Functionalizing graphene decorated with phosphorus-nitrogen containing dendrimer for high-performance polymer nanocomposites

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ABSTRACT

In this paper, we demonstrate a novel strategy for fabricating advanced polymer composites based on functionalized graphene oxide decorated with phosphorus-nitrogen-containing dendrimers (PND-GO). Both X-ray diffraction and transmission electron microscopy results show that reduced PND-GO uniformly disperses within polymer matrix and is exfoliated in polyurethane (PU) via in situ polymerization. Cone calorimetry results show that incorporating 2 wt% reduced PND-GO into PU decreases the peak heat release rate by 53% and prolongs the time to ignition by 28 seconds as compared with the PU bulk. Besides, the tensile strength and Young's modulus are remarkably enhanced by about 2 times and 5 times, respectively.

Key words: A. Polymer-matrix composites (PMCs); A. Nano-structures; B. Thermal properties; Graphene

1. Introduction

The flame-retarding polymer nanocomposite, as an important branch of polymer nanocomposites, has shown dramatic improvements in the mechanical, thermal, flame retardant and barrier properties with very low loading (usually less than 5%) of nanofillers, compared with those filled with traditional flame retardants. The carbon-based nanofillers graphene (oxide) is emerging as a rising star in the field of flame retardancy for its prominent intrinsic properties[1-6]. Song [2] and Huang [3] et al have found that graphene can more effectively decrease the heat release rate of polymer, prolong the time to ignition of materials, and enhance the char structure during combustion relative to layered silicates and carbon nanotubes. Unfortunately, most of polymer/graphene nanocomposites usually do not extinguish and burn slowly until most of the fuel has been burnt. To further improve fire performance of polymer/graphene nanocomposites, intumescent flame retardants (IFRs) have been used for their high flame retarding efficiency [4-6]. During combustion, the IFRs produce swollen multicellular char layers, which acts as a physical barrier against heat transmission and oxygen diffusion and protects the underlying material from the action of the fire [7].

As is well-known, the dispersion quality of nanofillers in the polymer matrix directly determines its effectiveness in improving performances of a material. However, the insolubility of nanofillers renders them difficult to be well-dispersed in the polymer matrix. Although chemical modifications with surfactants for nanofillers has been believed as a feasible method to improve the dispersion within the most hydrophobic polymers [8], there are still many obstacles that remain a huge

challenge. For example, the majority of current as-used surfactants with long alkyl chains reduce the thermal stability and flame retardancy of polymer nanocomposites for the inherent flammability. Moreover, due to its low stability (normally degrade at 200 °C), it is not suitable to process these polymers under a high temperature condition.

So far, much effort has been dedicated to the functionalization of nanofillers to improve the dispersion of nanofillers in the polymer matrix and flame retardancy of the polymer nanocomposites. Recently, nanofillers modified with IFRs have been considered as a promising candidate because of their halogen-free flame retardancy and high efficiency. For instance, Fang and Song et al has prepared the functionalized carbon nanotubes (CNTs) or fullerene (C₆₀) by grafting IFRs, and the functionalized CNTs or C₆₀ is found to be better dispersed in polymer matrix, and thus greatly improve the flame retarded properties of nanocomposites [9-11]. Besides, much work about layered silicates [12,13] modified with IFRs has been done in our group to study the flame retardancy effect on polymers. It is found that the composition, chain length and polarity of IFRs modification reagents are closely related to the formation of nanocomposites, which directly affects the performance of materials. Therefore, the functionalization with IFRs is able to improve the dispersion of nanofillers in polymer matrix, and enhance the synergistic effect between nanofillers and IFRs, which leads to the greater improvement in the performance of nanocomposites. However, there are still some challenges for creating high-performance polymer nanocomposites, especially in controlling the grafting degree of IFRs-functionalized

nanofillers. In fact, the grafting degree of IFRs on the surface of nanofillers has been very low until now, thus leading to limited flame retardancy efficiency and the performance improvements of materials. This paper aims to develop a novel class of graphene-based nano-flame retardants containing high loading of IFRs, which are then used to prepare high-performance polymer composites.

