Graphene oxide sheets covalently functionalized with block copolymers via click chemistry as reinforcing fillers†

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Herein, by taking advantage of click chemistry, we propose a general and effective methodology to covalently functionalize graphene oxide sheets (GOSs) with block copolymers, namely poly(styrene-ethylene-co-butylene-ethylene) triblock copolymers as an example in this study. The covalent attachment of SEBS to GOSs, as well as the individual nature of the hybrids, was confirmed by detailed investigations. For the potential applications of the block copolymer-clicked GOSs, they were incorporated into polystyrene (PS) as reinforcing fillers. The SEBS-clicked GOSs showed excellent compatibility with a PS matrix, and as a consequence, remarkably improved mechanical properties and thermal stability of the resulting composite films were achieved. This protocol is believed to offer possibilities to fully combine the extraordinary performances of GOSs with the multifunctional properties of block copolymers, and thus be useful in a variety of technological fields.

1. Introduction

Emerging as atomically thin two-dimensional carbon nanostructures, graphene sheets (GSs) have attracted tremendous attention from both the theoretical and experimental scientific communities in recent years.1 These fascinating carbon nanomaterials hold great promise in many potential applications such as polymer composites,2–4 lithium-ion batteries,5 organic photo-voltaic cells6 and biosensors.7 Especially, the extraordinary properties combined with inexpensive sources (graphite powders) of GSs have spurred intensive interest in developing high-performance, cost-effective polymer composites.8 For the actual implementation of GSs in technological uses, their mass production at low cost appears to be a key challenge. An effective approach in this regard is based on the deoxygenation of graphene oxide sheets (GOSs),9 which can be easily obtained from nature graphite flakes by strong oxidation and subsequent exfoliation.10 As heavily oxygenated carbon monolayers, GOSs are decorated with various oxygen functional groups (e.g. hydroxyl, carboxyl, epoxy, ketone, etc.) on their basal planes and edges.11 These active surface functionalities on GOSs can not only facilitate their exfoliation in a range of solvents12,13 but also enhance their compatibility with polar polymeric matrices.14–16 Therefore, in addition to their reduction to GSs, GOSs have also been suggested as ideal fillers for polymer composites.17

For the successful development of GOS-based polymer composites with satisfactory properties, two important issues have to be addressed: the uniform dispersion of GOSs in the polymer hosts, and the favorable interfacial interactions between these two phases.18 Because of the active oxygen functional groups located at their surfaces, GOSs can be dispersed in polar polymers such as poly(vinyl alcohol),14 polyurethane15 and polyamide16 at a molecular level with strong adhesions. However, nonpolar polymers, which constitute the family of the most influential and versatile polymer materials (e.g. polystyrene, polypropylene, polyethylene, etc.), are incompatible with GOSs. GOSs tend to form agglomerates or even restack in nonpolar polymer matrices because of their incredible interlayer cohesive energy,18 thereby making the fabrication of high-performance GOS-based nonpolymer composites unfeasible. In this regard, several strategies including covalent bonding18–21 and noncovalent functionalization22 of GOSs have been proposed. Wherein, based on the reactive oxygen functionalities at GOS surfaces, covalent modification of GOSs with nonpolymer polymers is suggested to be a promising method for achieving excellent compatibility between GOSs and nonpolymer polymers in that it can minimize the interfacial tensions between them.18,19 For example, Song and co-workers reported a facile route to covalently functionalize GOSs with polyethylene (PE) and found that the PE grafted GOSs can be well dispersed in a PE matrix without any observed aggregation.18

