

# Enhanced Dielectric and Electrical Properties in Polyurethane Composites with Graphene Nanosheets

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**Abstract.** The Electrical properties of polyurethane (PU) filled with graphene nanosheets (GRN) at low frequency is investigated. In last decade, polyurethane elastomers have attracted attention in transducer and actuator applications. The dielectric constant is one of the key factors for increasing actuator ability. Graphene nanosheets as conducting fillers have to be filled to increase the dielectric constant. In order to prove this idea, polyurethane composites with various graphene contents have been characterized by SEM and DSC. And their electrical capability has been measured at various frequencies of  $10^1$ - $10^4$  by using LCR meter. To gain the films, polyurethane composites filled with various graphene contents were prepared by solution casting method. The results showed a well homogenous dispersion of the graphene filler in the polyurethane matrix. In addition, it was found that the glass transition temperature ( $T_g$ ) of the PU/GRN increase as the content of filler increased and it can be affected the interfacial polarization between PU matrix with the GRN fillers. Therefore, it is found that graphene in the polyurethane matrix exhibit high enhanced the electrical properties and the optimal dielectric constant at 2wt% graphene of 9.74.

## Introduction

Recent work, it has been greatly studied about energy harvesting, sensor and actuator applications [1-2]. Among the various material, electroactive polymers (EAPs) are of the promising candidate materials which have the capability to convert energy from mechanical energy to electrical energy and vice versa. Compared to other materials, EAPs have various advantages such as flexibility, large dimensional change, easy processing, light weight, and low cost [3]. In several types of research have presented Polyurethane elastomers (PUs) are great interest for high-strain actuator due to large mechanical deformations  $> 10\%$  strains [4]. Moreover, PU has high dielectric constant because of a strong polarization to be induced under an electric field. It has reported in a recent study that the increase of the dielectric constant is one of the key factors for enhancing the energy conversion capability. The traditional approach of the increasing the dielectric constant is to disperse metals, ceramics, and carbon black into the polymer matrix. However, their disadvantages such as easily agglomerated and flexibility loss at a high filler concentration giving rise to the focus on the conductive filler composites. In fact, by using conductive fillers to increase the dielectric constant is interested. The various concept has been explained about conductive fillers can give achieving to the dielectric constant [5]. A theoretical according to the percolation threshold has been proposed to predict the dielectric constant, it is given by [5]

$$\varepsilon = \varepsilon^0 \left| \frac{f_c - f}{f_c} \right|^{-q} \quad (1)$$

Where  $\varepsilon$ ,  $\varepsilon^0$ ,  $f_c$ ,  $f$ , and  $q$  are the dielectric constant of the polymers matrix, the permittivity of free space, the percolation threshold, the volume content of conducting fillers, and the critical exponent, respectively.

In this present work, PU filled with graphene (GRN) at the various content of filler have been fabricated by solution casting. The dielectric constant including loss tangent and conductivity was measured by using LCR meter. Moreover, Scanning electron microscopy (SEM) and differential

scanning calorimetry have been used to prove the relationship between electrical properties with filler distribution and the glass transition.

## Experimental

Thermoplastic polyurethane elastomers (DP 9370A) were supplied from Covestro Deutschland AG. This PU used as a matrix is based on MDI (4,4 methylene bis(phenyl isocyanate) BDO (1,4-butanediol) as the hard segment and PTMO (poly (tetramethylene oxide)) as the soft segment. Graphene nanosheets were used as a filler as provided by Sigma Aldrich. The conductivity and particle size of graphene are about 4-6 S/cm and 2-3  $\mu\text{m}$ , respectively. The 1-Methyl-2-pyrrolidone with the 99% purity as a solvent was purchased from Sigma Aldrich.

Figure 1 shows the schematic preparation of PU filled with GRN films. Firstly, The PU granules were dried at 80 °C for 24 hours. Then PU granules were dissolved in 1-Methyl-2-pyrrolidone (NMP, 99% purity, M79603, Sigma Aldrich) under mixing at 80 °C for 45 minutes to obtain a homogeneous solution. Graphene nanosheets were added into the NMP and dispersed for 20 minutes by using ultrasonic. And then graphene solution was added into PU matrix and continuous mixing at 80 °C for 3 hours to gain homogeneous solution. The final solution was cast onto a glass surface at 60 °C by a casting method and dried in the oven for 24 hours to remove the solvent. Finally, the PU/GRN film was taken off from the glass surface and annealed at 125 °C for 3 hours to remove remaining solvent.