2. Experimental details

2.1. Materials

Graphene oxide (GO) was prepared by the modified Hummer's method from graphite colloidal and vacuum-dried under phosphorus pentoxide at room temperature for above a week [14]. 1,6-hexamethylene diisocyanate (HDI) was provided by Bayer Co. Amine terminated poly (amidoamine) (PAMAM, G1) dendrimer, where G represents generation, was purchased from Chenyuan Silicon Materials Co. Ltd (Weihai, China). 2,2-dimethyl-1,3-propanediol phosphoryl chloride (DPPC) was synthesized by reacting phosphoryl trichloride with neopentyl glycol according to previous literatures [12,13]. Ester-based polyol (molecular weight $M_n=2000$ g/mol), 4,4'-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol (BDO) were supplied by Shanghai Hersbit Chemical Co. Ltd (Shanghai, China).

2.2. Fabrication of PND-GO

To load as much as phosphorus-nitrogen containing dendrimer on the graphene oxide surface and consider the synergistic effects of P-N system, the mole ratio of HDI, PAMAM and DCCP grafted onto the surface of GO was pre-controlled at about 1:1:7. The typical synthetic route to graphene oxide modified with

phosphorus-nitrogen containing dendrimer (PND-GO) is shown in Scheme 1 mainly consisting of three steps. The first step is the synthesis of HDI-GO, 2.0g GO was dispersed into 200 mL of anhydrous N,N-Dimethylformamide (DMF) to form a brownish black slurry with the aid of sonication for 2 h at room temperature. Then, about 20 mL of anhydrous DMF solution containing 0.336 g HDI was added dropwise into the GO slurry and the mixture was then sonicated at 60°C for 8h. After reaction, the slurry was filtered and the precipitate was washed with anhydrous DMF for three times. The products were termed HDI-GO.

The second step involves the grafting reaction of dendrimer PAMAM (G1) onto GO surface. Briefly, 1.429 g of PAMAM (G1) was added into a 100 mL of anhydrous DMF suspension containing 1.168 g HDI-GO. Then, the mixture was sonicated at 30 °C for 10 h. After the reaction was over, the slurry was filtered and the precipitate was washed with anhydrous methanol for three times and then dried under vacuum at 60 °C for 12 h. The products were termed D-GO.

The final step is the reaction of phosphorus oxychloride with the terminal group (amidine) of D-GO. Typically, 1.30 g of D-GO powders were dispersed in 100 mL of anhydrous DMF with the assistance of sonication for 2 h at room temperature, 1.414 g of triethylamine and 20 mL of anhydrous DMF containing 0.644g DCCP was subsequently added dropwise into the above suspension and the mixture was allowed to stir at 30 °C for 6 h. The product was filtered and washed with methanol and then deionized water three times to remove by-product. The resultant product was termed PND-GO.

2.2. Fabrication of PU nanocomposites

PU composites filled with reduced PND-GO were prepared via situ polymerization in DMF as follows. 1.0 g of PND-GO was dispersed into 100 mL of anhydrous DMF with the aid of sonication for 2 h. Subsequently, 74.25 g of dry polyol and 20.66 g of MDI were added to the above mixture, and a prepolymer formed by heating the mixture at 80 °C under N₂ for 3 h. The chain extender, BDO (4.09 g) and catalyzer, stannous octanoate was added to the mixture and the mixture was allowed to continue stirring for another 5 h. Then, 0.8 mL of hydrazine solution and 3.5 mL of ammonia solution (28%) were added into the above homogeneous dispersion and the mixture was stirred at 95 °C for 1 h. Finally, the solvent was removed in the vacuum oven at 110 °C for 24h and the solid compound was pressed on a curing machine at 180 °C for 8 min to be shaped into 4.0 ± 0.1 mm thick sheets for further measurements. PU composites filled with 1 wt% and 2 wt% reduced PND-GO were designated as PU/PND-G1 and PU/PND-G2. The parallel samples of PU filled with 1 wt% and 2 wt% reduced GO were designated as PU/G1 and PU/G2, which were prepared as the above steps (reduction temperature : 95 °C, reduction time: 1h).

