



# Effects of functional groups on the graphene sheet for improving the thermomechanical properties of polyurethane nanocomposites



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## ABSTRACT

Dispersibility of graphene sheets in polymer matrices and interfacial interaction are challenging for producing graphene-based high performance polymer nanocomposites. In this study, three kinds of nanofillers; pristine graphene nanoplatelets (GNPs), graphene oxide (GO), and functionalized graphene sheet (FGS) were used to prepare polyurethane (PU) composite by in-situ polymerization. To evaluate the efficacy of functional groups on the graphene sheets, PU reinforced with GNPs, GO, and FGS were compared through tensile testing and dynamic mechanical thermal analysis. The Young's moduli of 2 wt% GO and FGS based PU nanocomposites were found significantly higher than that of same amount of GNPs loading as an evidence of the effect of functional groups on graphene sheets for the mechanical reinforcement. The strong interaction of FGS with PU was responsible to exhibit notably high modulus (25.8 MPa) of 2 wt% FGS/PU composite than the same amount of GNPs and GO loading even at elevated temperature (100 °C).

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## 1. Introduction

Polyurethane (PU) is a block copolymer that consists of two phase morphology due to the thermodynamic incompatibility of the hard and soft segments [1]. Generally, the phase separation between the hard and soft segments and hydrogen bonding between urethane bonds determine the mechanical properties of PU. PU is the material of choice for a broad range of applications such as coatings, adhesives, rollers and tyres, composite wood panels, insulation of refrigerators and freezers, building insulation, cushioning for furniture, car parts, shoe soles, sportswear, etc [1,2]. After the study of PU on biocompatibility and biostability evaluation, it has been widely used in the preparation of implants and medical devices such as drug-controlled release carriers, cardiovascular implants and medical supplies [3]. Nanofillers such as carbon black (CB), carbon nanofibers, carbon nanotubes (CNTs), graphene, and

functionalized graphene sheet have been incorporated into polymer for the efficient reinforcement and superior functional properties [2,4–15]. Among the various nanocomposite systems, graphitic based fillers are superior to improve electrical and thermal conductivities, mechanical and tribological properties, dielectric performances and gas barrier properties of the all elastomeric matrices [2,12–16]. The interfacial interaction between the matrix and thin layer of graphene sheet plays a vital role in significantly improving the mechanical properties [15–17]. After a proper structural and interfacial organization of graphene with polymer matrix, the resulting nanocomposite can exhibit outstanding structural performance and multifunctional properties. The mechanical performances as well as thermal, electrical, and barrier properties of graphene based polymer nanocomposite depend on the processing techniques and morphological organization [9,14,15].

The surface properties of graphene can be chemically modified for specific purposes [11,18]. Oxidized form of graphene i.e. graphene oxide (GO) has been widely used as a nanofiller for the reinforcement of polymer-matrix composites [12–17]. The reactive functional groups of GO such as epoxide, carboxyl, carbonyl,

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and hydroxyl are very useful for the further modification with long chain of organic molecules or polymers. There are many reports in the literature that show the surface modification of carbon nanotubes (CNTs) and graphene by using different modifying agents [18–24]. The surface of CNTs has been already modified by silane compounds having ethylene, amine, epoxy, and thiohydroxy functional groups [22,25]. Such modification of CNTs was found effective to improve the compatibility of CNTs with the polymer matrix. Furthermore, the grafting of silane moieties on the surface of GO was very effective to further improve the interface between the filler and matrix, resulting superior mechanical properties of polymer nanocomposites [18,21]. Ou et al. [24] reported a self assembled monolayer of aminosilane on the silicon wafer via a self-assembly process, where the GO was grafted onto a silicon substrate covered with aminosilane through chemical reactions between the epoxy and amine groups. The covalently functionalized GO with aminosilane has been already used to prepare composite with silica monoliths [21], where the improvements of 19.9% compressive failure strength and 92% toughness of composite were observed with 0.1 wt% loading of filler. Chemically grafted GO with 3-aminopropyltriethoxysilane in aqueous medium generates many hydroxyl groups on the surface of graphene sheet due to the hydrolysis of ethoxy groups of aminosilane [12,13]. Costa et al. [26] observed the effect of functional groups on the carbon nanotube on the electrical, thermal and mechanical properties of carbon nanotube/styrene-butadiene-styrene for the preparation of electro-mechanical composites. In their study, even the dispersion of CNTs was improved by covalent functionalization, the electrical percolation threshold was achieved at ~8 wt% loading of covalently functionalized CNTs whereas pristine CNTs showed percolation threshold lower than 1 wt%. Bose et al. [27] reported various types of pre-treatments of carbon nanotubes on the properties of polymer/carbon nanotubes composites and discussed briefly about the various strategies designed to alter the dispersion stability and quality of nanotubes in the composites. The effects of the oxidative debris in the GO for a stronger interface with the poly(methyl methacrylate) matrix relative to base washed GO are also reported in the previous study [28], where improved mechanical properties of the GO based nanocomposites than base washed GO was observed due to the better dispersion of the GO sheets.

