene structures in rubber composites for enhanced conductive, mechanical and barrier properties

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Experimental

Materials

SBR latex (Intex 132, solid content of 60 wt %, styrene content is 25 wt%), was manufactured by Lanzhou Petrochemical Co. Ltd. Graphite powder was purchased from Shanghai Colloidal Co. Ltd. The reagents used for the synthesis of GO were based on a modified Hummer's method[1]. Ethanol, toluene, sodium hydroxide (NaOH), calcium chloride ($CaCl_2$) and hydrazine hydrate was provided by Guangzhou Chemical Reagent Factory. 2,2'-Azobisisobutyronitrile (AIBN), styrene (St), Octyl phenol 10 (OP-10) and polyvinylpyrrolidone (PVP, M_w=8000) were supplied by Sinopharm Chemical Reagent Co. Ltd.

Zinc oxide (ZnO), stearic acid (stA), N-cyclo-hexylbenzothiazole-2-sulphenamide (CZ), 2,2'-dibenzothiazole disulfide (DM), 2-Mercaptobenzimidazole (MB) and

Sulfur (S) were purchased from Guangzhou Longsun technology Co., Ltd. All the rubber ingredients were industrial grade and were used as received.

Synthesis of polystyrene (PS) microspheres

A typical procedure for the synthesis of PS microspheres by dispersion polymerization was as follows: St (22 g), PVP (5 g), and AIBN (0.022 g, 0.1 wt% relative to St) were dissolved in 70 mL of ethanol in a 150 mL of flask. The mixture was constantly stirred under nitrogen atmosphere and kept at 70 °C for 20 h. After the polymerization, the PS microspheres were obtained by the repeated washing with ethanol several times, and finally drying at 60 °C in a vacuum oven.

Synthesis of 3D macroporous graphene structure (3D-GE)

To integrate graphene sheets into a macroscopic assembly, graphite oxides were initially prepared by the modified Hummers method, detailedly described in our recent work and the yield of GE is about 45% from GO.[2] Graphite oxides were firstly dispersed in ethanol/deionized water (4/5, v/v) solution for getting well-dispersed graphene oxide (GO) suspensions by a sonication process, then chemically reduced to prepare the GE suspensions. And the PS microspheres solution was prepared by dispersing PS particles (10 wt %) in deionized water at PH=2. The GE and PS solutions (95:5 in weight ratio) were uniformly mixed. Noteworthily, the effect of the weight ratio of GE and PS on the morphology of the synthesized 3D-GE was detailedly discussed in the Fig. S6. At pH 2, as shown in Fig. S4(a), both PS and GE were positively charged (zeta potential values of +17.1 mV for GE and +32.6 mV for PS) and were thus hardly agglomerated. Then, when the pH was raised to 6, both components had oppositely charged (zeta potential values of -31.5 mV for GE and +28.5 mV for PS) and thus stimulate the electrostatic interaction between both components, leading to the formation of PS@GE hybrids (Fig. S4(b)). Then, as-synthesized PS@GE hybrids were purified by repeated centrifugation and re-suspension in ethanol three times, whereafter, the hybrids were freeze-dried under vacuum for 12h. Next, the 3D macroporous graphene structures (3D-GE) were obtained by removing the PS microspheres with toluene exposure. Finally, the black product is washed with water for several times, and freeze-dried under vacuum for 24 h.

