

Electrically Conductive and Flame Retardant Graphene/Brominated Polystyrene/Maleic Anhydride Grafted High Density Polyethylene Nanocomposites with Satisfactory Mechanical Properties

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Abstract Electrically conductive and flame-retardant maleic anhydride grafted high-density polyethylene (MA-HDPE) nanocomposites with satisfactory mechanical properties are fabricated by melt compounding MA-HDPE with polyethyleneimine (PEI)-modified reduced graphene oxide (PEI@RGO) as the conductive nanofiller and brominated polystyrene (BPS) as the flame retardant. The modification with PEI significantly improves the interfacial compatibility and dispersion of the RGO sheets in the MA-HDPE matrix, leading to electrically conductive nanocomposites with enhanced mechanical properties. Furthermore, the addition of 25 wt% of BPS makes the nanocomposite flame-retardant with a UL-94 V-0 rating. Thus, the multifunctional RGO/MA-HDPE nanocomposites with good electrical, flame-retardant, and mechanical properties would have potential applications in construction and pipeline fields.

Keywords Polymer nanocomposites; High density polyethylene; Graphene; Electrical conductivity; Flame retardancy

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INTRODUCTION

Currently, polymer nanocomposites are widely applied in various areas including electronics, automobiles, and transports due to their easy processability, tunable properties, and excellent corrosion resistance.^[1] Nevertheless, most polymers are electrically insulating and flammable, which may cause electrostatic charges and induce a risk of fire. Therefore, it is necessary to develop electrically conductive and flame-retardant polymer nanocomposites for targeted applications. Generally, satisfactory electrical properties of polymer composites are obtained by filling large quantities of conductive fillers, such as metal particles, carbon black, and graphite.^[2–8] However, the high loadings of these conductive fillers often cause deterioration in processability and mechanical properties of ultimate polymer composites. Compared with traditional conductive fillers, two-dimensional graphene sheets have shown their great potential in fabricating highly conductive polymer materials due to their high aspect ratio and excellent electrical conductivity.^[9,10] Fundamentally, realization of the intriguing properties of graphene sheets greatly depends on their compatibility with polymers and their dispersion in polymer matrices, especially

for inert polyolefins.^[11,12] Till now, various pioneering works have been reported to improve the dispersion of graphene sheets in different polymers by melt compounding, solution mixing, and *in situ* polymerization.^[13–16] Chemical modification of graphene is the most effective way to enhance the interfacial interaction with polymer matrices.^[17–19] Quiles-Diaz *et al.* adopted maleic anhydride-grafted polypropylene to modify graphene sheets, leading to obvious enhancements in thermal stability as well as electrical and mechanical performances of isotactic polypropylene.^[18] In our previous work, styrene-maleic anhydride copolymer was used to improve the interfacial interaction between graphene sheets and polystyrene matrix, resulting in remarkable rheological behavior and electrical properties.^[19] Despite the promising advances, however, an efficient approach is still required to ensure the uniform dispersion of graphene sheets in nonpolar polyolefins.

In addition, satisfactory flame-retardancy is also necessary for electrically conductive polymer nanocomposites, especially used as pipes in coal mines and electronics.^[20–25] Although the halogen-containing flame retardants are more effective than other flame retardants,^[26–30] their applications are increasingly limited due to the severe pollution and great damages. Therefore, environmentally friendly flame retardants with high flame-retardant efficiency are extensively studied. The main topic is how to achieve excellent flame-retardant performance at the minimal additive loadings. Parti-

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cularly, when high electrical and flame-retardant properties are demanded for the polymer composites, it becomes more challenging to maintain satisfactory mechanical properties.

The purpose of the present work is to simultaneously enhance electrical, flame-retardant, and mechanical properties of nonpolar polyolefins. Polyethyleneimine (PEI)-modified reduced graphene oxide (PEI@RGO) sheets are prepared as the conductive component to improve their dispersion in MA-HDPE matrix. The effects of PEI on chemical structure, thermal stability, and dispersion of RGO are investigated in detail. Moreover, brominated polystyrene (BPS) is used as an eco-friendly macromolecular flame-retardant to improve the flame retardancy of the PEI@RGO/MA-HDPE nanocomposites. The binary and ternary nanocomposites are well characterized in terms of electrical conductivity, flame-retardancy, and mechanical properties.

EXPERIMENTAL

Materials

PEI, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), and *N*-hydroxysuccinimide (NHS) were purchased from Sigma-Aldrich (USA), and graphite flakes (1000 mesh) were provided by Huadong Graphite Factory (China). NaNO_3 , H_2SO_4 , KMnO_4 , H_2O_2 , HCl , and xylene were bought from Sinopharm Chemical Reagents (China), and hydrazine hydrate solution (80%) was supplied by Aladdin Reagents (China). Maleic anhydride grafted high density polyethylene (MA-HDPE, CMG9804, 0.9% grafting degree) and BPS (3010) were bought from Qilu Petrochemical Co. (China) and Albemarle Co. (USA), respectively.

