Electrostrictive Properties of Polyurethane Three-Phase Composites

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Thesis Title	Electrostrictive Properties of Polyurethane Three-Phase Composites
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ABSTRACT

Recently, electroactive polymers such as polyurethane (PU) are the one promising for an actuator application and energy harvesting. The dielectric permittivity is one of the key factors for increasing the electrostrictive properties. The conductive polymer and carbon have to be filled in order to increase the dielectric permittivity. The first experiment of this work, the conductive carbon such as graphene was used to improve the dielectric permittivity. Second, the PU three-phase composites were prepared with graphene combined with polyaniline. To gain the films, the solution of PU three-phase composites were prepared by films casting method. The effect of three phase composite in term of dielectric permittivity, electrical, mechanical, and electrostrictive properties was investigated. The dielectric and electrical properties were monitored via LCR meter, while the mechanical properties were determined using a strain gauge setup. The results show that the dielectric permittivity and electrical properties improve with increase filler concentration, which was related to a combined effect in the PU three-phase composites. The characterized results from SEM, FTIR, and DSC was used to support the idea. Finally, the electrostrictive behavior of PU three-phase composites was assessed by measuring the deformation under high voltage with a photonic displacement apparatus. In comparison, the result of the elctrostrictive properties of the PU three-phase composites is greater than their separate composites. Therefore, the PU three-phase composite has considered to be a great polymer for actuator applications and energy harvesting.

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“In the name of Allah, the Most Gracious and the Most Merciful”

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The Relevance of the Research Work to Thailand

The objective of this Master of Science Thesis in Physics is to study the electrostrictive properties of polyurethane three-phase composites for actuators and energy harvesting applications at low frequency. In Thailand, the polyurethane polymers was used for several applications such as footwear soles, automotive seats, and coating. The other benefits of the polyurethane polymers for actuators and energy harvesting applications were discussed in this research work. The major work involved the electrostriction of the polyurethane three-phase composite which using graphene nanosheets and polyaniline nanopowders as fillers. The modified electroactive polymers in this work can be applied for actuators and energy harvesting in several parts of Thailand such as:

- Artificial muscles
- Micro-actuators in low frequency devices
- Energy converter applications
- Micro-fluidic and valves
- Medical devices
- Acoustic transducer

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LIST OF ABBREVITIONS AND SYMBOLS

A	Area of sputtered electrode
C_p	Capacity
d	Lattice spacing
ε_0	Dielectric permittivity of vacuum (ε_0 = 8.854 x 10^{-12} F/m)
ε	Permittivity of dielectric constant
E	Electric field
f	Frequency
ΔH_m	Enthalpy change
M_{33}	Electrostrictive coefficient
M_M	Maxwell stress induced-strain coefficient
P	Polarization
Q	Polarization-related electrostriction coefficient
S	Strain
S_E	Strain from electrostriction effect
S_M	Maxwell strain
t	Sample thickness
Y	Young’s modulus
AFM	Atomic Force Microscopy
BDO	1,4-butanediol
CB	Carbon black
CNT	Carbon nanotube

CP	Conductive polymer
DSC	Differential Scanning Calorimeter
EAPs	Electroactive Polymers
FTIR	Fourier Transform Infrared Spectrometer
GRN	Graphen nanoheets
HS	Hard-segment

LIST OF PUBLICATIONS

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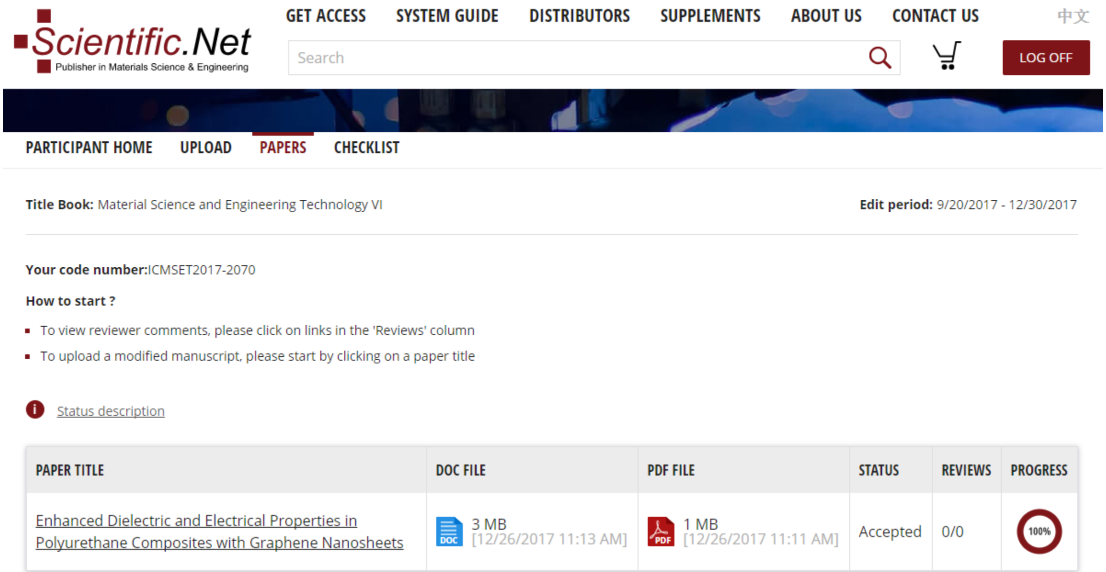

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Enhanced Dielectric and Electrical Properties in Polyurethane Composites with Graphene Nanosheets	3 MB [12/26/2017 11:13 AM]	1 MB [12/26/2017 11:11 AM]	Accepted	0/0	100%

Chapter 1 Introduction

1.1 Scientific background and motivation of the research

In recent decades, scientists have found a device to generate the electrical energy from the environment such as the windmill and the waterwheel. Converting or generating energy from the environment is called energy harvesting. As a potential energy source, the first important of mechanical vibrations is that they are present almost everywhere. Mechanical vibrations source occur in many environments such as transport, buildings, industrial, terrains, human activities, military devices, and etcetera (Seah et al., 2012). Considering the mechanical vibration source, electroactive polymers (EAPs) are kind of smart material polymers which perform energy conversion between the electrical and mechanical forms. The various advantages of EAPs are flexibility, large dimensional change, easy processing, light weight, and low coast (Li et al., 2004). EAPs can be used in the various application, such us actuators, vibration controls, medical ultrasound, electronics, automotive, energy conversion, and etc. (Lang and Muensit, 2006). Moreover, the electronic EAPs are activated by the electric field and it have a faster response than ionic EAPs (Bar-Cohen, 2010). The devices that can convert energy from mechanical energy or vibration into electricity and vice versa might be categorized in electromagnetic, electrostatic, electrostrictive, and piezoelectric converters.

Recently, electrostrictive polymers has good opportunities for actuators and energy harvesting, since their large >10% strains (Guyomar et al., 2012). Electrostrictive polymers have investigated for energy harvesting as well. The energy harvesting power can be increased by increasing the electrostrictive performance. Actually, electrostrictive abilities in a polymer is depend on dielectric permittivity and Young's modulus. Previous work mainly focuses on piezoelectric materials. However, due to piezoelectric has brittleness, problem in term of depolarization, and lead to crucial challenges in long-term operation. Compered to the piezoelectric materials, electrostrictive materials have advantages such as flexibility, large dimensional change, easy processing, light weight, and low cost. Therefore, the electrostrictive polymers have good promised because of their incredible capabilities as energy converter (Eddiai et al., 2012).

As an electrostrictive polymers, polyurethane is a great interest for actuator and energy harvesting applications due to their high specific energy, large deformations and fast response time (Wongtimnoi et al., 2011). The polyurethane as electrostrictive polymers can gain large actuator ability, it can change energy from electrical energy and mechanical energy and might be benefit in actuator applications. It can use for another application like energy harvesting due to they could convert mechanical energy to electrical energy. In recent work, polyurethane (PU) is large deformation under an applied electric fields of 20 MV/m. By the reason of PU having a high dielectric permittivity and due to a strong polarization occurred under an applied electric field. Moreover the better interactions of dipole lead to raise great electrostrictive ability (Jaaoh et al., 2016).

In recent work on polyurethane with conducting polyaniline composite presented the dielectric permittivity is increase to improve the electrostriction. The dielectric permittivity is an important key factor because it can directly affects the strain under electric field in actuators applications (Jaaoh et al., 2016). Moreover, modified polyurethane with highly conductive fillers such as polyaniline is the most popular methods that improve the interfacial polarization in composites. The interfacial polarization is one of the key factors for increasing the dielectric permittivity. In previous work Polyaniline emeraldine base dope with hydrochloric evidently exhibit a homogenous dispersion and lead to increase strain response (Putson et al., 2016).

In the previous literature, 2D conducting filler like graphene nanosheets have good attention in the field of polymer nanocomposites where the graphene has incredible electrical properties which can achieve the high dielectric permittivity of PU/CNT-GRN of 225 in the low frequency (Chen et al., 2015).

Consequently, large strain induced-electric field base on electrostrictive polyurethane can occur when the combination of fillers between the conducting polymer polyaniline and graphene were used. The main education advantages of the work are to produce large electrostriction from obtained polyurethane composite films and understand their mechanisms based on the correlation of the accumulated charges and interfacial polarization effects. Effect of fillers depend on their, dielectric, mechanical properties and electrostriction of all samples will be studied.

1.2 Aims of the research

The aim of the research is to enhance the electrostriction performance of the electrostrictive polymer. Three strategies were carried out as follows:

Strategy I: the electrostrictive PU was prepared with the various conductive fillers to enhance the electrostrictive coefficient.

Strategy II: the graphene nanosheets was filled with the electrostrictive polyurethane in order to improve the electrical properties **(Paper I)**.

Strategy III: study the electrostrictive effect of the modified electrostrictive polyurethane three-phase composites **(Paper II)**.

1.3 Thesis organization

The thesis is divided by five chapters. The first chapter presents the scientific background, motivation of the research and general concept of electroactive polymers (EAPs), particularly the electrostrictive polymers.

Chapter 2 shows the preparation and characterization of the electrostrictive polyurethane modified with the conductive fillers such as graphene nanosheets and polyaniline.

Chapter 3 presents the dielectric and electrical properties of polyurethane filled with graphene nanosheets. The theoretical is described to understand the effect of conductive filler to the dielectric and electrical performance.

Chapter 4 proposes the electromechanical ability of the modified electrostrictive polyurethane three-phase composites and discussion is provided as well.

Finally, the last chapter summarizes of the respective conclusions in the several chapters of the thesis and the future research suggestions are given to improve the present work.

1.4 Concept of EAPs

1.4.1 Electroactive polymers (EAPs)

In recent studies, electroactive polymers (EAPs) are smart materials that can change their size or shape due to the electrical stimulaton to be induced in polymer matrix (Pelrine et al., 1998). The electronic EAPs materials are driven by an electric field. While, the ionic EAP are deformed their shape because of ion motion under the electroactive EAPs are classified to be two categories such as electronic and ionic electroactive polymers. The types of EAPs are presented in Table 1.1.

Table 1.1 Classification of Electroactive EAPs in two main groups and representing some of their selected subdivisions

EAPs	
Electronic EAPs	Ionic EAPs
Dielectric elastomer	Ionic polymer-metal composite (IPMC)
Piezoelectric polymer	Ionic polymer gel (IPG)
Electrostrictive polymer	Conductive polymer (CP)
Electrostrictive paper	Conductive carbon

Electroactive polymers (EAPs) can convert the mechanical energy under the applied electric field, it has been studied by researchers as alternative materials for wide range applications such as actuators or artificial muscles. In recent studied, electrostrictive polymer is the one promising for several actuator applications and from vibration sources such as human motion perhaps can be used for harvesting energy (Cottinet et al., 2010). Summary of the advantages and disadvantages of two basic EAPs group are listed in Table 1.2.

Table 1.2 advantages and disadvantages of the electronic polymer (EAPs)

EAPs type	Advantages	Disadvantages
Ionic EAPs	- Large bending displacements - Provides mostly bending actuation - Requires low voltage	- Do not hold strain under DC voltage - Slow response - Bending EAPs induces a relativity low actuation force - Difficult to produce a consistent material
Electronic EAPs	- Long life in room conditions - Rapid response - Hold strain under DC activation - Induces relativity large actuation force	- Requires high voltage (150 MV/m) - Requires compromise between strain and stress - Glass transition temperature is inadequate for low-temperature actuation task

1.4.2 Electrostrictive polymers

Electrostrictive polymers are kind of electroactive polymers. It is the new category of smart materials (Jaaoh et al., 2016). Electrostrictive generally presents a quadratic of the strain under the electric field, as presented in Figure 1.1. This phenomenon is called electrostriction effect and occurs in all dielectric materials.

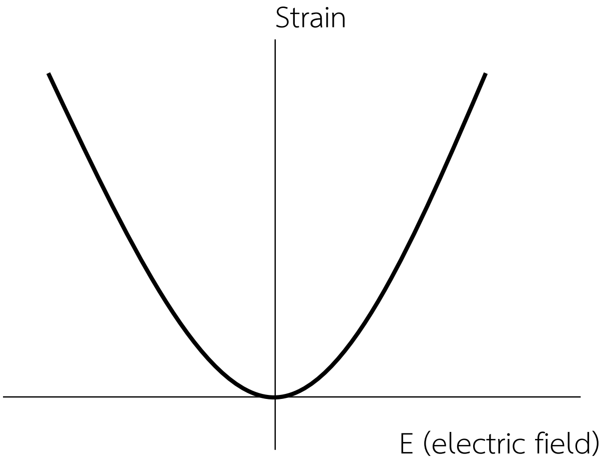

Figure 1.1 Schematic representation strain with electrical field (Guyomar et al., 2012)

Electrostriction effect depends on two distinct contributions. It is known as S_E which corresponds to true electrostriction while other contribution known as S_{max}, is strain due to the electrostatic stress (Maxwell) and occur between the two electrodes. For the strain due to electrostriction S_E may be given by (Su et al., 2003):

$$S_E = Q.P^2 \tag{1.1}$$

Where ***P*** is the polarization induced by an electric field ***E*** in polymer films and ***Q*** is the intrinsic electrostrictive coefficient. Then, ***P*** depends on the dielectric permittivity is written as:

$$P = \varepsilon_0.(\varepsilon_r' - 1).E \tag{1.2}$$

Where $\boldsymbol{\varepsilon}_r$ is the relative dielectric permittivity real part commonly called the dielectric permittivity and the strain due to electrostriction might be given as:

$$S_E = Q.\varepsilon_0{}^2.(\varepsilon_r' - 1)^2.E^2 \tag{1.3}$$

In the contrary, the strain caused by the Maxwell stress effect, it is called electrostatic strain $\boldsymbol{S_{max}}$, may be expressed as (Pelrine et al., 2000):

$$S_{Max} = \frac{-\varepsilon_r'.\varepsilon_0.E^2}{Y} \tag{1.4}$$

Where $\boldsymbol{Y}$ is the Young's modulus of the polymer films. The total of the strain is given by:

$$S = S_E + S_{Max} = M.E^2 \tag{1.5}$$

Where $\boldsymbol{M}$ is the electrostrictive coefficient, in condition of the thickness strain in the same direction with the applied electric field. In fact of experiments, these both contributions such as electrostrictive and Maxwell stress are very difficult to diveded from each other (Wongtimnoi et al., 2011). For the electrostrictive polymers such as polyurethane, $\boldsymbol{S_E}$ might be larger value than compared with $\boldsymbol{S_{max}}$, and $\boldsymbol{M}$ is related to the intrinsic electrostrictive coefficient $\boldsymbol{Q}$ through

$$M = \varepsilon_0{}^2.(\varepsilon_r' - 1)^2.Q \tag{1.6}$$

Moreover, intrinsic electrostrictive coefficient $\boldsymbol{Q}$ is inversely proportional to the value of the dielectric permittivity and Young's modulus (Guillot and Balizer, 2003) according to:

$$Q \propto \frac{1}{\varepsilon_0 . \varepsilon'_r . Y} \qquad (1.7)$$

Therefore in dielectric material for $\boldsymbol{\varepsilon'_r}$ >> 1, electrostrictive scoefficient $\boldsymbol{M}$ is proportional to the dielectric permittivity and inversely proportional to the Young's modulus of the dielectric material (Guillot and Balizer, 2003):

$$M \propto \frac{\varepsilon_0 (\varepsilon'_r - 1)^2}{\varepsilon'_r Y} \qquad (1.8)$$

Nowadays, polyurethanes (PU) are interesting material for the large strains in applied low electric fields. Compared to another polymer, polyurethane was highest strain as shown Table 1.3.

Table 1.3 Strain and the Young's modulus comparison of polymers

Polymer	**Strain (%)**	**Young's Modulus (Mpa)**
Polyurethane	11	17
Silicone	32	0.7
Fluoro silicone	28	0.5
Ethylene propylene	12	1.8
Polybutadiene	12	1.7
Isoprepene	11	0.85

1.4.3 Conducting polymers

In fact, the conventional materials such as metal and alloys are present agglomeration in polymer matrix when increasing the filler loading. Therefore, polymer matrix filled with conductive polymer are of interest for enhanced electrical properties. Polyaniline is a kind of conductive polymer which common used in electrical engineering applications due to the highly dielectric permittivity, however its relatively high conductivity in polymer matrix (Jaaoh et al., 2014).

Table 1.4 is shown a comparison of dielectric permittivity and power density of various polymer composites. In summaries, polyurethane with polyaniline filler is presented the highest dielectric permittivity and electrotrictive coefficient. Even if PU/PANI has the higher Young Modulus than PU pure, moreover the electrostrictive properties still high since the electrostrictive coefficient depends on dielectric permittivity.

Table 1.4 comparison of dielectric permittivity and power density between polymer composites

Sample	ε_r (at 20 Hz)	Y (MPa)	M_{31} ($\times 10^{-18}$ m^2/V^2)
PU PURE	4.68	22.5	1.91
PU/PANI 2%	12.40	24.5	2.77
PU (DMF)	6.77	25.3	1.70
PU 1%C	8.30	40.0	9.87
PU 0.5%SiC	5.10	80.0	4.11
PU/nCu 3%	7.80	50.4	12.56

1.4.4 Conducting Carbon

According to the electrostrictive equation, in order to gain a good dielectric polymer with large deformation strain under low electric field, the electromechanical capability is the important point, as we know before that the electrostrictive coefficient defined as the value of the dielectric permittivity versus Young's modulus (Hu et al., 2014). Hence, an good suggestion is to increase dielectric permittivity and largely decrease Young's modulus in the dielectric elastomer (Zhao et al., 2013). Almost all dielectric polymers, such as polyurethane, silicones, and crylics have poor dielectric permittivity of less than 10. Another method to increase the dielectric permittivity is fabricate the composite which is nanofillers are added into polymer matrix, this method has been carried out with the high dielectric permittivity in polymer composites. These nanofillers might be seperated into four categories such as ceramic nanofillers (e.g., $PbZrTiO_3$, $BaTiO_3$), organic semiconductor (e.g., CuPc), organic dipoles (e.g., Nally-N-methyl-p-nitroaniline), and conductive carbon (e.g., CNT, CB, GRN). The typical nanocarbon materials like graphene nanosheets 2D, which have much attention in term of polymer composites because of their incredible electrical properties, it has used for conducting carbon filler and It can improve other properties such as mechanical properties and electromechanical properties at very low loading contents.