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet -5700 FT-IR spectrometer using KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Kratos AXIS Ultra DLD electron spectroscopy. Scanning transmission electron microscopy (STEM) and elemental mapping were carried out under a high-angle annular dark field (HAADF) mode on a Tecnai

G2F30S-Twin transmission electron microscope. X-ray diffraction patterns were obtained in Bruker AXS D8 Advance diffractometer using a Cu-K α radiation generator. The diffraction patterns were collected within the 2θ range 2-40 ° using scanning rate of 0.6 °/min. Transmission electron microscopy (TEM) samples were cut using a diamond knife and RMC MTXL ultramicrotome. The ultrathin sections were then placed on 400 mesh copper grids and photographed using a JEM-1230 transmission electron microscope. Thermogravimetric analysis (TGA) was carried out on a Q600SDT thermogravimetric analyzer. The sample weight is in the range of 12.0~14.0 mg. TGA tests were done from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen (N₂) condition. The flame retardant properties of PU composites were tested using cone calorimeter (ISQ 5660-1) with a heat flux of 35 kW/m². All samples have dimensions of 100×100×4 mm³ were wrapped in aluminum foil and then put in a box with the same dimension in the horizontal direction. The cone data reported here were the average values of three replicated measurements. Char residue was examined by scanning electron microscopy (SEM) using Hitachi S-4800(II) scanning electron microscope.

3. Results and Discussion

3.1. Characterization of PND-GO

Figure 1a shows the FT-IR spectra of GO, HDI-GO, D-GO and PND-GO. Compared with GO, two new absorption peaks respectively located at 2930 cm⁻¹ and 1489 cm⁻¹ appear in the FT-IR spectrum of HDI-GO. These two peaks belong to the stretching and bending vibrations of -CH₂ group from HDI, indicating the successful

grafting of HDI on the surface of GO. As for the D-GO sample, two absorption peaks at $\sim 3340\text{ cm}^{-1}$, 1575 cm^{-1} and the absorption peak at 1621 cm^{-1} respectively arising from N-H and C=O groups of PAMAM are observed in the FT-IR spectrum of D-GO relative to HDI-GO, indicating that HDI-GO is successfully grafted with PAMAM due to the reaction of isocyanic acid and amine. After the amidocarbonylation reaction, the new peaks at 1206 cm^{-1} , 1059 cm^{-1} and 1011 cm^{-1} arising from P=O and P-O groups of DPPC appears in the FT-IR spectrum of PND-GO, strongly suggesting that D-GO has been chemically grafted by phosphorus oxychloride.

XPS measurements are used to determine the chemical composition of various functionalized graphene. As presented in Figure 1b, compared with the starting GO which only shows two binding energy (BE) peaks at 284.6 eV (C1s) and 533.1 eV (O1s), HDI-GO and D-GO display characteristic BE peaks N1s at $\sim 399.6\text{ eV}$ and $\sim 398.9\text{ eV}$ suggesting the presence of N in HDI-GO and D-GO. Besides BE peaks of C1s, N1s and O1s, P2d peak (134.2 eV) and P2s (191.3 eV and 199.1 eV) are also observed in XPS spectrum of PND-GO, further proving the successful grafting of phosphorus-nitrogen containing dendrimer onto GO surface in PND-GO sample. Besides, the relative contents of elements are summarized in Table 1. HDI-GO shows about 5.4 wt% of nitrogen due to the grafting of HDI. Similarly, chemical grafting action of PAMAM makes D-GO exhibit a much higher content of nitrogen as compared with HDI-GO. Most impressively, for PND-GO sample, besides 9.8 wt% nitrogen, the content of phosphorus reaches 7.1 wt%, indicating the the presence of DCCP in PND-GO.

Figure 2 shows C1s spectra of GO and various functionalized grapheme. BE peaks for C-C (284.19 eV), C-O (286.41 eV) and C=O (288.12 eV) are clearly found in C1s scan of GO.³⁶⁻³⁹ The C1s spectrum of HDI-GO displays two BE peaks at 285.08 eV and 286.11 eV, respectively, which are attributed to the C-H and CO-N groups in HDI molecules. Similarly, a peak at 286.63 eV corresponds to the CO-N bond in C1s spectra of D-GO. Moreover, BE peak areas of CO-N increase obviously after HDI-GO being chemically grafted by PAMAM. For C1s spectra of PND-GO, BE peaks for C-C (284.49 eV), C-H (285.50 eV), CO-N (286.09 eV), C=O (288.24 eV) are found, and the BE peak area of C-H are larger than that of C-C, which further supports that GO sheets are covered by a high amount of phosphorus-nitrogen containing dendrimer. N1s spectra and P2p spectra for PND-GO are shown in Figure 2e and Figure 2f. BE peaks for PND-GO show two types of bonded N: one peak at 399.31 eV (C-N) and 401.12 eV (CO-N). Additionally, the peak at 131.30 in P2p spectrum of PND-GO is attributed to the P-O in DCCP molecules, which strongly confirms that phosphorus oxychloride DCCP reacts with the terminal group (amidine) of D-GO.