Reinforcement of an elastomeric composite is evaluated by studying the enhancement of the elastic modulus and the elongation at break with the addition of nanofiller. A hydrodynamic effect on elastomeric composite [29] depends on the filler volume fraction, but the polymer chain trapped within the filler agglomerates may increase the effective filler volume. The shape factor of filler also contributes to alter the modulus of elastomeric compounds. The basic methods and molecular mechanisms which provide to the reinforcement of elastomeric materials have been widely discussed. Active fillers can improve the modulus of elastomeric composites as the product of two terms. Hydrodynamic effect arising from the inclusion of rigid particles is considered as the first term as it is quantitatively taken into account by the Guth and Gold expression [29,30]. The increased cross-linking density created by polymer–filler interactions is considered as the second term. Recently, Modkour et al. [31] investigated the non-Gaussian behavior of self assembled thermoplastic PU using constant stress–strain relaxation and molecular modeling techniques. Mooney–Rivlin approach [29–33] has been used to explain the deviation of the elastomeric compounds from ideality. Bokobzaa et al. [34] showed the reinforcement effect of in situ generated silica in natural rubber. They noticed that silica particles generated before vulcanization appeared to inhibit the cross-linking reaction of

natural rubber compound by sulfur, and form a silica–silica network via the silanol groups present on the silica surface. The hydrodynamic reinforcement effect is mostly accountable for pristine CNTs or GNPs based elastomeric composites due to the inclusion of rigid nanofillers in the polymer matrix. On the other hand, functionalized graphene and CNTs based polymer nanocomposite prepared by in situ polymerization possibly can increase the crosslink density in their composites. Thus, both hydrodynamic and cross-linking effects are accountable for functionalized graphene and CNTs based PU nanocomposites.

In our previous study, the hydroxyl and carboxyl groups on the graphene sheet has been utilized for the grafting of PU chain by in-situ polymerization which results the dramatically improvement on the thermal and mechanical properties of PU nanocomposites [6,14,15,17]. A literature survey revealed that there are many reports on the nanocomposites prepared by solution mixing of graphene, GO or functionalized graphene in a polymer [2,7–9,12,13]. However, there was no any comparative studies that showed the effects of functional groups on the graphene sheet for improving the thermomechanical properties of PU nanocomposites. We believe that the optimal reinforcement in nanocomposites can achieve through the development of a strong interface between the filler and the polymer matrix. In that respect, a proper modification of GO is a major subject of our study to improve the thermomechanical properties of PU nanocomposites. Thus, GO was modified with aminosilane to increase the reactive site on the surface of GO for the grafting of PU chain. The changes on the morphologies, thermal and mechanical properties of PU nanocomposites with changing the fillers: GNPs, GO, and functionalized graphene were systemically investigated.

## 2. Experimental

### 2.1. Materials

Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), 3-Aminopropyltriethoxysilane (APTES), 4,4'-Methylene diphenyl diisocyanate (MDI), poly(tetramethylene glycol) (PTMEG, average Mw = 1000 g/mol), and 1,4-butanediol (BD) were purchased from Sigma–Aldrich. PTMEG and BD were kept in a vacuum oven for dehydration at 70 °C for 24 h before used. The NCO content in MDI was calculated by back titration with n-dibutyl amine (ASTM D2572-80). GNPs were synthesized from the natural graphite by previously reported ion-exchanged induced intercalation and exfoliation method [35]. GO was synthesized from a synthetic graphite using modified Hummers method [36,37].

### 2.2. Preparation of FGS

Colloidal suspension of GO (1 g) in water (1 L) was prepared by ultrasonication at room temperature for 3 h. Then, APTES (10 mL) was added drop-wise into the GO dispersion followed by additional ultrasonication for 1 h. A homogeneous brown precipitate of aminosilane grafted graphene sheet (AGS) was observed after the vigorous reaction between GO and APTES. A small portion of reaction mixture was separated and washed several times with ethanol to remove the free APTES completely, and labeled as AGS. Next, the reaction mixture was heated at 65 °C for 24 h, as a result the black suspension of functionalized graphene sheet (FGS) was observed. The mixture was washed several times with absolute ethanol and stored in a solution form with ethanol for the preparation of PU nanocomposites. Both AGS and FGS were dried in a vacuum oven at 65 °C for 24 h for the analysis by TGA, IR, and XRD.

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