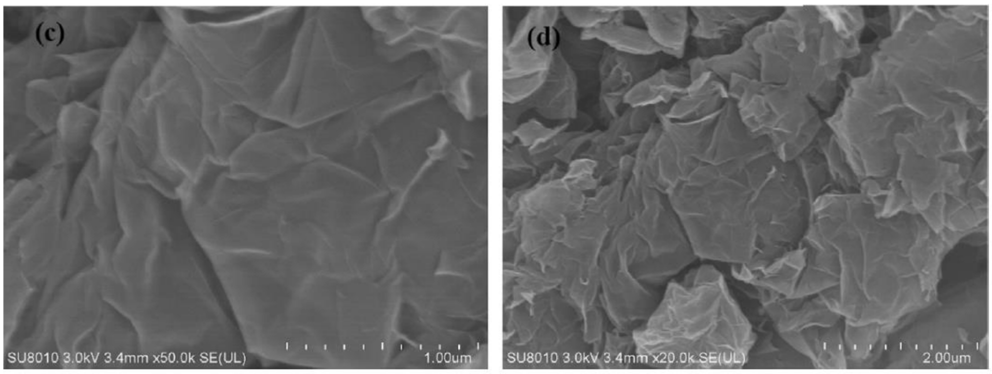

Figure 1.2 SEM images of GRN in PU matrix (Chen et al., 2015)

Figure 1.2 displays micrographs of PU/GRN, The GRN nanosheets present well dispersion in polymer matrix. GRN nanosheets are homogenously dispersed due to their chemical structure. It confirmed that GRN consists of nanosheets which is randomly aggregated and good interaction with each other.

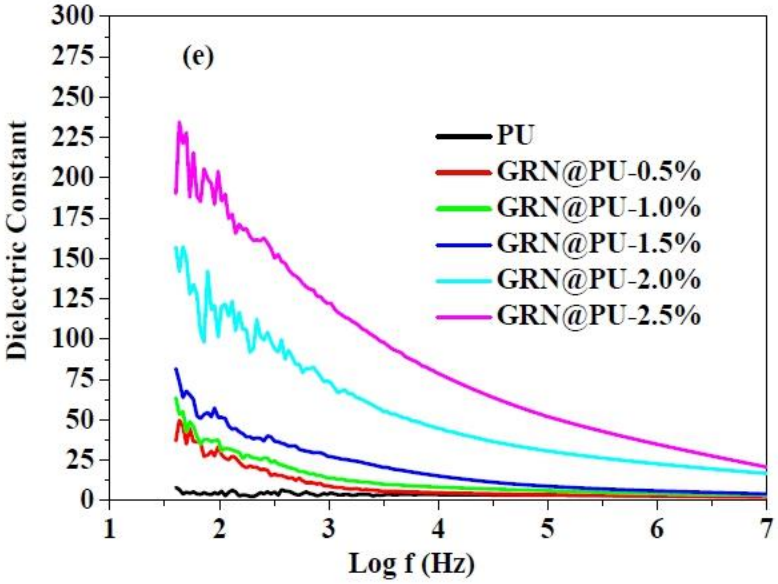

Figure 1.3 Dielectric properties of PU pure and PU/GRN composite (Chen et al., 2015)

Frequency-dependent dielectric properties at room temperature are shown in Figure 1.3, of both pure PU and variation filler of PU/GRN. As we can see that the dielectric permittivity in all samples decrease when increasing the frequency. Moreover, the dielectric permittivity of the PU filled with GRN is higher than the PU pure because of interfacial polarization effect between the PU matrix with the conducting fillers.

1.5 Conclusions

Electrostricitve polymers are considered great interest for several actuator and transducer applications, in consequence of large strain under applied electric field, high specific energy, and faster response. While the ionic EAP subdivisions, the conductive polymers such as polyaniline have high electrical properties and leads to generate large deformation. The graphene nanosheets offer extraordinary electronic due to strong dispersion in the elctrostrictive polymer. Therefore, the electrostrictive polyurethane and both fillers was studied to discover the effect of fillers for high electromechanical properties.

Chapter 2 Preparation and characterization of electrostrictive polyurethane three phase composites

2.1 Introduction

In order to improve the electromechanical ability, the electrostrictive polymers require a high dielectric permittivity and low Young’s modulus as previous mention. Regarding the comparison of various polymer matrix, thanks to the high dielectric permittivity over 5 and their elasticity, polyurethane is the best candidate for the actuator and sensor applications (Jaaoh et al., 2014). In addition, to gain the prospective high electrostriction ability, the dielectric permittivity and low modulus of electrostrictive polyurethane need to be improved. In the previous literatures, the conductive polymers and carbon such as polyaniline and graphene have a good electrical properties (Mondal and Khastgir, 2017). Hence, the main interest of this work is to prepare the combination electrostrictive polyurethane with the polyaniline and graphene in the purpose of improving the electrical properties. In present work, the electrostrictive polyurethane were prepared by solution casting method, for comparison electrical and mechanical behavior, the electrostrictive polyurethane were modified by adding the polyaniline nanopowder and graphene nanosheets. To supporting the idea, the morphology, chemical structure and the thermal behavior of electrostrictive polyurethane and their composites were assessed by a scanning electron microscope (SEM), Fourier Transform Infrared Spectrometer (FTIR) and Differential Scanning Calorimeter (DSC). These primarily properties are discussed upon the effect to electrical and electrostriction properties that are discussed in the details in chapter 3 and, respectively.

Polyurethane (PU) is commercially available polymers which were used in this work due to their larger dielectric permittivity at low frequency. In addition the increasing dielectric permittivity can be increased by filled the graphene nanosheets and polyaniline nanopowders in the polymer matrix. Their blends were prepared in the laboratory, the polyurethane filled with both fillers was blended by a magnetic stirrer. In order to gain the films, the solutions were cast onto glass plate. Their morphologies, chemical structure and termal behavior are also explained in this section.

2.2 Literature reviews of polyurethane, polyaniline and graphene

2.2.1 Polyurethane

The chemical structure of PU is presented in Figure 2.1. The hard segment content is about 46% and the physical properties depend on partially on the phase separation degree between hard and soft phases. The hard-segment domains act as physical cross-links in the soft-segment matrix. The soft segment is represented the flexible character of the polymers. Figure 2.2 shows three basic building blocks such as a polyether as a soft-segment, a diisocyanate as a hard-segment, and urethane bonded interphase.

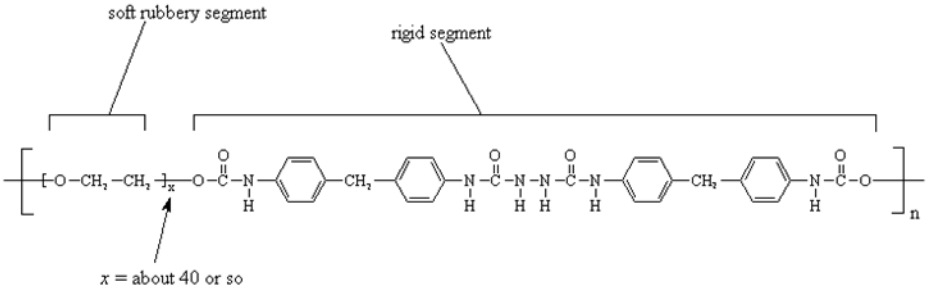

Figure 2.1 structure of Polyurethane (Wallace et al., 2002)

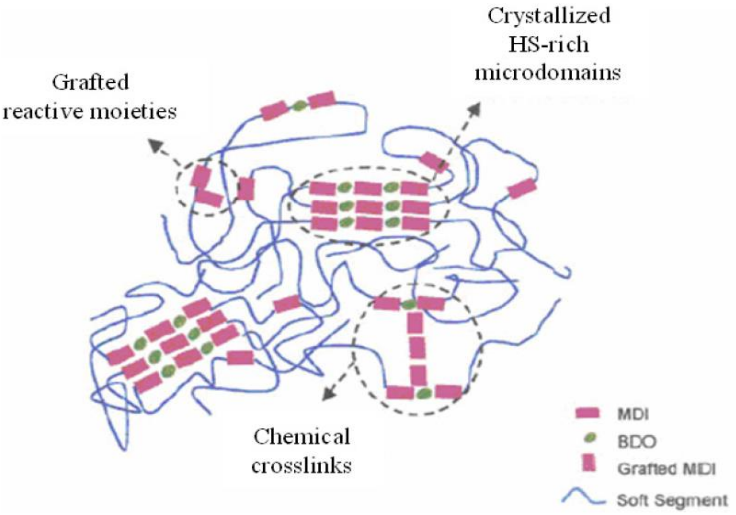

Figure 2.2 schematic representation of chains urethane and micro-separation of rigid segments (Lapprand et al., 2007)

2.2.2 Polyaniline

PANI have six structural forms, ranging from fully reduction state to the full oxidation state (Wallace et al., 2008) as shown in Figure 2.3 the production of polyaniline would be rather simple if processing could be achieved with the most desired oxidation state, emeraldine salt (PANI-ES). However, the insolubility of PANI-ES, the only conductive form of polyaniline, requires an alternative approach to processing. The insolubility has been improved with the use of a polar (hydrophilic) aprotic solvent, for instance DMF (Goncalves et al., 2005). Moreover, polyaniline emeraldine base dope with hydrochloric evidently exhibit a homogenous dispersion and lead to increase strain response, morphology of PU/PANI-ES are presented in Figure 2.4.

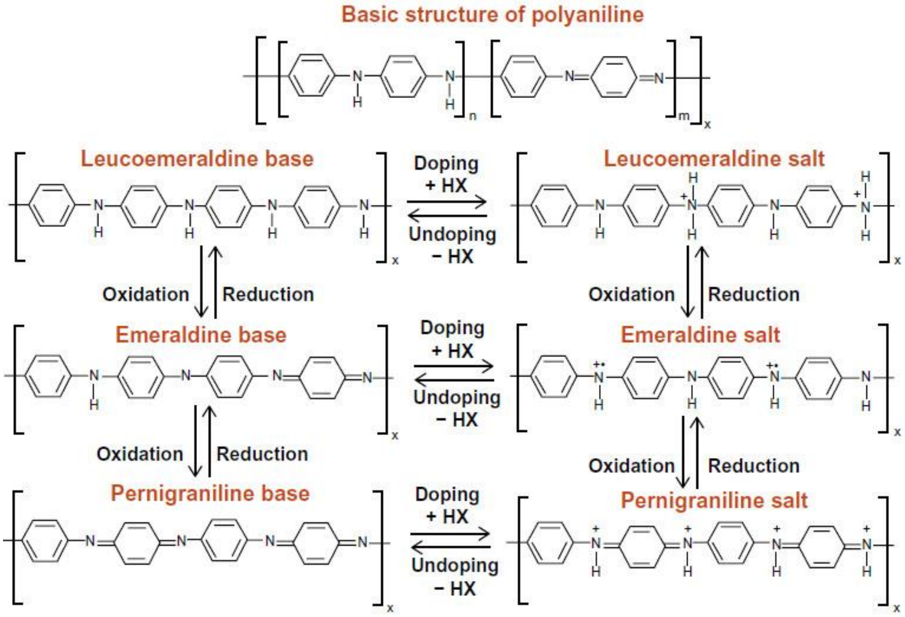

Figure 2.3 structural form of polyaniline (Tian et al., 2016)

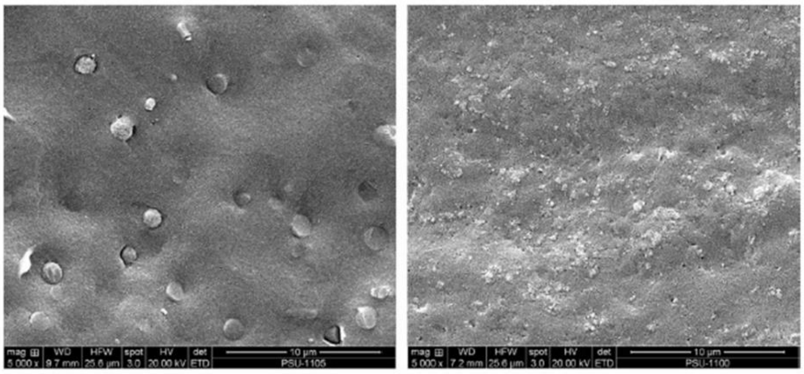

Figure 2.4 Morphology of PU with PANI conducting polymers dope without HCl and with HCl (Jaaoh et al., 2016)

2.2.3 Graphene

In particular, the Conducting Carbon fillers divide into three structural as shown in Figure 2.5. Graphene (GRN) is single layer conjugated sp^2 hybridized carbon atom arranged into a planner 2D honeycomb lattice and may also be described as the starting building block of graphitic structure, while 1-5 lattices of graphene is known as graphene nanosheets and more than 9 lattices of graphene is known as graphite (Mondal and Khastgir, 2017). The unique properties of graphene are exceedingly high young's modulus and high electrical conducticvity. All these characteristics make graphene a promising material for various applications.

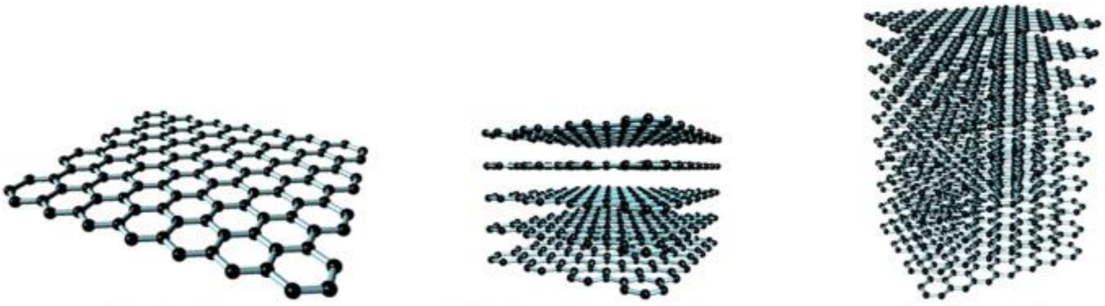

Figure 2.5 the differential structure of graphene (a), graphene nanosheets (b) and graphite (c) (Yadav and Cho, 2013)

2.3 Preparation and Characterization of electrostrictive polyurethane and their composite

2.3.1 Preparation of the PU three phase composites

Thermoplastic polyurethane elastomers (DP 9370A) used as matrix were supplied from Covestro Deutschland AG. Thermoplastic PU 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 and polyaniline nanopowders were used as a filler as provided by Sigma Aldric, while conductivity and particle size of graphene are about 4-6 S/cm and 2-3 μm, respectively. The 1-Methyl-2-pyrolidon with the 99% purity as a solvent was purchased from Sigma Aldrich.

Figure 2.6 shows the schematic preparation of PU filled with GRN films. For the PU three-phase composites films follow the same preparation as well. The first step, The PU granules were dried at 80 °C for 24 hours to evaporation. Then PU granules were dissolved in 1-Methyl-2-pyrrolidone (NMP, 99% purity, M79603, Sigma Aldrich) at 80 °C for 45 minutes in order to obtain a homogeneous solution in polymer matrix. Graphene nanosheets and polyaniline nanopowders were added into the NMP and dispersed using ultrasonic for 20 minutes. And then graphene and polyaniline solution was added into PU matrix and continuous mixing to gain a homogeneous solution at 80 °C for 3 hours. The last solution was cast onto a glass surface with the same condition of the thickness at 60 °C by a casting method and dried for 24 hours to remove the solvent. Finally, the PU/GRN film was annealed at 125 °C for 3 hours to remove remaining solvent as shown in Figure 2.7.

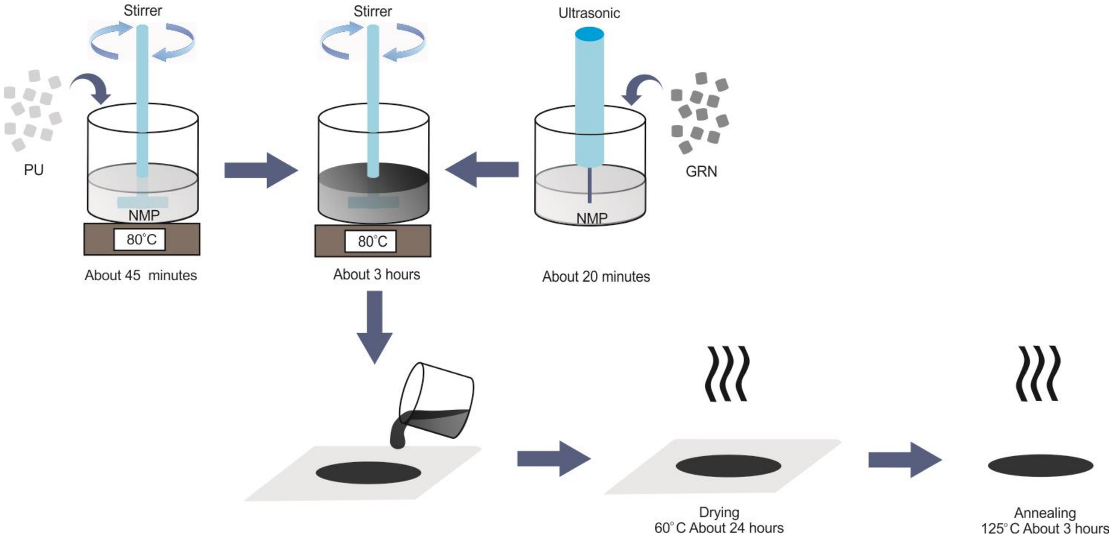

Figure 2.6 Schematic illustration of PU/GRN films preparation

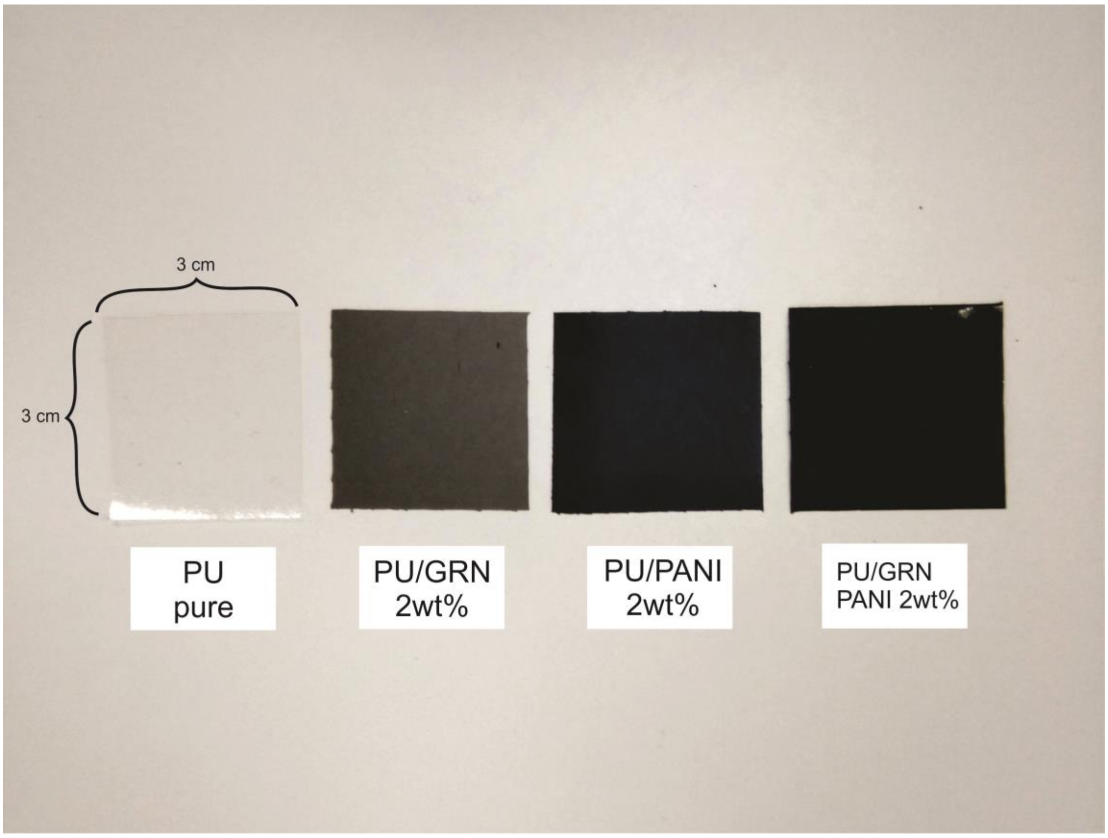

Figure 2.7 a photograph of specimens for PU pure, PU/GRN, PU/PANI, and three phase composites

2.3.2 SEM and AFM characterization

The morphology and dispersion of PU pure and PU composites were characterized using scanning electron microscopy (SEM, FEI Quanta 400, USA). the magnification of 5000x and the high voltage was conducted at 20 kV. Figure 2.8 despicts the SEM images of PU pure and PU/GRN composites in the cross-section. The results present that the tickhness all of samples around 100 μm and PU pure was smoothest than other. It is seen that the GRN nanosheets in the PU matrix has a good dispersion at 2wt% content of filler. 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 permittivity is due to the increasing content of filler.