Modification of RGO with PEI

Graphene oxide (GO) was prepared by the modified Hummers method and subsequent ultrasonication.^[31] PEI@RGO was obtained by modifying GO with PEI and reducing GO with a typical reduction agent of hydrazine hydrate. In details, after 250 mL of an aqueous suspension with uniformly dispersed GO ($2 \text{ mg} \cdot \text{mL}^{-1}$) was prepared by ultrasonication of GO for 15 min with a JY92-IIDN ultrasonicator, 0.5 g of EDC, 0.4 g of NHS, and 1.0 g of PEI were added with vigorous stirring in an ice-bath, and the mixture was treated for 30 min in a KQ-600DB ultrasonic cleaning machine, vigorously stirred for 12 h at a room temperature, and then transferred to an oil-bath for heating 3 h at 95 °C. Finally, an appropriate amount of hydrazine hydrate solution was added to reduce the GO component. The resultant product was denoted as PEI@RGO, washed with ethanol three times, and dispersed in xylene for storage.

Fabrication of PEI@RGO/MA-HDPE Nanocomposites

PEI@RGO/MA-HDPE nanocomposites were fabricated by solution-mixing and precipitation approach. Therein, 10 g of MA-HDPE was dissolved into xylene, and the solution was heated at 140 °C with vigorous stirring until MA-HDPE dissolved. Meanwhile, xylene solution with uniformly dispersed PEI@RGO was obtained by ultrasonic treatment for 30 min using the KQ-600DB ultrasonicator, and then mixed with the xylene solution of MA-HDPE under vigorous stirring for 6 h. Finally, the mixture was precipitated in

methanol. The resultant PEI@RGO/MA-HDPE nanocomposite was washed with methanol three times and dried at 80 °C in a vacuum oven. The nanocomposites were compressed into round samples ($\Phi 25 \text{ mm} \times 1 \text{ mm}$) and rectangular samples ($130 \text{ mm} \times 13 \text{ mm} \times 3.2 \text{ mm}$) by a vacuum hot press (China) for electrical conductivity and flame-retardant measurements, respectively, and injection-molded to standard samples with a micro injection molding machine for mechanical properties measurement.

To confirm the important roles of MA-HDPE in improving the filler-matrix compatibility and dispersion of graphene in HDPE matrix, PEI@RGO/HDPE nanocomposites were also fabricated with the prepared PEI@RGO/MA-HDPE nanocomposite as conductive master batch.

Fabrication of PEI@RGO/BPS/MA-HDPE Nanocomposites

The fabrication of PEI@RGO/BPS/MA-HDPE nanocomposites was similar to that of PEI@RGO/MA-HDPE nanocomposites. The difference is that, after the xylene suspension of PEI@RGO was mixed with the xylene solution of MA-HDPE under vigorous stirring for 2 h, an appropriate amount of BPS was added. After vigorous stirring for 4 h, the resultant product was precipitated by methanol, washed with methanol three times, dried at 80 °C by a vacuum oven, and finally denoted as PEI@RGO/BPS/MA-HDPE nanocomposites.

Characterization

Fourier-transform infrared (FTIR) spectra of GO, PEI, PEI@GO and PEI@RGO were recorded using a Nexus 670 FT-IR spectrometer. X-ray photoelectron spectra (XPS) of GO, PEI@GO, and PEI@RGO were obtained with a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. A Renishaw inVia laser confocal Raman spectrometer was used to characterize the structural evolution of GO, PEI@GO, and PEI@RGO. X-ray diffraction (XRD) patterns of GO, PEI@GO, and PEI@RGO were recorded on a Rigaku D/Max 2500 X-ray diffractometer. Thermogravimetric analysis (TGA) curves were acquired with a TA Instruments Q50 thermogravimetric analyzer under an argon atmosphere. Microstructures of all nanocomposites were observed using a Hitachi S4800 scanning electron microscope (SEM). Electrical conductivities were measured with a 4-probes Tech SX1934 (SZ-82) resistivity meter ($> 10^{-4} \text{ S} \cdot \text{m}^{-1}$) and a Keithley 6517B electrometer/high resistance meter ($< 10^{-4} \text{ S} \cdot \text{m}^{-1}$). Notched impact energy of MA-HDPE and its nanocomposites was acquired on a XC-22 cantilever beam impact tester. The dimension of the specimens for notched impact property testing was $80 \text{ mm} \times 10 \text{ mm} \times 4 \text{ mm}$ with a 45° V notch (2 mm depth). Moreover, tensile properties were measured on an Instron 1185 universal testing machine with dumbbell-shaped samples according to GB/T 1040.2. Five samples were tested for each item and the average value was reported. A CZF-01 horizontal and vertical burning tester was used to determine flame-retardant performances of PEI@RGO/BPS/MA-HDPE nanocomposites.

RESULTS AND DISCUSSION

Interfacial compatibility between nanofillers and polymer

matrices is critically important for manipulating microstructure and various properties of polymer nanocomposites. GO sheets are modified by long chain PEI with abundant amino groups and reduced to RGO by hydrazine hydrate. Fig. 1 illustrates the synthesis procedure of PEI@RGO. After grafted with PEI, the RGO sheets show a uniform dispersion in MA-HDPE matrix, benefiting the formation of an electrical conductance network and prevent the deterioration of mechanical properties. In addition, the chemical reduction of GO with hydrazine hydrate improves the electrical conduction of RGO sheets and further favors an enhanced conductivity of the resultant polymer-based nanocomposites.

