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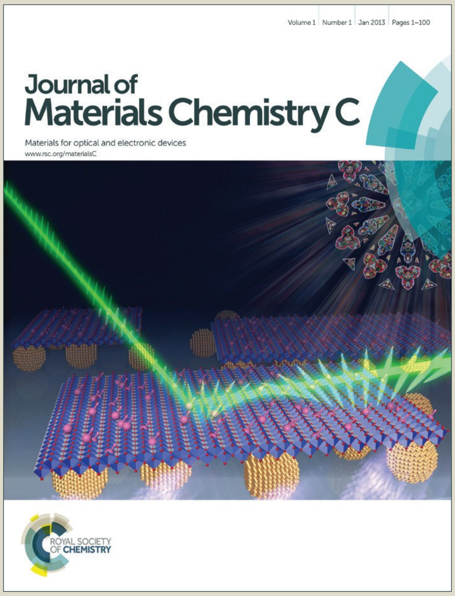

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ARTICLE

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

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The styrene butadiene rubber/graphene (SBR3GE-DH) composites with segregated graphene networks, synchronously having high electrical conductivity, mechanical strength and gas barrier property, were firstly fabricated by a pre-construction strategy combined static hot pressing. A ‘‘three dimensional graphene (3D-GE) network’’ with percolation conductive paths was efficiently constructed with an extreme low percolation threshold of 0.55 vol%. Remarkably, a conductivity of 0.033 $S\cdot m^{-1}$ at a 3D-GE content of 1.66 vol% was 8 orders of magnitude higher than that of the sheet-like GE-based composites (SBRGE) prepared by conventional latex compounding. All those outstanding properties were attributable to the well-constructed ‘‘3D-GE segregated networks’’ in the SBR, and the strong interfacial adhesion between 3D-GE and the SBR matrix resulting from the geometric confinement of 3D-GE networks. Such performances make SBR3GE-DH composites very competitive for potential applications in high conductive sealing gasket in aerospace industry, sealed packages, and gas transport and storage devices, *etc*.

Electrically conductive polymer composites, generally tailored by the incorporation of conductive fillers into the essentially insulating polymer matrix, have attracted enormous academic research and industrial attention due to their potential applications in sensors[1,2], conductors[3] and electromagnetic interference shielding[4,5] and photovoltaic devices[6,7], *etc*. Particularly, the utilization of graphene (GE) as an electrically conductive filler in composites shows significant potential for practical applications due to its outstanding electrical conductivity (up to 6000 $S\cdot cm^{-1}$).To date, there have been numerous studies reporting that the GE can dramatically endow the polymer with a great electrically conductivity compared with other conductive fillers at a lower content. For example, Araby *et al.*[8] developed a solution mixing to prepare the conductive styrene butadiene rubber/GE composites with a percolation threshold of 5.3 vol%, and a percolation threshold of 2 wt% was reported by Chen *et al*.[9] for polyurethane/GE composites fabricated by ball milling process. Ruoff *et al.*[10,11] also found that a certain amount of GE dramatically enhance the electrical properties of natural rubber (NR). However, a relatively high GE content was employed to improve the conductivity of the composites fabricated by the abovementioned approaches. Therefore, reducing the content of GE (lowering the percolation threshold) with maintaining or even enhancing the conductivity of the composites has been a major challenge.

Nowadays, a detailed analysis by Ruoff *et al.*[10] and Li *et al.*[12] demonstrated that the segregated network conduces to forming a conductive pathways at a certain filler loading, thus a low percolation threshold can be achieved. For example, Xia *et al.*[13] fabricated the NR/GE composites with a segregated GE network structure synthesized by a latex compounding method, contributing to a low conductive percolation threshold (0.62 vol%) of composites. Luo *et al.*[14] demonstrated the segregated graphene networks in NR composites led to a low percolation threshold (0.21 vol%). Unfortunately, these conductive polymer composites with segregated GE network structures always exhibit inferior mechanical properties, and it is of high difficulty and randomicity for constructing the intact segregated GE network structure without the defects. Therefore, a novel method to attain high conductivity and low percolation threshold without severe damage in the mechanical performance of composites, as well as a desirable GE network structure, is urgently needed.