Over the past few decades, numerous studies have been reported on the use of block copolymer-based hybrids, which allow for the fine tuning of desirable properties in the resulting...
The introduction of block copolymers into inorganic nanoparticles has also been actively pursued, as it can yield a vast range of functional properties for potential technological applications. Shin et al. utilized block copolymers as a template to produce mesoporous SiO$_2$ films. As demonstrated by Mountrichas et al., block copolymers could be used as surfactants to disperse otherwise insoluble fullerenes in water. Cho and co-workers covalently attached block copolymers to carbon nanotubes (CNTs) and found that the block copolymer-grafted CNTs could be homogeneously dispersed in the polymer matrix, thus remarkably enhancing its mechanical performances. Very recently, the incorporation of block copolymers into GSs and GOSs with the aim of altering their surface properties has been carried out in some pioneering works. Shen et al. realized the synthesis of amphiphilic GSs by grafting amphiphilic block copolymers on them. Han and co-workers found that poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) triblock copolymers could be adsorbed onto GSs through noncovalent interactions between the hydrophobic PPO segments and hydrophobic GS surfaces. Utilizing the ability of PEO segments to penetrate into $\alpha$-cyclodextrin cavities and form supramolecular assemblies, they further presented a facile method to prepare GS-based hydrogels. Although the promising prospect of the hybridization of block copolymers with GSs and GOSs has been shown in these studies, to the best of our knowledge, it lacks a general and effective approach to covalently functionalize GSs and GOSs with block copolymers, especially, for the fabrication of high-performance polymer composites.

In our previous study, we developed an effective strategy to immobilize well-defined polymers onto GOSs using click chemistry. Because of the high reactivity (proceeding in the presence of all functional groups), selectivity (affording 1,4-regioselective 1,2,3-triazoles) and reliability (not affected by H$_2$O, O$_2$, etc.) of click chemistry, this strategy can be applied to various polymers for their covalent linkage to GOSs. Herein, we focus on the usage of click chemistry to covalently attach block copolymers, namely poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) triblock copolymers as an example in this study, to GOSs. This synthetic approach can be expanded to other functional or template block copolymers for their covalent bonding onto GOS surfaces. To illustrate one of the potential applications of these block copolymer-clicked GOSs, they were incorporated into PS as reinforcing fillers, fabricating high-performance nonpolar polymer composites.

2. Experimental

Materials

Graphite oxide solids were synthesized from expandable graphite powders (EGPs, Yingtai Company, China) using a modified Hummers method. SEBS triblock copolymers, Kraton G1651 with a molecular weight of 170 000 g mol$^{-1}$ and a PS composition of 0.29, were provided by Shell Company. PS (Sigma-Aldrich) employed to fabricate composite films has a molecular weight of 139 000. Unless otherwise stated, all other reagents and solvents were purchased from commercial suppliers and used as received.

Synthesis of azido-modified SEBS (SEBS–N$_3$)

SEBS–N$_3$ was synthesized by chloromethylation of SEBS and subsequent azidation of chloromethylated SEBS (SEBS–CH$_2$Cl), as reported elsewhere. For the chloromethylation of SEBS, 2.5 g of SEBS and 2.7 g of trioxane were dissolved in 150 mL of distilled chloroform, yielding a clear solution. Then, 11.4 mL of chlorotrimethysilane (TMCS) and 1.5 mL of SnCl$_4$ were added dropwise to the above solution in an ice–water bath under vigorous agitation. The mixture was stirred at 0 °C for 0.5 h and further at room temperature for 6 h. After completion of the reaction, 50 mL of methanol–water solution (50% v/v) was added to stop the reaction. Finally, the reaction mixture was precipitated in methanol, purified by three cycles of dissolving–precipitation in chloroform–methanol, and dried overnight in a vacuum oven at room temperature, producing SEBS–CH$_2$Cl. The Fourier transform infrared (FTIR) spectrum of SEBS–CH$_2$Cl is shown in Fig. 1. An obvious band at 1265 cm$^{-1}$ due to C–Cl stretching indicates the successful chloromethylation of SEBS.

For the azidation of SEBS–CH$_2$Cl, 2.5 g of SEBS–CH$_2$Cl and 218 mg of NaN$_3$ were dissolved in 50 mL of dimethylformamide (DMF). The reaction mixture was stirred at room temperature for 24 h and the polymer was precipitated in water to remove unreacted NaN$_3$. The white flocculence was filtered under vacuum, and then dried overnight in a vacuum oven at room temperature, yielding SEBS–N$_3$. The FTIR spectrum of SEBS–N$_3$ is also presented in Fig. 1. The absorption at 2095 cm$^{-1}$ should be ascribed to N$_3$ stretching, suggesting that the azidation step succeeded.