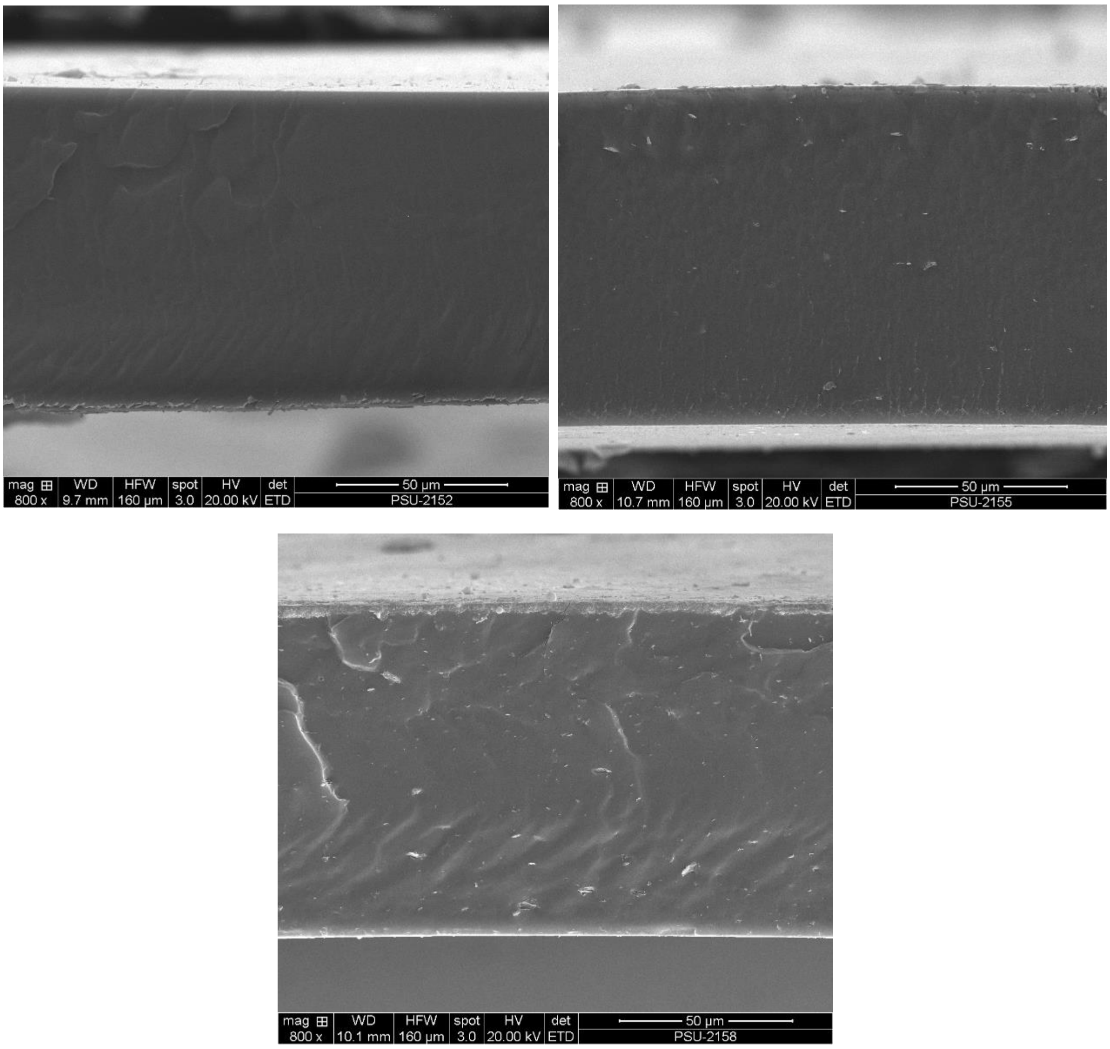

Figure 2.8 SEM images cross-section of the PU pure (a); the PU filled with GRN of 1wt% (b); the PU filled with GRN of 2wt% (c)

The morphologies of PU three-phase composites were provided in Figure 2.9. It also clearly that PU pure was smoothest compared to others with the magninifications of 5000x. Some nanosheets of GRN with different size are observed the homogenious distribution in the PU matrix as depicts in Fig 2.9b. This was indicated that the greater interfacial polarization and it leads to affect to high electrical properties. However, the agglomeration was found in PU/PANI composites as shown in Fig 2.9c and contributes to the high conductvity in PU composites. The better dispersion and distribution of both fillers in the PU matrix compared to the two-phase composites is clearly seen. The graphene and polyaniline are accidentally incorporate inside the polymer matrix. The better interface area could be seen in the GRN nanosheets and the PANI filler distribute such a filler-filler networks. This combination of two filler might be affected to the electrical and mechanical properties.

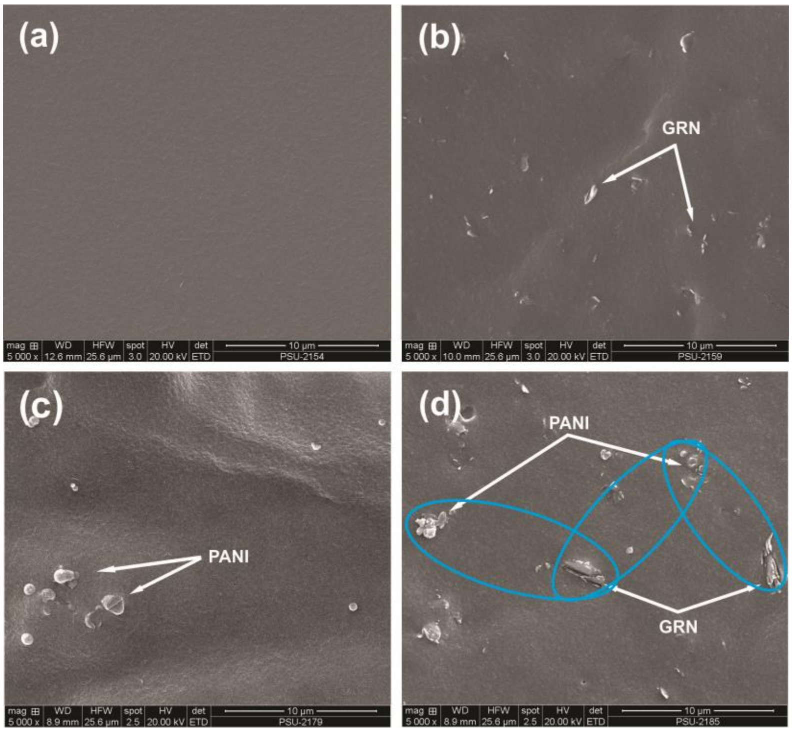

Figure 2.9 SEM images at high magnitude of the PU pure, PU two-phase and three-phase composites: the PU pure cross section (a); the PU filled with GRN of 2wt% (b); the PU filled with PANI of 2wt% (c); and PU three- phase composites with the same ratio content of 2wt% (d)

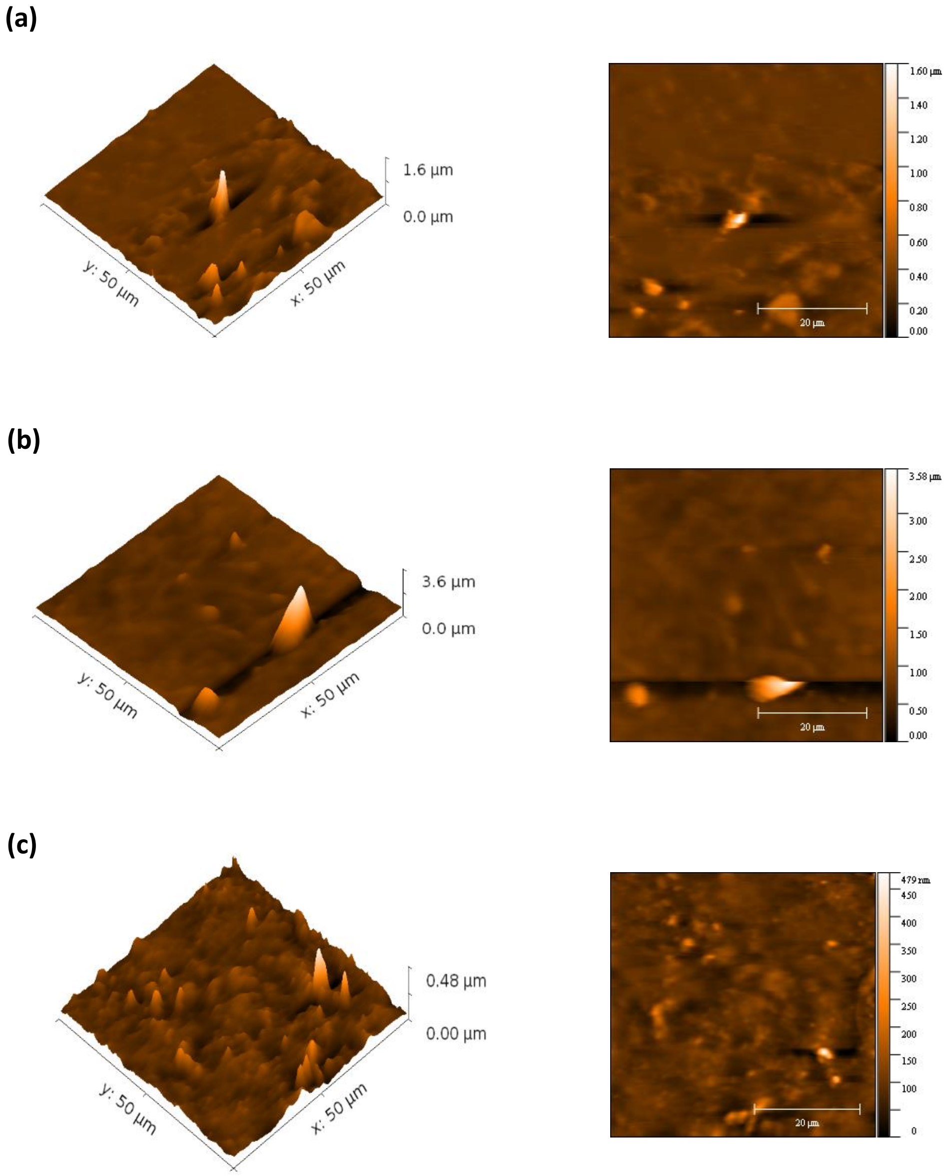

Figure 2.10 Topography images of the PU pure, PU two-phase and three-phase composites: the PU filled with GRN of 2wt% (a); the PU filled with PANI of 2wt% (b); and PU three- phase composites with the same ratio content of 2wt% (c)

The topography of PU two-phase composites was observed using Atomic Force Microscopy (AFM) as shown in Figure 2.10. The surficial and colorless areas interpret the dispersed fillers in PU matrix. In a good agreement with the SEM results, the nanosheets of GRN embedded in PU matrix with the surface roughness of 1.6 μm as presented in Figure 2.10a. However, the agglomeration of PANI nanopowders embedded in PU matrix with the surface roughness of 3.6 μm as shown in Figure 2.10b. In addition, the PU three-phase composite displayed a good distribution and dispersion and contributes to the high interfacial polarization.

2.3.3 FTIR characterization

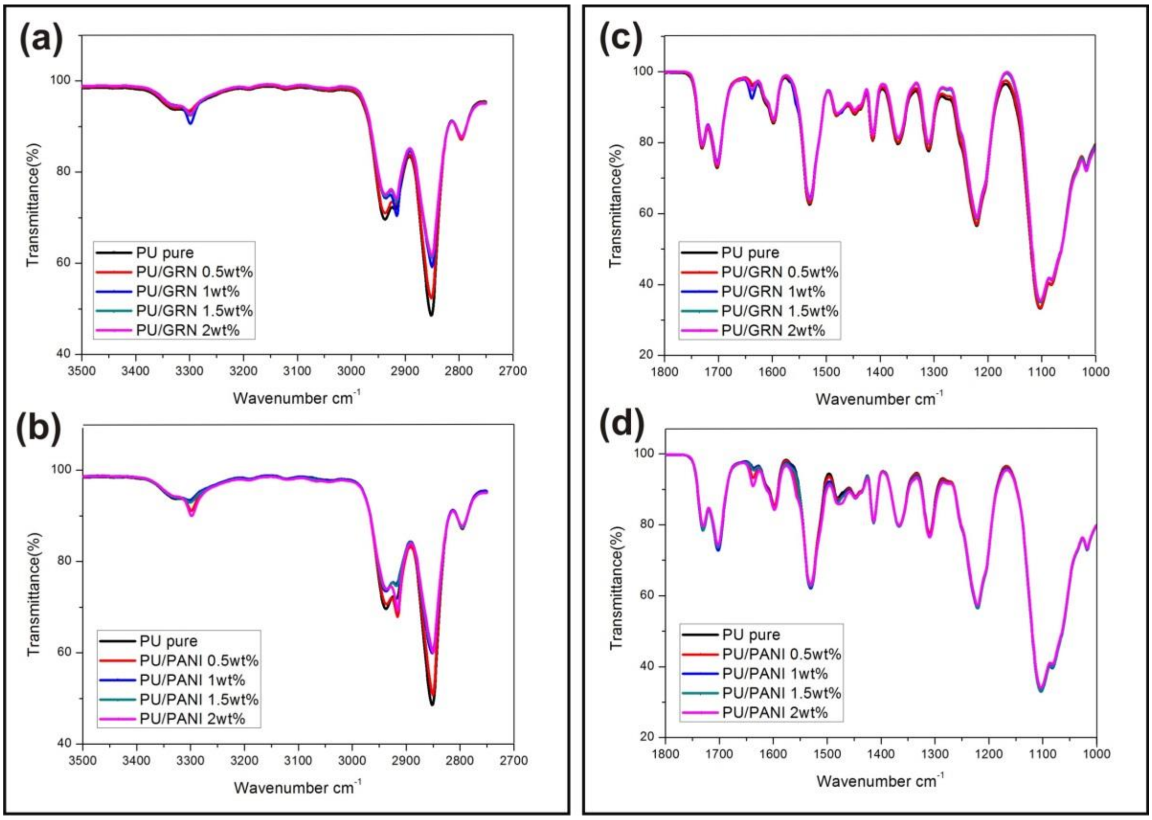

Figure 2.11 Curve-fitting results in the FTIR spectra of the PU pure and composites: (a) the PU/GRN composites in the region of 2700-3500 cm^{-1}, (b) 1000-1800 cm^{-1}, (c) and the PU/PANI composites in the region of 2700-3500 cm^{-1}, (d) 1000-1800 cm^{-1}

The infrared spectra were recorded from 800 cm^{-1} until 4000 cm^{-1} by using Fourier Transform Infrared Spectroscopy. The FTIR is used to determine the different aspect of functional groups in the PU composites. The infrared spectra were separated into two region which are 2700-3500 cm^{-1} as the amine region and 1000-1800 cm^{-1} as carboxyl region.

The infrared spectra amine of PU/GRN composites is shown in Figure 2.11a. It presents that new free N-H is formed at 3301.88 cm^{-1} when the content of GRN increase. The other transmittance of Hydrogen bond stretching around 3326.95 cm^{-1}. The hydrogen bond N-H at 3301.88 cm^{-1}, free N-H at 3326.95 cm^{-1}, symmetric hydrogen bond $C\text{-}H_2$ at 2852.50 cm^{-1}, and asymmetric hydrogen bond $C\text{-}H_2$ at 2937.36 cm^{-1} shift significantly to a higher frequency to 3321.16 cm^{-1}, 3298.01 cm^{-1}, 2850.57 cm^{-1} and 2935.43 cm^{-1}, respectively. The infrared spectra carboxyl of PU/GRN composites is presented in Figure 2.11b. The increasing of C=O bonding of 1703.01 cm^{-1} and C=C bonding of 1730.01 cm^{-1} indicated that the grapene nanosheets greatly influenced to the PU matrix. Figure 14c and 14d show the FTIR spectra of PU/PANI composites. The stretching transmittance peak at 3326.95 cm^{-1}, 2852.50 cm^{-1}, 1703.01 cm^{-1}, 1531.36 cm^{-1}, and 1365.59 cm^{-1} corresponded to hydrogen bond N-H, symmetric $C\text{-}H_2$, hydrogen bonded carbonyl C=O, symmetric amine N-C-N, and C-N stretching, respectively. Compared with the PU filled with GRN 2wt% stretching band, all their stretching band shift to the lower wavenumber, the shifting peak of N-H And C-N may correspond to the interaction between urethane segment in PANI and carbonyl groups in the PU matrix (Putson et al., 2016). In addition, after incorporating PANI into PU matrix, the FTIR spectra N-C-N shifts to the higher frequency due to the –NCO groups influenced by N-H and indicates that the PANI has better interaction with the PU matrix than GRN. The conductive network may be formed in between GRN and PU matrix.