In this work, we have developed a novel pre-construction method to fabricate high electrically conductive, high strength and gas barrier vulcanized rubber composites with a three dimensional conductive segregated graphene network (3D-GE). The electrical conductivity of the segregated SBR composites at a 1.66 vol% content of 3D-GE improves by more than 8 orders of magnitude compared with that of the SBR/GE composites prepared by conventional latex compounding. The rubber composites with an interconnected 3D-GE network exhibit very competitive for applying to highly conductive sealing gasket in aerospace industry, sealed packages, and gas transport and storage devices, *etc*.

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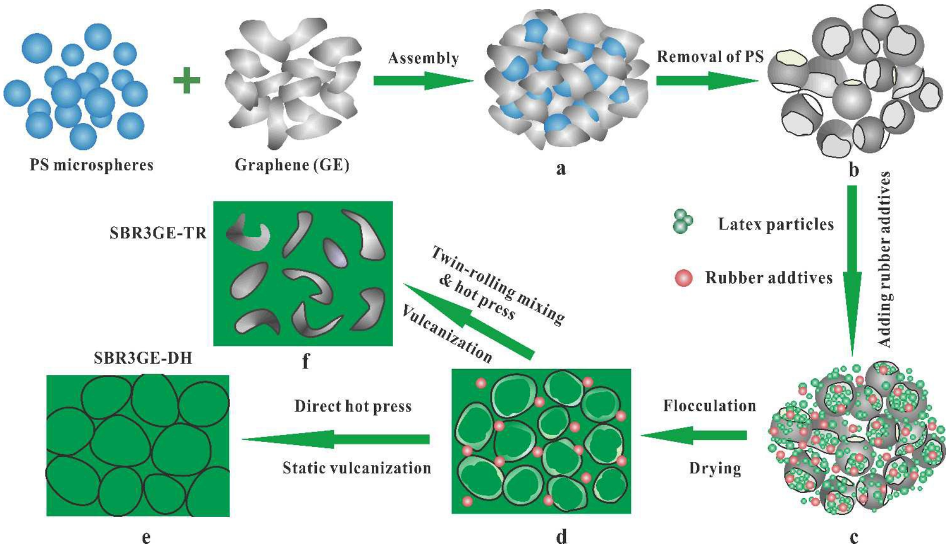

Scheme 1 The preparation of SBR/GE composites with a 3D-GE segregated network by a pre-construction method and direct hot press. (a) PS@GE hybrids prepared by self-assembly process; (b) 3D-GE obtained by removal of PS microspheres; (c) 3D-GE and rubber additives uniformly dispersed in latex, and SBR/3D-GE latex acquired by in situ reduction in latex; (d) SBR compounds with 3D-GE network after latex flocculation and drying; (e) the crosslinked SBR composites with the 3D-GE network fabricated by direct hot press; (f) the crosslinked SBR/3D-GE composites fabricated by twin-rolling mixing and hot press.

The pre-construction method for preparing SBR composites with a segregated 3D-GE network is schematically illustrated in Scheme 1. Firstly, polystyrene (PS) microspheres and graphene oxide (GO) were prepared by dispersion polymerization and the modified Hummers method, respectively. All the homogeneous PS and the reduced GO suspensions were dispersed in water by a sonication process. PS@GE hybrids were then prepared by self-assembly process (Scheme 1a), subsequently, the final 3D-GE with macroporous structure were fabricated by removing the PS microspheres with toluene exposure (Scheme 1b). The 3D-GE and rubber additive (*i.e.* sulfur, accelerator) were uniformly added into the SRB latex. The latex particles at 30~100 nm (Fig. S2(a)) and rubber additives can easily swarm into the macroporous structure of 3D-GE (Scheme 1c). Next, the black SBR/3D-GE latex was obtained and then the latex was coagulated and filtrated (Scheme 1d). The obtained solids were dried and then hot pressed directly and static vulcanized at 160 °C to obtain the SBR3GE-DH composites. In the vulcanization, although an extrusion effect originated from the rubber particles potentially exert a force for the 3D-GE network, the segregated 3D-GE network structure can be efficiently retained after vulcanization (Scheme 1e) due to the high viscosity of the molten rubber matrix and van der Waals force between the GE sheets. If the obtained rubber solids were subjected to the twin-roll mixing, the 3D-GE segregated network in SBR3GE-TR composites may be seriously destroyed (Scheme 1f).