Preparation of alkyne-functionalized GOSs

Alkyne-functionalized GOSs were prepared according to a procedure that we have previously reported. Briefly, 100 mg of graphite oxide powders were refluxed in 20 mL of SOCl$_2$ at 70 °C for 24 h. After removing excess SOCl$_2$ by rotary evaporation, the product was vacuum dried at room temperature overnight. Subsequently, a mixture of propargyl alcohol (2 mL), distilled chloroform (2 mL) and anhydrous triethylamine (TEA, 1 mL) was added dropwise to the chloroacylated GOSs in an ice–water bath under vigorous agitation. The mixture was stirred at 0 °C for 1 h and further at room temperature for 24 h. The solids
were obtained by filtering the reaction mixture through a 220 nm PTFE membrane. The collected solids were redispersed in chloroform (150 mL) and separated by filtration three times. Then, they were redispersed in ethanol (200 mL) and separated by filtration for another three times. After purification, the resulting powders were vacuum dried at room temperature overnight, and alkyne-functionalized GOSs were obtained.

**Coupling of SEBS–N₃ to alkyne-functionalized GOSs via click chemistry**

A 100 mL flask was charged with 40 mg of alkyne-functionalized GOSs, 400 mg of SEBS–N₃ 12.4 mg of CuBr, 20 µL of pentamethyldiethylenetriamine (PMDETA) and 40 mL of DMF. After three freeze–pump–thaw cycles, the mixture was stirred under nitrogen at room temperature for 24 h. Obtained from the reaction mixture by vacuum filtration, the solids were redispersed in 150 mL of tetrahydrofuran (THF) and separated by vacuum filtration. This purification cycle was repeated four times, and the final products were dried at 40 °C for 1 h at room temperature, yielding SEBS-clicked GOSs (SEBS-c-GOSs). In the last cycle, the filtrate was carefully collected for a FTIR spectroscopic measurement. The FTIR spectrum of the filtrate is almost the same as that of pure THF, and the absorption at 1601 cm⁻¹ for C=O stretching of PE segments in SEBS cannot be observed (Fig. S1†), indicating that the filtrate is free of SEBS or its derivatives.

**Fabrication of neat PS and PS–SEBS-c-GOS composite films**

All films were fabricated using a solution drop-casting method. Briefly, a specific amount of SEBS-c-GOSs or mixtures of SEBS and GOSs were dispersed in 5 mL of THF with the aid of sonication at room temperature. Subsequently, 250 mg of PS was dissolved in the same medium. After sonication for an additional 1 h at room temperature, the obtained homogeneous suspension was cooled in an ice–water bath, slowly dropped onto a Teflon plate, evaporated in an airtight container at room temperature overnight, and further dried at 50 °C under vacuum for another 12 h. Finally, the film was peeled off from the substrate for mechanical and thermal tests.

**Characterization**

FTIR spectra were recorded using a Nicolet Nexus 470 spectrometer. Thermogravimetric analysis (TGA) assays were carried out under air atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 20 °C min⁻¹. Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 514 nm laser excitation. X-ray diffraction (XRD) patterns were acquired by a PANalytical X’pert diffractometer with Cu-Kα radiation ($\lambda = 0.154$ nm). Atomic force microscopic (AFM) images were acquired using a Multimode Nano 4 in the tapping mode. Mechanical properties were evaluated at 23 °C using a universal testing machine (CMT-4102, SANS Group, China) for dog-bone type specimens. The dimensions of the specimens were 50 mm (length) × 9 mm (width) × 20 mm (narrow portion length) × 4 mm (narrow portion width) × 0.07 ± 0.005 mm (thickness). A load cell of 50 N was employed and the tensile rate imposed was 1 mm min⁻¹. At least four tests were conducted for each sample, from which the mean values and standard deviations were derived. The tensile-fractured surfaces were observed with field emission scanning electron microscopy (FESEM, Hitachi, S-4800).