2.3.4 Thermal behavior

The thermal behavior of PU pure and their composites such as the melting temperature (T_g), the glass transition temperature (T_m) and the enthalpy changes (ΔH_m) was determined by a Differential Scanning Calorimeter (DSC). The samples of 10 mg was cooled from -150°C and heated to 250 °C with the heating rate at 5 °C/min. The glass transition temperature (T_g), the melting transition temperature (T_m) and the enthalpy changes (ΔH) every composite are shown in Table 2.1. The glass transition are observed around -67 °C. The glass transition increased in the PANI or GRN filler incorporated with PU matrix. It has been known that the increasing the glass transition indicated the crystalline dissolved in the soft segment. In addition, the endotherm transition can be found within the range 140 °C-180 °C which corresponds to the melting temperature of crystalline in the hard segments. In addition, the disruption of the structure PU matrix was observer by the mixing micro transition (T_{MMT}) around 130 °C. In comparison, the melting temperature of PU three phase composite has highest value compared to others. It may indicate that the crystallinity is increased in corporation of PU matrix. The crystallinity also depends on the enthalpy changes of the samples (Wang et al., 2017). It has observed that the enthalpy changes of PU three phase composite is the highest compared to the PU two phase composite and can be attributed to the agglomeration of PANI in the two phase composites.

Table 2.1 The parameters obtained from the DSC thermograms of PU pure, PU/GRN, PU/PANI and PU three-phase composites

Sample	Tg (°C)	T_{MMT} (°C)	Tm (°C)	**Δ**H_m (J/g)
PU Pure	-67.37	123.22	143.17	16.03
PU/GRN	-66.86	123.72	147.90	21.84
PU/PANI	-67.00	133.91	153.08	24.58
PU/GRN_PANI	-65.86	136.99	174.80	27.82

2.4 Conclusion

A solution casting is the method to prepare the PU pure and their composite films. The GRN nanosheets and PANI nanopowders was used as fillers. The morphologies, chemical structure, and thermal behavior are investigated. The morphology and phase distribution was observed using SEM and AFM, respectively. The results show that the GRN nanosheets have a rather good dispersion than the PANI nanopowders in PU matrix. The PANI nanopowders present the agglomeration, however the results of PU three phase composite image show both fillers have a homogeneously distribution and leads to high interfacial polarization. The infrared spectra were of PU pure and their composites recorded using Fourier Transform Infrared Spectroscopy. The increasing of C=O bonding and C=C bonding indicated that the grapene nanosheets greatly influenced to the PU matrix. The interaction between urethane segments in PANI was showed by shifting peak of N-H And C-N and carbonyl groups in the PU matrix the FTIR spectra N-C-N shifts to the higher frequency. The –NCO groups influenced by N-H and indicates that the PANI has better interaction with the PU matrix than GRN and leads to build conductive network. The last characterization is about thermal behavior that the glass transition, melting temperature and the enthalpy changes was determined using DSC. The results in temperature glass and melting slightly increase and it presented the strong interaction between PU matrix with their composites.

Chapter 3 Dielectric and electrical properties of polyurethane filled with graphene nanosheets

3.1 Introduction

It has greatly studied about Polyurethane for energy harvesting, sensor and actuator applications. The polyurethane elastomers (PUs) are great interest for high-strain actuator due to large mechanical deformations > 10% strains (Guyomar et al., 2012). In addition, PU has high dielectric permittivity because of a strong polarization when the electric field to be induced. One of the key factors to increase the dielectric permittivity is to disperse metals, ceramics, alloys, or carbon black into the polyurethane matrix. By the reason of metals, ceramics and alloys are easily agglomerate and flexibility loss at higher content of fillers, so several papers have been presented the concept of conductive fillers can increase the dielectric permittivity without any agglomeration and flexibility loss. So in this chapter will present the interesting conductive fillers such as grahene nanosheets to increase dielectric permittivity.

In addition, this chapter will describe the dielectric permittivity including loss tangent and conductivity of PU filled with graphene at various content of filler using LCR meter. In addition, electrical properties with filler distribution and the glass transition was determined to prove the idea by using scanning electron microscopy (SEM) and differential scanning calorimetry, respectively.

3.2 Dielectric and electrical properties

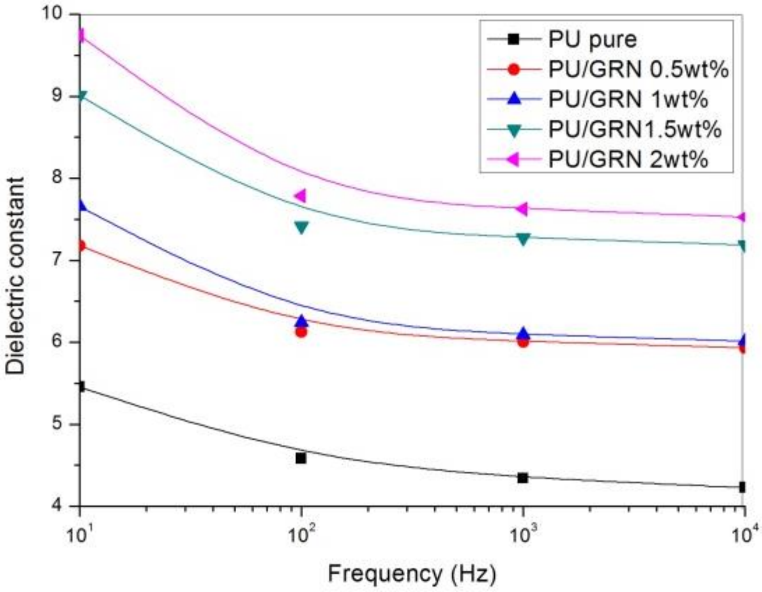

Figure 3.1 Effect of frequency on dielectric permittivity for PU filled with various content of GRN

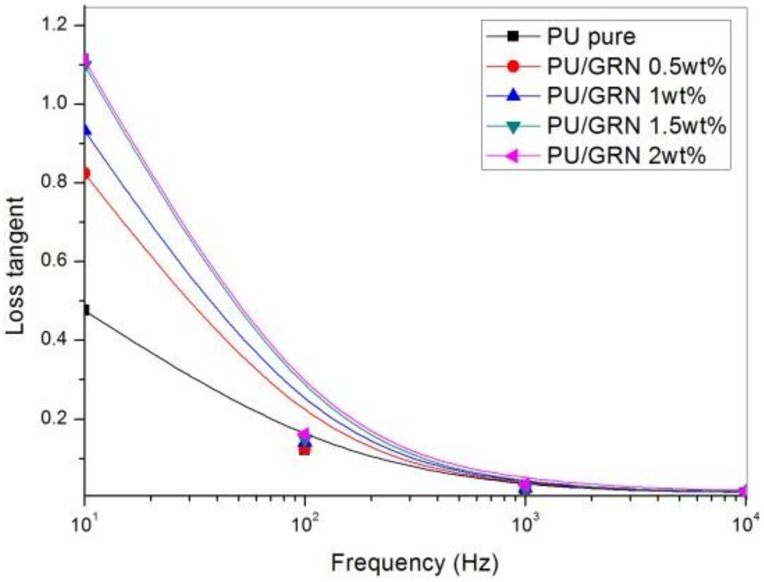

Figure 3.2 Effect of frequency on loss tangent for PU filled with various content of GRN

Figure 3.1 and Figure 3.2 show the dielectric permittivity and loss tangent as a function of frequency. The decreasing dielectric permittivity when the frequency increase can be attributed to the unresponsive dipoles of GRN to align themselves because of the fast frequency in the AC electric field, while the loss tangent decrease as well when the frequency is increase. The increasing dielectric permittivity and loss tangent in the low frequency lead to the maximum value of interfacial polarization between PU matrix with the GRN fillers. However, the value of interfacial polarization to be minimum when the frequency is increased.

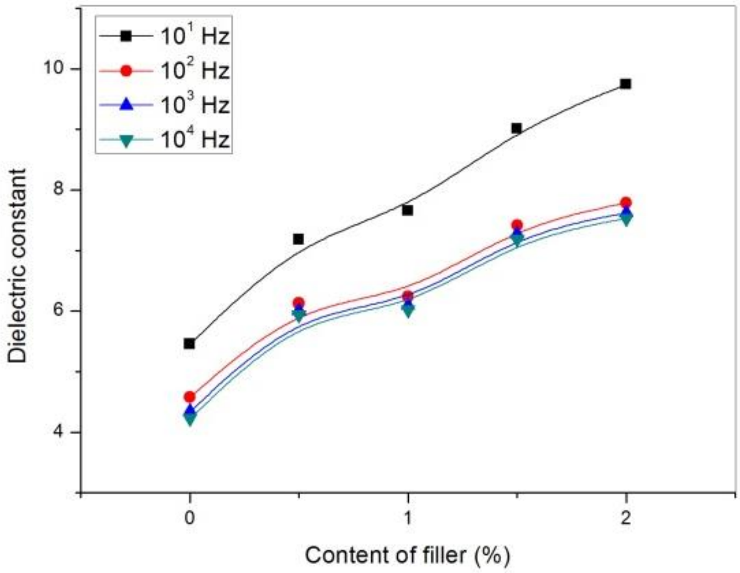

Figure 3.3 Effect of GRN content on dielectric permittivity at various frequencies.

In addition, Figure 3.3 depicts that the dielectric permittivity of PU/GRN composites increases with the increasing content of fillers. The GRN fillers were incorporated in PU matrix acts as a minute capacitor which provides the capacitor ability in the PU matrix. Hence, the dielectric permittivity of polymer composites is propotional to the number of capacitor. The various concept has been explained about conductive fillers can give achieving to the dielectric permittivity such as percolation threshold theory. A theoretical according to the percolation threshold has been proposed to predict the dielectric permittivity, it is given by (Lallart et al., 2012)

$$\varepsilon = \varepsilon^0 \left| \frac{f_c - f}{f_c} \right|^{-q} \tag{3.1}$$

Where $\varepsilon, \varepsilon^0, f_c, f,$ and q are the dielectric permittivity of the polymers matrix, the permittivity of free space, the percolation threshold, the volume content of conducting fillers, and the critical exponent, respectively. It can be clearly seen that the increasing content of filler leads to increasing the dielectric permittivity in the polymer composites. Moreover, recently study has been predicted theoretical based on percolation threshold which is accurate with experimental results only at the higher content of filler.

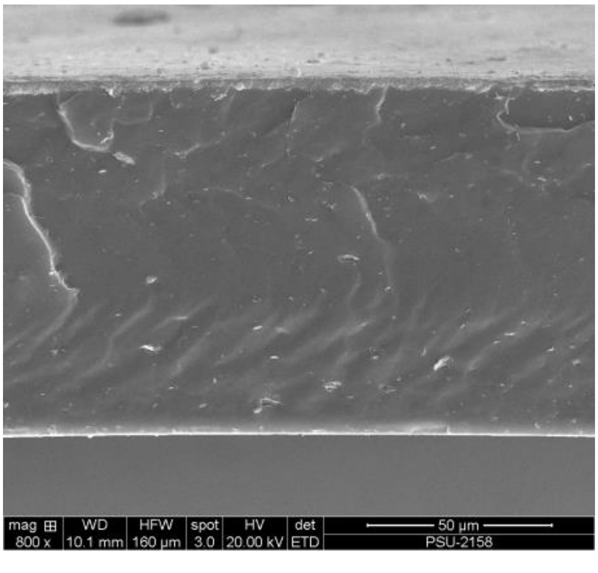

Figure 3.4 SEM cross section image of PU filled with GRN at 2wt%

The conductivity of PU/GRN composites versus the frequency at various content fillers of GRN as depicted in Figure 3.5. The conductivity for all sample is presented to be permittivity at the frequency below 10^2 Hz. However, the conductivity is found to be slightly increased in the frequency below 10^3 Hz, while the large deformation is observed in the frequency upper 10^3 Hz. 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. Moreover, there is no different with variation of conductivity as a function of GRN volume fraction. It can be seen that the increasing value of conductivity due to content filler of GRN increase. The increasing conductivity might be due to the incorporation of charge carriers of GRN nanosheets and the variation of filler content increases the number of charge carriers. In addition, the conductivity depends on the effective loss tangent as according to the Equation 3.2 (Wang, 2010).

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} + \frac{\sigma}{\omega\varepsilon_0\varepsilon'} \qquad (3.2)$$

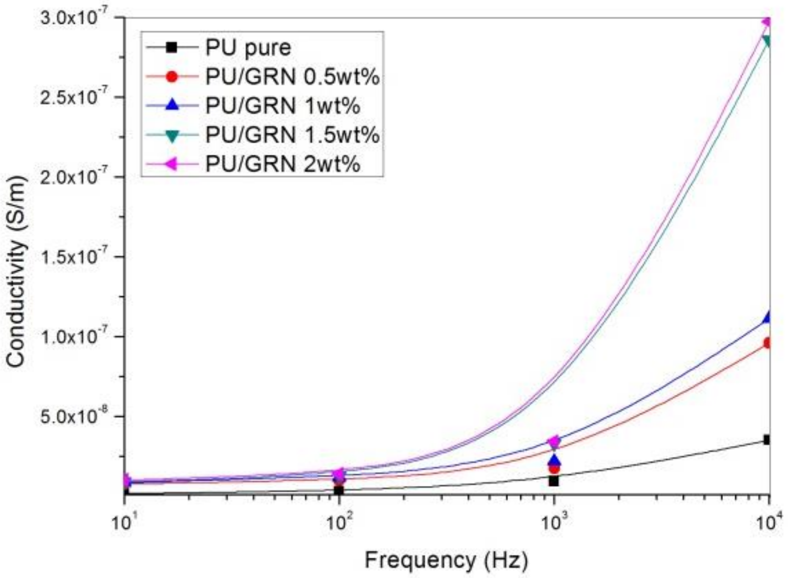

Figure 3.5 Effect of frequency on the conductivity for PU filled with various content of GRN

3.3 Mechanical properties

The young's modulus of the PU/GRN composites was evaluated using strain gauge machine, with the help of force gauge. The specimens were stretched with a strain rate 50 mm.min^{-1}. The strain versus the stress was plotted and then the Young's modulus was calculated. The Young's modulus in various content of GRN filler is obtained as shown in Figure 3.6. The reinforcement effect of PU/GRN composites may occur because of the wide area of GRN sheets and it might be exhibited relatively higher interface areas and leads to the strong adhesion of the polymer matrix. The strong interaction of covalent bonding between the PU matrix and GRN that leads to improve the Young's modulus as well.

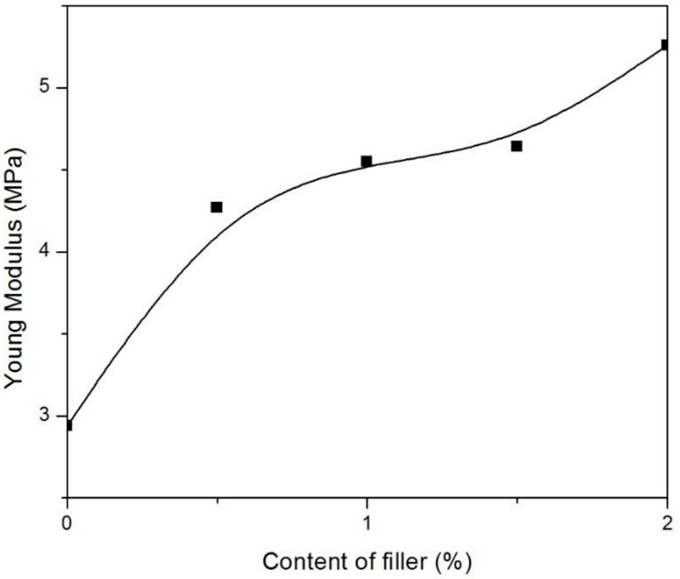

Figure 3.6 The Young's Modulus as a function of increased content of GRN filler in the PU matrix

3.4 Conclusion

In this chapter, it has studied about the dielectric and electrical properties of polyurethane composite films filled with graphene nanosheets. The dielectric permittivity was studied over a broad range of frequencies. The effect of graphene nanosheets leads to increase the dielectric permittivity and loss tangent. The dielectric permittivity increased due to the capacitor ability of GRN nanosheets and a great interaction between the matrix and the 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.

Chapter 4 Electrostriction of the polyurethane three-phase composite

4.1 Introduction

Previously work, the polyurethane has been modified with conductive fillers such as polyaniline, carbon black, carbon nanotube and etc. the conductive fillers are the one promising in order to enhance the electrostrictive polymer such as polyurethane and it can usefull for actuators applications, energy conversion and sensors. The polyurethane as matrix were filled with conductive fillers such as graphene nanosheets and polyaniline. In order to gain the composite films, the PU three-phase composite were prepared by solution casting method. The electrical and mechanical properties of polyurethane filled with both composites were investigated by an LCR meter and strain gauge setup. In previous work, the dielectric permittivity is the important key factor to affecting the electrostriction behavior. The last chapter shows the PU/GRN composites enhanced approximately 30% of the dielectric permittivity at 2wt% content of fillers. In order to study the electrostriction behavior, the electric field induced strain of polyurethane three-phase composite films were monitored via lock-in amplifier at a low frequency of 1 Hz. In addition, the electrostrictive coefficient was calculated by theoretical analysis and it was indicated the electrostriction coefficient of the polyurethane three-phase composites up to 0.03% transfer strain at a low electric field. In this chapter will discuss the effect of combination of polyurethane three-phase composites in the electromechanical performance.

