Graphene oxide grafted with polydimethylsiloxane modified polyurethane

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Funding information National Natural Science Foundation of China, Grant/Award Number: 21174063; Aeronautical Science Foundation of China, Grant/Award Number: 2018ZF52068

Abstract
In order to improve the dispersion of graphene oxide (GO) in polymers, we synthesized polyurethane (PU) chains with long polydimethylsiloxane (PDMS) chains as the “soft segment” and hexamethylenediisocyanate (HDI) as the “hard segment”, then the PU chains were grafted onto GO. The results of compatibility in solvents and TEM images of composites indicated that the modified GO (GO-PU) would present two different shapes in non-polar and polar solvents (cocoon-like shape and stretched shape, respectively). The two shapes made it have a good dispersion in both non-polar and polar polymers, it was expected to be applied in both non-polar and polar polymer matrixes. This provided a method for covalent modification of GO.

KEYWORDS covalent modification, dispersion, graphene oxide, polyurethane

1 INTRODUCTION
Graphene oxide (GO) is one of the important derivative of graphene. It not only has the same structure as graphene, but also has oxygen-containing functional groups such as hydroxyl and carboxyl.[1–4] So GO is widely used as a filler in polymer-based composites to improve the dielectric properties[5,6] mechanical properties[7–9] and anti-corrosive properties[10,11] However, due to the strong van der Waals force between the GO nanosheets; moreover, graphene-based nanocomposites are usually fabricated by the method of solution casting, it is difficult to uniformly disperse GO in polymers, especially in non-polar polymers. Generally, a good dispersion of GO within the polymer matrix is necessary to improve the properties of composites. As a result, the aggregation of GO will make the performances of composite unsatisfactory and even defective.

Covalent modification with molecules can destroy the van der Waals force between the GO nanosheets and improve the compatibility of GO with polymer matrixes, is one of the effective modification methods, and also give GO some new performances.[12,13] So covalent modification of GO is an important area of GO research.

In this work, PU chains were synthesized with long PDMS chains as the “soft segment” and HDI as the “hard segment”, and grafted onto GO. Isocyanate group is very reactive and can undergo a gradual polymerization reaction with hydroxyl, carboxyl, etc. This reaction process is gentle and easy to be controlled, widely used in the preparation of polyurethane (PU).[14,15] We adjusted the ratio of isocyanate group to hydroxyl group to make the synthesized PU chains have isocyanate groups, and then the PU chains were used to react with the hydroxyl and carboxyl groups of GO to complete the modification. The schematic
The GO grafted with PU (GO-PU) was characterized by FT-IR, XRD, Raman spectroscopy, TGA, and TEM analyses. The dispersion of GO-PU was analyzed with different organic solvents, and the fracture surface of GO-PU/SEBS and GO-PU/PU composites were investigated by SEM analyses. The results demonstrated that PU chains were successfully synthesized with PDMS and grafted onto GO, the compatibility of GO-PU with solvent increased with the increasing of solvent polarity, and the excellent flexibility and ultra-low crystallinity of PDMS made GO-PU have two different shape changes. In non-polar solvents, the hard segments of PU acted as physical cross-linking points, and the soft segments PDMS would swell to cocoon the GO nanosheets and the hard segments. Moreover, in polar solvents, the PU chains would present a stretched state. The two shape changes gave GO-PU a good dispersion in both non-polar polymers and polar polymers. It was expected to be applied not only in non-polar polymers but also in polar polymers.