### 3. Results and discussion

**Covalent functionalization of GOSs with SEBS**

The schematic procedure for covalent functionalization of GOSs with SEBS is depicted in Scheme 1. This process includes (a) preparation of SEBS–N₃ by means of chloromethylation and subsequent azidation of SEBS, (b) grafting of alkyne moieties to GOSs through an acylation reaction on the basis of carboxylic groups at GOS edges, and (c) click coupling of SEBS–N₃ to alkyne-functionalized GOSs. In the click coupling step, excess SEBS–N₃ was used in an attempt to drive the click reaction to high conversion, and the unreacted polymer was easily removed by filtration and prolonged washing with THF (see Experimental). It is worth noting that this procedure can be applied to covalently attach other functional or template block copolymers onto GOS surfaces in virtue of the high reactivity, selectivity and reliability of click chemistry.

The dispersibility of the final products in common solvents was checked as the simplest qualitative test to determine whether SEBS is clicked to GOSs. As demonstrated in Fig. 2, the SEBS-c-GOSs can be homogeneously dispersed in DMF, THF, toluene, etc., which are all good solvents for SEBS. Conversely, the poor solvents of SEBS, such as water and methanol, are incapable of dissolving SEBS-c-GOSs. Therefore, it is the grafted polymer that dictates the dispersing properties of the resulting products.

The evidence for our successful clicking of SEBS onto GOS surfaces can be proved by FTIR spectral comparison between GOSs and SEBS-c-GOSs, as shown in Fig. 3. There are two characteristic bands at 1722 and 1615 cm⁻¹ for SEBS-c-GOSs, corresponding to C=O and C=C stretching vibrations in carboxyl and skeleton respectively. The click reaction introduces several new absorptions apparently arising from SEBS into the products. For example, the doublet at 2924 and 2854 cm⁻¹ is assigned to asymmetric C–H stretching of methyl and methylene groups in SEBS. Note that these absorptions belong not to free SEBS but to grafted SEBS, because the SEBS-c-GOSs underwent a harsh rinsing step until the filtrate did not have SEBS or its derivatives (see Experimental). Moreover, the appearance of the peak at 1647 cm⁻¹, which is due to the formation of triazole ring, provides powerful evidence for the success of this click reaction.

To quantitatively determine the extent of SEBS grafting, TGA measurement of SEBS-c-GOSs was performed, with the results presented in Fig. 4. Two major mass loss peaks can be observed from the derivative TG (DTG) plot. The first one, which appears at approximately 470 °C, should be ascribed to the decomposition of SEBS (Fig. S2a†), while the second one at around 580 °C corresponds to the oxidation of bulk materials (Fig. S2b†). The weight loss due to polymer decomposition is about 35%, indicating that the loading of SEBS in SEBS-c-GOSs is about 35 wt %. Such a grafting efficiency is higher than that in our previous work, where PS was immobilized onto GOS surfaces via click chemistry. It may be ascribed to the high molecular weight of SEBS used in this study. Furthermore, SEBS-c-GOSs exhibit no
weight loss at 225 °C, suggesting that the oxygen functionalities of GOSs are absent in them. The oxygen functional groups disappear, probably due to their removal in the functionalization process, as well as their conversion into more stable triazole rings. The minor mass loss peak near to 280 °C may be assigned to the decomposition of the triazole rings.

Generally, both oxidation and covalent modification of graphitic materials would introduce defects in them. Raman spectroscopy, a powerful tool to verify the structural integrity of carbon-based structures, was utilized to gather information regarding these defects. Raman spectra for the pristine EGPs, GOSs and SEBS-c-GOSs are shown in Fig. 5. In all samples, two prominent peaks are clearly visible, corresponding to the so-called D and G bands at 1348 and 1576 cm\(^{-1}\), respectively.

For graphitic materials, the intensity ratio of D and G bands, \(I_D/I_G\), can be used to calculate crystallite size \(L_a\) according to the following equation:

\[
L_a (\text{nm}) = \frac{2.4}{l^2} \left( \frac{I_D/I_G}{10} \right)^{1/4},
\]

where \(l\) is the laser excitation wavelength (514 nm in this study). This equation allows one to indirectly assess the density of defects in terms of crystallite size. Based on the data in Fig. 5, the crystallite sizes of the EGPs, GOSs and SEBS-c-GOSs are 118.8, 20.2 and 16.1 nm, respectively. The defect density introduced by oxidation is remarkable, as deduced from the greatly reduced crystallite size. Upon the click functionalization, the defect
density exhibits a further increase, supporting the assertion that covalent bonding occurs between GOSs and SEBS. In addition, as illustrated in Fig. 5, only EGPs show a peak at 2721 cm\(^{-1}\), which is the so-called 2D band. Since the 2D band is sensitive to the stacking order of graphitic structures, the barely visible 2D band for GOSs and SEBS-c-GOSs suggests that their stacking structures are nearly disordered.