4.2 Electrostriction effect

In the last chapter has mentioned that the dielectric permittivity and the Young’s modulus are the key factors to enhance the electrostrictive abilities in the PU composites. The increasing of dielectric permittivity in polyurethane is due to a strong polarization under electric field. The electrostrictive coefficient could be enhanced by increasing the dielectric permittivity. The enhancement strain deformation (***S_{33}***) depends on the dielectric permittivity based on the Equation 4.1.

$$S_{33} = Q.{\varepsilon_0}^2.(\varepsilon_r - 1)^2.E_3^2 \tag{4.1}$$

Where ε_r is the real part of the relative dielectric permittivity, ε_0 is permittivity of free space, ***Q*** is the intrinsic electrostrictive coefficient, and ***E*** is electric field. Therefore, the relationship with the electrostrictive coefficient (***M***) could be defined as

$$M_{33} = {\varepsilon_0}^2.(\varepsilon_r - 1)^2.Q_{33}^2 \tag{4.2}$$

So the electrostrictive coefficient from (4.1) and (4.2) equals. Therefore the electrostrictive coefficient (***M_{33}***) is proportional to the dielectric permittivity (***ε_r***) and the inversely proportional to Young’s modulus (***Y***) (Putson et al., 2012). Therefore, it clearly understands that the dielectric permittivity is the important key factors for improving electromechanical properties as presented in Equation 4.3.

$$M_{33} \propto \frac{\varepsilon_0(\varepsilon_r - 1)^2}{\varepsilon_r Y} \tag{4.3}$$

4.3 Dielectric and Electrical Properties

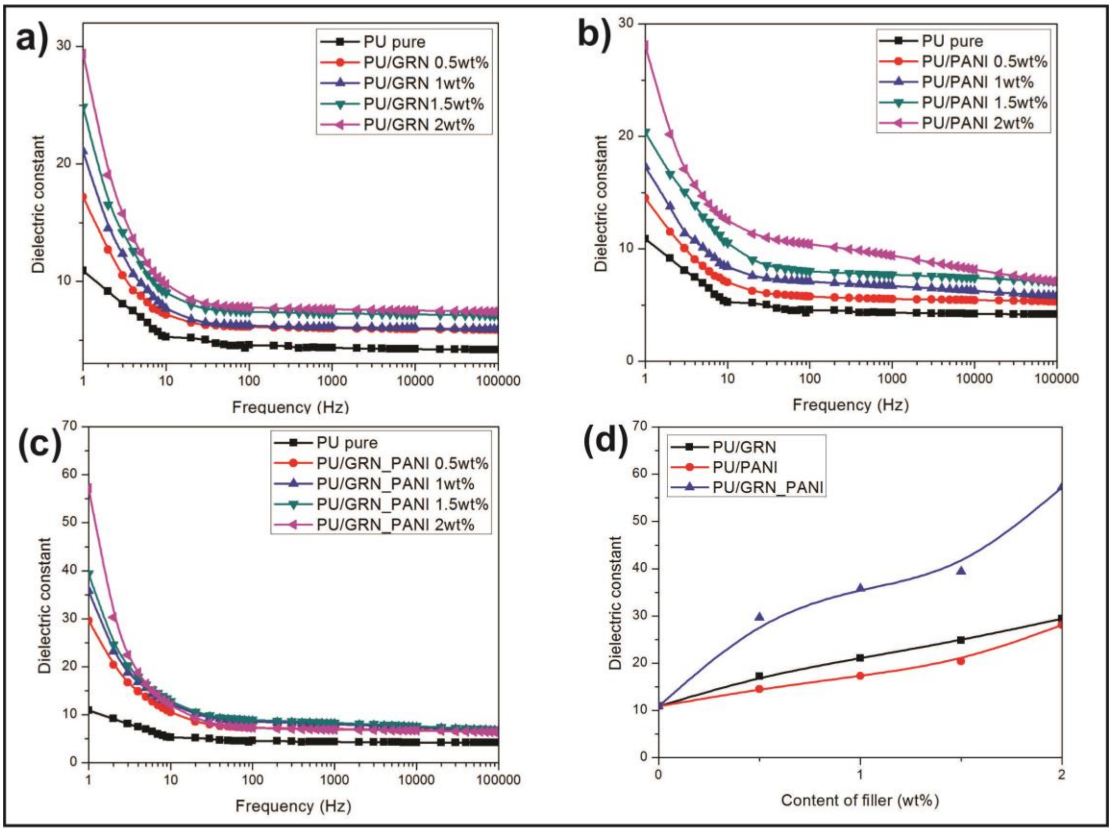

Figure 4.1 Plot of dielectric permittivity for PU two composites and PU three composites. The dielectric permittivity versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (d) the dielectric permittivity of PU two-phase composites and PU three-phase composites as a function of content

The dielectric permittivity and electrical properties were assessed across 10^0-10^5 Hz by an LCR meter (IM 3533 HIOKI). The sample was placed on between two electrodes with the diameter size of 21.38 nm and the same thickness of 100 µm. The dielectric permittivity and the electrical conductivity were calculated by the value of parallel capacitance and conductivity readings, respectively. Figure 4.1 shows the dielectric permittivity of PU pure and PU three-phase composites as a function of frequency. In Figure 4.1a, 4.1b, and 4.1c it can be clearly seen that the dielectric permittivity at 10^0 Hz for all of samples is higher compare to others. By the reason of the Maxwell-Wagner type Polarization is disappeared when the frequency increase. The dielectric permittivity of PU filled with 2wt% GRN composites was observed two times higher compere to the PU pure as shown in Figure 4.1a. As well as the PU/GRN composites, the dielectric permittivity of PU/PANI composites higher than the PU pure as presented in Figure 4.1b. It was found that the dielectric permittivity increases as both filler contents increased. According to the percolation threshold theory, it has been known that the dielectric permittivity of the two-phase composites depends on the percolation threshold and the fraction of filler. In addition, it has explained the contribution of conducting filler that the charge quantity will increase due to the polarization of the conducting filler interface is increased (Dang et al., 2004) (Li et al., 2017). That means an increase of charge carriers because of the incorporation of effective areas of the conductive filler interface. In recent work, the increase of the dielectric permittivity depending on the crystal fraction of the polymer (Liu et al., 2017). The increase of dielectric permittivity can be attributed to the increase of the melting enthalpy of crystallinity in the hard segment domain of the polyurethane.

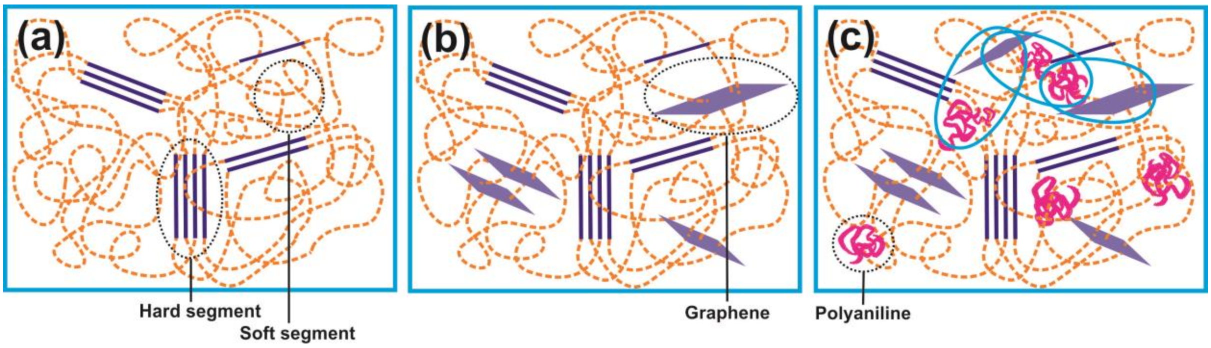

Figure 4.2 The schematic of structure deformation of PU pure (a), PU/GRN (b), and PU three-phase composites (c)

With the same ratio of GRN and PANI at 0.5wt%, the dielectric permittivity of PU/GRN slightly higher than the PU/PANI composites. The different morphology of both fillers is the factor to improve the dielectric properties. The larger surface area of GRN nanosheets lead to increasing the dielectric permittivity. As we know that the GRN has excellent electrical properties because of the surface lattice of GRN nanosheets have larger quantities of free π electron. The dielectric of the PU three-phase composites with the same percentage of filler has highest dielectric permittivity and it was raised up to 59 at 1 Hz as shown in figure 4.1d. It clearly shows strong Maxwell-Wagner interfacial polarization in the GRN nanosheets as conductive filler. Moreover, it has been known the behavior of conducting filler that the PANI as conducting filler can be able to build filler-filler networks between the gaps of GRN with the hard segment (HS) domain (Mondal and Khastgir, 2017). The better dispersion of PANI in the soft segment of polyurethane as presented in Figure 4.2c. It can be assumed that the cooperative interaction between GRN and PANI can possibly produce a combined effect behavior which is greater than their separate effects and it can achieve the greatly dielectric permittivity of PU three-phase composite.

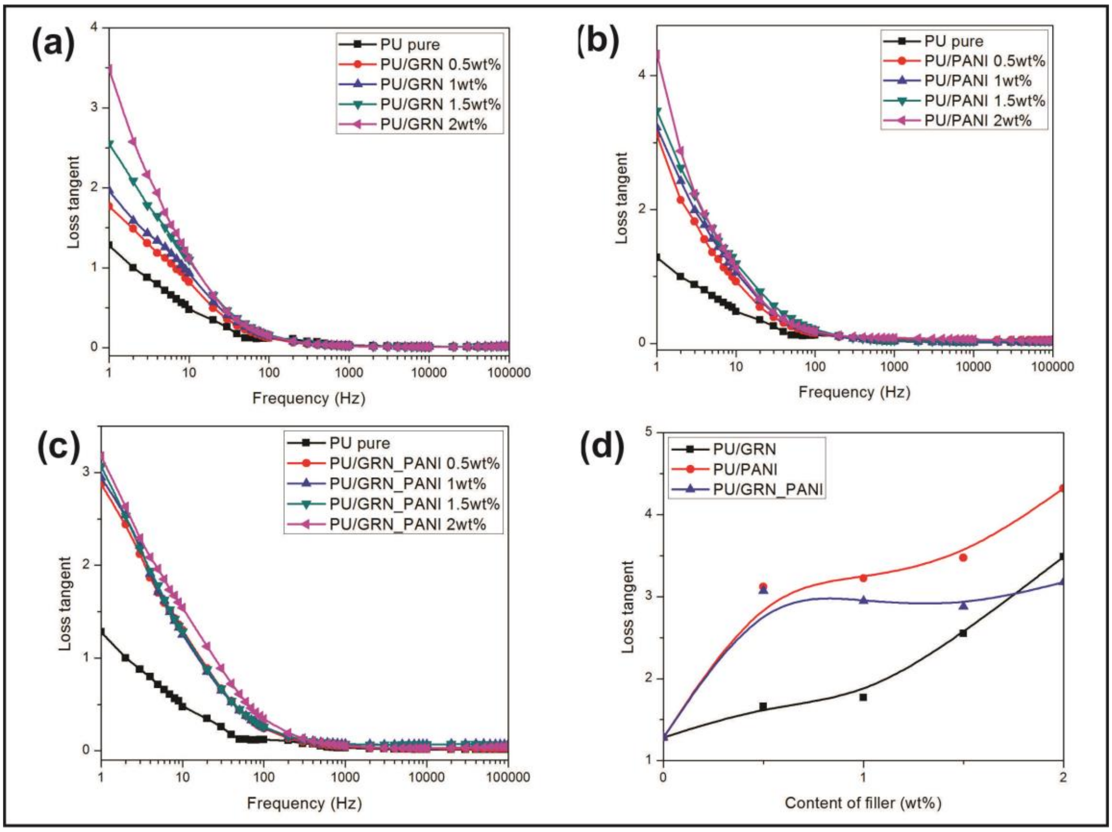

Figure 4.3 Plot of dielectric loss for the PU two-phase composites and PU three-phase composites. The dielectric loss versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (d) the dielectric loss of PU two-phase composites and PU three-phase composites as a function of content

Figure 4.3a, 4.3b, and 4.3c present the dielectric loss is increased as the frequency is decreased. This is due to the effect of agglomeration of PANI in the polymer matrix and the effect can improve the dielectric loss of PU/PANI composites. In the good agreement with the dielectric loss equation where the dielectric loss depends on the imaginary part of dielectric permittivity which is given by $tan\,\delta = \frac{\varepsilon''}{\varepsilon'}$, where $\tan\delta$ is dielectric loss, ε'' is the imaginary parts of the complex dielectric permittivity, and ε' is the real parts of the complex dielectric permittivity. Moreover, the reducing the dielectric loss effect due to the increasing dielectric permittivity. It shows that the dielectric loss could be reduced by the great amount crystalline of the graphene sheets caused by the isolation effect to the PANI crystallites. In the Figure 4.3d presents that the dielectric loss depend on filler content of the tree phase composites and when the filler of three-phase composite at 2wt%, the dielectric loss of 3.12 which has lowest dielectric loss.

In Figure 4.4a, 4.4b, and 4.4c show the electrical conductivity of all composites as a function frequencies at 10^1-10^5 Hz with various content of filler. All graphs show the electrical conductivity increases when the increasing frequency and this might be attributed to the polarization of bound charge (Wang et al., 2017). Moreover, Figure 4.4d presents the electrical conductivity also increases with the increasing amount of filler content, this can be attributed that the greatly number of charge carries (Putson et al., 2012). The electrical conductivity of PU/GRN and PU/PANI composites slightly different. As we can see, the electrical conductivity of PU/PANI is higher than the electrical conductivity of PU/GRN, it caused by the conducting networks of PANI has been formed and the free electrons can easily pass through. Moreover, the dielectric loss also affect the electrical conductivity.

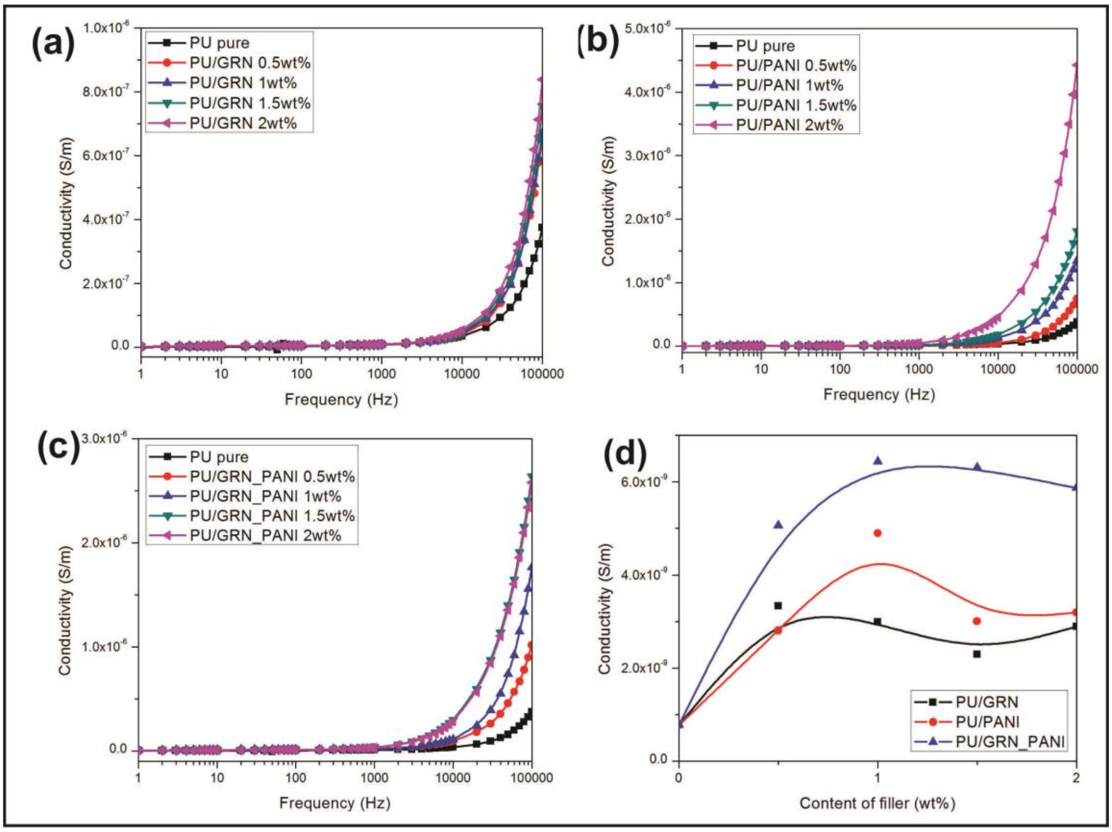

Figure 4.4 Plot of conductivity for PU two-phase composites and PU three-phase composites. The conductivity versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (a) the conductivity of PU two-phase composites and PU three-phase composites as a function of content

Figure 4.5 presents the dielectric permittivity of PU three-phase composite with different ratio of fillers. The result indicates that the ratio 1:1 of three-phase composite has a highest dielectric permittivity compared with another ratio. This trend can be attributed to contribution of greater combined effect between GRN and PANI in ratio 1:1 compared to another ratio. Therefore, this could be the reason of this work using ratio of 1:1.

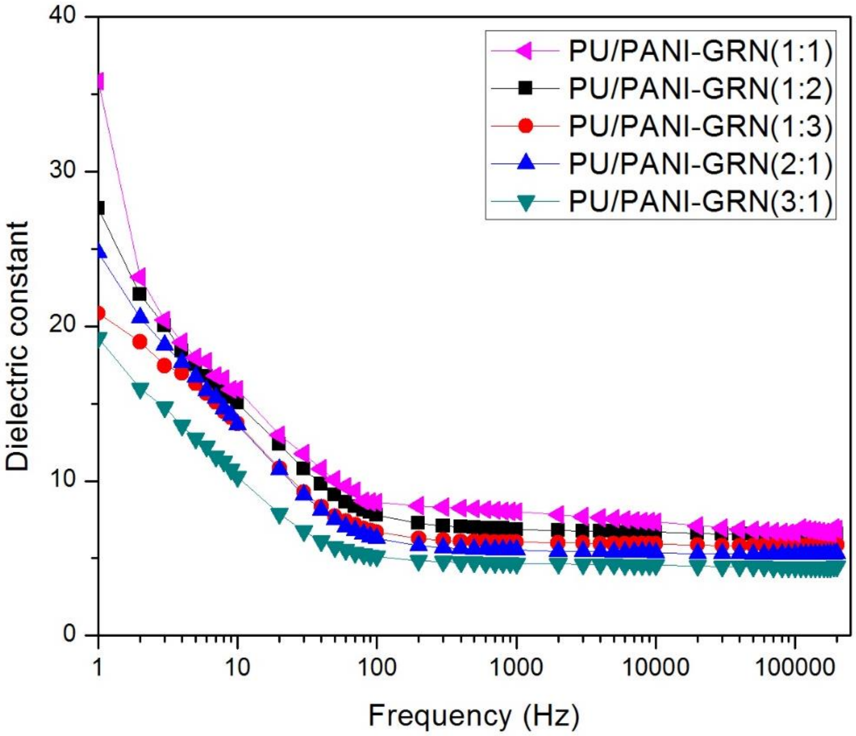

Figure 4.5 Plot of dielectric permittivity for PU three-phase composites with various ratio of fillers

4.4 Mechanical properties

The elasticity of composite films was determined by the strain gauge setup with the assist of force gauge (BFG50N, Mecmesin, UK). The dimension of the sample was 3 x 0.5 cm and the thickness was 100 μm. the piece of sample was stretched with the strain maximum of 10 % at 5 mm/min elongation rate in the length direction. The fixed side of the sample was clamped to the force gauge and the other side was clamped to the moving motor (RC ROBO Cylinder Model RCP 2CR-SA6, 220 mm long). The strain versus stress was determined to obtain their Young's modulus (***Y***). Figure 4.6 presents the Young's modulus versus content of the filler. The Young's modulus every samples were calculated from the slope of stress versus strain. As we can see that the

Young’s modulus exhibits slowly increased when increasing the content of filler. It indicates the Young’s modulus strongly depends on the stiffness in the composite. If the filler content increase, it leads to increasing the stiffness. The result shows that the Young’s Modulus of PU matrix with 2wt% GRN was slightly larger than PU/PANI composites of 5.26 MPa. The reinforcement effect of GRN may occur due to the wide area of GRN lattice compared to the PANI. The lattice area of GRN exhibits larger than PANI, the lattice area of GRN nanosheets lead to the strong adhesion with the polymer matrix. In the recent work has reported that the strong interaction of covalent bonding might affect the Young’s modulus. Then this leads to improved efficient load transfer between the filler with the Polymer matrix (Yadav and Cho, 2013). The T_g might be ascribed to the increase of HS domain and it may indicate the HS restrict to the SS mobility. The restricted of the SS increase following the significant increase in the T_g, in which a high reinforcement is achieved. However, it can be seen that the Young’s modulus is not affected by the maximum content of GRN and PANI filler.