The structural evolution of GO sheets is determined by comparing XRD patterns of GO, PEI@GO, and PEI@RGO (Fig. 2a). It is well known that graphite has a characteristic peak at 26.5° , indicating a lamellar spacing of 0.34 nm.^[32] After oxidation, the typical peak of graphite is replaced by a diffraction peak at 10.9° due to the introduction of the oxygen-containing groups. Compared to GO, PEI@GO exhibits a weak diffraction peak at a lower region (around 7.5°), suggesting the enlarged interlayer spacing upon the successful intercalation of macromolecular PEI between the sheets. Meanwhile, a new peak at 21.7° reflects the partial reduction of GO during the process of PEI grafting. The reduction of PEI@GO with hydrazine hydrate further removes the residual oxygen-containing groups, leading to a reduced lamellar spacing and an intensified diffraction peak at 21.7° for PEI@RGO sheets. The structural changes are also confirmed by the Raman spectra of GO, PEI@GO, and PEI@RGO (Fig. 2b). As expected, typical D and G bands that relate with the degree of defects and graphitization of graphite materials are observed, wherein the intensity ratio of D band and G band (I_D/I_G) is used to monitor the structural variation of graphene. It is seen that the I_D/I_G value of PEI@GO (1.14) is much higher than that of GO (0.88) due to the grafting of PEI macromolecules. After being reduced with hydrazine hydrate, the removal of residual oxygen-containing groups

leaves more defects, as evidenced by the even larger I_D/I_G value of PEI@RGO (1.28).^[33,34]

Moreover, the change of chemical compositions is also monitored by comparing the FTIR spectra of GO, PEI, PEI@GO, and PEI@RGO (Fig. 2c). In the case of GO, the presence of carbonyl and epoxide groups is confirmed by the bands at 1723 and 1065 cm^{-1} , respectively, which are greatly weakened or even disappear upon the grafting of PEI. At the same time, two emerging bands of PEI@GO at 1556 and 1170 cm^{-1} are assigned to the stretching vibration of N—H and C—N bonds in the secondary amide (C—NH—C), respectively. All these results indicate that the PEI macromolecules are grafted on the GO sheets. In contrast to GO and PEI@GO, the significantly weakened characteristic bands of PEI@RGO that are related to oxygen-containing groups imply the reduction by hydrazine hydrate.

The thermal stabilities of GO, PEI, PEI@GO, and PEI@RGO are evaluated (Fig. 2d). GO shows 5% weight loss at $\sim 100^\circ\text{C}$ due to the removal of adsorbed water, and then 10% weight loss for the decomposition of oxygen-containing groups. When the temperature is higher than 225°C , most of the oxygen-containing groups begin to decompose and release CO and CO_2 gases, leading to a significant weight loss of 43%. After 600°C , the two-dimensional carbon skeleton of GO decomposes rapidly, leaving a low carbon residue of 1.95%. Owing to the excellent thermal stability of PEI below 300°C , the PEI@GO has a better thermal stability than GO. The slow and gradual weight loss below 600°C is attributed to the removal of oxygen functionalities in GO and the decomposition of PEI. Consistent with the above-mentioned XRD, Raman, and FTIR results, PEI@RGO exhibits an even less weight loss and enhanced thermal stability than both PEI@GO and GO due to its low content of oxygen functionalities.

The grafting of PEI on GO and the reduction of GO in PEI@RGO can be well reflected in their XPS spectra (Fig. 3). Different from GO, both PEI@GO and PEI@RGO