2 RESULTS AND DISCUSSION

The FT-IR spectra of GO and GO-PU are exhibited in Figure 1A. In terms of GO, characteristic bands were observed at 3407, 1725, 1621, 1402, and 1118 cm\(^{-1}\), corresponding to O-H, C=O, and C=C groups stretching, bending vibration of C=O groups and stretching vibration of C-O-C groups,\(^{16,17}\) respectively. Compared with GO spectrum, there were new peaks appeared at 1583, 1538, 1261, 1095, 1024, 865, and 802 cm\(^{-1}\), where 1583 and 865 cm\(^{-1}\) were assigned to the vibration of benzene ring, 1538 cm\(^{-1}\) corresponded to NH groups,\(^{18,19}\) and 1261, 1095, 1024, and 865 cm\(^{-1}\) were attributed to the vibration of CH\(_3\), Si-O-C, Si-O-Si, and Si-C groups of PDMS,\(^{20,21}\) respectively. The absorptions of C=O and C-O-C groups had an overlaying with C=O groups of -NHCO- and Si-O-Si groups, the peaks shifted from 1725 and 1118 cm\(^{-1}\) to 1716 and 1095 cm\(^{-1}\). Moreover, the absorptions of aliphatic groups at 2962, 2933, and 2857 cm\(^{-1}\) were strengthened because the PU chains contained a lot of CH\(_3\) and CH\(_2\) groups.

The results of Raman spectroscopy are given in Figure 1B. The D band and the G band were observed at 1350 and 1592 cm\(^{-1}\) in the spectrum of GO, respectively. The D band was related to disorders or different types of structural defects and the G bands was due to the first order scattering of the E\(_{2g}\) mode.\(^{22,23}\) For GO-PU, a D band and a G band were also observed at 1338 and 1585 cm\(^{-1}\) in the spectrum of GO-PU, respectively. And the D and G bands were shifted to lower wavenumbers compared with GO.
spectrum, the degree of deviation was not as large as the general PU grafted but like PDMS grafted.[20] It was because that long PDMS chains were the main part in the ternary PU chains. For GO-PU, the ratio of $I_D/I_G$ decreased from 1.01 to 0.95 compared with GO. It was probably due to the existence of hydrogen bonds between PU chains and GO surface. This indicated that stacking state of GO could be easily disordered by grafting.[24,25]

XRD patterns of GO and GO-PU are shown in Figure 1C. In XRD pattern of GO, the diffraction of plane (002) appeared at $2\theta = 9.5^\circ$ with dspacing = 0.93 nm. For GO-PU, the peak of plane (002) was shifted to $2\theta = 9.3^\circ$ with dspacing = 0.95, it barely shifted compared with GO and the intensity of the peak was reduced, which verified the grafted PU chains effectively blocked the van der Waals forces between GO nanosheets, made the GO nanosheets of GO-PU become difficult to regularly arranged between GO-PU nanosheets. But this change was not big, the main reason was that the synthesized PU chains were large, it was not easily to intercalate into the interlayers of GO as small molecules during the synthesis process. And there was a sharp peak at $2\theta = 11.6^\circ$ and a dispersion peak around $2\theta = 20.8^\circ$ which meant PU chains had regular crystalline regions and irregular crystalline regions, one reason was that the movement of hard segments connected to GO was restricted, this limited the hard segments connected to GO nanosheets crystalline ability, another reason was that long PDMS chains had extremely low crystallization ability.

The TGA curves of GO and GO-PU are shown in Figure 1D. There was a major weight loss from 110 to 300°C due to decomposition of the oxygen-containing functional groups.[26,27] For GO-PU, it displayed two major weight
FIGURE 2 TEM images of GO-PU (B) was the enlarged view of the red box area in (A)

loss: the first step (weight loss of 18.12%) from 110°C to 231°C was the same reason as the weight loss of GO and the second step (weight loss of 34.47%) from 363°C to 590°C was attributed to the loss of PDMS segments. The decomposition of fatty chains and amide groups occurred from 231°C to 363°C. And it could be observed a little weight loss from room temperature to near 100°C on both curves, 5.93 and 5.65 wt%, respectively, it was the removal of the physically absorbed water molecules. After calculating, the grafting degree of PU was 0.1828 mmol g⁻¹.

The TEM images of GO-PU has been shown in Figure 2. GO nanosheets were evenly cocooned by polymers compared with the TEM images of GO (Figure S1), and the thickness of “cocoon” was about 5–10 nm. This confirmed the result of XRD that the grafted PU chains destroyed the van der Waals force between GO nanosheets made GO nanosheets of GO-PU become difficult to regularly arrange between GO-PU nanosheets.