The procedure for establishment of 3D-GE is schematically illustrated in Scheme 1. The PS microspheres with particle size 1~2 μm were firstly synthesized by the dispersion polymerization (Fig. S1a), and the GO, as a crumpled and transparent ‘‘paper’’, is observed by TEM observation (Fig. S1b). The electrostatic interactions between PS microspheres and reduced GO sheets were subsequently integrated into PS@GE hybrids through a self-assembly process. The SEM image in Fig. S1(c) clearly demonstrate that GE sheets are tightly wrapped around PS microspheres, forming wrinkled and folded textures. Evidently, after removal of the PS microspheres by etching with toluene, microporous 3D GE with holed structure is formed as displayed in Fig. 1a,b, and the size of the pore is approximately 1~2 μm. Also, some interconnected points were observed between the 3D-GE (Fig. S3), which can serve as efficient electrical bridges with the 3D-GE. Notably, the microporous structure does not collapse due to the interconnected nature of the GE shells in the assembled 3D structure. Withal, the microporous structure is favorable for providing large containable space for filling up latex particles and rubber additives (Fig. S2(b)), and such architecture provides necessary precondition for building the composites with the segregated 3D-GE network.

Furthermore, Fig. 1c shows that the segregated network structure of 3D-GE is formed in the matrix prepared by direct hot pressing. The 3D-GE shells cap the partial rubber particles, uniformly dispersed into the rubber matrix and

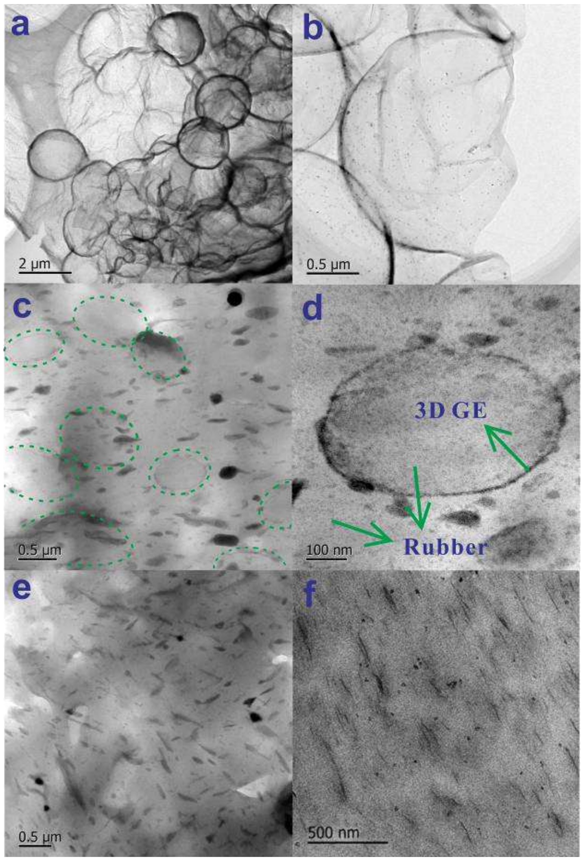

Fig. 1 TEM images of 3D-GE (a-b), SBR3GE-DH-2 composites (c-d), SBR3GE-TR-2 composites (e) and SBRGE-DH-2 composites (f). SBR3GE-DH: the SBR composites with the 3D-GE network prepared by latex compounding and direct hot pressing. SBR3GE-TR: the SBR composites with 3D-GE network prepared by latex compounding and twin-roll mixing. SBRGE-DH: the SBR composites with GE sheets prepared by conventional latex compounding and direct hot pressing. SBRGE-TR: the SBR composites with GE sheets prepared by conventional latex compounding and twin-roll mixing. SBRGE-DTR: the SBR composites prepared by direct twin-roll mixing of GE powders and SBR.

thus constructing a segregated conductive network. A much clearer view of segregated 3D-GE network at high magnification is shown in Fig. 1d. Also, it can be clearly seen in Fig. S7 and S8 that some interconnected points exist between the 3D-GE structures, which serve as electrical bridges for constructing the conductive paths. Such phenomenon effectively guarantees the enhancement of electrical conductivity of SBR composites. What we do know is that it is the first time for preparing such intact 3D-GE structure in the rubber matrix. By contrast, due to the strong shear force, the segregated 3D-GE networks in the matrix are seriously destroyed after the twin-rolling mix, resulting in that the GE networks are stripped away, stretched or squeezed in the matrix, as illustrated in Fig. 1e. Moreover, Fig. 1f displays that the majority of GE sheets are uniformly distributed in the SBR/GE composites with 1.66 vol% GE sheets prepared by latex compounding & direct hot pressing, without forming a segregated GE networks.