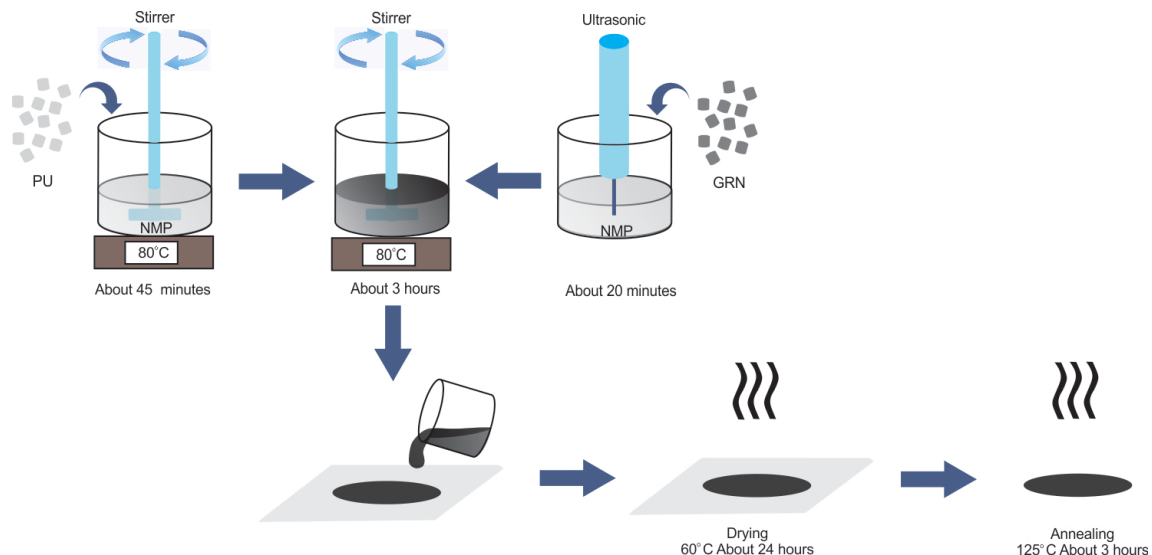


Fig. 1 Schematic illustration of PU/GRN films preparation

The PU/GRN composites were characterized in the matter of their dielectric properties, electrical properties, morphological structure, and thermal stability. Structure and morphology of the three-phase composite films were observed by using scanning electron microscopy (SEM, FEI Quanta 400, USA). The electrical properties such as dielectric permittivity, loss tangent, and conductivity were assessed across  $10^0$ - $10^5$  Hz by an LCR meter (IM 3533 HIOKI) as shown in figure 2. A Differential Scanning Calorimeter (DSC, Perkin Elmer DSC7, USA) was used to investigate the melting temperature ( $T_g$ ) where the samples of 10 mg were cooled under liquid nitrogen till  $-150^\circ\text{C}$  and after that heated till  $250^\circ\text{C}$  with the heating rate at  $5^\circ\text{C}/\text{min}$ .



Fig. 2 LCR meter and Scanning Electron Microscopy

## Results and Discussion

The dielectric constant and loss as a function of frequency from 10 Hz to  $10^4$  Hz for the PU with various GRN filler contents have been shown in Fig. 3 and 4, respectively. It is found that both the dielectric and loss tangent are decreased with the progressive increase of frequency. The decrease of dielectric constant and loss tangent might be due to unresponsive dipoles of GRN to align themselves with the fast frequency in the AC electric field and it leads to the minimum value of interfacial polarization between PU matrix with GRN fillers. In the contrary, the interfacial polarization responded at the low frequency. Furthermore, it is shown that the dielectric increases with the increasing GRN filler content, as can be seen in Fig 5. GRN fillers were blended in the PU matrix acts as a minute capacitor. It means that GRN provides capacitor ability in the polymer matrix. The dielectric constant of polymer composites is linearly to the proportional of the number of the capacitor, increase the dielectric constant depends on increasing filler volume fraction, as explained in the equation 1. Moreover, recently study has been predicted theoretical based on percolation threshold which is accurate with experimental results only at the higher content of filler [6]. Figure 6 shows the random homogeneous dispersion of GRN fillers in the PU matrix. It can be clearly seen the great interface between nanosheets of GRN fillers in the PU matrix. The great interface provides evidence of interactions and good compatibility and can be confirmed why the increase dielectric constant is due to the increasing content of filler.

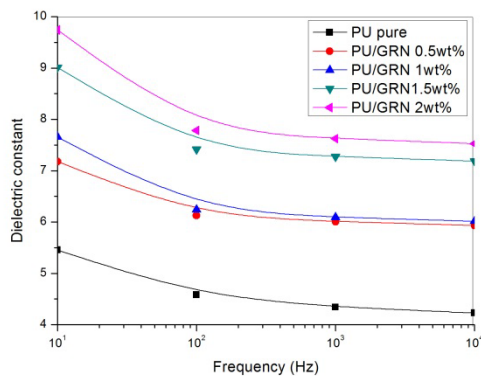


Fig. 3 Effect of frequency on dielectric constant for PU filled with various content of GRN

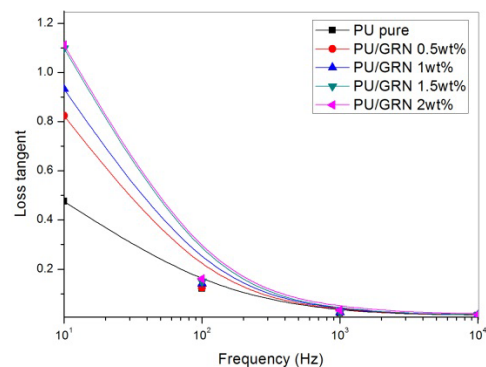


Fig. 4 Effect of frequency on loss tangent for PU filled with various content of GRN