Figure 3A and B shows the digital photographs of GO and GO-PU standing for 3 and 6 hours at a concentration of 0.5 mg mL⁻¹ after sonicating for 10 minutes in toluene, acetone, DMF and DMSO. GO had a good dispersion in DMF and DMSO, there was no obvious settlement within 6 hours standing. For GO-PU, the sedimentation rate of GO-PU was decreased as the polarity of the solvent increasing. Compared with GO, the sedimentation rates in toluene and acetone were significantly improved, especially in acetone. That was because the PU chains with PDMS as soft segment not only had a good solubility in DMF and DMSO but also had a good compatibility with toluene and acetone. However, due to the grafting of PU chains, GO nanosheets became hyperbranched nanosheets and the long PDMS chains had a poor solubility in DMF and DMSO, these made GO-PU unable to continue to be suspended in polar solvents as well as GO.

The SEM images indicate the fracture surface of 2 wt% GO-PU/SEBS and 2 wt% GO-PU/PU composites, where Figure 4A and B were the images of GO-PU/SEBS composite and Figure 4C and D were the images of GO-PU/PU composite. It could be seen from Figure 4A that GO-PU fillers were uniformly dispersed in matrix without the appearance of agglomeration. As seen in Figure 4B, the GO-PU fillers showed a smooth flat sphere shape (as marked by the red box) not like the normal shape of GO (Figure S2) and there was a clear interface between GO-PU fillers which meant fillers had a good dispersion in matrix. And the size of filler was significantly larger than the size of filler in TEM images. This could be explained by followings, as shown in Figure 5A. The isocyanate groups of PU could form hydrogen bonds with each other, and could also form hydrogen bonds with oxygen-containing functional groups of GO. These hydrogen bonds could not be destroyed in non-polar solvents such as toluene, and polydimethylsiloxane had excellent flexibility and ultra-low crystalline properties (polydimethylsiloxane with a molecular weight of 2000 was a liquid) and was dissolved in non-polar solvents such as toluene. So the hydrogen bonds between “hard segments” HDI and oxygen-containing functional groups would provide physical crosslinking points, and polydimethylsiloxane segments would swell in toluene solution of SEBS and it would cocoon the “hard segments” and GO nanosheets like a cocoon to block the formation of hydrogen bonds between GO-PU nanosheets which avoided them linking together, then GO-PU was filled with paraffin oil, that was also the purpose of adding paraffin oil in the process of preparing composite material, to demonstrate the shape change of GO-PU. As shown in Figure 4C and D, the fracture surface of GO-PU/PU was smooth and uniformly covered with gullies, like the fracture surface of GO/PU (Figure S3), but not like the fracture surface of GO-PU/SEBS, which indicated that the GO-PU presented two different shapes in SEBS and PU composites. This could be explained by followings, as shown in Figure 5B. The hydrogen bonds could be destroyed in polar solvents such as DMF, so the PU chains would be in a state...
Figure 3  The dispersion of (A) GO and (B) GO-PU in different organic solvents at 3 and 6 hours. From left to right, the solvents were toluene, acetone, DMF and DMSO, respectively.

Figure 4  SEM images of fracture surface of (A, B) GO-PU/SEBS and (C, D) GO-PU/PU composites. GO-PU nanoparticle was marked with red box in (B).
4 | EXPERIMENTAL SECTION

4.1 | Materials

Graphite powder (extra pure, particle size ~150 μm), sulfuric acid (H2SO4, 98%), hydrochloric acid (HCl, aqueous 37% solution), hydrogen peroxide (H2O2, 30%), potassium permanganate (KMnO4, 99%), N,N-dimethylformamide (DMF, AR) and phenol were purchased from Nanjing Chemical Reagent Co., Ltd. China. Sodium nitrate (NaNO3, >99%) was obtained from Shanghai Zhenxin Reagent Factory, China. Hexamethylene diisocyanate (HDI, 99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. China. Hydroxy terminated polydimethylsiloxane (PDMS, Mw = 2000 g mol⁻¹) was purchased from Shenzhen Jipeng Silicon Fluorine Material Co., Ltd. China. SEBS (YH-501T) was purchased from Baling Petrochemical Co., Ltd.