Figure 3a and 3c show TEM images of D-GO and PND-GO, and their SEM images together with elemental maps are presented in Figure 3b and 3d. EDX elemental mapping along with high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) are performed simultaneously to study in detail the composition of the D-GO and PND-GO samples. As shown in Figure 3b, elemental maps confirm the presence of C, O and N in the D-GO, suggesting the

grafting reaction of PAMAM with HDI-GO. Similarly, besides these elements, P is also detected in the PND-GO (Figure 3d). Moreover, the elemental map of P clearly indicates its homogenous distribution on the surface of GO sheets. The results further prove the FT-IR and XPS results for the successful fabrication of PND-GO.

To determine how much phosphorus-nitrogen containing dendrimer is grafted to GO, TGA of GO and PND-GO under a nitrogen atmosphere is conducted (Figure 4). Because the oxygen-containing groups of GO are very easy to decompose under high temperatures, the main degradation for GO takes place at 200 °C~260 °C, and the residue at 260 °C is 47.6 wt% decomposes above 260 °C and leaves the residue of 83.2 wt% at 260 °C. As for PND-GO, its weight loss tendency is similar to that of GO below 260 °C, and 71.3 wt% of residue is left at the above temperature. Since GO itself may be reduced by the amino groups of PAMAM under high temperatures, it is likely to affect the degradation of GO and thus theoretically the residue at 260 °C was not accurate in a strict sense. According to the calculation methods in a previous report [9,15], it's obtained that the grafting degree of GO reaches ~200 wt%. Compared with IFRs-functionalized CNTs or GO with the grafting degree of 60~70 wt% [9,15], the IFRs loading of PND-GO is very high, and the grafting degree increases by several times.

3.2. Morphology

Figure 5 shows the wide-angle X-ray diffraction (WAXD) patterns of GO, PND-GO, PU and its composites. The diffraction peaks in the pattern of GO appear at 10.0 °, corresponding to the layer-to-layer distance of ~0.90 nm. It is significantly

larger than that of pristine graphite (~ 0.33 nm), due to the intercalating oxygen-containing functional groups [16]. The pattern for PND-GO presents a graphene peak near $2\theta = 25.2^\circ$ and an additional peak near $2\theta = 8.9^\circ$, indicating the presence of phosphorus-nitrogen containing dendrimer between adjacent sheets in the PND-GO structure. The reduced interlayer distance in the PND-GO paper structure is primarily attributed to the loss of oxygen-containing functional groups for the grafting of phosphorus-nitrogen containing dendrimer, and similar results were also reported in previous literatures [17]. For the PU matrix, only a broad diffraction peak around $2\theta = 21.4^\circ$ is observed. After chemical reduction of GO and PND-GO dispersed in the PU matrix, the broad peak in GO disappears in the PU/G2 and PU/PND-G2 composites (under 2 wt% loading), indicating the exfoliation of the graphene.

The TEM images shows that the graphene sheets in PU/PND-G2 sample (Figure 6a) is dispersed better compared with PU/G2 sample (Figure 6b). Figure 6c reveals that most of graphene sheets agglomerate together in the PU/G2 composite. Nonetheless, at higher magnifications (Figure 6e), some reduced GO sheets are still exfoliated. Figure 6d shows that graphene sheets are dispersed better compared with PU/G2 sample for the grafting of phosphorus-nitrogen containing dendrimer onto the surface of graphene sheets. Furthermore, at higher magnifications (Figure 6f), the majority of functionalized graphene are exfoliated as dark-grey or dark lines in the matrix in PU/PND-G2 composites. The functionalized graphene sheets have a number of polar groups, such as amide, phosphoramidate, carbamate and so on, which contributes to the stronger interactions between the graphene sheets and the PU chains, thus leading to

the improvement of the dispersion of graphene sheets in the polymer matrix. In addition, the chemical reduction not only decreases the oxygen content of GO, but also weakens the interactions of polar functional groups of GO and promotes the exfoliation during in situ intercalative polymerization. Some exfoliated graphene-based polymer nanocomposites have been created via in situ polymerization with hydrophobic polymers such as PMMA [18], epoxy[19] and PU [20] in previous literatures.