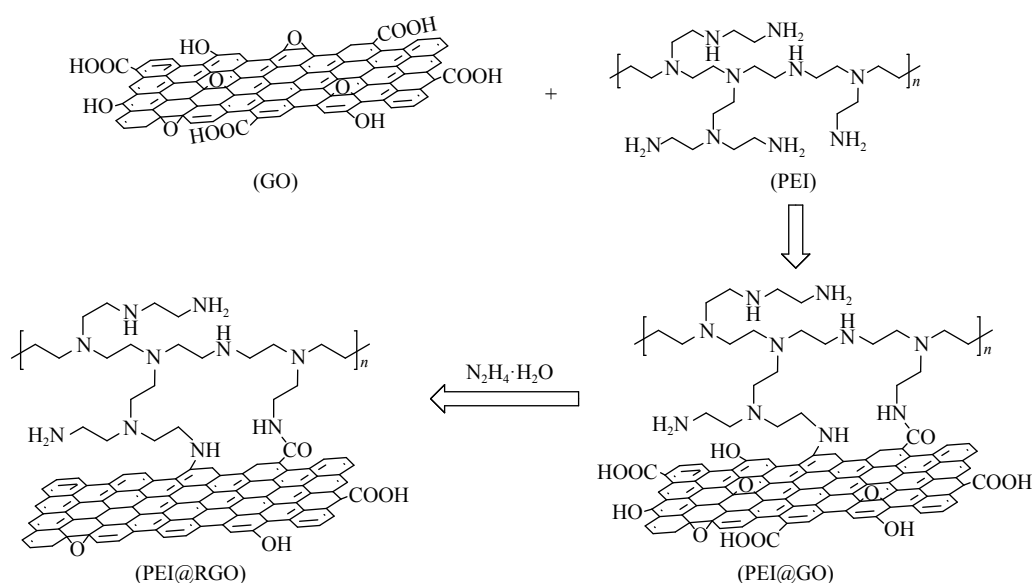


Fig. 1 Schematic illustrating the synthesis procedure of PEI@RGO sheets

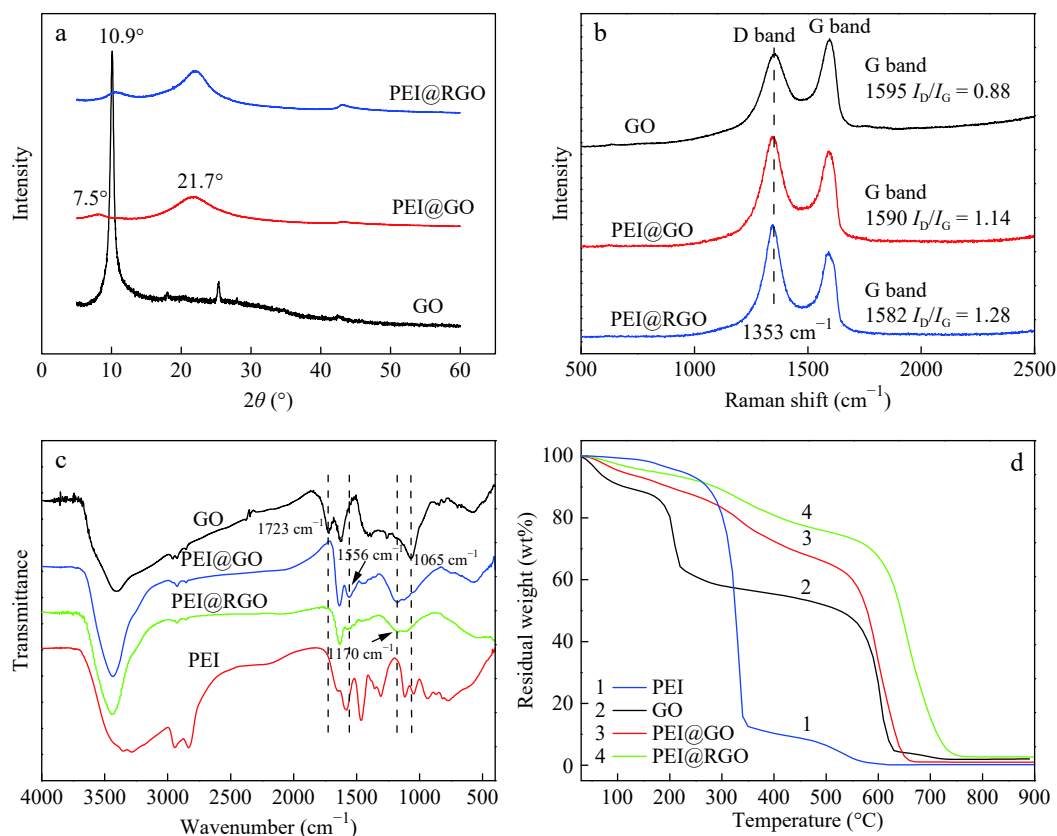


Fig. 2 (a) XRD patterns and (b) Raman spectra of GO, PEI@GO, and PEI@RGO; (c) FTIR spectra and (d) TGA curves of GO, PEI, PEI@GO, and PEI@RGO