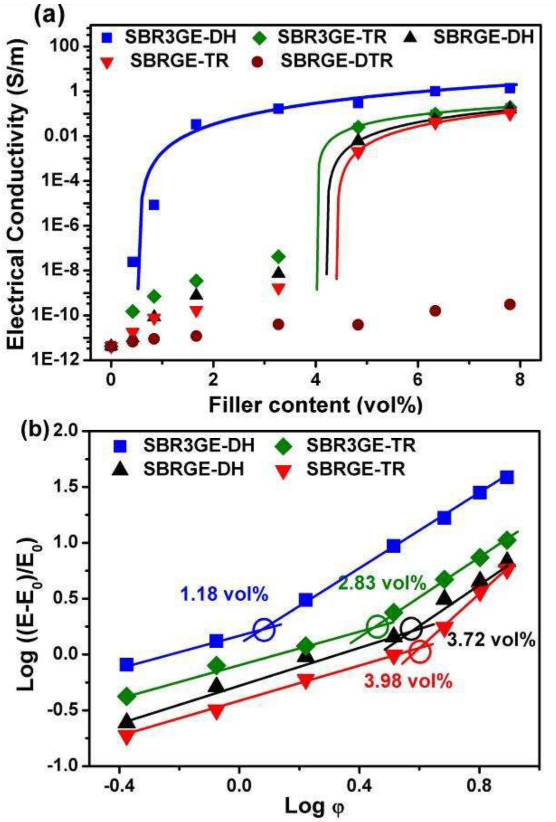

Fig. 2 (a) The electrical conductivity as a function of the GE content for the SBR/GE composites prepared by the different methods. (b) Double logarithmic plot of the excess tensile modulus as a function of the GE content. The straight lines are the fitting curves.

It has been admitted that constructing a continuously conductive network in the composites is of crucial importance for achieving high conductivity at low filler contents, and effectively reducing the percolation threshold.[13,15,16] Fig. 2a presents the electrical conductivity of the composites prepared by different methods as a function of GE content. All the SBRGE-DH and SBRGE-TR prepared by the conventional latex compounding of GE have a low conductivity value of 10^{-8} S·m^{-1} at the GE content of 3.27 vol%. Additionally, SBRGE-DTR obtained with a direct twin-roll mixing exhibits a lower conductivity value of 10^{-10} S·m^{-1} at a higher GE content of 7.8 vol%. That is because the direct twin-roll mixing cannot be in favour of exfoliation and dispersion of GE powders, and construction of conductive network in the matrix.

Noting that the electrically conductivity and conductive percolation threshold of SBR3GE-DH is comparable to those of the SBRGE-DH. For instance, the electrical conductivity of the SBRGE-DH-2 composites is 7.7×10^{-10} S·m^{-1}, while it can reach up to 0.033 S·m^{-1} for the SBR3GE-DH-2, significantly enhanced by 8 orders of magnitude. Particularly, the electrical conductivity of SBR3GE-TR is slightly higher than those for SBRGE-DH and SBRGE-TR, and extremely lower than that of SBR3GE-DH.

Such performances can be attributed to the different networks in the composites. These are schematically illustrated in Fig. 3. At low filler concentrations, GE sheets exist as individual units rather than connected networks in the SBRGE composites (Fig. 3(I)). And though

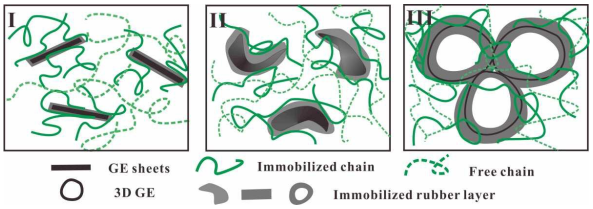

Fig. 3 A simplified schematic showing the GE network in the SBRGE-DH (I), SBR3GE-TR (II) and SBR3GE-DH composites (III).

the rubber chains are immobilized on the surface of GE sheets and regarded as ‘‘bridges’’ to connect the GE sheets, only a few electrons can be dictated by the immobilized rubber layer surrounding the GE sheets. This is the reason why the conductivity of the SBRGE composites has no significant enhancement in comparison with the neat SBR. This phenomenon is also observed for the SBR3GE-TR (Fig. 3(II)), because the collapse of 3D-GE network is occurred under the action of shear force. As for SBR3GE-DH composites, even low 3D-GE concentration is enough to form a conductive network *via* a direct contact between 3D-GE, thereupon, an intact segregated 3D-GE network can be efficiently constructed (Fig. 3(III)) and hence the high electrical conductivity is observed. Within this segregated network, the motion of rubber chains can be impeded by the geometric confinement of the segregated 3D-GE network, forming a higher density immobilized rubber layer in the vicinity of 3D-GE as shown in Fig. 3(III).

