Enhanced physical mechanics properties of hydroxyl-terminated polybutadiene based polyurethane crosslinking with modified graphene oxide

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Abstract. In this work, a series of composites with enhanced tensile strength and fracture strain were obtained via the crosslinking between modified graphene oxide (MGO) and hydroxyl-terminated polybutadiene (HTPB) chain. The preparation, characterization and physical mechanics properties of the prepared composites have been displayed detailedly. As a result, the tensile strength of composite containing 0.1wt% of MGO (PUM-0.1) increased by 57.8%. Impressively, the fracture strain of PUM-0.1 composite was 1292.6%, which is higher than that of polyurethane without MGO. Moreover, the resistance capability to deformation of the composites has also been enhanced significantly.

1. Introduction

HTPB-based polyurethane (PU) has attracted many attentions in various field due to its excellent properties, like well elasticity, wonderful toughness, good chemical resistance, and sub-ambient glass transition temperature (Tg)[6]. The physical mechanics properties of HTPB-based PU are important during their application, and researchers are committed to enhancing its physical mechanics properties to extend its service life[10]. To date, numerous methods, like chemical modification and nanoparticles addition[8, 10], have been adopted to enhance their physical mechanics properties, and the carbon-based nanomaterials have been regarded as a potential materials[7].

Graphene oxide (GO) is one of derivatives of graphene. It has been widely used as a reinforcing filler to enhance the properties of polymer[11]. Generally, due to the strong van der Waals force between go layers, it tends to aggregate in polymeric matrix, which has an adverse effect on polymer[5]. Fortunately, GO possesses abundant oxygen-containing groups on its surface[2], which can be used to achieve surface modification and improve the interfacial interactions between GO and polymer, thus achieving uniform dispersion of GO. As far as we know, modifiers like some small-molecule compounds and polymer chains have been widely used to enhance the performance of various polymers[1, 9]. By comparison, among various compounds, hyperbranched polymers have aroused many attentions in reinforcing polymer recently[6].

In this work, we synthesized modified GO (MGO) via using amine-terminated hyperbranched polyamide as modifier. Then, the MGO-filled PU were obtained through cross-linking reaction between MGO and PU matrix. Various characterization methods have been conducted on MGO to determine the
successful modification. Moreover, the physical mechanics properties of composites have been evaluated carefully.

2. Materials and experiments

2.1. Materials
Hydroxyl-terminated polybutadiene (HTPB, 99.9%) was provided by Liming Research & Design Institute of Chemical Industry Co., Ltd., Luoyang, China. O-(7-azabenzotriazole-1-yl)-N,N,N,N’-tetramethyluronium hexafluorophosphate (HATU, 99%), Isophorone diisocyanate (IPDI, 99%), triphenylbismuthine (TPB), Dibutyl phthalate (DBP, 99.5%), N,N-dimethylformamide (DMF, ≥99.8%), ethanol (≥99.7%) and other reagents were obtained from Aladdin Co., Shanghai, China. GO (>99%) was provided by Nanjing XFNANO Material Technology Co., Ltd, China.

2.2. Modification of GO (MGO)
50mg of GO was added in 20mL DMF (solvent) and sonication for 1h. Then, 0.5g of HBPA was added in 10mL DMF and mixed with GO suspension. Subsequently, 5mg of HATU (catalyst) was added and sonicated for 3h at room temperature. Afterwards, the mixture was centrifuged, and the filter cake was washed with ethanol for at least 5 times. After that, the obtained solid(MGO) was dried at 60°C for 24h.

2.3. Preparation of composites
Composites were prepared via a facile solution blending method: (1) A certain amount of MGO was added in DMF through 1h of sonicating; (2) HTPB was mixed with the MGO suspension by mechanical stirring at 70°C for 6h; (3) The DBP (plasticizer) accounting for 13wt% of HTPB, IPDI (curing agent) accounting for 11.5wt% of HTPB and TPB (catalyst) accounting for 0.1wt% of HTPB were added. (4) The obtained mixture was injected into polytetrafluoroethylene molds and allowed them to curing at 60°C for 36h. By contrast, PU without any fillers and composites filled with GO were also fabricated. For convenience, the PU without any fillers was denoted as P-PU, the composites filled with GO were denoted as PUG-x, and the composites filled with MGO were denoted as PUM-x, where x is the mass fractions of GO or MGO.

3. Results and discussion

3.1. Modification of GO
Fourier transform infrared spectroscopy (FTIR) spectrum of GO are shown in Figure 1(a). It displays the characteristic peaks at 1728cm⁻¹, 1628cm⁻¹, 1053cm⁻¹, and 3300-3000cm⁻¹ corresponding to the stretching vibration of C=O, C=C, C-O, and the stretching vibration of O-H in hydroxyl and carboxylic acid of GO, respectively[11]. After modification, the peak of MGO at 1728cm⁻¹ disappeared. Meanwhile, the spectrum displayed some new peaks at 3250cm⁻¹, 2959-2850cm⁻¹, 1640cm⁻¹ and 1555cm⁻¹, which assigned to the stretching vibrations of N-H groups and -CH₃/-CH₂ groups, amide C=O stretching, the bending vibration of secondary amide, respectively, implying that GO was successfully modified by HBPA[4].