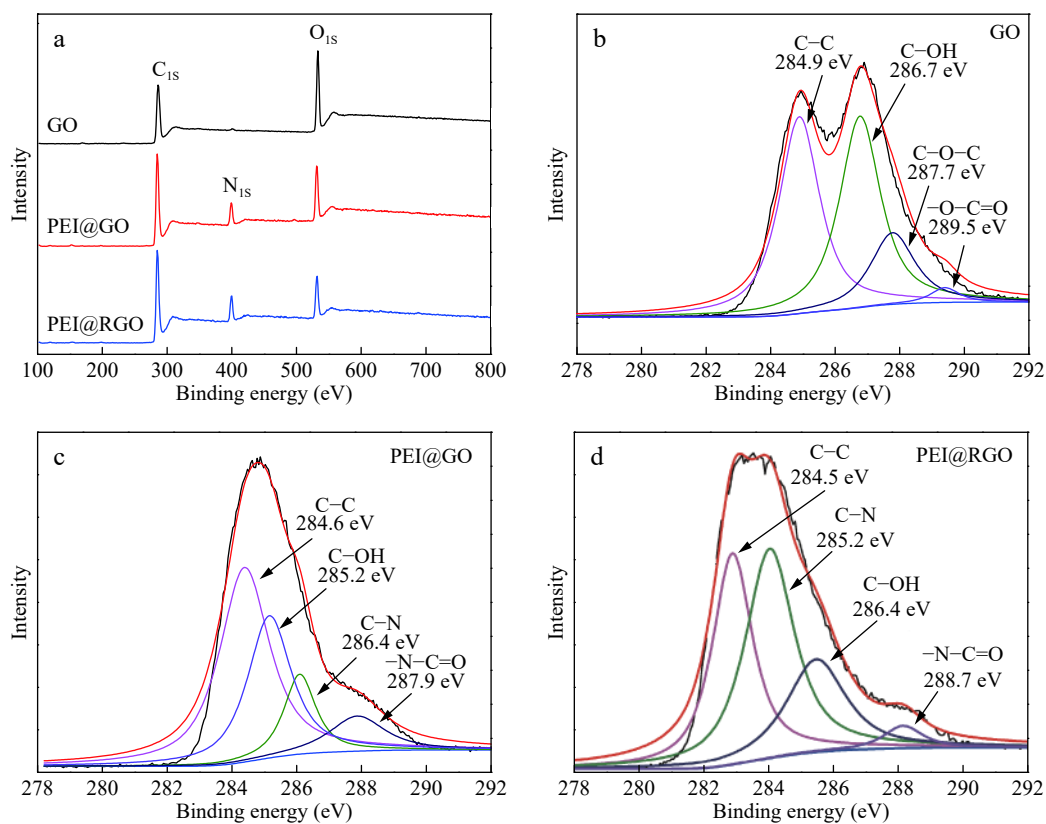


Fig. 3 (a) XPS survey spectra of GO, PEI@GO and PEI@RGO; C_{1s} XPS spectra of (b) GO, (c) PEI@GO, and (d) PEI@RGO

present new characteristic peak of N element in their survey XPS spectra, indicating the presence of PEI on sheets. This is also confirmed by C1s spectra of GO, PEI@GO, and PEI@RGO, where the characteristic peaks of oxygen-containing groups are dramatically weakened and even disappear, accompanied with the emergence of peaks assigned to nitrogen groups. The elemental compositions (C, O, and N) of GO, PEI@GO, and PEI@RGO are calculated based on the XPS results and listed in Table 1. Again, the introduction of PEI on GO and partial reduction are verified by the N element and the decreased oxygen content in PEI@GO and PEI@RGO, as compared to GO. The further increases in C and N contents for PEI@RGO are another evidence for the reduction effect of hydrazine hydrate.

Table 1 Element contents of GO, PEI@GO, and PEI@RGO

Sample	C (%)	O (%)	N (%)
GO	69.6	30.4	—
PEI@GO	73.0	17.2	9.8
PEI@RGO	76.0	13.3	10.7

The PEI@RGO sheets obtained as electrically conductive nanofillers can endow MA-HDPE with a satisfactory antistatic feature, which could avoid fire hazards caused by accumulated charges. Meanwhile, BPS as a flame retardant is added into the nanocomposites to prevent the spread of fire hazards. Figs. 4 and 5 show the microstructures of the MA-HDPE nanocomposites filled with electrically conductive filler of PEI@RGO and flame retardant of BPS. Similar to neat MA-HDPE, there are no obvious filler aggregates and clear filler-matrix interfaces for PEI@RGO/MA-HDPE nanocomposites, which can even be maintained at loadings of 1.5 wt% and 2 wt%, suggesting the good dispersion of PEI@RGO sheets and their interfacial compatibility with the matrix. The favorable results derive from the unique molecular structure of PEI combining polar amino groups and long alkyl chains, which alleviates the agglomeration of RGO sheets and improves the interface between RGO and the MA-HDPE matrix. With the assistance of PEI, PEI@RGO sheets are promising as electrically conductive nanofillers for MA-HDPE to achieve high electrical conductivity at low

loadings of the fillers. After the incorporation of BPS, there are numerous BPS particles that uniformly dispersed in the MA-HDPE matrix, forming an island-like structure (Fig. 5). The unique microstructure of the MA-HDPE nanocomposites will guarantee the expected electrical, mechanical, and flame-retardant properties.

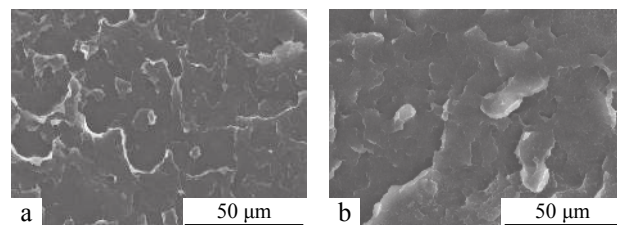


Fig. 4 SEM images of (a) MA-HDPE and (b) PEI@RGO(2 wt%)/MA-HDPE nanocomposite

Fig. 6 shows the influences of PEI@RGO and BPS contents on electrical conductivity of the MA-HDPE-based nanocomposites. Clearly, the electrical conductivity of PEI@RGO/MA-HDPE nanocomposites increases rapidly with the increasing content of PEI@RGO. With only 1.5 wt% of PEI@RGO, the nanocomposite shows a conductivity of $4.3 \times 10^{-6} \text{ S} \cdot \text{m}^{-1}$, surpassing the minimum value for antistatic application. A higher value of $0.023 \text{ S} \cdot \text{m}^{-1}$ is achieved at 2.0 wt%. These intriguing electrical properties are superior to those of most polyolefin-based nanocomposites filled with graphene and other conductive nanofillers,^[35,36] which are attributed to the conductance network formed with the well-dispersed PEI@RGO sheets in the matrix. Therefore, the resultant PEI@RGO/MA-HDPE nanocomposites can be used as a master batch for the preparation of HDPE nanocomposites. As expected, PEI@RGO/HDPE nanocomposites with MA-HDPE as the compatibilizer indeed also show excellent electrical conductivities, although they are slightly lower than the values of their counterparts with MA-HDPE as the matrix (Fig. 6a). This also reflects the crucial role of MA-HDPE in improving the filler-matrix compatibility and dispersion of graphene in HDPE matrix.