Preparation of SBR composites

For the preparation of SBR/3D-GE composites, the 3D-GE suspensions were firstly obtained by sonication, and the sonication power and sonication time are set as 100 W and 20 min, respectively. The ultrasonic process was performed by KQ-500DV ultrasonic cleaner (Kun Shan Ultrasonic Instruments Co., Ltd.). The specific parameters are designed with ultrasonic power 100~500W, ultrasonic time 1~480 min, frequency 40 kHz or as request, and interior tank size (length, width, thickness) with 500 × 300 × 180 mm. Transducers are matched onto the bottom of the cleaning tank, heating power 800 W, with external stainless steel heating plate. Herein, we have investigated the effect of sonication time on the structure of 3D-GE, as shown in the Fig. S5. Evidently, the increased sonication time has little effect on the structure of 3D-GE when the sonication time is less than 40 min. Then the 3D-GE suspensions were evenly dispersed in SBR latex to prepare SBR/3D-GE latex. Subsequently, the crosslinking agent sulphur and other rubber additives were well-dispersed into the latex by violently stirring for 1h. Then, the mixture was co-coagulated by adding $CaCl_2$ (2.0 wt%) solutions as the flocculating agents. The co-coagulated compounds were thoroughly washed with de-ionized water several times until no chloride ion was detected, and vacuum dried at 50 °C over night. After that, the dried solid compounds were directly hot pressed and vulcanized at a temperature of 160 °C and a pressure of 10 MPa for cure time (T_{90}) and then were cooled under a pressure of 5 MPa at room temperature for 3 min. The obtained SBR/3D-GE composites were coded as SBR3GE-DH-x. For a comparison, the above dried solid compounds were further mixed on a twin-roll mill. The rolls were set to a temperature of 30 °C, a speed of 15 rpm with a friction ratio of 1.27:1, and a nip gap of 1 mm. The milling time for all the compounds was about 10 min. Then, these compounds were hot pressed and vulcanized following the same procedures of the above SBR3GE-DH. The obtained SBR/GE composites after the twin-roll mixing were designated as SBR3GE-TR-x. Additionally, SBR/GE composites without segregated network structure, coded as SBRGE-DH-x, were prepared by conventional latex compounding and directly hot press. And SBR/GE composites without segregated network structure, coded as SBRGE-TR-x, were obtained by conventional latex compounding and twin-roll mixing. Thereinto, x represents the 3D-GE or GE content as parts per hundred parts of rubber, which was controlled to be 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10 phr (parts per hundred parts of rubber) in the composites. The formulation of the SBR composite is listed in Table S1.

Characterization

The surface morphology of the samples was analyzed by a Nova NANOSEM 430 scanning electron microscopy (FESEM) and a JEOL2100 transmission electron microscopy (TEM). For TEM observations, thin sections (50~100 nm) of vulcanized SBR3GE-DH composites were cut using a cryoultramicrotome (Leica EM UC7, DiATOME cryo 35° diamond blade) with a -120 °C chamber temperature and a knife temperature of -95 °C. Slicing speed is 0.05~100 mm/s and the feed accuracy is from 1 nm~15 microns. The sections were collected onto 200 mesh Gilder Cu grids. Finally, the TEM digital micrographs were acquired using a JEOL 2100 at 200 kV. The mechanical properties were all measured by a U-CAN UT-2060 instrument at room temperature with relative humidity about 65%. 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. 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. The stress-strain curves were recorded. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 instrument in a nitrogen atmosphere, at a heating rate of 10 °C/min.

The electric conductivity of all of the samples was measured by a two-point measurement using a digital source-meter (Keithley 2450) (below 10^8 Ω) and a high-resistivity meter (Keithley 6517B) (above 10^8Ω). Rectangular strip samples (40mm×10mm×1 mm) were employed and painted using silver paste for the electrical measurements. Five specimens were measured for each sample to achieve an average value. The measured volume resistance (Ω), R_v was converted to volume resistivity, ρ_v according to ASTM D4496 and D257 using the formula:

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

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

A gas permeability tester (VAC-V2, Labthink Instruments) was performed to measure the nitrogen permeability of SBR composites. All the samples were circular-shaped specimens with 50 mm diameter and 1 mm thickness.

