



# High performance polyurethane nanocomposite films prepared from a masterbatch of graphene oxide in polyether polyol

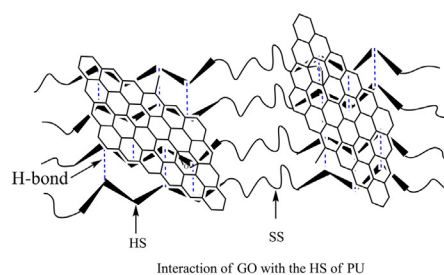
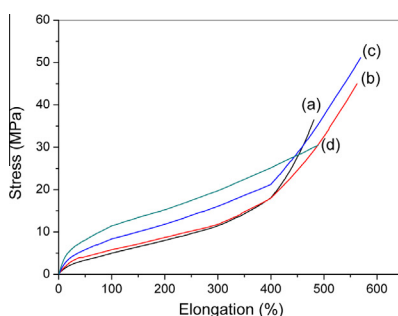
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## HIGHLIGHTS

- A masterbatch of GO in polyol was prepared and used for the preparation of PU composites.
- Grafted PU chain on the surface of GO facilitated the stress transfer benefit between matrix and filler.
- The effect of GO on the strain hardening of PU was investigated.
- The improvement of tensile strength without sacrificing the elongation of PU composites was most significant ever reported.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A masterbatch of graphene oxide (GO) in polyol was prepared and used for the preparation of polyurethane (PU)/GO nanocomposites by bulk in-situ polymerization. The prepared nanocomposites were characterized in terms of their thermal, mechanical, and morphological properties as a function of GO loading. Here, grafted PU chains on the surface of GO facilitated the beneficial stress transfer from the PU matrix to GO. This stress transfer occurs due to the reaction of the hydroxyl and carboxyl groups of GO with the isocyanate groups of 4,4'-methylene diphenyl diisocyanate (MDI) and the PU pre-polymer. The Young's modulus of the PU was improved by 280.5% through the incorporation of 3 wt% GO. Additionally, an improvement of 40.5% in the tensile strength and 19% in the elasticity was achieved at 1 wt% GO. Strain hardening of PU was improved with GO loadings up to 1 wt% due to the synergetic orientation of the soft segment and the PU-grafted GO in the strain direction. However, the large increase in cross-link density that occurred at 2 wt% GO prevented strain hardening, and the ultimate tensile strength decreased. The Halpin–Tsai model was used to predict the orientation of GO in PU nanocomposites. The randomly oriented 3D arrangement of GO in PU showed better agreement between the theoretically calculated and experimentally determined moduli compared to the 2D alignment. These results demonstrate that the preparation of PU nanocomposites using masterbatch dilution is an excellent method to attain well-dispersed GO. This technique can also be used to overcome the environmental problems associated with volatile organic compound (VOC) emission, as well as addressing some of the difficulties found in the plastics processing industry.

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## 1. Introduction

Graphene consists of a single atomic layer of graphite that can be fabricated by different exfoliation methods [1–7]. Transferring the exceptional electrical, thermal, and mechanical properties of graphene to polymer matrices allows for a substantial

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enhancement of multifunctional properties [8–18] at much lower loading fractions than polymer composites with conventional fillers [19,20]. One of the most versatile synthetic soft materials is polyurethane (PU), which is a popular commercial polymer that has been used in a diverse range of industrial applications [21]. Composites of PU with nanoclays and carbon nanotubes (CNTs) have shown a strong ability to comprehensively improve the physical properties of PU in order to develop next-generation PU materials for broader industrial applications [19–22].

Graphene oxide (GO) is an excellent filler for the reinforcement of PU [23–24] and contains oxygen groups at the basal plane and edges [23–27]. Using ultrasonication, GO can be simply exfoliated into thin carbon sheets in organic solvents [23–25], providing good dispersion in polymeric matrices. Liang et al. [28] employed isocyanate-modified graphene, sulfonated graphene, and reduced graphene as nanofillers in PU matrices by solution mixing processes. In their study, thermal degradation of an isocyanate-modified graphene/PU composite occurred at a much higher temperature compared to the sulfonated graphene and the reduced graphene/PU composites. Furthermore, the graphene/PU composite containing 1 wt% sulfonated graphene exhibited intriguing and reproducible infrared-triggered actuation performance with a significant improvement in mechanical properties. Nanoscale dispersion of functionalized graphene sheets (FGSs), at even small loadings in the PU matrix, effectively enhances the electrical conductivity of PU nanocomposites. However, the deleterious effects of FGS on the crystallization of the soft segment of PU can overshadow the reinforcement effect in nanocomposites [9].