4.2 | Synthesis of GO

GO was synthesized from graphite flake powder through a modified Hummer’s method. For this purpose, graphite powder (3 g) and NaNO3 (1.5 g) were slowly added to concentrated H2SO4 (80 mL) in an ice bath, and kept stirring for 30 minutes. Then KMnO4 (9 g) was gradually added to the suspension below 10°C. After stirring for 1.5 hours, stirred at 35°C for another 30 minutes, following deionized water (80 mL) was slowly added. Then kept the reaction at 90°C for another 30 minutes. When the reaction was over, H2O2 was continuously added to the mixture until the color of the suspension turned into yellow brown. Following HCl (5 mL, 1 M) solution was added at room temperature. The PH of the suspension was adjusted to 7.0 by Centrifugal washing, finally GO was obtained by freeze drying.

4.3 | Synthesis of GO grafted with PU (GO-PU)

HDI (0.2 mL), DMF (2 mL) and PDMS (1.248 g) were added into three-necked flask, and stirred for 10 minutes, following reacted at 90°C for 2 hours under nitrogen protection. Then cooled the solution to 60°C, a certain amount of phenol was added, and stirred for 10 minutes, then reacted at 90°C for another 2 hours. After that cooled the solution to 60°C again, the GO suspension containing GO (200 mg) obtained by sonicating for 40 minutes in DMF (170 mL) was add into flask and stirred for another 10 minutes, reacted at 90°C for 2 hours again. In the end, cooled the mixture to the room temperature.

3 | CONCLUSION

The PU chains modified with long polydimethylsiloxane (PDMS) chains as the “soft segment” was used to covalent modified GO. The compatibility of GO-PU with solvents was increased as the polarity of solvent increasing. And thanks to the excellent flexibility and ultra-low crystallinity of PDMS, GO-PU had two different shape changes in non-polar and polar solvents, made it have a good dispersion in both non-polar and polar polymers. It was expected to be applied in both polymers. For example, it was used as a dielectric filler in SEBS, and used in PU to improve the mechanical properties etc. Moreover, the special shape change in non-polar solvent made it expected to be used in nano-carrier materials.

FIGURE 5  A, The schematic diagram of shape change of GO-PU in toluene. B, The schematic diagram of shape change of GO-PU in DMF or DMSO. The red straight lines and blue curves represented “hard segments” and “soft segments” of PU, respectively.
temperature, filtered, washed with hot DMF, and dried in vacuum.

4.4 Preparation of GO-PU/SEBS and GO-PU/PU composites

GO-PU/SEBS was prepared by adding the GO-PU into the toluene solution containing SEBS and same quality paraffin oil as SEBS and stirred for 30 minutes, then poured into a mold and dried it under vacuum for 24 hours. GO-PU/PU was prepared by adding the GO-PU into the DMF solution of PU and stirred for 30 minutes, then poured into a mold and dried under vacuum for 24 hours.

4.5 Characterization

Fourier transform infrared spectrum (FT-IR, Bruker Tensor 27, Bruker Daltonics, Germany) was employed to characterize the structure of GO-PU and GO. Raman spectra of GO and GO-PU were recorded using a Raman spectrometer (Horiba LabRAM HR Evolution) with 532 nm. X-ray diffraction (XRD, ARL XTRA, Thermo Fisher, Switzerland) was employed to characterize the structure of GO-PU and GO. Ramanspectra of GO-PU with a heating rate of 10°C min⁻¹. Transmission electron microscope (TEM, JEM-2100, JEOL, Japan) was used to observe microstructure of GO-PU. Scanning electron microscope (SEM, JSM-6510, JEOL, Japan) was used to observe microstructure of the surface morphology of GO-PU/TPE and GO-PU/PU composites.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant number 21174063), the Aeronautical Science Foundation of China (grant number 2018ZF52068).

DATA AVAILABILITY STATEMENT

Research data are not shared.

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How to cite this article: D. Liu, J. Wang, X. Gao, H. Wang, H. Ren, Nano Select 2021, 1.
https://doi.org/10.1002/nano.202100063