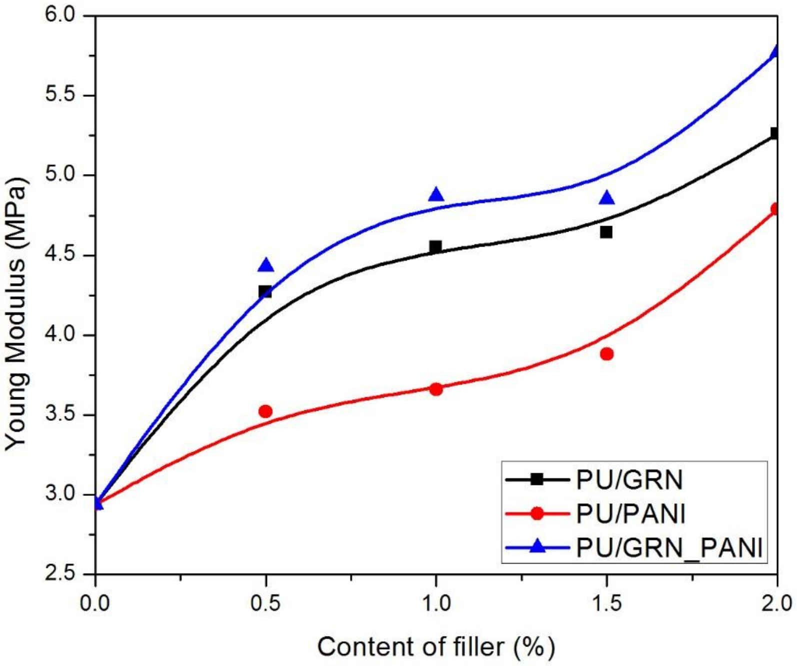

Figure 4.6 The Young's Modulus as a function of increased content of filler for the PU two-phase composites and PU three-phase composites

4.5 The electromechanical ability of the modified electrostrictive polyurethane three-phase composite

The electrostriction of polyurethane three-phase composites was assessed by measuring the deformation in the low electric field (*E* ≤ 6 MV/m) using a photonic displacement apparatus (MTI-2100 Fotonic sensor, sensitivity 0.0058 μm/mV) as illustrated in Figure 4.7. The composite films were sandwiched between two brass electrodes (diameter 20 mm) and it was connected to the high voltage. The small displacement of the composite films was detected by the photonic sensor and a lock-in amplifier (Trek model 610E) will measure as voltage peak-to-peak.

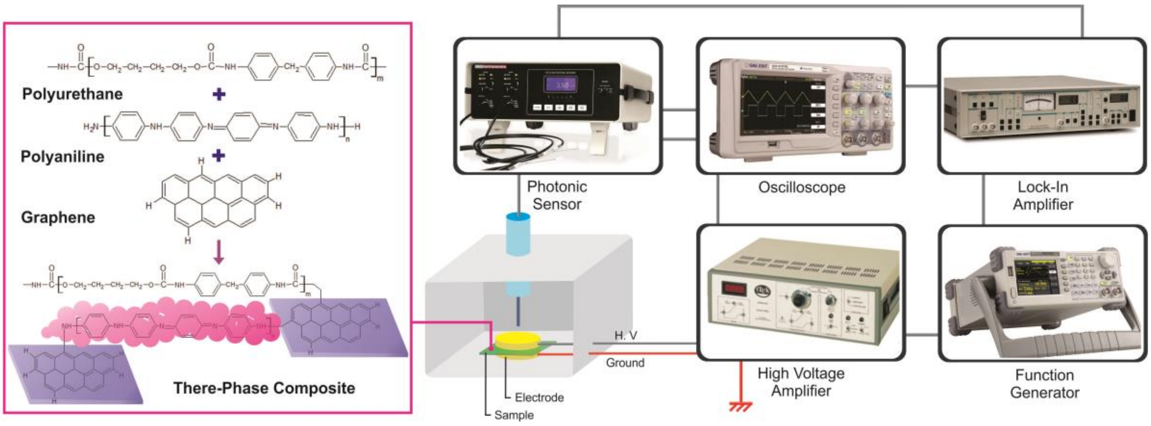

Figure 4.7 the electrostriction measurement setup

The photonic sensor was used to measure the electromechanical performance of PU three-phase composites. In Figure 4.8 depicts the thickness electric field-induced strain under the applied electric field. The increase of percentage electric field-induced strain with increased of the electric field is shown. The strain of all the samples was quadratically increased proportionally to the applied electric field. And the saturation of the strain was shown beyond 3 MV/m and it is due to the hard segment mobility and the saturation of the electric field induced polarization (Eddiai et al., 2013) (Sukwisute et al., 2013). So that the maximum thickness strain in the applied electric field observed at 3 MV/m before saturated. The PU matrix filler with PANI content of 0wt% to 2wt% shows transfer the approximately strain percentage of 27.7%, and for the PU filled with GRN has larger strain percentage of 30%. Moreover, the modified PU three-phase composites can increase the strain-induced electric field performance at 3 MV/m. And compered to others samples, the PU three-phase composites have highest percentage of strain response of 40%. Previously discussion, the PU three-phase composites contributes to the greatly dielectric permittivity due to the great polarization which can increase electromechanical performance at low electric field.

In a good agreement with the following equation, that the strain depended on polarization of PU three-phase composites might be presented by $S_3 = Q_{33}.P_3^2$, with the same direction of the strain and the applied electric field (Guiffard et al., 2009). In addition, the saturation was occurred in the high electric field area due to the saturated polarization. So when the samples were applied under an electric field, their electric polarization appears. After turning off the electric field in the composite film, there is no residual polarization anymore. The generated polarization is supposed to be saturated after the maximum electric field requirements every composites films.

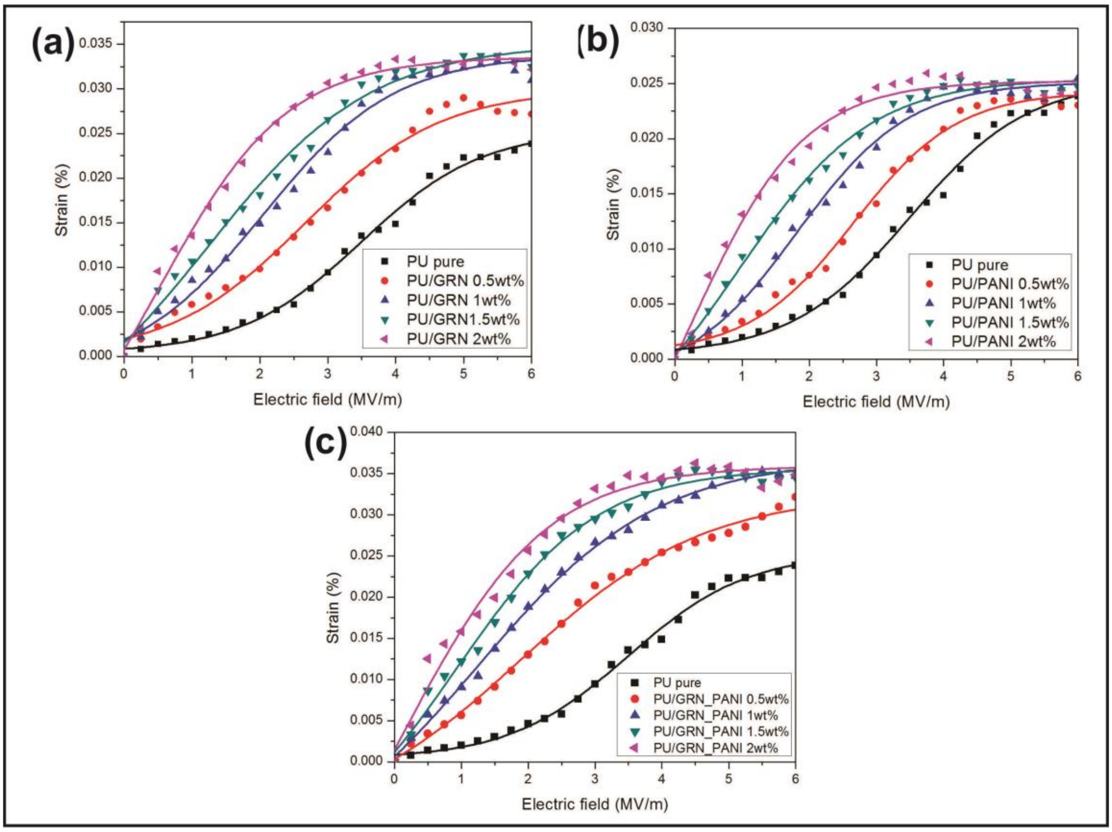

Figure 4.8 Variation of strains induced in the PU composites as a function of the electric field for (a) PU/PANI, (b) PU/GRN, and (c) PU three-phase composites

The summaries of their dielectric permittivity and Young's modulus is given in Table 4.1, and also it shows the comparison between electrostrictive coefficient (M_{33}) with the Maxwell stress effect. The electrostrictive coefficient (M_{33}) was calculated from the slope of the transverse strain versus quadratic electric field, which can be given by following equation $S_{33} = M_{33}E_3^2$, Where S_{33} is the strain and E_3 is the electric field. In comparison, the Maxwell stress effect has lower value than the electrostrictive coefficient. It can be conclude that when the electric field was applied to the samples there is no electrostatic interaction beetwen the electrode with the polymer matrix, so it can be assumed that the Maxwell stress effect can be minor influenced (Zhang et al., 2012). Hence, in this case can be concluded that the tranverse strain occured due to the electrostrictive effect. Figure 4.9 presents the electrostrictive coefficient versus percentage of filler content for PU three-phase composites at E = 4 MV/m. The electrostrictive coefficient every samples was significantly enhanced with increased content of filler. As we know before that the electrostrictive coefficient is depends on the dielectric permittivity and the Young's modulus by following the Eq. 2 (Guillot and Balizer, 2003b). In several works have been reported that the electrostrictive effect of PU can be enhanced with various conductive filler (Liu et al., 2015) (Jaaoh et al., 2016b) (Petit et al., 2008). The interfacial charge in the conducting fillers can contribute to improve the dielectric permittivity and it can enhance the electrostrictive effect. In our case works, the electrostrictive coefficient of PU/GRN composites is larger than the electrostrictive coefficient of PU/PANI composites. In comparison of the GRN and PANI, it is not only the interfacial charge of consucting fillers is affected but also in term of the distribution and the shape of fillers in PU matrix, the nanosheets of GRN wider than PANI which contributes to the increase the free electrons and enhance the dielectric permittivity, nevertheless somewhat the electrostrictive coefficient of PANI was occurred due to the PANI agglomerate in polymer matrix where affected to the increasing dielectric loss. Therefore, the electrostrictive coefficient of the PU three-phase composites is significantly higher than the electrostrictive coefficient of PU two-phase composites.

Table 4.1 The comparison of the dielectric permittivity ($\boldsymbol{\varepsilon}_r$), Young's modulus (*Y*), M_{33} coefficient, and the Maxwell stress effect for the synthesized PU two-phase composites and PU three-phase composites

Sample	ε_r at 1 Hz	*Y* (MPa)	M_{33} (m^2/V^2) at 1 Hz	$\frac{\varepsilon_r \cdot \varepsilon_0}{Y}$
PU pure	10.89	2.94	0.91×10^{-15}	3.28×10^{-17}
PU/GRN 0.5wt%	17.19	4.27	1.45×10^{-15}	3.56×10^{-17}
PU/GRN 1wt%	21.08	4.55	1.87×10^{-15}	4.10×10^{-17}
PU/GRN 1.5wt%	24.86	4.66	1.92×10^{-15}	4.72×10^{-17}
PU/GRN 2wt%	29.41	5.26	2.11×10^{-15}	4.95×10^{-17}
PU/PANI 0.5wt%	14.52	3.52	1.32×10^{-15}	3.65×10^{-17}
PU/PANI 1wt%	17.31	3.66	1.43×10^{-15}	4.18×10^{-17}
PU/PANI 1.5wt%	20.39	3.88	1.59×10^{-15}	4.65×10^{-17}
PU/PANI 2wt%	28.09	4.79	1.75×10^{-15}	5.18×10^{-17}
PU/GRN_PANI 0.5wt%	29.63	4.43	1.95×10^{-15}	5.92×10^{-17}
PU/GRN_PANI 1wt%	35.82	4.87	2.22×10^{-15}	6.51×10^{-17}
PU/GRN_PANI 1.5wt%	39.44	4.85	2.28×10^{-15}	7.19×10^{-17}
PU/GRN_PANI 2wt%	57.24	5.77	2.31×10^{-15}	8.78×10^{-17}

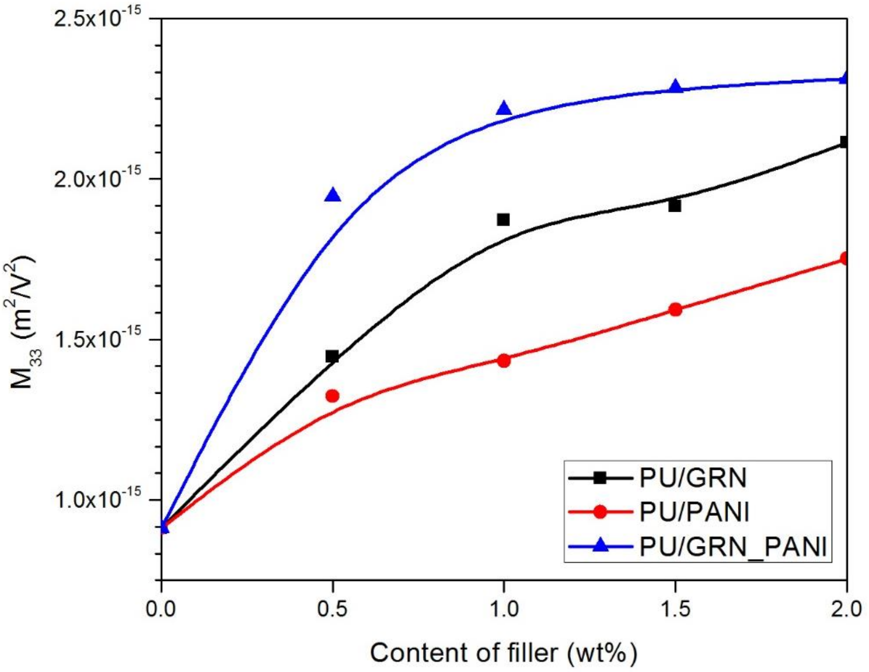

Figure 4.9 variation of the electrostrictive coefficient as a function of filler content at 1 Hz

4.6 Conclusion

The graphene nanosheets give a good electrical properties due to strong dispersion in the PU matrix. The PU two-phase composite and PU three-phases composite films were synthesized with GRN nanosheets and PANI as the conducting fillers in the PU matrix using solution casting method. The electrostrictive effect with the various fillers was observed using the electrostrictive setup with help from the photonic sensor. The PU three-phase composites presented the incredible electrostrictive effect, the PU three-phase composites showed a good dispersion which improved the interfacial charge. The increasing dielectric properties of the PU three-phase composites indicated that the cooperative interaction between matrix and fillers. As larger free charge quantities, filler network formed and charge carrier effect has increased, a combined effect behavior is achieved. Compared to the two-phase composites, Young’s modulus of PU three-phase composites slightly increased. In the last experimental result, the electrostrictive effect of PU three-phase composites presented significantly better than separate composite.

Chapter 5 Conclusions and future work

5.1 Main conclusions

Electrostricitve polymers are considered great interest for several actuator and transducer applications, in consequence of large strain under applied electric field, high specific energy, and faster response. While the ionic EAP subdivisions, the conductive polymers such as polyaniline have high electrical properties and leads to generate large deformation. A solution casting is the method to prepare the PU pure and their composite films. The GRN nanosheets and PANI nanopowders was used as fillers. The morphologies, chemical structure, and thermal behavior are investigated. The morphology and phase distribution was observed using SEM and AFM, respectively. The results show that the GRN nanosheets have a rather good dispersion than the PANI nanopowders in PU matrix. The PANI nanopowders present the agglomeration, however the results of PU three-phase composite image show both fillers have a homogeneously distribution and leads to high interfacial polarization. The infrared spectra were of PU pure and their composites recorded using Fourier Transform Infrared Spectroscopy. The increasing of C=O bonding and C=C bonding indicated that the graphene nanosheets greatly influenced to the PU matrix. The interaction between urethane segments in PANI was showed by shifting peak of N-H and C-N and carbonyl groups in the PU matrix the FTIR spectra N-C-N shifts to the higher frequency. The –NCO groups influenced by N-H and indicates that the PANI has better interaction with the PU matrix than GRN and leads to build conductive network. The last characterization is about thermal behavior that the glass transition, melting temperature and the enthalpy changes was determined using DSC. The results in temperature glass and melting slightly increase and it presented the strong interaction between PU matrix with their composites. In this chapter, it has studied about the dielectric and electrical properties of polyurethane composite films filled with graphene nanosheets. The dielectric permittivity was studied over a broad range of frequencies. The effect of graphene nanosheets leads to increase the dielectric permittivity and loss tangent. The dielectric permittivity increased due to the capacitor ability of GRN nanosheets and a great interaction between the matrix and the 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.

The graphene nanosheets offer extraordinary electronic due to strong dispersion in the elctrostrictive polymer. Therefore, the electrostrictive polyurethane and both fillers was studied to discover the effect of fillers for high electromechanical properties**.** The electrostrictive effect with the various fillers was observed using the electrostrictive setup with help from the photonic sensor. The PU three-phase composites presented the incredible electrostrictive effect, the PU three-phase composites showed a good dispersion which improved the interfacial charge. The increasing dielectric properties of the PU three-phase composites indicated that the cooperative interaction between matrix and fillers. As larger free charge quantities, filler network formed and charge carrier effect has increased, a combined effect behavior is achieved. Compared to the two-phase composites, Young’s modulus of PU three-phase composites slightly increased. In the last experimental result, the electrostrictive effect of PU three-phase composites presented significantly better than separate composite.

5.2 Future work

The results showed a closely relation of the electrical properties, mechanical properties and the electrostrictiove properties. The effect of three phase composite have studied to improve the electromechanical ability. Following these work, the future work may focus on the following issues:

a) To gain the larger electromechanical ability, the dielectric permittivity of the electrostrictive polymer should be increased. The promising conductive polymer with another electrostrictive polymer should be investigated in advance.

b) To effect of three-phase composite with another electrostrictive polymer should be studied to enhance the electromechanical ability.

c) These present work can be extended for study in term of energy harvesting.

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Paper I

Enhanced Dielectric and Electrical Properties in Polyurethane Composites with Graphene Nanosheets

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Enhanced Dielectric and Electrical Properties in Polyurethane Composites with Graphene Nanosheets

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Keywords: Electrical properties, dielectric, electrical conductivity, polyurethane, graphene

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 (Tg) 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 coast [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]

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

Where ε, ε^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 Aldric. The conductivity and particle size of graphene are about 4-6 S/cm and 2-3 µm, respectively. The 1-Methyl-2-pyrolidon 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.