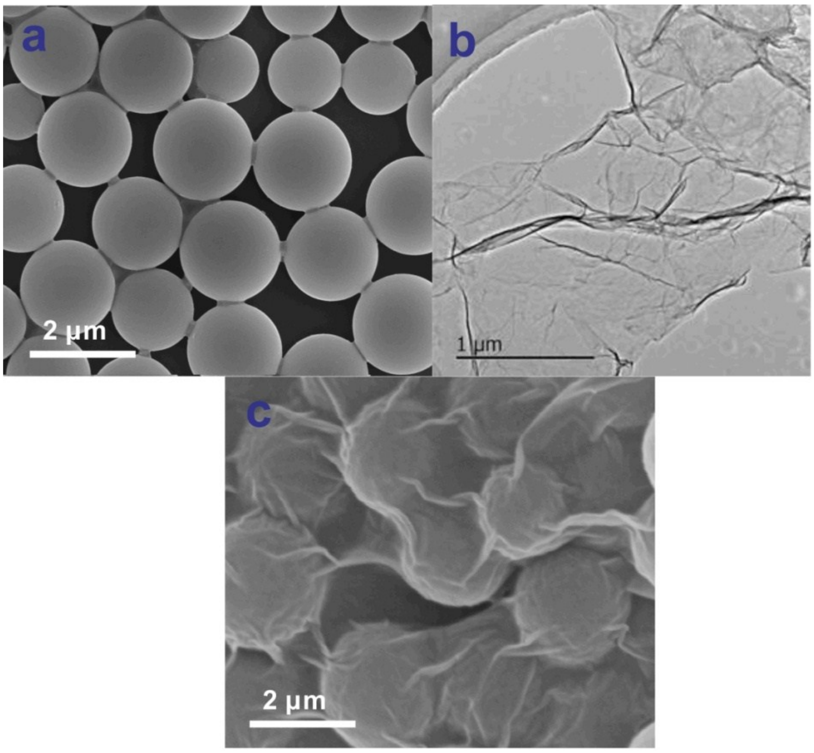

Fig. S1 SEM images of PS microspheres (a), PS@GE hybrids (c), and TEM image of the GO sheets (b).

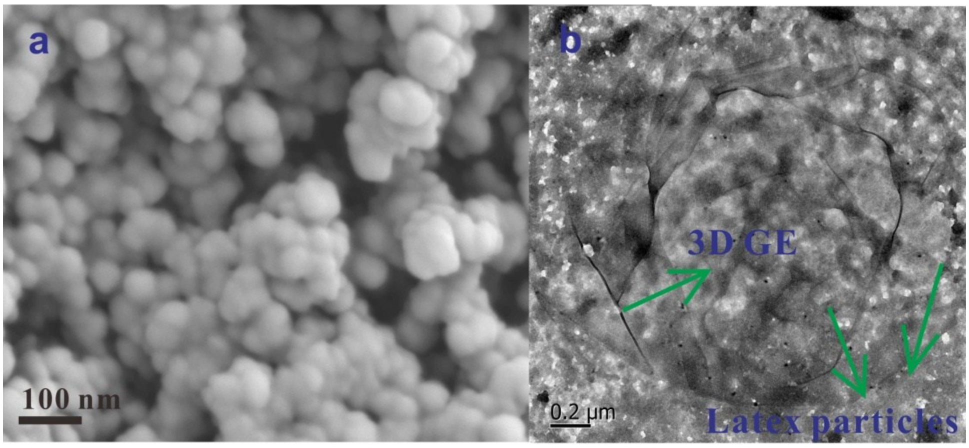

Fig. S2 (a) SEM image of SBR latex particles. (b) TEM image of SBR compounds with 1.66 vol% 3D-GE prepared by latex compounding & coagulantion.

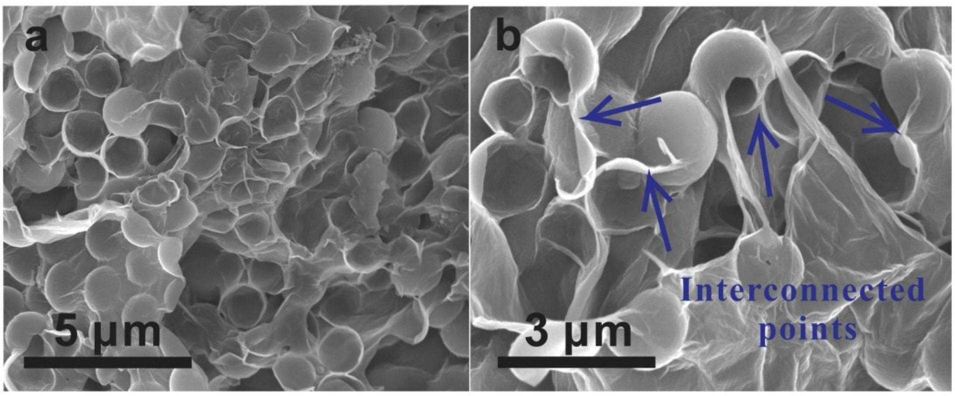

Fig. S3 SEM images of 3D-GE.