Interestingly, the presence of BPS significantly improves the electrical conductivity of PEI@RGO/MA-HDPE nano-

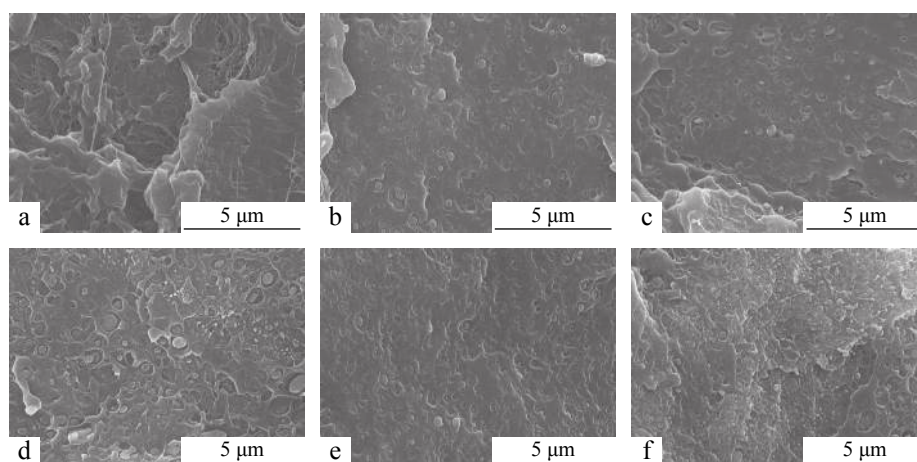


Fig. 5 SEM images of PEI@RGO (1.5 wt%)/MA-HDPE nanocomposites filled with (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, (d) 15 wt%, (e) 20 wt%, and (f) 25 wt% of BPS

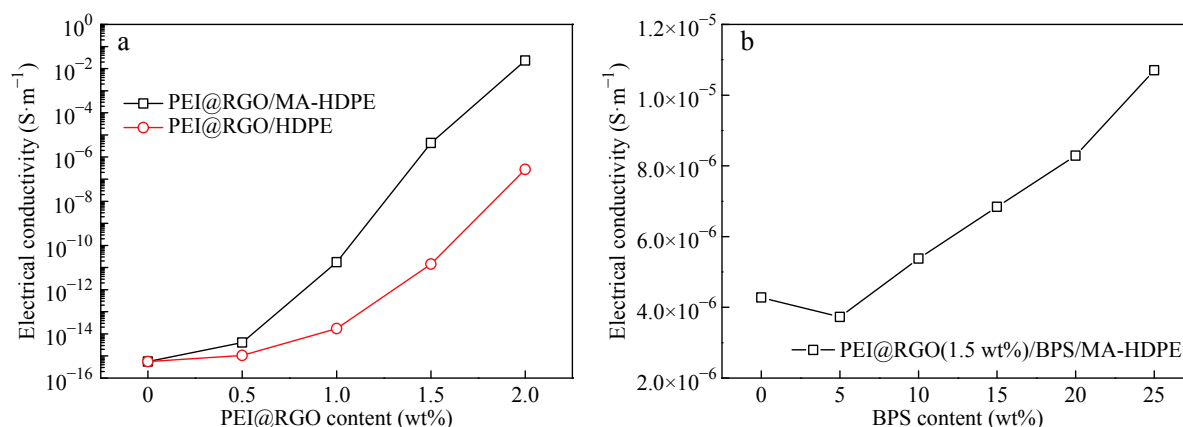


Fig. 6 Electrical conductivities of (a) PEI@RGO/MA-HDPE and PEI@RGO/HDPE nanocomposites and (b) PEI@RGO(1.5 wt%)/BPS/MA-HDPE nanocomposites

Table 2 Flame-retardant property of PEI@RGO(1.5 wt%)/BPS/MA-HDPE nanocomposites with different BPS contents

Code	BPS content (wt%)	UL-94	<i>t</i> ₁ (s)	<i>t</i> ₂ (s)	Whole time (s)	Flame to clamp	Dripping
1	5	Failed	> 30	> 30	> 60	Yes	Yes
2	10	Failed	> 30	> 30	> 60	Yes	Yes
3	15	Failed	> 30	> 30	> 60	Yes	Yes
4	20	V-1	< 10	< 30	< 60	No	No
5	25	V-0	< 10	< 10	< 10	No	No

composite due to the favorable volume exclusion effect of BPS. With the increase of BPS content, the electrical conductivity of nanocomposites with the same PEI@RGO content of 1.5 wt% steadily rises even up to ten times of its counterpart despite the insulating nature of BPS. The beneficial effect of BPS arises from the enhanced integrity of the conducting graphene network, because the presence of BPS reduces the volume occupied by fillers and makes the conducting network more compact and efficient for electron transport, resulting in excellent electrical performances of PEI@RGO/BPS/MA-HDPE nanocomposites.