The near-absence of a stacking order for GOSs and SEBS-c-GOSs can be confirmed by their XRD patterns in comparison with that of EGPs. As demonstrated in Fig. 6, compared with the XRD trace of EGPs, which exhibits a strong diffraction peak at 26.5° (corresponding to an interlayer spacing of about 0.34 nm), that of GOSs only presents a weak and broad diffraction peak at 10.7°. This peak indicates that the interlayer spacing of the GOSs increases to 0.83 nm, and the remaining stacking of the GOSs is rather loose. Upon SEBS clicking, the XRD line of SEBS-c-GOSs has no visible peak, suggesting that their remaining stacking is disordered.

This disruption of the structure reduces the attractive interactions among SEBS-c-GOSs, making their exfoliation into individual sheets possible. To illustrate the complete exfoliation of SEBS-c-GOSs in the solvent, their AFM observations were conducted. As displayed in Fig. 7, SEBS-c-GOSs have an average height of 7 nm. Obviously, they are much thicker than GOSs, whose thickness is 1.4 nm (Fig. S3† matching well with the reported thickness of individual GOSs\(^{13}\)). Similar thickness increases have been widely reported for polymer-functionalized GSs and GOSs.\(^{19,27,28,31,34,38}\) For example, Xu et al. found that the \textit{in situ} polymerization of caprolactam on GOSs would increase their height to 8 nm.\(^{18}\) Therefore, we can expect that the observed sheets are uniform monolayers. In addition, it is found that the lateral dimension of SEBS-c-GOSs is only 30–50 nm (Fig. 7), which is much smaller than that of GOSs (about 1 \(\mu\)m, Fig. S3†). Such a decrease in the GOS size has also been reported by Pan and co-workers.\(^{39}\) They found that the thermal reduction of GOSs in the solvent would cut them into ultrafine sheets with an average diameter of 10 nm through a complete breakup of their linear defects.\(^{39}\) In this study, the chloroacylation of GOSs, which constitutes the first step in the functionalization process, is a solvothermal step. The AFM image of chloroacylated GOSs suggests that after this step, the sheet size has already been cut to 30–50 nm (Fig. S4†). Therefore, it is in the chloroacylation stage that the reduction of sheet size occurs.

Reinforcing effect of SEBS-c-GOSs in polymer composite films

The ability of as-synthesized SEBS-c-GOSs to be dispersed in a wide variety of organic media as individual sheets allows their homogeneous incorporation into polymer matrices. Since GOSs have been predicted to exhibit excellent mechanical stiffness (fracture stress = 63 GPa) by Monte Carlo simulations, our products appear to be attractive reinforcing fillers in polymer composites. To investigate the compatibility and reinforcing effect of our prepared SEBS-c-GOSs in polymer composites, PS was employed as a typical polymer host, and films of neat PS and PS–SEBS-c-GOS composites with filler loadings of 0.5, 1.0 and 2.0 wt% were fabricated using a solution drop-casting method (see Experimental). The photograph of these films (dog-bone type, for mechanical tests) is displayed in Fig. 8a. Apparently, the films of PS–SEBS-c-GOS composites show homogeneous appearances by visual inspection, indicating uniform distributions of SEBS-c-GOSs in the PS matrix. The uniform dispersion of SEBS-c-GOSs in the PS matrix can be proved by XRD measurements. As presented in Fig. 8b, the XRD pattern of PS–2.0 wt% SEBS-c-GOS composite film is almost the same as that of neat PS film, with no graphite layer structure peak at 26° or graphite oxide peak at 12° detected. According to Ramanathan \textit{et al.}, this result indicates that the dispersion of SEBS-c-GOSs in the PS matrix is close to single-sheet level.\(^4\) The XRD traces of

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**Fig. 5** Raman spectra of EGPs, GOSs and SEBS-c-GOSs (excitation wavelength 514 nm).