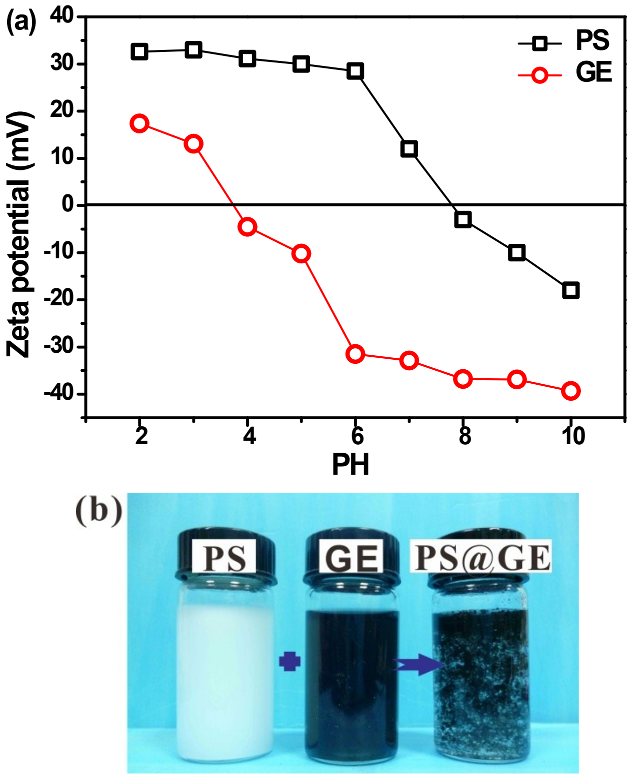

Fig. S4 (a) Zeta potentials of PS microspheres and GE solutions with various pH values. (b) Digital photographs during the synthesis of the PS@GE hybrids.

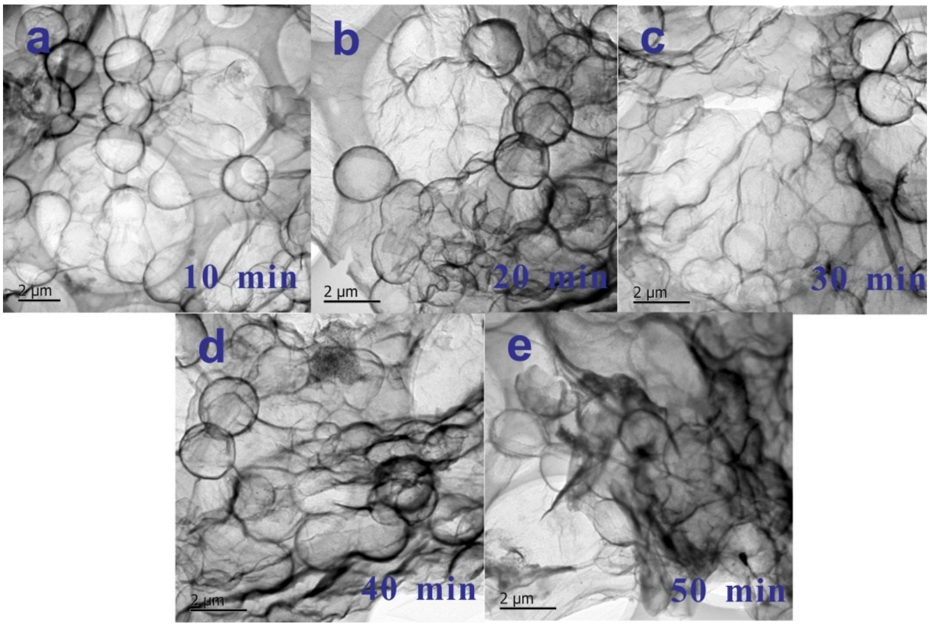

Fig. S5 TEM images of 3D-GE treated with different sonication time. (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 50 min.

Herein, the sonication process is effective method to obtain the homogeneous suspensions, which further makes 3D-GE clusters well-dispersed in SBR latex. Controlling the sonication time is conductive to protecting the 3D-GE structure. As shown in the Fig. S5. Evidently, the increased sonication time has little effect on the structure of 3D-GE when the sonication time is less than 40 min. Thus, the sonication power and sonication time in the present work are set as 100 W and 20 min, respectively.