To meet the requirements for polymer nanocomposites applied in electronics and mines, the PEI@RGO (1.5 wt%)/BPS/MA-HDPE nanocomposites are evaluated by UL-94 vertical burning test (Table 2). When the BPS content is lower than 15 wt%, the nanocomposites have a serious flammable dripping and cannot self-distinguish. When the BPS content is increased to 20 wt%, a UL-94 V-1 rating without flammable dripping for the ternary nanocomposite is achieved, but it is too long for the afterflame time after the second ignition. Fortunately, adding 25 wt% of BPS finally affords a UL-94 V-0 rating for the PEI@RGO/BPS/MA-HDPE nanocomposite. Moreover, both the two afterflame time (*t*₁ and *t*₂) and the whole time are less than 10 s, and no flammable dripping occurs during the combustion process.

It remains a great challenge for polymer nanocomposites to simultaneously achieve both excellent functionalities and satisfactory mechanical properties, especially at large filler loadings. Here, the mechanical properties of MA-HDPE nanocomposites filled with PEI@RGO are tested to assess their overall performance for practical applications (Fig. 7). Interestingly, the addition of PEI@RGO sheets does not reduce the overall mechanical properties including notched im-

pact strength, tensile strength, and elongation at break. The values of Young's modulus show steady increases with the increasing loading of PEI@RGO. Although the other mechanical performances of the nanocomposites are not improved by PEI@RGO, the preservation of essential mechanical properties is valuable for its nanocomposites with high filler loadings (1.5 wt% and 2.0 wt%). Generally, polymer nanocomposite with excellent mechanical properties can be prepared at low graphene loadings,^[37,38] and high loadings often cause filler aggregation and defects, and thereby deteriorate mechanical properties of the nanocomposites. The satisfactory mechanical properties of the PEI@RGO/MA-HDPE nanocomposites in this work are attributed to the uniform dispersion of modified RGO sheets and their enhanced interactions with the matrix derived from the enhanced interfacial compatibility.

The influences of BPS on mechanical properties PEI@RGO/BPS/MA-HDPE nanocomposites are further investigated (Fig. 8). It is seen that the notched impact strength and elongation at break decrease with the increasing BPS content within acceptable limits. The hard BPS particles with phase-separated structure are responsible for the slight decline in these two ductile properties of polymer nanocomposites.^[39] Fortunately, the tensile strength of the resultant nanocomposites shows no significant loss and is well retained with the increased BPS content. This is because the unique molecular structure of BPS offers good interaction and compatibility with the MA-HDPE matrix to ultimately preserve the mechanical properties.^[40,41] Similar to the PEI@RGO/MA-HDPE nanocomposites, the addition of BPS leads to slight increase in Young's modulus of the nanocomposites due to higher intrinsic modulus of the introduced component.^[39,42,43]