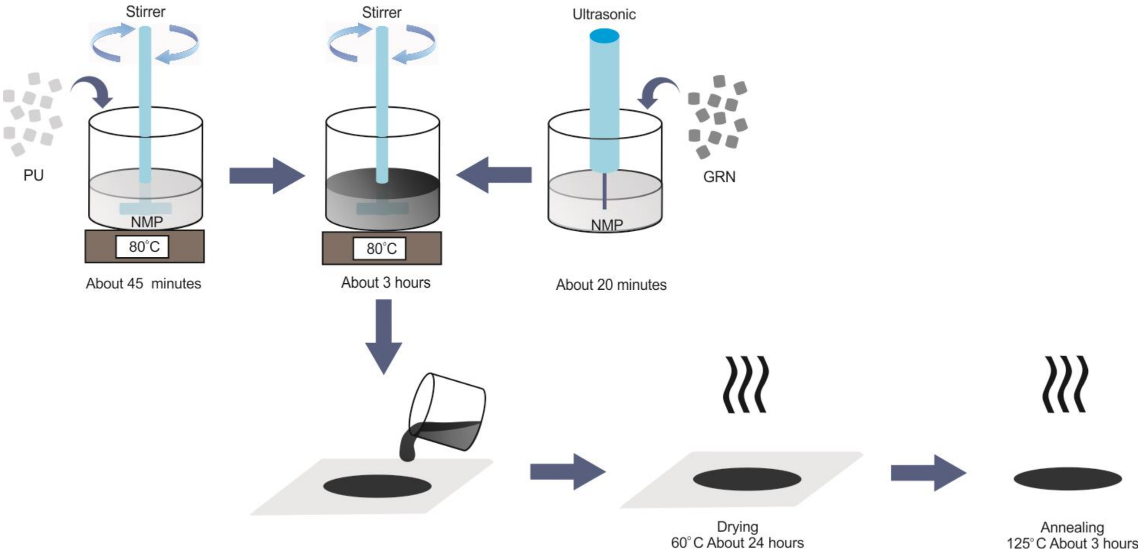


Fig. 1 Schematic illustration of PU/GRN films preparation

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 (Tg) where the samples of 10 mg were cooled under liquid nitrogen till -150˚C and after that heated till 250 ˚C with the heating rate at 5 ˚C/min.

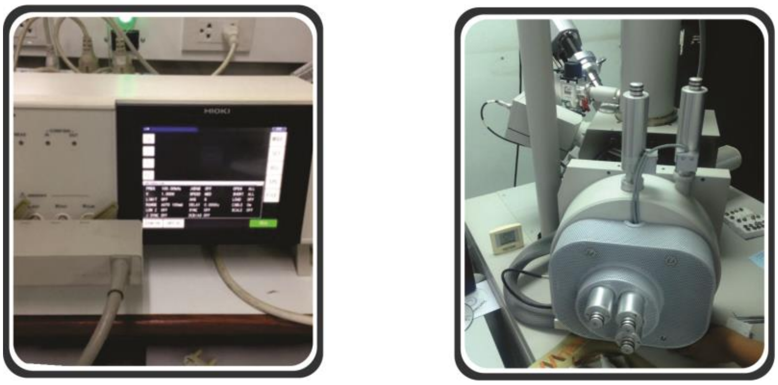
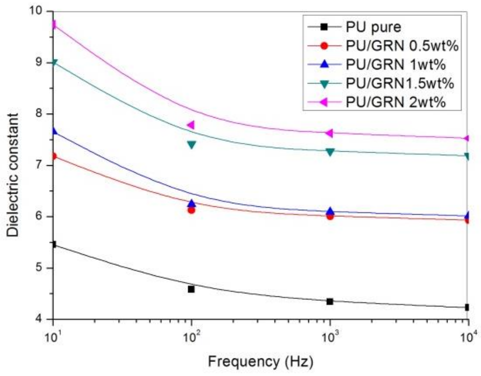


Fig. 2 LCR meter and Scanning Electron Microscopy

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.



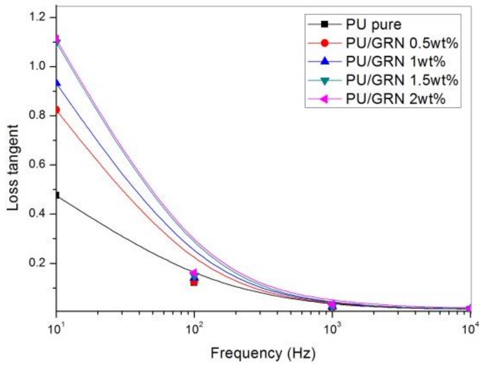


Fig. 3. Effect of frequency on dielectric constant for PU filled with various content of GRN

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

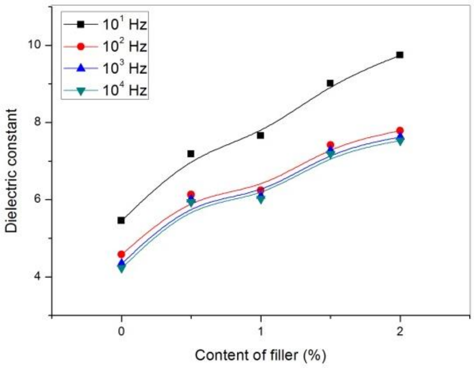


Fig. 5. Effect of GRN content on dielectric constant at Various frequencies.

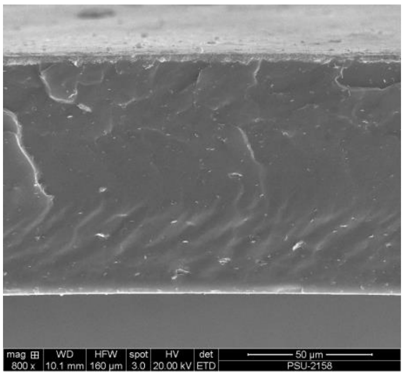


Fig. 6. SEM cross section image of PU filled with GRN at 2wt%

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 10^2 Hz. However, it is found to be slightly increased and large deformation in the range 10^2-10^3 Hz and upper 10^3 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].

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} + \frac{\sigma}{\omega\varepsilon_0\varepsilon'} \qquad (2)$$

In order to study The glass transition temperature (Tg) 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 Tg occurred at -67.37 ˚C. The increase value of Tg was due to the interaction of GRN with the hard segments of PU that can be retricting the mobility of soft segments [8].

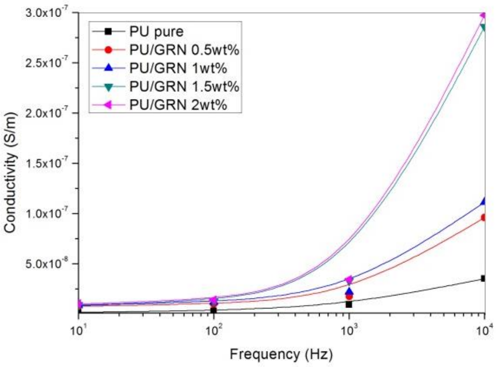


Fig. 7. Effect of frequency on the conductivity for PU filled with various content of GRN

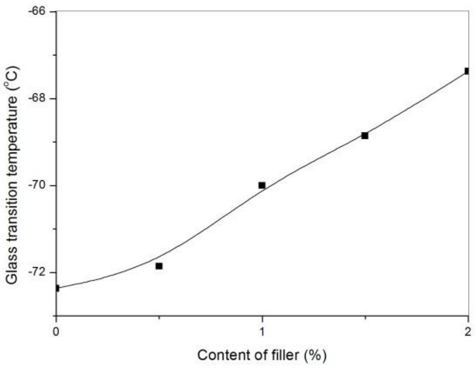


Fig. 8. Effect of GRN content on the glass transition temperature

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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Paper II

High Electromechanical Performance of Modified Electrostrictive Polyurethane Three-Phase Composites

Ardimas, Putson, C.

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High Electromechanical Performance of Modified Electrostrictive Polyurethane Three-Phase Composites

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ABSTRACT

In order to enhance the electrostrictive polymer, the polyurethane has been modified with conductive fillers that are the one promising for an actuator applications, energy conversion, and sensors. The polyurethane matrix and the conductive fillers such as graphene nanosheets and polyaniline nanopowder were prepared to gain the films by solution casting method. The morphology, structure and thermal behavior of PU three-phase composite were observed by SEM imaging, FTIR, and DSC techniques. In addition, the electrical and mechanical properties of polyurethane filled with both composites were investigated by an LCR meter and strain gauge setup. As recently mentioned, the dielectric constant is the important key factor to affecting the electrostriction behavior. The results show the PU three-phase composites enhanced approximately 50% of the dielectric constant. In order to study the electrostriction behavior, the electric field induced strain of polyurethane three-phase composite films were monitored via lock-in amplifier at a low frequency of 1 Hz. In addition, the electrostrictive coefficient was calculated by theoretical analysis and it was indicated that the electrostriction coefficient of the polyurethane three-phase composites up to 0.03% transfer strain at a low electric field. Therefore, it was known that the combination of polyurethane three-phase composites could be increased two times of the electromechanical performance.

Keywords: Electrostriction, Electromechanical properties, Three-phase, Polyurethane, Polyaniline, Graphene.

Introduction

Over the last decade, much interest on current technology has been devoted to the polymers due to the limited performance of conventional materials for instance metals, ceramics, and alloys. Electroactive polymers (EAPs) are kind of smart materials which has the capability to convert energy from mechanical energy to electrical energy and vice versa. Thanks to it have been greatly studied for energy harvesting, sensor and actuator applications.

Compared to other materials, the EAPs, especially the dielectric elastomers (DEs), have various advantages such as flexibility, large dimensional change, easy processing, light weight, and low cost [1-4]. EAPs can be categorized into electromagnetic, dielectric elastomers, electrostatic, electrostrictive, and piezoelectric. Electrostrictive polymers and dielectric elastomers are one of the promising candidates for high-strain actuator due to their strain gives quadratic on the electric field. They can be found in every dielectric material. Moreover, previous work mainly focused on piezoelectric materials. In comparison to the electrostrictive polymers, the piezoelectric materials have brittleness, heavy, large stress and depolarization problems in long-term operation. Therefore, new smart electrostrictive polymers have suggested as great promising materials for energy harvesting, actuator application, artificial muscles, et cetera [5].

In recent work has been studied on the enhancement electrostrictive coefficient based on polyurethane composites. As an electrostrictive polymer, polyurethane is a great interest for a wide range of actuator and transducer applications because of large deformations, high specific energy, and short response time. The dielectric permittivity and Young's modulus are the key factors to enhance the electrostrictive abilities of polyurethane. The last results show that polyurethane enhanced the dielectric permittivity because of a strong polarization to be induced under an electric field. Increasing the dielectric constant leads to the enhance of electrostrictive coefficient. Based on the Eq. 1 that the enhancement strain deformation (S_{33}) depends on the dielectric permittivity through

$$S_{33} = Q.\varepsilon_0{}^2.(\varepsilon_r - 1)^2.E_3^2 \qquad (1)$$

Where ε_r is the real part of the relative dielectric permittivity, ε_0 is permittivity of free space, Q is the intrinsic electrostrictive coefficient, and E is electric field. hence, the relationship with the electrostrictive coefficient (M) might be defined as

$$M_{33} = \varepsilon_0{}^2.(\varepsilon_r - 1)^2.Q_{33}^2 \qquad (2)$$

So the electrostrictive coefficient from (1) and (2) equals

$$M_{33} \propto \frac{\varepsilon_0(\varepsilon_r-1)^2}{\varepsilon_r Y} \qquad (3)$$

Thus the electrostrictive coefficient (M_{33}) is proportional to the dielectric constant (ε_r) and the inversely proportional to Young's modulus (Y) [6]. It is clearly understandable that the dielectric permittivity is one of the key factors for affecting electromechanical properties as shown in Eq. 3.

Several papers presented in order to enhance the dielectric constant, the synthesized conductive carbon such as carbon black, carbon nanotubes (CNTs) and graphene nanosheet (GRN) have to be incorporated in the polymer matrix [7] [8]. In fact, the larger aspect ratio of GRN lattice could be corresponded to the high number of micro-capacitor and leads to great electrical conductivity, hence the GRN has been considered to be a good candidate for high dielectric permittivity filler [9]. The other difference type of filler such as polyaniline also has been proposed to influence the electrostrictive effect [10]. As the great interfacial polarization, the addition of 2wt% polyaniline in PU matrix has the dielectric permittivity of 23.75 and gain the electrostrictive coefficient up to 6.12 x 10^{-16} under 2MV/m electric field [11]. Furthermore, the latest article proposes the effect of hybrid blend where graphene coupled with the variation of carbon for instance CB and MWCNT. The effect of hybrid blend exhibited improve the electrical conductivity and mechanical properties on account of the good dispersion and high interaction with the elastomer matrix [12]. Therefore, the three-phase composites included the polymer matrix, the conductive carbon, and conductive polymer are the great interest due to their high electromechanical performance.

Having considered from the previous mentions in several papers, therefore in this work, the two-phase composites and three-phase composites were prepared with the different type of filler for example graphene nanosheets (GRN) and polyaniline (PANI) in corporate with PU matrix. All of the composites were prepared via solution casting method. In order to keep the similar variation, all of the samples were prepared with the same thickness of 100 µm. The morphological structure, chemical bonds, and phase structure were assessed by using SEM, FTIR, and DSC, respectively. The dielectric coefficient was determined as functions of filler content and frequency with the range of 10^0-10^5 Hz, while Young's modulus is determined as well. In addition, the strain deformation was assessed as a function of DC electric field and the electrostrictive coefficient was calculated and compared each other in order to gain new understanding.

1. Materials and methods

2.1. Materials preparation

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 and Polyaniline powders used as fillers were provided by Sigma Aldric. The conductivity and particle size of graphene about 4-6 S/cm and 2-3 µm. The 1-Methyl-2-pyrrolidone with the 99% purity as a solvent was purchased from sigma Aldrich.

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 and polyaniline were added into the NMP and dispersed for 20 minutes by using ultrasonic. Then graphene and polyaniline solutions were 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-PANI film was taken off from the glass surface and annealed at 125 ˚C for 3 hours to remove remaining solvent and the final thickness of the films was 100 µm.

2.2. Characterization methods

2.2.1. Structure and Morphology

The PU three-phase composites were characterized in the matter of their morphology and dispersion of the fillers by using scanning electron microscopy (SEM, FEI Quanta 400, USA). In order to observe the cross-section, the specimens were sliced using liquid nitrogen, whereas the magnification and the high voltage was conducted in the specimen of 5000x and 20 kV, respectively.

2.2.2. FTIR characterization

By using Fourier Transform Infrared Spectroscopy (FTIR, Bruker EQUINOX 55), the infrared spectra were recorded in the region of 4000-800 cm^{-1}. The FTIR was used to determine the different aspect of functional groups in the PU composites. The curve-fitting results of the specimen were divided into two region where the first region was in the amine region of 2700-3500 cm-1 and the second region was carboxyl region of 1000-1800 cm-1.

2.2.2. Thermal Analysis

A Differential Scanning Calorimeter (DSC, Perkin Elmer DSC7, USA) was used to investigate the thermal stability, including the glass temperature (T_g), the melting transition temperature (T_m) and the enthalpy changes (ΔH) of the composites. The specimen of 10 mg was sealed in the hermetically aluminum crucible, and then with the help of liquid nitrogen, the DSC cell was maintained in an atmosphere equilibrated. The specimen was cooled by using liquid nitrogen, then it was heated from -150˚C to 250 ˚C with the heating rate at 5 ˚C/min

2.2.3. Electrical Properties

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). All of that was determined along the frequency range of 1-10^5 at room condition. The sample was placed in between two electrodes with the diameter size of 21.38 nm and the same thickness of 100 µm. The dielectric constant and the electrical conductivity were calculated by the value of parallel capacitance and conductivity readings, respectively.

2.2.3. Mechanical Properties

The strain gauge setup with the assist of force gauge (BFG50N, Mecmesin, UK) was developed to determine the elastic modulus of each composite film. The dimension of the sample was 3 cm long, 0.5 cm wide and the thickness 100 µm. the piece of sample was stretched with the strain maximum of 10 % at 5 mm/min elongation rate in the length direction. The fixed side of the sample was clamped to the force gauge and the other side was clamped to the moving motor (RC ROBO Cylinder Model RCP 2CR-SA6, 220 mm long). The strain versus stress was determined to obtain their Young's modulus (Y).

2.2.4. Electrostrictive Properties

The electrostriction of polyurethane three-phase composites was assessed by measuring the deformation in the low electric field ($E \leq 6$ MV/m) using a photonic displacement apparatus (MTI-2100 Fotonic sensor, sensitivity 0.0058 µm/mV) as illustrated in Fig. 1. The composite films were sandwiched between two brass electrodes (diameter 20 mm) and it was connected to the high voltage. The small displacement of the composite films was detected by the photonic sensor and a lock-in amplifier (Trek model 610E) will measure as voltage peak-to-peak.

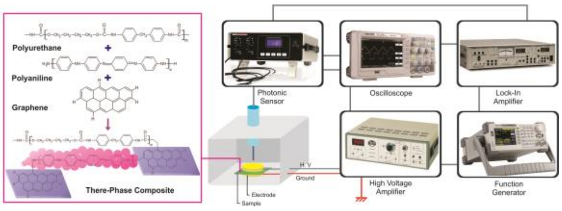

Fig. 1. The Electrostriction Setup

2. Result and Discussion

3.1.SEM characterization

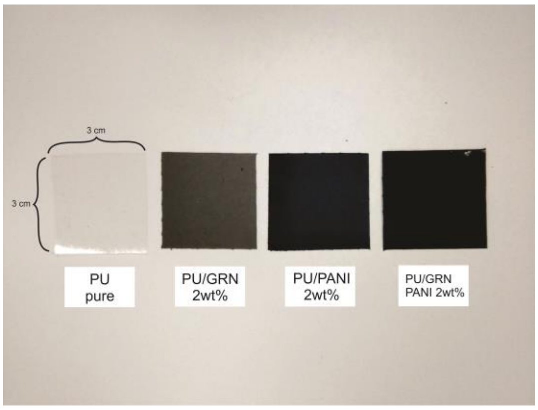

Fig. 2. A photograph of specimens for PU pure, PU/GRN, PU/PANI, and three phase composites

Fig 2 presents a photograph of the specimens for PU pure, PU/GRN, PU/PANI, and PU three-phase composites. Fig. 3 shows morphologies of the PU pure and PU three-phase composites by using the SEM with the magnifications of 5000x. It can be clearly seen that PU pure without the filler was the smoothest than other as presented in Fig. 3a. The SEM images of PU filled with GRN as depicted in Fig. 3b, some nanosheets with different size in the PU matrix is presented. The GRN sheets are observed a good dispersion in the PU matrix. The good dispersion of filler can be affected by the high electrical properties. However, only a few folded and wrinkled nanosheets of GRN are observed. In addition, the micro-agglomerates can be found when the content of filler to be change to PANI which is displayed in Fig. 3c and this lead to increase the conductivity of the polymer matrix [6]. The micro-agglomerates in PU matrix exhibit greater than PU/GRN composites. In the same magnification, the strong interfacial interaction was seen in PU three-phase composites which are shown in Fig. 1d. It can be clearly seen that the better dispersion and distribution of both fillers in the PU matrix compared to the two-phase composites. Both fillers are accidentally incorporate into the PU matrix. It can be said that the GRN nanosheets have a better interface area than PANI nanopowders, while the PANI fillers taking action as filler-filler networks. This synergistic effect might be improved to the electrical and mechanical properties.