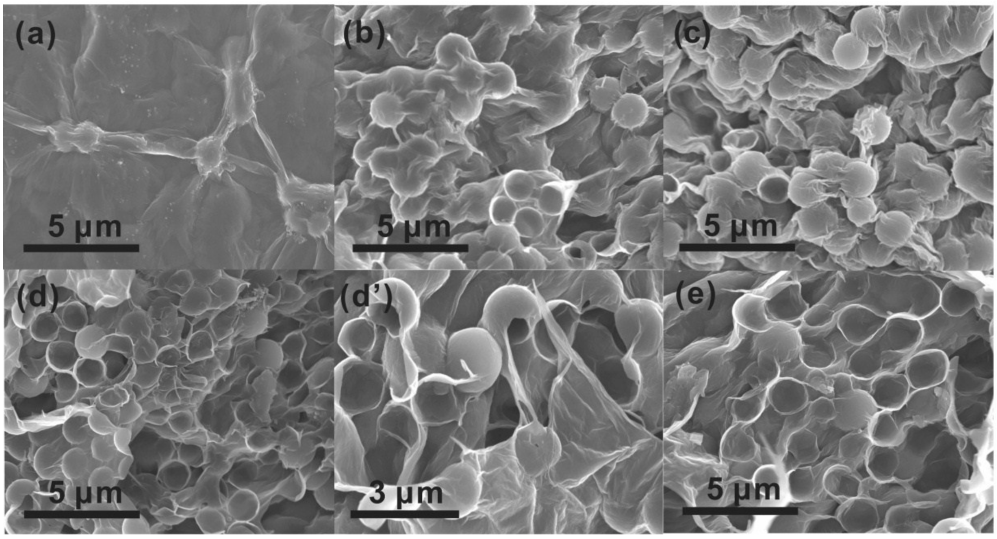

Fig. S6 SEM images of the synthesized 3D-GE in different weight ratio of GE and PS. (a) 90:1; (b) 45:1; (c) 30:1; (d and d') 19:1; (e) 10:1. For preparing the homogeneous suspensions using for the SEM observation, the sonication power and sonication time are set as 100 W and 20 min, respectively.

In the synthesized process, the weight ratio of GE and PS is the crucial factor for affecting the size of the synthesized 3D-GE clusters. As shown in the Fig. S6, it can be clearly seen that the formation of 3D-GE clusters is greatly influenced by the weight ratio of GE and PS. When the weight ratio of GE and PS is 90:1 and 45:1 (Fig. S6(a, b)), the porous 3D-GE structure is not formed. This phenomenon is ascribed to that the excessive amounts of GE sheets leads to an irreversible aggregation and stack. When the weight ratio of GE and PS decreases to 19:1 (namely, 95:5, as adopted in the present work), the macroporous 3D-GE structure can be clearly observed in the Fig. S6(d, d'). With further increasing the weight ratio of GE and PS to 10:1 (Fig. S6(e)), the imperfect porous structure is formed, mainly due to the lack of GE sheets coated on PS microspheres. Thus, the weight ratio of GE and PS is set at 19:1, which is in favor of the formation of perfect macroporous 3D-GE clusters. As observed in

Fig. S6(d,d’), the size of 3D-GE clusters is about 10 μm. Such clusters size can be further verified by the morphology of 3D-GE in the rubber matrix, as shown in the Fig. S8 of the *Electronic Supplementary Information*. Accordingly, the weight ratio of GE and PS affects the size of the formed 3D-GE clusters and their morphology in the rubber matrix, and further determines the percolation threshold in the rubber composites. And the appropriate sonication process can conduce to making 3D-GE clusters well-dispersed in SBR latex, effectively contributing to preparing the conductive rubber composites with high electrical performance.