Figure 1(b) presented the X-ray diffraction (XRD) spectra of GO and MGO. Obviously, the spectrum of GO shows a broad peak at 2θ=10.46°, and its interlayer spacing can be calculated as ~0.85nm. After modified by HPBA, the 2θ peak of the spectrum of MGO has moved to ~9.05°, which can be calculated as a larger interlayer spacing of ~0.97nm. Additionally, there is a broad peak appearing ranging from ~15° to 25°, indicating that the MGO layers are loosely stacked during modification process[10].
Figure 1. (a, d) FTIR and TGA spectra of materials. (b, c) XRD and XPS spectra of materials. (e) STEM images of MGO. (f) elemental mapping of nitrogen on the surface of MGO.

X-ray photoelectron spectroscopy (XPS) can further determine the chemical composition of MGO and GO. As displayed in Figure 1(c), GO shows a C1s peak and O1s peak at 284.5eV and 533eV, respectively. After modification, it is apparent that the C1s/O1s intensity ratio of MGO increased. It is worth noting that a new N1s peak appears at 399.3eV on the spectrum of MGO, which further demonstrated the successful modification of GO. Then, the modification of GO can be further confirmed via the thermogravimetric analysis (TGA), and the results were summarized in Figure 1(d). It is clearly that there are two obvious weight loss stages of GO. The first weight loss stage is caused by the evaporation of absorbed water, and the second weight loss stage is attributed to the decomposition of oxygen-containing functional groups of GO[3]. Due to the modification of HBPA, the weight loss the second weight loss stage of MGO is significantly slow, and the third decomposition stage corresponding to the thermal decomposition of HBPA appeared, which further proved the successful modification of GO. Moreover, the modification of MGO was further demonstrated by the elemental mapping, and the images are shown in Figure 1(e) and (f). It can be seen that the nitrogen element, which are provided by HBPA, can be found on the surface of MGO.

3.2. Physical mechanics properties of composites

The physical mechanics properties of composites were tested and the corresponding curves are displayed in Figure 2. As seen in Figure 2(a), both tensile strength and fracture strain show the trend of first increasing and then decreasing with the increase of nanofiller content. Apparently, the composites filled with MGO showed better reinforcement in tensile strength and fracture strain than that of composites filled with GO. Specifically, when 0.05wt% nanofiller was added, the tensile strength of PUG-0.05 and PUM-0.05 increased by 31.9% and 33.9%, respectively, relative to P-PU. However, the PUM-0.05 can reach up a high elongation of 1158%, which is 170% higher than that of PUG-0.05. Additionally, the reinforcement effect of MGO become more remarkable at the same content of 0.1wt% compared to GO. The tensile strength of PUM-0.1 can reach up to about 0.4MPa, 57.8% higher than that of P-PU. It can be inferred that this outstanding reinforcement effect mainly owing to below factors: (1) the abundant -NH2 groups on its surface, which can react with IPDI to form well interfacial interactions between MGO sheets and matrix; (2) the unique molecular structure of HBPA improve the compatibility of MGO with matrix. Meanwhile, the fracture strain of PUM-0.1 increased simultaneously (1292.6%). Nevertheless, when MGO contents higher than 0.1wt%, both tensile strength and elongation
at break declined due to the aggregation of MGO. The high density of MGO in the matrix leads them to react with each other through IPDI to generate aggregates.

![Stress-strain Curve](image1.png)

![Creep Test Curves](image2.png)

**Figure 2.** (a) Stress-strain curves of various composites. (b) Tensile strength and fracture strain of various composites. (c) Creep tests curves of various composites for 3 successive cycles. Afterwards, creep tests are carried out to evaluate the resistance to deformation and recovery capability (Figure 2(c)). Obviously, P-PU exhibits high creep strain and residual strain, which also increase with successive cycles. As for composites filled with MGO, both their creep strain and residual strain all lower than that of P-PU, and only present little change after three creep cycles. But upon increasing nanofiller contents to PUG-0.2 and PUM-0.3, neither of them presents the same creep performance as PUM-0.2 due to the aggregation of GO and MGO.

**4. Conclusion**

In conclusion, we modified GO by using the HBPA as modifier through a facile method. The composition and structure of MGO are demonstrated by XPS、FTIR、TGA and TEM. The results of physical mechanics properties tests demonstrated that MGO can dramatically enhance the physical mechanics properties of PU. The tensile strength of PUM-0.1 increased by 57.8% compared with P-PU. In addition, creep tests exhibit the excellent deformation resistance and recovery capability of PUM composites when the MGO content is below 0.2wt%.

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