It is generally known that closely related to the electrical conductivity of the composites is that of filler content. Evidently, a significant increase for the electrical conductivity of SBR3GE-DH composites is displayed at a critical concentration (Fig. 2). For having an insight into the electrical conductive behaviour of the composites from the critical concentration of fillers, a power law relation can be employed to compute the electrical conductive percolation threshold (φ_c).[17,18]

$$\sigma \propto (\varphi - \varphi_c)^s \, (\varphi \geq \varphi_c)$$

where σ is the conductivity of the composites, φ is the volume fraction of the fillers, and *s* represents the critical exponent. The conductivity of the composites as a function of filler content is displayed in Fig. 2a. Obviously, the percolation threshold of the SBR3GE-DH composites is only 0.55 vol%, much lower than those of SBR3GE-TR, SBRGE-DH and SBRGE-TR composites, which are as high as 4.05, 4.24 and 4.43 vol%, respectively. Such prominent superiority for SBR3GE-DH is attributable to that the majority of the 3D-GE can greatly enhance their inter-GE connections and efficiently construct a continuously conductive network by direct static hot press, and hence the percolation threshold is much lower. For SBR3GE-TR system, the strong shear force can cruelly destroy the 3D-GE networks, leading to the breakdown of conductive paths. Noteworthily, we find that the electrical behaviour of our composites is better than those reported for NR/GE[13], polyurethane/GE[9], SBR/GE[19], polycarbonate/GE[20] and epoxy/GE composites[21], *etc*.

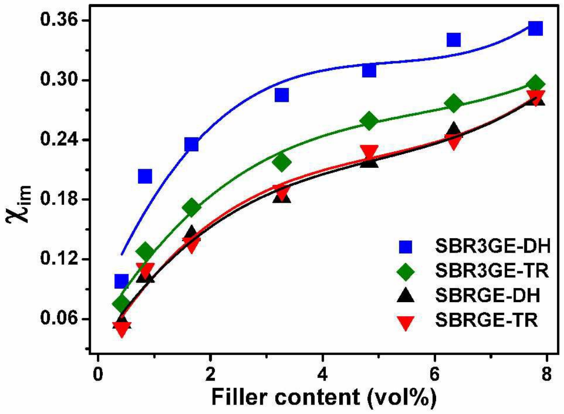

Fig. 4 Weight fraction of immobilized rubber chains (χ_{im}) of SBR/GE composites obtained by different methods as a function of filler content.

It has been testified that the critical exponent (*s*) depends on the system dimensionality of the composites. As reported, the value of *s* reflects the status of a polymer-fillers network.[22,23] Concretely, the value of *s* lower than 2.1 suggests a polymer-bridged filler network in the matrix, whereas the value of *s* higher than 3.75 indicates the existence of a strong interconnected network, directly constructed between the fillers. As displayed in Table S2, the *s* values of 1.33, 1.73 and 1.95 correspond to SBR3GE-TR, SBRGE-DH and SBRGE-TR composites, respectively. Such results are indicative of the formation of a polymer-bridged GE network. Moreover, a *s* value of 4.18 for SBR3GE-DH reveals the existence of the interconnected GE networks in the matrix. Hence, this low electrical percolation threshold and high value of the critical exponent can be attributed to the pre-construction 3D-GE interconnected networks in the SBR matrix, as demonstrated by the TEM observations.