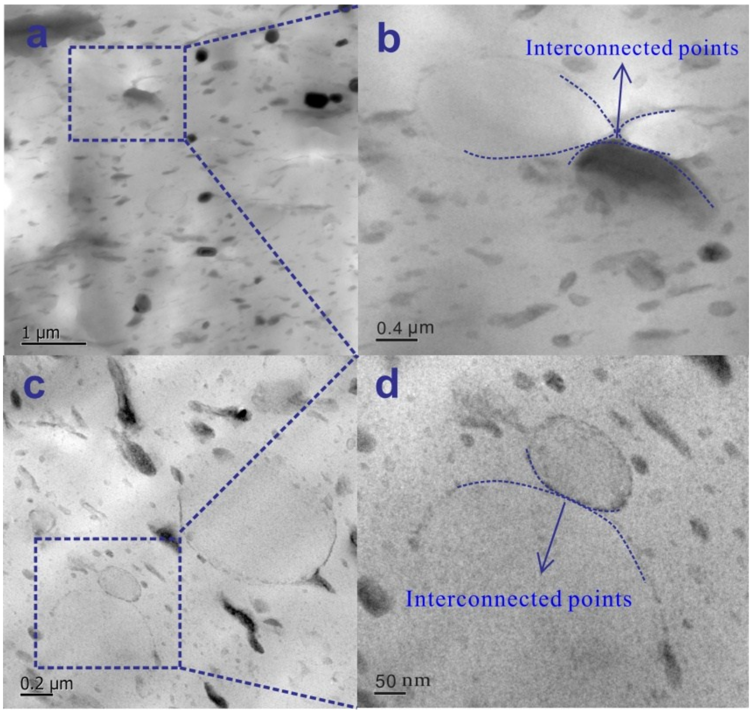

Fig. S7 TEM images of SBR3GE-DH-2 composites (a, c) and the magnified images corresponding to the areas outlined in blue (b, d).

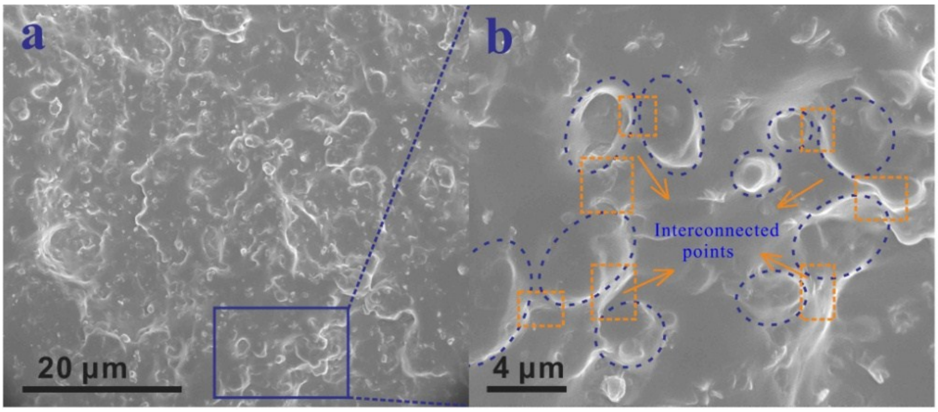

Fig. S8 SEM images of SBR3GE-DH-2 composites (a) and the magnified images corresponding to the rectangular areas outlined in blue (b). The circles outlined in blue represent the 3D-GE, and the rectangular areas outlined in orange refer to the interconnected points.

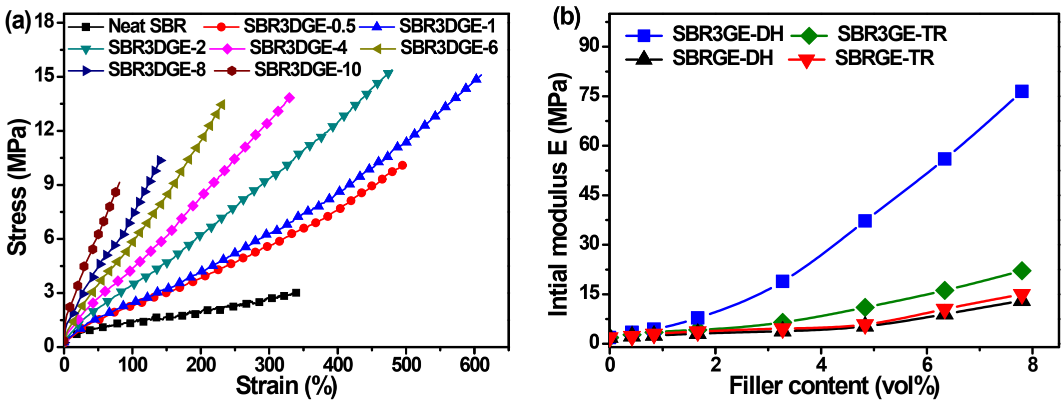

Fig. S9 (a) The stress-strain curves for the SBR3GE-DH composites with a segregated 3D-GE network. (b) Initial modulus for the SBR composites as a function of the filler content.