3.3. Mechanical properties

The typical stress-strain curves of PU and its composite is shown in Figure 7, and the results are summarized in Table 2. Similar to dynamic storage modulus, both tensile modulus (E) and tensile strength (σ) of PU composites are remarkably enhanced with the addition of reduced GO and PND-GO, despite the reduction in the elongation at break (ϵ). Compared with the pure PU resin, PU/G2 shows a nearly 4-fold increase in E (~33.6 MPa), and about 40% enhancement in σ (~17.6 MPa), indicating that the strong reinforcement effect of graphene sheets for PU.^{40,45} By contrast, PU/PND-G2 display nearly 5-fold increase in the E (from 8.5 MPa for pure PU to 39.7 MPa), and about 2-fold increase in the σ from 12.5 MPa to 24.9 MPa. Both E and σ of PU/PND-G2 are higher than those of PU/G2, and furthermore, the ϵ of PU/PND-G2 still remains above 620% and is far more than that of PU/G2 (~330%). In fact, incorporating small amounts (~0.7 wt %) of graphene improves tensile strength and of in situ polymerized TPU significantly. A 5-fold increase in tensile modulus of PU resin is observed by incorporating small amounts (~0.7 wt%) of

graphene for PU/PND-G2 composites prepared in our work, whereas similar or even less improvements were obtained by adding above 3 wt% reduced GO as reported in previous literatures[20-23]. Such significant enhancements in mechanical properties are mainly ascribed to the fine dispersion of reduced PND-GO in the polymer matrix and reinforcement effect of functionalized graphene nanosheets, as already evidenced by XRD and TEM results. By contrast, the addition of traditional flame retardant, e.g. halogen derivatives [24], phosphorus-based compounds[25] or intumescent flame retardants [26], basically leads to a prominent decrease in the strength and toughness for polymers owing to the poor interfacial interaction between flame retardants with polymer matrix.

3.4. Thermal stability

Figure 8 shows TGA and DTG curves of PU and its composites with different loading levels of reduced GO and PND-GO, with detailed data summarized in Table 3. The PU resin starts to decompose at about 302 °C (T_i) leaving negligible char at 600 °C, and the maximum mass loss temperature (T_{max}) reaches 394 °C. However, adding reduced GO into PU resin increases the T_i and T_{max} to different extent. Compared with pure PU resin, the T_i and T_{max} of PU/G2 are increased by 12°C and 16°C respectively, and the residual weights display a slight change, which indicates that the thermal enhancing effect of graphene sheets delay effectively the degradation of PU resin. The similar results were also found in other graphene-based polymer nanocomposites [27,28]. For PU composites filled with reduced PND-GO, T_i of reduced PND-GO contained samples is lower than that of pure PU resin due to the

adding of graphene sheets grafted by phosphorus-nitrogen containing dendrimer, which accelerates the early degradation of PU matrix. However, $T_{\max}$ of reduced PND-GO contained samples increases 20~31°C during the major degradation step relative to pure PU resin or reduced GO contained samples. Moreover, the residual weights increase greatly with adding the reduced PND-GO. For instance, the residual weights of PU/PND-G2 increase about three times as compared with pure PU resin. This indicates that this functionalized graphene has the excellent char-forming effect on the PU matrix. Results from TGA and DTG show that the addition of reduced PND-GO reduces the thermal degradation temperature but the enhances the char-forming capability of PU matrix.

3.5. Flammability

As presented in Figure 9a and Table 4, the neat PU resin is of an inherently ignitable and flammable polymeric material and the peak heat release rate (PHRR) reaches a value of around 678 kW/m². In the case of the reduced GO contained PU samples, the PHRR values are obviously reduced, while the time to ignition (TTI), the average mass loss rate (AMLR) slightly changes in comparison with the neat PU resin. However, incorporating reduced PND-GO is capable of effectively prolonging the TTI and reducing the PHRR, total heat release (THR) and average mass loss rate (AMLR), strongly indicating great enhancements in the flame retardancy of PU resin. For instance, with respect to the neat PU resin, PU/PND-G1 exhibits a 42% reduction (389 kW/m²) in PHRR and a slightly longer TTI of 19 s. When the content of reduced PND-GO reaches 2 wt% (PU/PND-G2), the TTI is prolonged by 28 seconds (~94

