



## Dielectric properties of modified graphene oxide filled polyurethane nanocomposites and its correlation with rheology



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### ABSTRACT

This study aims at investigating the dynamic mechanical, dielectric and rheological properties of reinforced polyurethane (PU) nanocomposites containing hydrophilic graphene oxide (GO) and/or hydrophobic modified graphene oxide (mGO) sheets. The organic modification of GO was performed with 4,4'-methylenebis (phenyl isocyanate) (MDI) and the samples were prepared by solvent mixing. We found that addition of mGO provides a more significant increase in the dielectric permittivity as compared to the addition of GO. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy demonstrate the more effective dispersion of thin exfoliated sheets of mGO in the PU matrix as compared to unmodified GO. This qualitative morphology observation is correlated with the quantitative results inferred from the dynamic mechanical analysis, rheology and dielectric studies. The viscoelastic Payne effect is noticed for all nanocomposites and the filler–filler and polymer–filler interactions are studied by applying the Kraus and Maier and Goritz models. The non-linear viscoelastic behavior of the PU nanocomposites is in good agreement with the Maier and Goritz model, which includes the effects of the adsorption/desorption of PU chains on the filler surface. The observed results underline the possibilities of PU composites with organically modified GO sheets in capacitor applications.

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### 1. Introduction

Polyurethane (PU) is an industrially important synthetic elastomer due to its excellent flexibility, elasticity and damping ability. These properties together with its high melt processability and tunable physical properties make this thermoplastic elastomer applicable in coatings, adhesives, foams, biomimetic materials and various diversified fields of modern technologies [1]. PU also possesses a high tensile strength, abrasion, tear resistance, and solvent resistance and combines properties of elastomers as well as thermoplastics. However, the applicability of PU (especially PUs having a small amount of hard segments) is still limited by its low stiffness, inferior gas barrier properties and poor conductivity [2]. Among various nanofillers employed for composite fabrication

with the objective to enhance the physical properties of PU, graphene and graphene oxide (GO) have utmost importance owing to their unique properties such as stiffness, strength, specific surface area, thermal conductivity and gas impermeability [3].

Since the properties of polymer nanocomposites largely depend on the dispersion of nanofillers within the matrix and the filler–polymer compatibility and interfacial interaction, several modifications of graphene fillers have been employed; often depending on the polymer nature [2]. A number of studies report on GO and functionalised graphene filled PU [4–6]. Khan et al. reported extremely stiff PU containing 55 wt% graphene [7], but the elasticity of PU was seriously deteriorated. GO consist of many polar groups such as hydroxyl, epoxide, ether and carboxylate groups as the result of oxidation [8]. Due to its polar nature, GO has only limited solubility in organic solvents and nonpolar polymers; thus necessitating surface treatments to improve the performance of the nanocomposites. Stiffness and scratch resistance of PU significantly enhance by GO addition [9]. However Nguyen et al. disclosed non-covalent interfaces leading to poor reinforcing effect of GO [10]. Thus the ideal

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interface for stress transfer was proposed to be covalent bonds forming between graphene/GO and the matrix PU [5,11,12].

In the present work the quality of dispersion of GO in PU is enhanced by introducing methylene diphenyl diisocyanate (MDI). The isocyanate (NCO) group at the end of the linear PU interacts with the oxygen groups on the GO. Solution mixing is employed in order to achieve a better dispersion of GO in the PU matrix and the filler concentration is varied from 0 to 3 wt%. Using MDI the GO filler surface is also modified. The dynamic mechanical, dielectric and rheological properties of the PU/GO nanocomposites were determined and compared with those of PU/isocyanate modified GO (mGO) nanocomposites and neat PU. Here the stiffness and toughness are enhanced without deteriorating the storage modulus. The qualitative information of dispersion from rheology is related with its quantitative assessment from dielectric property and dynamic mechanical analysis (DMA) depending on the filler concentration and reinforcement state. The extent of GO exfoliation in the final composites was characterized by X-ray diffraction scattering and electron microscopy. The entire study aims at developing a GO nanocomposite applicable in electronics.

## 2. Experimental section

### 2.1. Materials

The monomers, MDI and 1,4-Butanediol (1,4-BD) for PU synthesis were purchased from Interchemol S.A., Poland and BASF, Germany respectively. The polyol, poly (tetramethylene ether) glycol (PTMG, 1889 g/mol) was obtained from BASF, Hungary. Graphite, dibutyltindilaurate (DBTL), N,N-dimethyl formamide (DMF) and other reagents such as  $H_2SO_4$ ,  $HNO_3$ , HCl,  $KMnO_4$  and  $H_2O_2$  were procured from Sigma–Aldrich. PTMG and 1,4-BD were dried separately at 100 °C with stirring under reduced pressure. MDI was melted at 46 °C and filtered before use. All other reagents were used as received.