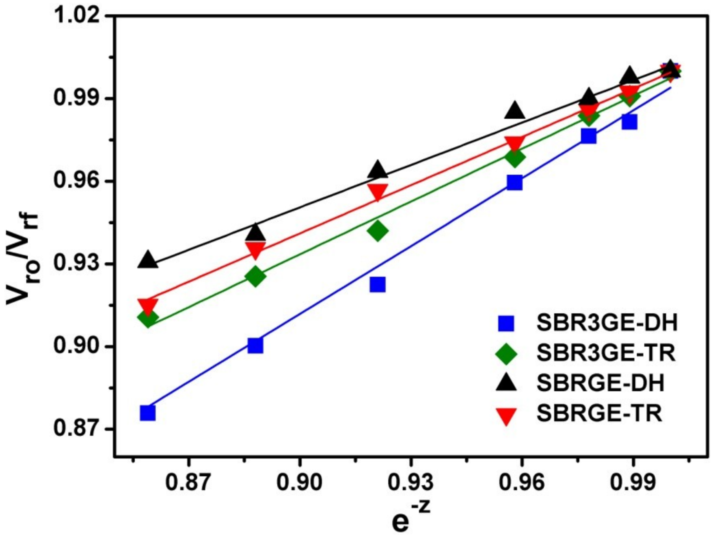

Fig. S10 Cunneen-Russell plot of SBR composites obtained by different methods.

The Cunneen-Russell equation[3] can be utilized to analyze the interfacial interaction between rubber and 3D-GE, which is given in the following equation:

$$\frac{V_{r0}}{V_{rf}} = ae^{-z} + b$$

where V_{r0} and V_{rf} represent the volume fractions of the rubber in the neat SBR and SBR composites, respectively, swollen in a solvent. a and b are two constants, and z is the weight fraction of the 3D-GE in the rubber. Thereinto, the value of V_{r0}/V_{rf} serves as an indicator reflecting the rubber-filler interactions in the composites.

Fig. S10 documents the filler content-dependent V_{r0}/V_{rf} of neat SBR and various SBR composites. Also, a basic note is that the higher slope of the plot of V_{r0}/V_{rf} against e^{-z} indicates stronger rubber-filler interactions. All of these results suggest the stronger interfacial interaction in SBR3GE-DH by contrast with those for other SBR/GE composites. Particularly, it can reasonably interpret the superior mechanical performance for SBR3GE-DH as compared to those of other SBR/GE composites.

Table S1. The experimental formula for preparation of SBR composites.

Content (phr)	Neat SBR	SBR GE-0.5	SBR GE-1	SBR GE-2	SBR GE-4	SBR GE-6	SBR GE-8	SBR GE-10
GE	0^{α}	0.5	1	2	4	6	8	10
SBRL	166.7	166.7	166.7	166.7	166.7	166.7	166.7	166.7
ZnO	5	5	5	5	5	5	5	5
StA	2	2	2	2	2	2	2	2
MB	1	1	1	1	1	1	1	1
CZ	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DM	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
OP-10	2	2	2	2	2	2	2	2

$^{\alpha}$ parts per hundred parts of rubber

Table S2. The percolation threshold (φ_c) and critical exponent (s) for SBR composites.

Percolation parameters	φ_c (vol%)	s
SBR3GE-DH	0.55	4.18
SBR3GE-TR	4.05	1.33
SBRGE-DH	4.24	1.73
SBRGE-TR	4.43	1.95

Table S3. The comparison for the electrical conductivity and mechanical properties of neat SBR, SBR3GE-DH, SBR3GE-TR, SBRGE-DH and SBRGE-TR composites with 1.66 vol% filler content.

Sample	Electrical conductivity (S/m)	Tensile strength (MPa)	Elongation at break (%)
Neat SBR	4.2×10^{-12}	3.0	313
SBR3GE-DH-2	3.3×10^{-2}	16.6	455
SBR3GE-TR-2	3.1×10^{-8}	13.8	468
SBRGE-DH-2	7.7×10^{-10}	13.0	474
SBRGE-TR-2	1.7×10^{-10}	12.1	480

Table S4. DSC results for the glass transition of SBR composites.