Among the various polymer-compounding approaches for the preparation of GO/PU nanocomposites, such as melt mixing, solution mixing, and in-situ polymerization [24], in-situ polymerization followed by solution mixing is recommended for obtaining the highest degree of GO dispersion in the PU matrix. Wang et al. [29] reported an efficient method to prepare graphene nanosheet-reinforced PU composites by in-situ polymerization in which covalent bonding between graphene and PU was well suited to form composites by the reaction of the hydroxyl functional groups of graphene with the NCO groups of the PU pre-polymer and MDI [24,29,30]. Pei et al. [31] showed ultrahigh tensile strength and strain-to-failure with a greatly improved modulus by adding cellulose nanocrystals during the preparation of the PU pre-polymer. In their report, the amount of reactive hydroxyl groups on the cellulose nanocrystals was calculated using back titration with dibutylamine in order to determine the number of excessive isocyanate groups after reacting the cellulose nanocrystals with a known amount of MDI. Raghu et al. [12] prepared FGS-based waterborne polyurethane (WPU) nanocomposites by mixing an FGS dispersion in acetone and WPU with a solid content of ~30 wt%. Although they observed a large improvement in the electrical conductivity ( $1.31 \times 10^{-5} \text{ S cm}^{-1}$ ) of the composite film after the incorporation of 2 phr FGS, the tensile modulus of the composites decreased continuously until the filler concentration reached 5 phr. Kim et al. [24] prepared PU nanocomposites by incorporating isocyanate-modified GO (iGO) and thermally reduced GO (TRG) using three different methods: in-situ polymerization, solvent casting, and melt blending. A large improvement in the tensile stiffness, along with a decrease in nitrogen permeation, was observed with the addition of iGO by in-situ polymerization. To overcome the rapid growth in viscosity during in-situ polymerization, N,N-dimethylformamide (DMF) was added in their study.

The solvent casting method is not an attractive route to prepare PU nanocomposites due to the adverse effect of the solvent on the mechanical properties of PU, as well as volatile organic compound (VOC) emission during PU composite film formation [23,24]. Melt mixing is the most economically viable method from an industrial point of view and is desirable for the preparation of thermoplastic

polymer nanocomposites. However, the melt mixing method is limited for the preparation of PU nanocomposites due to the small difference between the degradation and melting temperatures of PU. Furthermore, melt mixing is not a suitable method to prepare GO/PU nanocomposites due to the poor dispersion of the GO in PU in the melt state; as a result, the mechanical properties of the nanocomposite decline with increasing GO content [24]. Additionally, the handling of carbon nanomaterials in the plastic parts manufacturing industry is often a key issue. Emission of carbon nanomaterials like CNTs, graphene, and GO into the environment, due to the potential widespread usage of carbon nanomaterials in industry, could result in an increase in human exposure. Serious toxicity by inflammatory and fibrotic reactions in the lungs can occur after exposure to carbon nanomaterials [32]. For this reason, strict preventive and protective measures should be taken to limit inhalation exposure to carbon nanomaterials. Production of a GO masterbatch in polyol is an attractive alternative as it offers a dust-free processing method with lower health and safety risks compared to the bulk carbon nanofillers dispersion process and the solution casting methods used for the production of GO-based polymer nanocomposites. Other benefits of using a masterbatch include elimination of dispersion difficulties and the need for formulation development, as well as an easier method for handling the material. The masterbatch processing route is attractive for most polymer nanocomposites manufacturing industries where the carbon nanomaterials are bound in a polymer or are a polymer component, which makes them easier to handle.

In comparison to nanocomposites prepared by solution mixing of GO in a polymer [23,24], a literature survey reveals the lack of detailed reports investigating the properties of GO/polyol masterbatches for PU nanocomposites. In the present work, GO/PU nanocomposites were produced by varying the GO content through dilution of a GO/polyol masterbatch and subsequent bulk in-situ polymerization. The thermal and mechanical properties of the prepared nanocomposites were characterized. Here, thin layers of GO sheets were generated during sonication. Restacking of the GO sheets was prevented by the adsorption of polyol onto the GO surface even after the removal of the solvent. The molecular level interaction between GO and PU increased the effective cross-link density of the elastomer network through the superior GO reinforcement in the PU nanocomposite.

## 2. Experimental

### 2.1. Materials

Synthetic graphite (lateral size <20  $\mu\text{m}$ ), potassium permanganate, tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) were purchased from Sigma–Aldrich and used as received. Sulfuric acid and hydrogen peroxide were purchased from Junsei Chemical Co., Ltd., Japan. 4,4'-Methylene diphenyl diisocyanate (MDI), poly(tetramethylene glycol) (PTMEG, average  $M_w = 1000 \text{ g/mol}$ ), and 1,4-butanediol (BD) were purchased from Sigma–Aldrich for the preparation of PU composites by in-situ polymerization.

### 2.2. Preparation of graphite oxide

GO was synthesized from synthetic graphite using Hummer's method with minor modification [2,33]. Briefly, 250 ml of  $\text{H}_2\text{SO}_4$  was placed in a three-neck flask and cooled in an ice bath. This was followed by the addition of 10 g of graphite. The mixture was stirred for 15 min at temperatures below 5 °C, after which 35 g of  $\text{KMnO}_4$  was added slowly over 15 min. After 30 min, the mixture was heated to 35 °C and the reaction was continued for 5 h. Then, the mixture was cooled in an ice bath, and excess  $\text{H}_2\text{O}$  (~500 ml) was added slowly. Unreacted  $\text{KMnO}_4$  was reduced through the

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