### 2.2. Synthesis of PU

In order to synthesize PU, a calculated amount of MDI was added to the PTMG, and the mixture was stirred at 80 °C for 1 h to obtain a prepolymer (with a theoretical concentration of 6.6% unreacted NCO groups). The MDI:PTMG ratio was maintained to be 2.6:1. Then, the prepolymer was mixed with 1,4-BD at a NCO/OH molar ratio of 1 while stirring vigorously and was poured into a hot mold (90 °C). The reacting mixture was annealed at 100 °C for 24 h to complete the reaction. Finally non-modified soft PU (containing 33.3% of hard segments) was obtained. Due to the low level of hard segments, the PU does not have a sharp  $T_m$ .

### 2.3. Synthesis of GO and modified GO

The synthesis of GO was carried out by oxidizing graphite followed by the improved graphene oxide synthesis method [13]. Required amounts of GO and MDI were dissolved in DMF and sonicated for 10 min. The mixture was then refluxed for 48 h at 100 °C. The precipitate was filtered and washed several times with DMF to remove the extra phenylisocyanate. The product was dried in a vacuum oven at 60 °C to obtain the functionalised GO nanosheet-phenylisocyanate complex.

### 2.4. Preparation of nanocomposites

PU nanocomposites were prepared by solution mixing. GO was first dispersed in DMF by bath sonication and then mechanically stirred with the PU/DMF solution for 3 h at 3000 rpm at 130 °C.

Samples were casted on Teflon sheet and dried in the vacuum oven at 110 °C. PU represents the neat matrix. PG0.5, PG1.5 and PG3 denote GO filled PU nanocomposites and PMG0.5, PMG1.5 and PMG3, the mGO filled PU respectively at 0.5, 1.5 and 3 wt%.

## 2.5. Characterization techniques

Atomic force microscopy (AFM) images were recorded with diC-aliber Veeco Instrument. The water drop volume for the contact angle measurements was 5  $\mu$ l in all cases and the temperature was 25 °C. The images were captured by online microscopy (GBX Digidrop intelligent version, France) using Windrop++ software and the measurements were repeated six to ten times for each sample specimen. Morphology of the samples was studied with a JEOL SEM-1400 Scanning Electron Microscope (SEM) at an acceleration voltage of 100 kV. Ultra-thin samples were cut using a cryogenic ultramicrotome Leica ultracut UCT at –90 °C. Dielectric measurements were done on samples of ~0.300 mm thickness using an ALPHA dielectric analyzer (Novocontrol Technologies) in the frequency range  $10^{-2} < F/Hz < 10^6$ , at 25 °C. Rheological measurements were performed with a controlled-stress rheometer (AR2000, ARES), equipped with a parallel plate geometry with diameter 25 mm at 160 °C. For the analysis, samples in the form of disks with approximately 2 mm thickness and 25 mm diameter, were prepared by compression molding at 100 °C for 3 min. A strain sweep at strains of 0.1–100% at a constant frequency of 1 rad/s was performed to determine the linear viscoelastic region. In addition, the elastic modulus ( $G'$ ) was measured in the linear domain in the frequency range between 0.01 and 100  $rad\ s^{-1}$  at a constant strain of 0.05%. Dynamic Mechanical Analysis (DMA) was performed with a metraVib device using rectangular-shaped samples ( $4 \times 2.5 \times 0.5\ mm^3$ ) in tension mode.

## 3. Results and discussion

### 3.1. Morphology and nature of modified GO

By using atomic force microscopy (AFM), the morphology and thickness of the synthesized GO and mGO nanosheets were analyzed. Samples of GO and mGO were coated on oxidized silicon wafers for good contrast in AFM imaging and tapping mode images were obtained as shown in Fig. 1a and b. Imaging was carried out in height, amplitude and phase modes simultaneously. The planar morphology of the GO and mGO nanosheets is clear from the images. The interplanar distances of GO and mGO are found to be roughly 1.5 and 3.3 nm respectively.

Next, contact angles of water droplet on both GO and mGO platelets were measured at room temperature to elucidate the effect of surface functionalization on the wettability. Fig. 1c and d respectively give the contact angles for the GO and mGO films. With a tilt angle of 0°, the true contact angle was determined as the average of the left and right hand side values. The calculated average contact angle value for the GO film is  $96.5^\circ \pm 4$  whereas for mGO, it is  $152.5^\circ \pm 6$  (Fig. 1c), thus proving the hydrophilicity of GO and hydrophobicity of mGO. The thermogravimetric analysis performed on mGO (Supplementary Information Fig. 1a) further confirms its hydrophobicity as no mass loss is evidenced at <180 °C temperature due to the grafted benzyl groups (from MDI) on mGO surface. The FTIR (Supplementary Information Fig. 1b) spectrum also assures GO modification by MDI.

### 3.2. Composite microstructure

Composite morphology was monitored using SEM micrographs of the cryo cut surfaces of PG3 and PMG3 samples (Fig. 2). The effect of filler nanosheets on the microstructure of the PU is very

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