**Fig. 6** XRD patterns for EGPs, GOSs and SEBS-c-GOSs.

**Fig. 7** AFM image (left) and height profiles (right) of SEBS-c-GOSs.
tensile strength and Young’s modulus are largely enhanced, and yield behavior. However, after the addition of SEBS-c-GOSs, the composite films display slightly decreased elongations without Fig. 9a. Compared to a parallel PS sample, PS–SEBS-c-GOS neat PS and PS–SEBS-c-GOS composite films are given in of the host polymer. The representative stress-strain curves for dispersed SEBS-c-GOSs should have a significant reinforcement (a) Representative stress-strain curves of neat PS and PS–2.0 wt% SEBS-c-GOS composite films. other composite films are also similar to that of the neat PS film, and thus not shown here.

In polymer composites, a well dispersed state of reinforcing fillers ensures a maximized reinforced surface area, which will affect the neighbouring polymer chains and, consequently, the properties of the whole matrix. Therefore, the uniformly dispersed SEBS-c-GOSs should have a significant reinforcement of the host polymer. The representative stress-strain curves for neat PS and PS–SEBS-c-GOS composite films are given in Fig. 9a. Compared to a parallel PS sample, PS–SEBS-c-GOS composite films display slightly decreased elongations without yield behavior. However, after the addition of SEBS-c-GOSs, the tensile strength and Young’s modulus are largely enhanced, and their relationships with filler loading are shown in Fig. 9b. It is obvious that these two parameters have a remarkable increasing tendency with the increase of SEBS-c-GOS loading. With only 2.0 wt% SEBS-c-GOSs incorporated, the tensile strength increases by 78% from 23.0 (for PS parallel sample) to 40.9 MPa, while the Young’s modulus is raised by 73% from 1.22 (for PS parallel sample) to 2.11 GPa. It should be noted that further increasing the concentration of SEBS-c-GOSs to 3 wt% would deteriorate the tensile strength and Young’s modulus of the composite films (Fig. S5†). The tendency of the overall mechanical parameters of polymer composites to fall off at high filler content has also been found by other researches, who used polymer-grafted CNTs or GOSs as reinforcing agents. According to their suggestions, these downturns should be assigned to the aggregation of reinforcing fillers, which would create defects in the final composites.

Such mechanical improvements are much more prominent than those reported in our previous study. In that work, the uniform introduction of GOSs into poly(lactic acid) only caused a 26% increase in tensile strength and a 18% raise in Young’s modulus, which is presumably due to the poor interface interactions (no functionalization was taken on GOSs in that study). Therefore, the remarkable mechanical improvements in this study should be attributed not only to the homogeneous dispersion of SEBS-c-GOSs, but also to the favorable adhesions between fillers and polymer host, which allow the efficient load transfer between these two phases. In general, the hydrogen bonding formed between the oxygen functionalities of GOSs and polar polymers is the main source of strong interfacial adhesions. For example, as demonstrated by Liang et al., in poly(vinyl alcohol)–GOS composites, the external tensile loads could be successfully transferred to GOSs across the interface via strong hydrogen bonding, and a 76% increase in tensile strength and a 62% raise in Young’s modulus were achieved. However, in the present system, since PS is a nonpolar polymer without hydrogen bonding with GOSs, the favorable interface interactions result from the covalent bonding of the PS segments in SEBS onto GOS surfaces. To verify the significance of SEBS bonding on the efficient load transfer between matrix and fillers, a control film with the same composition as the PS–2.0 wt% SEBS-c-GOS composite film but no covalent coupling of SEBS onto GOSs (i.e., a PS film filled with 0.7 wt% SEBS and 1.3 wt% GOSs) was fabricated. The mechanical reinforcement in the control film is limited (Fig. S6†), suggesting that the SEBS grafting is crucial to the efficient load transfer between matrix and fillers.