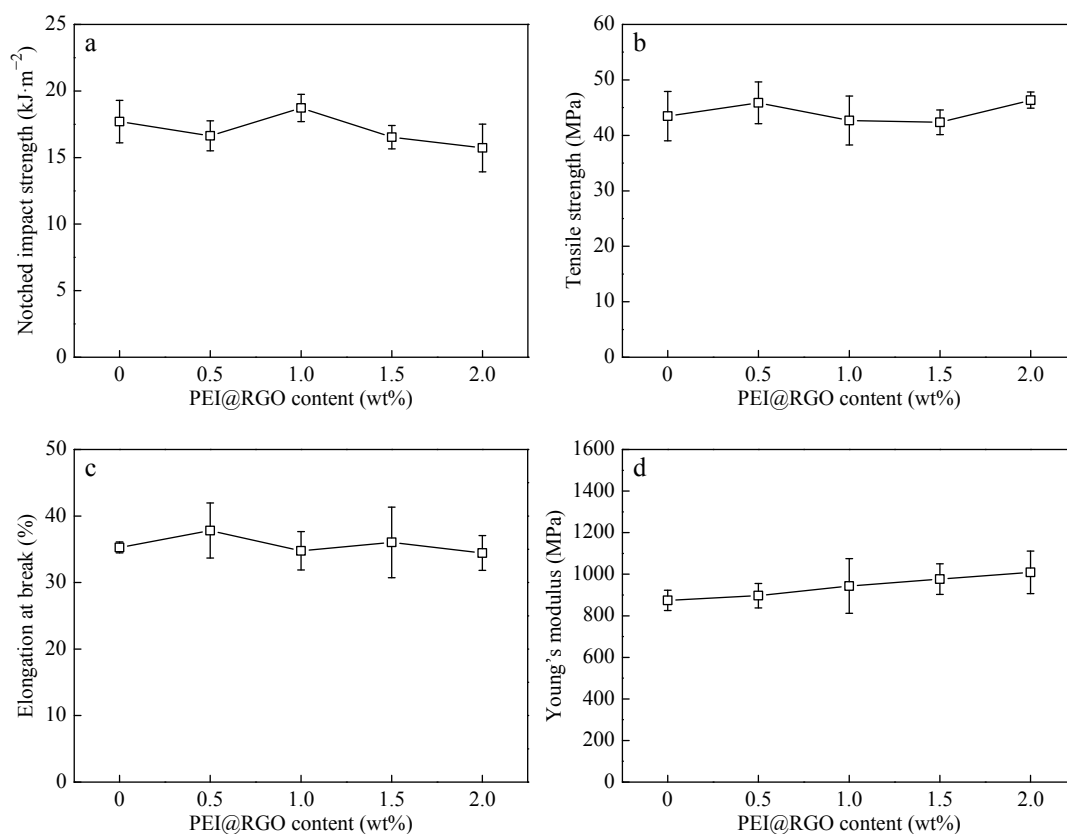


Fig. 7 (a) Notched impact strength, (b) tensile strength, (c) elongation at break, and (d) Young's modulus of PEI@RGO/MA-HDPE nanocomposites with different contents of PEI@RGO

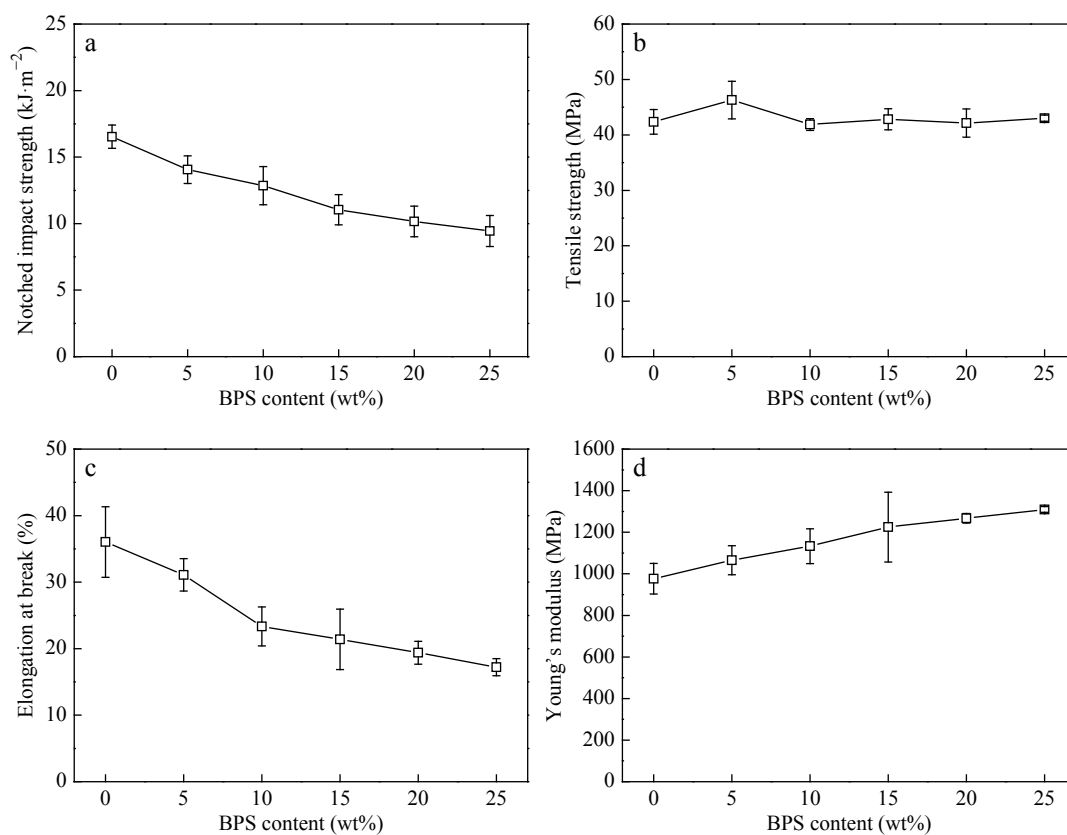


Fig. 8 (a) Notched impact strength, (b) tensile strength, (c) elongation at break, and (d) Young's modulus of PEI@RGO(1.5 wt%)/BPS/MA-HDPE nanocomposites with different BPS contents

CONCLUSIONS

Electrically conductive PEI@RGO/MA-HDPE nanocomposites with outstanding flame-retardant performance are fabricated by a solution precipitation method. The grafted PEI chains improve the dispersion of RGO sheets in the matrix by providing good interfacial compatibility. The addition of 1.5 wt% of PEI@RGO endows the nanocomposite with high electrical conductivity to meet the antistatic requirements. When the PEI@RGO content is increased to 2.0 wt%, the electrical conductivity of $0.023 \text{ S} \cdot \text{m}^{-1}$ is achieved for the nanocomposite. Importantly, the mechanical properties of the composites are ultimately retained even at high loadings. Additionally, the incorporation of BPS yields an excellent retardant performance of UL-94 V-0 rating to the PEI@RGO/BPS/MA-HDPE nanocomposites, but does not significantly sacrifice the valuable mechanical properties. Consequently, the prepared PEI@RGO/BPS/MA-HDPE nanocomposites combine satisfactory electrical, flame-retardant, and mechanical properties uniquely, holding a great promise for potential applications in the electronics and coal mines.

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