seconds) and the PHRR is decreased by up to 53% ($\sim 320 \text{ kW/m}^2$). Such remarkable prolongation in TTI and reduction in PHRR are very crucial for reducing the fire hazards of PU since they allow people more time to escape from the fire and save their properties. Meanwhile, the THR and AMLR are reduced by 8 % and 23 %, respectively, indicating that some polymer chains participate into the carbonization process due to the flame retardancy of phosphorus-nitrogen containing dendrimer grafted onto the surface of graphene. By contrast, 3wt% of GO functionalized by hyper-branched IFRs only make the PHRR and THR of polyethylene to decline by 28 % and 6%, respectively [29], which further indicates that graphene functionalized with phosphorus-nitrogen containing dendrimer has a significant improvement in the flame retardancy efficiency compared with existing state-of-the-art compounds.

The smoke production rate (SPR) is another critical parameter to evaluate the fire safety of a material since the toxic smoke not only reduces the visibility, thus making it difficult for trapped people in the fire to escape, but also is readily to be inhaled by the trapped, causing the trapped to be poisoned. As shown in Figure 9b and Table 4, the addition of reduced GO decreases the peak SPR (PSPR) of PU resin, but changes slightly the value of total smoke production (TSP). As for PU composites filled with reduced PND-GO, the PSPR and TSP significantly decrease compared with neat PU resin, and both PSPR and TSP steadily reduce with increasing loading level of reduced PND-GO. PU resin shows a PSPR of $0.117 \text{ m}^2/\text{s}$ and a TSP of $9.38 \text{ m}^2/\text{s}$, while the presence of only 1.0 wt% of reduced PND-GO makes the PSPR and TSP to decline by 56 % and 23%, respectively. When the loading level of reduced PND-GO

increases up to two times, PSPR and TSP are of 0.042 m²/s and 6.82 m²/s, respectively decreased by 64% and 27% relative to that of neat PU resin.

To elucidate effects of reduced PND-GO on the char-forming capability of PU resin, the microstructure and morphology as well as the chemical composition of the char residue after combustion is examined by SEM and EDX. As shown in Figure 10a, the chars of PU resin shows a rather flattened morphology, where some loose and continuous carbonaceous particles were observed on the surface of the thin residues (Figure 10b). For the char for PU/G2, a continuous and denser charred layer with some micro-size holes is observed (see Figure 10c). At high magnifications, many wrinkled graphene nanosheets joint each other and form a barrier in the chars of PU/G2, which helps enhance the char strength and thus improves the flammability properties of PU nanocomposites. In comparison, after combustion PU/PND-G2 presents a totally different char morphology, and a much more continuous, compact and denser char, filled with finely dispersed graphene nanosheets, is clearly observed (Figure 10e, f). Such char layer is able to form protective shields on the surface of the residues, thus effectively inhibiting the transfer of heat and diffusion of oxygen when the material is exposed to the flame or heat flux, and leading to largely improved flame retardancy properties.

Figure 11 presents the EDX spectra of char residue of PU composites after cone calorimeter testing. Around 71 wt% C and 29 wt% O are detected in the char residue of PU. Compared with PU resin, the carbon content of the char for PU/G2 is increased ~8 wt%, indicating that the addition of reduced GO enhances the intensity of the char

layers of PU after combustion. For the char of PU/PND-G2, the carbon content reaches 82 wt% and is higher than that of the char PU and PU/G2, which indicates that the char-forming capability of PU is improved by phosphorus-nitrogen containing dendrimer grafted onto graphene surface. Meanwhile, around 4 wt% phosphorus still remains in the char of PU/PND-G2, supports the fact that some phosphoric acid or phosphide is formed during combustion which play a very important role for improving the char-forming capability of PU. During the formation of carbonaceous char, the phosphoric acid generated from flame retardant reduced PND-G2 under heating condition, acts as the catalyst for the dehydration process, which promotes the oxidative dehydrogenation crosslinking-charring process and increases the char yield thus improves flame retardancy of PU nanocomposites. The result is in good agreement with results of the above cone calorimeter tests and TGA.