For well understanding the reinforcing efficiency of a segregated 3D-GE network towards the rubber matrix, the percolation threshold for mechanical performance were investigated through an analysis of the initial modulus according to a model proposed by Huber and Vilgis[24]. Based on this model, it posed a good linearity between the filler content (below the percolation threshold) and the excess modulus ($(E-E_0)/E_0$), where E_0 and E represent the initial modulus of unfilled and filled rubber, respectively. Of particular note is that the initial modulus of composites was determined by the slope at the origin of the stress-strain curves (Fig. S9(a)). Fig. S9(b) shows the initial modulus as a function of GE content and the results reveals a significant trend for an increase in the initial modulus of composites with increasing GE content. However, it is clearly observed that the increment of the initial modulus with the

GE content is not linear, result of which indicates an existence of two regimes, at low and at high GE content, respectively. All these results testify the existence of the percolation threshold in the rubber/GE composites.

Furthermore, the Huber and Vilgis model has also been developed to determine the percolation threshold, which is precisely evaluated by the intersection of the two fitted straight lines of the two regimes. Fig. 2b shows a double logarithmic plot of the excess modulus as a function of the GE content. For the SBR/GE composites without the segregated network, the percolation threshold for the SBRGE-DH and SBRGE-TR composites is 3.72 vol% and 3.98 vol%, respectively. In comparison, as for the SBR3GE-DH composites, the estimated percolation threshold lowers to 1.18 vol%, whereas for SBR3GE-TR composites, the percolation threshold is 2.83 vol%. As a whole, the percolation threshold evaluated by the Huber and Vilgis model and that computed by the data of electrical conductivity are in an expectant consistency. So, these results strongly suggest that the pre-construction method effectively facilitate the formed segregated 3D-GE network structure in the SBR3GE-DH composites. Notably, the strong shear force can lead to the breakage of the segregated 3D-GE network structure in the SBR3GE-TR composites obtained by the twin-roll mixing. Besides, none of the present process can effectively contribute to building the segregated network structure of GE in the SBRGE-DH and SBRGE-TR composites, either by direct hot pressing or by twin-roll mixing.

Additionally, the mechanical properties of the composites were provided for a comparison and the results were tabulated in Table S3. We find that the mechanical properties of the SBR3GE-DH composites are more superior to those for the SBR3GE-TR, SBRGE-DH and SBRGE-TR composites. Remarkably, in contrast with neat SBR, the tensile strength of the SBR3GE-DH-2 composite (1.66 vol% 3D-GE content) is significantly increased by 453%, and the corresponding elongation at break is substantially improved as well. As known, at high filler content, a trade-off between the electrically conductivity and mechanical properties are generally inescapable. Surprisingly, the SBR3GE-DH composites with the segregated 3D-GE network simultaneously have the good electrically conductivity and mechanical properties at low GE content. These outstanding performances tremendously provide the basic for the further practical application.

It is well document that the outstanding performances of the composites crucially rely on the interfacial interactions between the filler and the matrix. More notably, the rubber chains immobilized on the surface of the fillers due to strong interfacial interactions, can effectively elaborates the reinforcement of fillers towards the rubbers. The weight fraction of rubber chains immobilized on the surface of GE (χ_{im}) can be quantitatively analyzed by the following equation[25]:

$$\chi_{im} = 1 - \frac{\Delta C_{pn}}{\Delta C_{p0}(1-\omega)}$$

where ΔC_{pn} is the heat capacity increment normalized to the rubber fraction, ΔC_{p0} represents the heat capacity increment of the neat rubber. ω is the weight fraction of GE in the composites.

The values of ΔC_p of neat SBR and SBR composites were calculated and the results were tabulated in Table S4. And the dependence of χ_{im} on the GE content was also shown in Fig. 4. Evidently, the value of χ_{im} for SBR3GE-DH is much higher than those achieved in SBR3GE-TR, SBRGE-DH and SBRGE-TR composites. As shown in Fig. 3, the segregated 3D-GE network is beneficial to the formation of immobilized rubber layer in the interfacial region of 3D-GE, result of which significantly decreases the mobility of 3D-GE and thus prevents the phase separation. So, the immobilized rubber layer acts as an interface modifier between the matrix and fillers, and the larger value of χ_{im} imply the stronger interfacial interaction between the 3D-GE and rubber. Furthermore, the Cunneen-Russell equation[26] can be utilized to analyze the interfacial interaction as shown in Fig. S10, and the results also indicate the stronger interfacial interaction in SBR3GE-DH by contrast with those for other SBR/GE composites. So, it can reasonably interpret the superior mechanical properties for SBR3GE-DH compared with those of other SBR/GE composites.