Sample	ω^{α} (%)	T_g (K)	ΔC_p (J/g·K)	ΔC_{pn} (J/g·K)	χ_{im} (wt%)
Neat SBR	0	222.65	0.625	0.625	-
SBR3GE-DH-0.5	0.446	222.95	0.561	0.564	9.76
SBR3GE-DH-1.0	0.889	223.15	0.494	0.498	20.32
SBR3GE-DH-2.0	1.762	223.55	0.470	0.478	23.52
SBR3GE-DH-4.0	3.463	223.95	0.451	0.467	28.48
SBR3GE-DH-6.0	5.106	224.25	0.430	0.453	30.97
SBR3GE-DH-8.0	6.695	224.65	0.405	0.434	34.05
SBR3GE-DH-10.0	8.230	224.95	0.372	0.405	35.19
SBR3GE-TR-0.5	0.446	222.75	0.575	0.578	7.52
SBR3GE-TR-1.0	0.889	222.95	0.540	0.545	12.80
SBR3GE-TR-2.0	1.762	223.25	0.507	0.517	17.20
SBR3GE-TR-4.0	3.463	223.55	0.473	0.490	21.76
SBR3GE-TR-6.0	5.106	223.95	0.439	0.463	25.92
SBR3GE-TR-8.0	6.695	224.25	0.422	0.452	27.68
SBR3GE-TR-10.0	8.230	224.55	0.404	0.440	29.60
SBRGE-DH-0.5	0.446	222.75	0.587	0.590	5.60
SBRGE-DH-1.0	0.889	223.05	0.556	0.561	10.24
SBRGE-DH-2.0	1.762	223.25	0.526	0.535	14.40
SBRGE-DH-4.0	3.463	223.45	0.493	0.511	18.24
SBRGE-DH-6.0	5.106	223.75	0.464	0.489	21.76
SBRGE-DH-8.0	6.695	224.05	0.439	0.470	24.80
SBRGE-DH-10.0	8.230	224.35	0.413	0.450	28.00
SBRGE-TR-0.5	0.446	222.65	0.590	0.593	5.12
SBRGE-TR-1.0	0.889	222.95	0.551	0.556	11.04
SBRGE-TR-2.0	1.762	223.25	0.530	0.540	13.60
SBRGE-TR-4.0	3.463	223.55	0.489	0.507	18.88
SBRGE-TR-6.0	5.106	223.95	0.457	0.482	22.88
SBRGE-TR-8.0	6.695	224.15	0.443	0.475	24.00
SBRGE-TR-10.0	8.230	224.55	0.409	0.446	28.40

$^{\alpha}\omega$, the weight fraction of GE in the composites; T_g, the glass transition temperature; ΔC_p, the heat capacity increment at T_g; ΔC_{pn}, heat capacity increment normalized to the rubber fraction; χ_{im}, the weight fraction of immobilized rubber in the composites.

Table S5. Gas permeability, conductivity and mechanical properties of GE, GO, graphite derivative/elastomer composites.

Rubber	Filler	Content	Permeant	Permeability reduction (%)	Conductivity (S·m^{-1})	Increase for mechanical property (%)
NR[4]	GE	2 phr	Water vapor	60	2.8×10^{-2}	37
NR[5]	GE	2 phr	Oxygen	50	---	160
SBR[6]	GE	3 phr	Oxygen	67.2	3.2×10^{-5}	700
XNBR[1]	GO	1.9 vol%	Nitrogen	55	---	344
NR[7]	SGO	2.0 wt%	Air	60	---	79
ENR[8]	GE	2.0 wt%	Oxygen	59	3.75×10^{-4}	---
SBR[9]	GO	2.0 wt%	Nitrogen	65	---	700
Silicone[10]	GE	8.0 wt%	---	---	3.0×10^{-9}	143
NR[11]	PDDA-GE	2.0 vol%	---	---	4.5×10^{-1}	-46.5
SBR[α]	GE	2 phr	Nitrogen	71.6	3.3×10^{-2}	453

[α] represents the properties of SBR3GE-DH-2 (1.66 vol%) composites prepared in our work.

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