It may be interesting to compare the reinforcing effect of GOSs with that of their 1D counterparts, CNTs. Since the reinforcing effect of GOSs and CNTs is suggested to be matrix dependent, our discussion is focused specifically on their PS composites. Lu and co-workers have developed a “grafting to” approach to covalently functionalize CNTs with a PS copolymer. They found that the addition of 0.3 wt% copolymer-grafted CNTs (0.06 wt% in CNT loading) led to 82% and 78% increases in tensile strength and Young’s modulus of the PS composite films. In this work, the improvements in tensile strength and Young’s modulus are comparable to those reported in their study. However, to achieve such a prominent mechanical reinforcement, the concentration of SEBS-c-GOSs should be up

Fig. 8 (a) Appearance for dog-bone type specimens of neat PS and PS–SEBS-c-GOS composite films; (b) XRD patterns for neat PS and PS–2.0 wt% SEBS-c-GOS composite films.

Fig. 9 (a) Representative stress-strain curves of neat PS and PS–SEBS-c-GOS composite films; (b) Relationships of tensile strength and Young’s modulus with SEBS-c-GOS concentration.
to 2.0 wt% (1.3 wt% in GOS content), which is much higher than that of copolymer-grafted CNTs. It is presumably due to the low aspect ratio of our prepared SEBS-c-GOSs because smaller aspect ratio often requires higher filler loading to form percolated networks.44

For direct evidence of the excellent compatibility between SEBS-c-GOSs and PS host, we took FESEM observations on the tensile-fractured surfaces of composite films (Fig. 10). Compared with the tensile-fractured surface of neat PS film, which is clear and smooth (Fig. S7†), that of PS–1.0 wt% SEBS-c-GOS composite film is rather coarse with no visible aggregation (Fig. 10a), indicating that the dispersion of SEBS-c-GOSs in the polymer matrix is very uniform. When the filler content increases to 2.0 wt%, there are many submicron pores appearing in the tensile-fractured surface (Fig. 10b). The emergence of pores at high filler loading has also been reported in carbon nanofiber-reinforced polymer composites,45 and was ascribed to a strong reinforcement derived from the high concentration of reinforcing agents and their favorable adhesions with host polymer. Therefore, the FESEM examinations confirm the satisfactory compatibility between SEBS-c-GOSs and PS matrix.

The effect of SEBS-c-GOS addition on the thermal stability of a polymer host was also investigated. Fig. 11 demonstrates the TG traces of neat PS and PS–SEBS-c-GOS composite films. Obviously, the introduction of SEBS-c-GOSs induces thermal stabilization of the matrix: the temperature for a 10% weight loss of PS exhibits a gradually increasing tendency with an increase of filler content. Upon the incorporation of 2.0 wt% SEBS-c-GOSs, the temperature for 10% weight loss increases by 26 °C from 325 °C (for PS parallel sample) to 351 °C. Such an enhancement in thermal stability is to be expected because GSs and GOSs are proposed to act as barriers in polymer matrices to delay the permeation of oxygen and the escape of volatile degradation products, thus improving the thermal stability of the resulting composites.17 Moreover, the homogeneous distribution of SEBS-c-GOSs in the polymer host also plays a key role because it can maximize the thermal stabilizing effect of fillers, as we suggested in our previous work.20

4. Conclusions

In conclusion, we have successfully developed a general and effective method to covalently functionalize GOSs with SEBS, a typical block copolymer, via click chemistry. The as-prepared SEBS-c-GOSs have a polymer loading of 35 wt%, and can be dispersed in a wide variety of organic media as individual sheets in virtue of the dissolubility of the clicked SEBS in these solvents. By taking advantage of click chemistry, this strategy can be expanded to other functional or template block copolymers for their covalent linkage to GOSs, and thereby holds great promise in many technological fields. To demonstrate one of the potential applications of the block copolymer-clicked GOSs, SEBS-c-GOSs were introduced into PS as reinforcing fillers. These reinforcing agents can be homogeneously dispersed in the polymer matrix with favorable interfacial adhesions, and thus exhibit a strong reinforcement of PS. Compared with neat PS, PS–2.0 wt% SEBS-c-GOS composite exhibits a 78% increase in tensile strength and a 73% raise in Young’s modulus. Moreover, the thermal stability of the polymer host is also remarkably improved after the incorporation of SEBS-c-GOSs. Therefore, this protocol is believed to greatly broaden the application scope of GOSs and promote the development of GOS-based materials.

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Notes and references