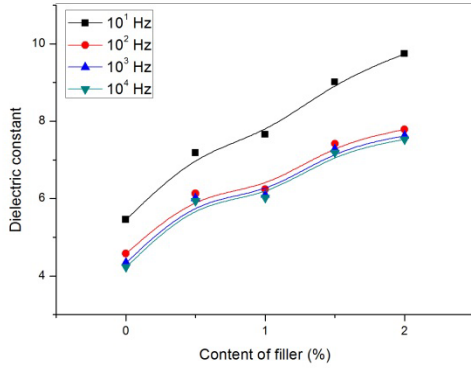


Fig. 5 Effect of GRN content on dielectric constant at Various frequencies

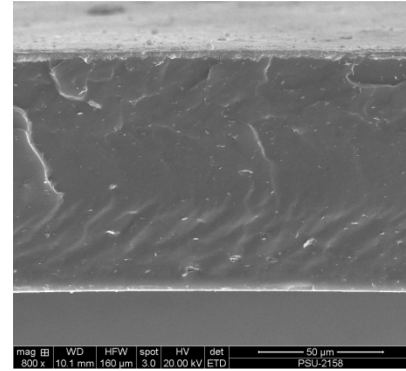


Fig. 6 SEM cross section image of PU filled with GRN at 2wt%

Fig. 7 depicts the conductivity of PU/GRN composites versus the frequency at a different volume fraction of GRN. The conductivity for all PANI/GRN composites is obtained to be constant at the frequency below 10<sup>2</sup> Hz. However, it is found to be slightly increased and large deformation in the range 10<sup>2</sup>-10<sup>3</sup> Hz and upper 10<sup>3</sup> Hz, respectively. The various phase may be due to a different kind of polarization around a charge in localized state. Another reason is that the increasing AC frequency influences the conductivity and lead to reducing the charge storage capability. In addition, no obvious different the variation of the conductivity as a function of content filler of GRN. It is found that the increasing content filler of GRN increases the value of the conductivity. In this case, the increasing conductivity may be due to nanosheets of GRN which provide the incorporation of charge carriers and the variation of filler content increases the number of charge carriers. In addition, the conductivity is depend on the effective loss tangent as according to the Equation 2 [7].

$$\tan \delta = \frac{\epsilon''}{\epsilon'} + \frac{\sigma}{\omega \epsilon_0 \epsilon'}$$
(2)

In order to study The glass transition temperature (T<sub>g</sub>) of PU/GRN composites, The DSC technique was used to confirm the interaction between PU matrix and GRN filler. The glass transition temperature significantly increased with increasing content of GRN as presented in Figure 8. The highest value of T<sub>g</sub> occurred at -67.37 °C. The increase value of T<sub>g</sub> was due to the interaction of GRN with the hard segments of PU that can be retraining the mobility of soft segments [8].

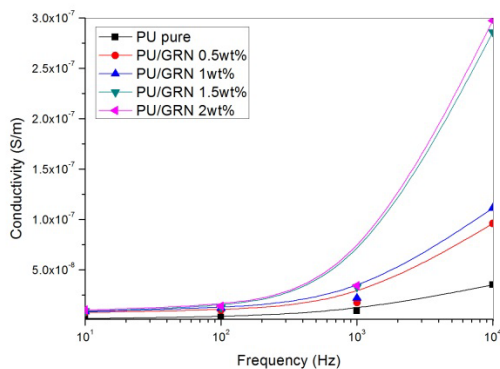


Fig. 7 Effect of frequency on the conductivity for PU filled with various content of GRN

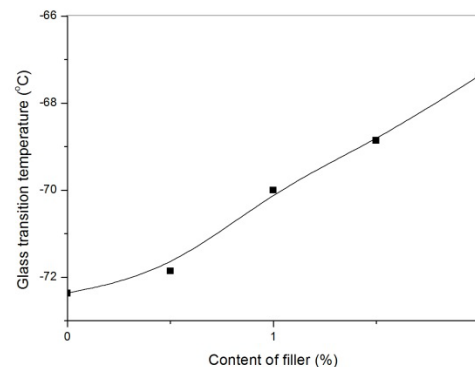


Fig. 8 Effect of GRN content on the glass transition temperature

## Summary

In this work, the dielectric and electrical properties of polyurethane composite films filled with graphene nanosheets were studied. The influences of graphene loading are enhanced the dielectric constant and loss tangent. The increasing dielectric constant might be due to capacitor ability of GRN fillers and also the great interaction between the PU matrix with GRN fillers. It is shown that the dielectric and loss of PU/GRN composite films are suddenly decreased when the frequency increases. Moreover, the conductivity increased at high frequency can be explained using theory of charge carrier. The DSC results show the glass transition of composites increase with increasing GRN content, this effect occurred because of interaction between fillers with the hard segments of PU matrix.

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