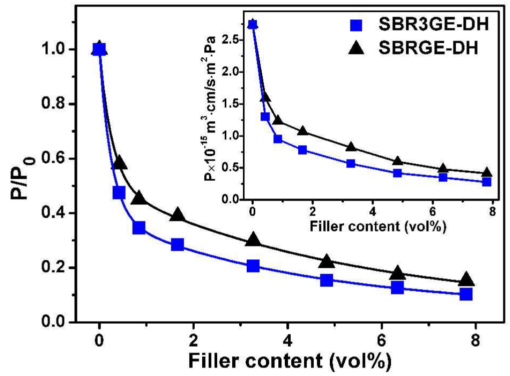

Fig. 5 Nitrogen permeability of SBR composites as a function of filler content, measured at 23 °C and 0% relative humidity (RH).

Based on the above analysis, such a low electrical threshold, excellent electrical conductivity and high mechanical performance can be ascribed to the well-constructed ‘‘3D-GE segregated networks’’ in the SBR matrix, and the strong interfacial interaction between 3D-GE and the SBR.

Considering that rubber materials are potentially needed to meet the special practical application, gas barrier property of materials should certainly be a study of renewed focus. Nitrogen permeability of the SBR composites measured at 23 °C and 0% RH is shown in Fig. 5. The nitrogen permeability decreases with increasing the content of GE for both the segregated SBR3GE-DH and not-segregated SBRGE-DH composites. For example, compared to neat SBR, the permeability of SBR3GE-DH-2 composites (1.66 vol% 3D-GE) dramatically decreased by 71.6%, while the permeability of SBRGE-DH-2 composites (1.66 vol% GE) decreased by 61.1%. The incorporation of the impervious GE sheets and 3D-GE to the rubber not only enhances the impervious area for penetrant flux, also increases the diffusion length in the matrix. It is noteworthy that the segregated SBR3GE-DH composites exhibit a more significant decrease in the permeability compared with that for the non-segregated SBR3GE-DH composites at all the investigated contents. The superiority of 3D-GE to GE sheets in improving the gas barrier property of SBR is ascribed to the formation of interconnected 3D-GE network, thus efficiently producing a reduced cross section and an extreme tortuous path for hindering the gas diffusion in the materials. In contrary, as to the rather flat structure of GE sheets, it is of difficulty to construct a dimensional barrier for restricting the gas diffusion. Delightedly, the gas barrier property of the fabricated SBR3GE-DH is superior to that of those GE-based rubber composites previously reported, such as the segregated NR/rGO[27], NRLGES[13], SBR/GE[17], XNBR/GO[28], ENR/SGO[29] and NR/GE[30]. Additionally, the comprehensive comparison of the mechanical performance, electrically conductivity and gas barrier property of graphene, graphene oxide, and graphene derivative/rubber composites previously reported is listed in Table S5. It can be noted that as-prepared SBR3GE-DH composites exhibit more excellent balance of electrically conductivity, mechanical performance and gas barrier property. Such promising overall properties make SBR3GE-DH composites very competitive for potential applications as the multi-functional structural materials, such as sealing gasket, sealed packages, and gas transport and storage devices, *etc*.

Conclusions

We firstly reported a novel approach, *i.e.* pre-construction method and static vulcanization, to fabricate rubber composites with a segregated graphene network exhibiting good electrical conductivity, gas permeability and high mechanical property. The 3D-GE with macroporous structure were prepared by self-assembly process and the etching techniques. Subsequently, the solid rubber compounds by coagulation with the 3D-GE and rubber additive were subjected to the static vulcanization, finally preparing the crosslinked SBR composites with a segregated 3D-GE network. The obtained 3D-GE network efficiently promotes the formation of the conductive path, dramatically enhancing the electrical conductivity and reducing the electrical percolation threshold of the composites. The electrical conductivity of the SBR3GE-DH composite (1.66 vol% 3D-GE) prepared by pre-construction method and static vulcanization is 8 orders of magnitude higher than that of the SBRGE composites prepared by conventional latex compounding. Importantly, the SBR3GE-DH composites with a 3D-GE segregated network synchronously possess the high mechanical performances and excellent gas barrier properties. This novel strategy of pre-constructed 3D-GE for fabricating an effective segregated GE structure in a rubber matrix can efficiently endow the composites with the multiple functions, and profitably broaden the application fields, such as highly conductive sealing gasket in aerospace industry, sealed packages, and gas transport and storage devices, *etc*.

Acknowledgements

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