4. Conclusion

A halogen-free flame retardant additive, PND-GO, has been successfully fabricated in this work. Results show that reduced PND-GO can be readily uniformly dispersed and most of graphene nanosheets are exfoliated in the PU matrix via in situ polymerization. Incorporating reduced PND-GO into the polymer matrix not only enhances the strength of PU composites, but also improves the thermal stability and flame retardancy of nanocomposites. The addition of 2 wt% reduced PND-GO reduces PHRR by about 53% and prolongs TTI by 28 seconds as compared with neat PU resin. Besides, the value of PSPR and TSP reduces by 56 % and 23%. Moreover, the tensile strength and Young's modulus are respectively enhanced by about 2 times

and 5 times. In brief, graphene functionalized with phosphorus-nitrogen containing dendrimer (reduced PND-GO) combines outstanding thermal, flame retardancy, smoke-suppression, reinforcing performances, which can be used to create high-performance polymer nanocomposites.

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Scheme 1. Schematic representation for synthetic route to PND-GO.

Fig. 1. (a) FT-IR spectra of pristine GO, HDI-GO, D-GO and PND-GO; (b) XPS spectra of GO, HDI-GO, D-GO and PND-GO.

Fig. 2. C1s spectra of (a) GO, (b) HDI-GO, (c) D-GO and (d) PND-GO, (e) N1s and (f) P2p spectra of PND-GO.

Fig. 3. TEM images of (a) D-GO and (c) PND-GO with STEM-HAADF images and elemental mapping for (b) D-GO and (d) PND-GO.

Fig. 4. TGA curves of GO, PND and PND-GO in N₂ condition.

Fig. 5. XRD patterns of GO, PND-GO, PU, PU/G2 and PU/PND-G2 composites.

Fig. 6. TEM images of (a, c, e) PU/G2 and (b, d, f) PU/PND-G2 composites.

Fig. 7. Stress-strain curves for PU and its composites.

Fig. 8. TGA curves (a) and DTG curves (b) for PU and its composites in N_2 condition.

Fig. 9. Heat release rate (a) and smoke production rate (b) curves for PU and its composites.

Fig. 10. Morphologies of the residues of PU composites. SEM images for residues of PU (a, b), PU/G2 (c, d) and PU/PND-G2 (e, f).

Fig. 11. EDX spectra of char residues of PU, PU/G2 and PU/PND-G2.

Table 1. Quantitative comparison of elements detected from XPS spectra (in wt %).

Sample	C	O	N	P
GO	57.7	42.3	-	-
HDI-GO	57.4	37.2	5.4	-
D-GO	54.3	30.9	14.8	-
PND-GO	53.4	29.7	9.8	7.1

Table 2. Mechanical properties of PU and its composites.

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PU	8.54±0.28	12.52±0.43	1120±115
PU/G1	19.89±0.33	14.27±0.45	534±24
PU/G2	33.63±0.35	17.55±0.52	336±19
PU/PND-G1	17.23±0.42	17.92±0.61	770±42
PU/PND-G2	39.69±0.54	24.87±0.83	624±33

Table 3. Data of TGA and DTG for various samples at a heating rate of 10 °C/min in N₂.

Sample	T _i ^a (°C)	T _{max} ^b (°C)	Residue at 600 °C (wt %)
PU	302	394	4.9
PU/G1	307	404	5.4
PU/G2	314	410	6.2
PU/PND-G1	298	414	13.5
PU/PND-G2	294	425	15.4

^a T_i and ^b T_{max} refer to the temperature where at 5 wt% loss and the maximum weight loss occurs, respectively. The residue is obtained at 600 °C.

Table 4. Detailed experimental results for PU and PU composites obtained from cone calorimetry.

Sample	TTI ^a	PHRR ^a	THR ^a	AMLR ^a	PSPR ^a	TSP ^a
	(s)	(kW/m ²)	(MJ/m ²)	(g/s)	(m ² /s)	(m ² /s)
PU	66±4	678±23	87±1.4	0.108±0.011	0.117±0.012	9.38±0.5
PU/G1	68±3	484±22	86±1.1	0.102±0.008	0.074±0.009	8.91±0.4
PU/G2	69±4	437±17	85±1.0	0.097±0.008	0.064±0.008	8.74±0.3
PU/PND-G1	85±4	389±15	83±0.9	0.088±0.006	0.051±0.006	7.24±0.3
PU/PND-G2	94±4	320±10	80±0.9	0.083±0.005	0.042±0.007	6.82±0.4

^a TTI: time to ignition, PHRR: peak release rate, THR: total heat release, AMLR: average mass loss rate, PSPR: peak smoke production rate, TSP: total smoke production.

Caption of Figures

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