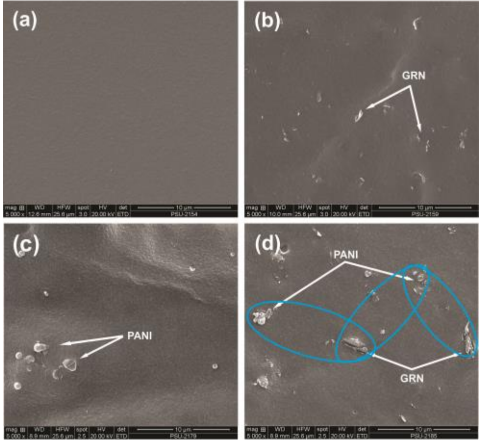

Fig. 3. SEM images at high magnitude of the PU pure, PU two-phase and three-phase composites: the PU pure cross section (a); the PU filled with GRN of 2wt% (b); the PU filled with PANI of 2wt% (c); and PU three- phase composites with the same ratio content of 2wt% (d)

3.2. FTIR characterization

Fourier transform infrared spectroscopy (FTIR) was used to investigate the functional group interactions between PU and both composites. The infrared spectra were recorded in the range of 800-4000 cm^{-1}. Curve fitting amine and carboxyl regions of the PU/GRN composites in their several contents of filler are interpreted in the Fig. 4a and Fig. 4b, respectively. It shows that all FTIR spectra transmittance of the PU pure was increased upon increasing content of GRN. However, new free N-H approximately stretching at 3301.88 cm^{-1} is formed. While the transmittance of hydrogen bond N-H approximately stretching at 3326.95 cm^{-1} is increased [13]. In addition, the hydrogen bond N-H at 3301.88 cm^{-1}, free N-H at 3326.95 cm^{-1}, symmetric hydrogen bond C-H$_2$ at 2852.50 cm^{-1}, and asymmetric hydrogen bond C-H$_2$ at 2937.36 cm^{-1} shift significantly to a higher frequency to 3321.16 cm^{-1}, 3298.01 cm^{-1}, 2850.57 cm^{-1} and 2935.43 cm^{-1}, respectively. The curve fitting of Carbonyl groups of PU/GRN composites is presented in Fig. 4b. The C=O stretching peaks at 1703.01 and 1730.01 reduce to the higher transmittance, except for C=C at 1635.51 cm^{-1} is increased. This confirmed the graphene nanosheets greatly influenced to the PU matrix [14]. The other hand, FTIR spectra of PU filled with the various content of PANI are dispayed in Fig. 2c and Fig. 2d. the stretching transmittance peak at 3326.95 cm^{-1}, 2852.50 cm^{-1}, 1703.01 cm^{-1}, 1531.36 cm^{-1}, and 1365.59 cm^{-1} corresponded to hydrogen bond N-H, symmetric C-H$_2$, hydrogen bonded carbonyl C=O, symmetric amine N-C-N, and C-N stretching, respectively. In comparison with the curve fitting of PU filled with GRN 2wt%, all of their stretching band shift to the lower wavenumber, the shifting peak of N-H And C-N may correspond to the interaction between urethane segment in PANI and carbonyl groups in the PU matrix [15]. Moreover, Miangwei Tian et al described that the FTIR spectra of N-C-N shifts to the higher frequency as a result of the –NCO groups influenced by N-H2 after incorporating PANI into PU matrix shift [16]. By that mean the PANI filler has a better interaction compared to the GRN nanosheets, thus such kind of conductive filler network between GRN nanosheets and hard segment domain of PU matrix is formed.

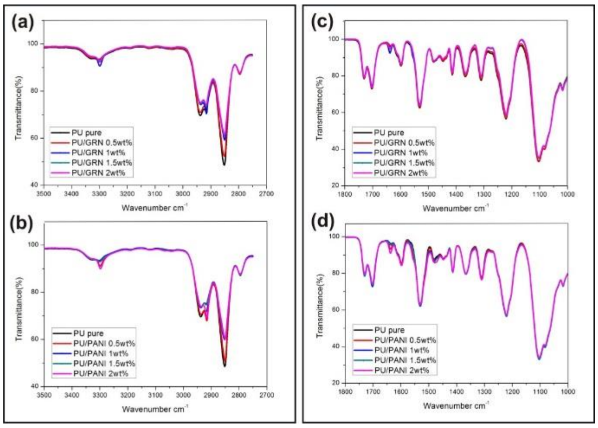

Fig. 4. Curve-fitting results in the FTIR spectra of the PU pure and composites: (a) the PU/GRN composites in the region of 2700-3500 cm^{-1}, (b) 1000-1800 cm^{-1}, (c) and the PU/PANI composites in the region of 2700-3500 cm^{-1}, (d) 1000-1800 cm^{-1}

3.3. Thermal Behavior

In order to study thermal behavior of PU pure and PU three-phase composites were obtained by DSC technique where the composite films of 10 mg were cooled under liquid nitrogen till -150˚C and after that heated till 250 ˚C with the heating rate at 5 ˚C/min. The glass transition temperature (T_g), the melting transition temperature (T_m) and the enthalpy changes (ΔH) every composite are presented in Table 1. The following thermal around -67 ˚C is attributed to the T_g of soft segment (SS). The T_g of PU pure and PU with various fillers are observed. It can be seen that the T_g of PU matrix filled with PANI or GRN is very slightly increased. However, the PU three-phase composites significantly increased up to -65.86 ˚C. The increase of T_g is indicated that micro-crystalline of GRN and PANI dissolved in the soft segments. The mixing micro transition (T_{MMT}) can be attributed to the disruption of the structure is observed at 130 ˚C. In addition, the endotherm transition can be found within the range 140 ˚C-180 ˚C which corresponds to the T_m of crystalline in the hard segments [17]. The T_m of the hard segment in the PU pure has the lowest value compared to the PU three-phase composites, it indicates that a greater crystallinity with increasing the hard segment domains [18-19]. In addition, the crystallinity of the polymer composites depends on the melting enthalpy [20]. It is observed the melting enthalpy of PU/PANI composites is greater than PU/GRN composites, thus can be attributed to the agglomeration of PANI filler inside the matrix as shown in SEM result.

3.4. Electrical properties

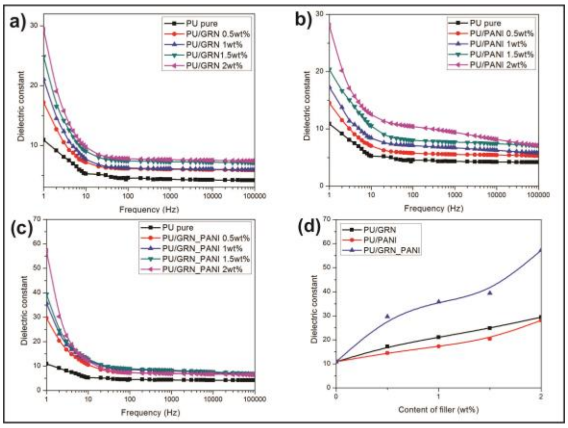

Fig. 5. Plot of dielectric constant for PU two composites and PU three composites. The dielectric constant versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (d) the dielectric constant of PU two-phase composites and PU three-phase composites as a function of content

Fig. 5 presents the dielectric constant of PU pure and PU three-phase composites as a function of frequency from 1 Hz to 100 kHz. In Figure 5a, 5b, and 5c for all composites have the high dielectric constant at the lowest frequency. The decrease of the dielectric constant observed when the frequency slightly increase since the Maxwell-Wagner type Polarization is disappeared. Consequence the contribution of conductive filler, the dielectric constant of PU filled with 2wt% GRN composites value is nearly 2 times higher than PU pure and no obvious difference result with PU/PANI composites as presented in Fig. 5a and Fig. 5b, respectively. It was found that the dielectric constant increases as both filler contents increased. According to the percolation threshold theory, it has been known that the dielectric constant of the two-phase composites depends on the percolation threshold and the fraction of filler. In addition, it has explained the contribution of conducting filler, that the charge quantity will increase due to the polarization of the conducting filler interface is increased [21] [22]. That means an increase of charge carriers because of the incorporation of effective areas of the conductive filler interface. In recent work, the increase of the dielectric constant is depending on the crystal fraction of the polymer [20]. In particular, the crystal fraction usually accompanied the dipole polarization, resulting in the increase of the melting enthalpy of crystallinity in the HS domain can greatly increase the dielectric constant.

It can be seen that the dielectric constant of PU filled with 0.5wt% GRN was higher than the dielectric constant of PU filled with 0.5wt% PANI. The different morphology of both fillers is being seen to be the cause of the dielectric properties improvement. The larger surface area of GRN nanosheets is the key to gain the dielectric constant. In a good agreement that GRN has excellent electrical properties due to larger quantities of free π electron in the surface lattice of GRN nanosheets. It has been explained too that the carrier mobility of GRN can achieve (15,000 $cm^2/V.s$) at room temperature [23].

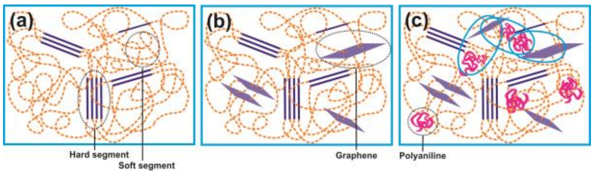

Fig. 6. The schematic of structure deformation of (a) PU pure (b) PU/GRN (c) PU three-phase composites

The dielectric of the PU three-phase composites with the same percentage of filler is higher than both dielectric of two-phase composites and it was raised up to 59 at 1 Hz as shown in figure 5d. It clearly exhibits that the GRN nanosheets as conductive filler has strong Maxwell-Wagner interfacial polarization. Moreover, it has been known that the behavior of conducting filler that the PANI as conducting filler can be able to build filler-filler networks between the gaps of GRN with the hard segment (HS) domain [12]. The PANI contributes to conducting polymer which is dispersed in the soft segment (SS) domain as presented in Fig. 6c. Therefore, the PU three-phase composites have cooperative interaction and possibly produce a combined effect behavior which is greater than their separate effects and leads to achieve the extremely high dielectric constant.

Meanwhile as well as the dielectric constant, the dielectric loss is increased as the frequency is decreased as presented in Fig. 7a, b, and c. This is related to the effect of agglomeration of PANI inside the matrix and it leads to increase the dielectric loss of PU/PANI composites. The result is in a good agreement with the dielectric loss equation which is given by $\tan\delta = \frac{\varepsilon''}{\varepsilon'}$, where $\tan\delta$ is dielectric loss, ε'' is the imaginary parts of the complex dielectric constant, and ε' is the real parts of the complex dielectric constant. In other hand, increase of the dielectric constant also relates to the reducing the dielectric loss effect. It presents that the great the amount crystalline of the graphene sheets can reduce the dielectric loss caused by the isolation effect to the PANI crystallites. In the Fig. 7d depicts that the dielectric loss versus filler content of the tree phase composites at 2wt% of 3.12 which has lowest dielectric loss compared with the other composites.

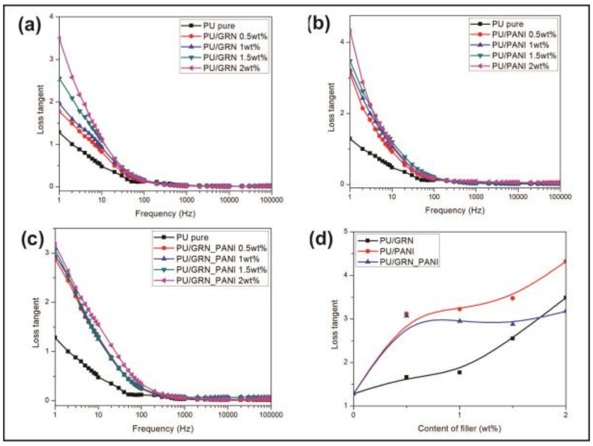

Fig. 7. Plot of dielectric loss for the PU two-phase composites and PU three-phase composites. The dielectric loss versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (d) the dielectric loss of PU two-phase composites and PU three-phase composites as a function of content

The electrical conductivity of all composites as a function frequencies at 10^1-10^5 Hz with various content of filler was shown in Fig. 8a, b, and c. As we can see, the electrical conductivity linearly increases when the frequency is increased. The observed increases in electrical conductivity may be attributed to the polarization of bound charge [24]. Moreover, Fig. 8d presents the electrical conductivity also increases with the amount of filler content, indicating that the number of charge carries is increased [6]. The results in the electrical conductivity slightly different between both of two-phase composites. The electrical conductivity of PU/PANI is higher than the electrical conductivity of PU/GRN, it might be attributed to the conducting networks has been formed between PANI with the matrix and the free electrons can easily transport. In addition, the electrical conductivity can be affected by the dielectric loss.

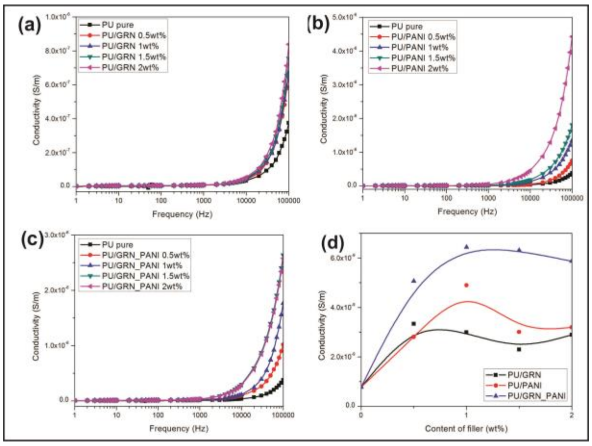

Fig. 8. Plot of conductivity for PU two-phase composites and PU three-phase composites. The conductivity versus frequency of (a) PU/GRN, (b) PU/PANI, (c) PU three-phase composites, and (a) the conductivity of PU two-phase composites and PU three-phase composites as a function of content

3.5. Mechanical properties

The representative Young's Modulus versus content of the filler is shown in Fig. 9. The Young's modulus was determined from the slope of stress versus strain. For all the composites, the Young's Modulus exhibits slowly increased when the content of filler was increased. It can be assumed that Young's Modulus strongly depends on the stiffness in the composite. Increasing the filler content leads to increasing the stiffness. The result indicates that the Young's Modulus of the incorporation of PU with 0.5wt%, 1wt%, 1.5wt%, and 2wt% GRN was significantly larger than PU/PANI composites of 4.27 MPa, 4.55 MPa, 4.64 MPa, and 5.26 MPa, respectively. In the case of GRN filler, the reinforcement effect may occur due to the larger area of GRN lattice [25-26].

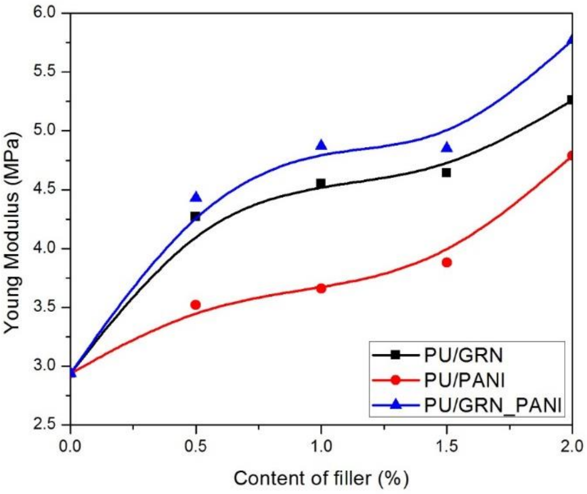

Fig. 9. The Young's Modulus as a function of increased content of filler for the PU two-phase composites and PU three-phase composites

The surface area of GRN is larger than PANI, there is a higher chance of GRN nanosheets exhibit relatively higher interface areas and leads to the strong adhesion of the polymer matrix. In the previous work also reported that the increased Young's modulus can be affected by the strong interaction of covalent bonding and subsequent improved efficient load transfer between the filler with the Polyurethane [27]. Furthermore, the aforementioned of the Tg might be ascribed to the increase of HS domain and it may indicate the HS restrict to the SS mobility. The restricted of the SS increase following the significant increase in the Tg, in which a high reinforcement is achieved. However, it can be seen that the maximum content of GRN and PANI filler does not have an impact on the increased Young's modulus.

3.6. Electrostriction

The electromechanical performance of PU three-phase composites was measured by using the photonic sensor. The results depicted in Fig. 10 show the thickness electric field-induced strain to the applied electric field. A typical increase of percentage electric field-induced strain with increased of the electric field was observed.

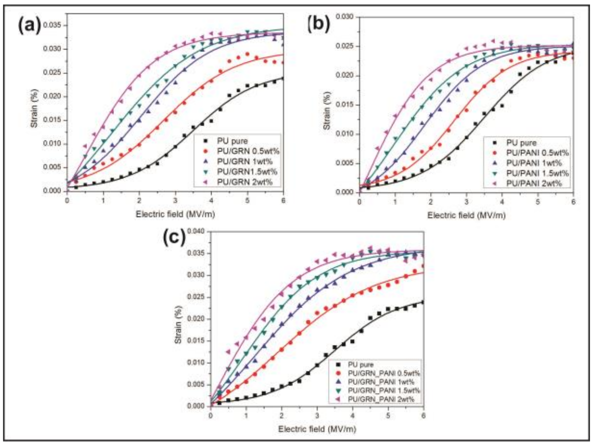

Fig. 10. Variation of strains induced in the PU composites as a function of the electric field for (a) PU/PANI, (b) PU/GRN, and (c) PU three-phase composites

The electric field-induced strain of all the composites was quadratically increased proportionally to the applied electric field. The saturated strain was occurred beyond 3 MV/m and might be caused by the saturation of the electric field induced polarization and the hard segment mobility [28] [29]. So that the maximum of the thickness strain induced the electric field observed at 3 MV/m before saturated. The PU/PANI composites with the content of filler from 0wt% to 2wt% exhibit transfer the approximately strain percentage of 27.7%, while for the PU/GRN exhibit larger strain response of 30%. In addition, the modified PU three-phase composites can improve the strain-induced electric field performance at 3 MV/m. And then the highest percentage of strain response was found from the PU three-phase composites of 40%. As the previous discussion, the PU three-phase composites contributes to the greatly dielectric constant as a result of the polarization which can enhance the strain response at low electric field. In addition, it can be approved that the strain depended on polarization of PU three-phase composites can also be presented by the following equation $S_3 = Q_{33}.P_3^2$, with the same strain direction with the applied electric field [30].

The saturation was occurred in the high electric field regime due to the saturated polarization. When the composite films were applied by an electric field, their electric polarization appears. After turning off the electric field in the composite film, there is no residual polarization anymore. The generated polarization is supposed to be saturated after the maximum electric field requirements every sample.

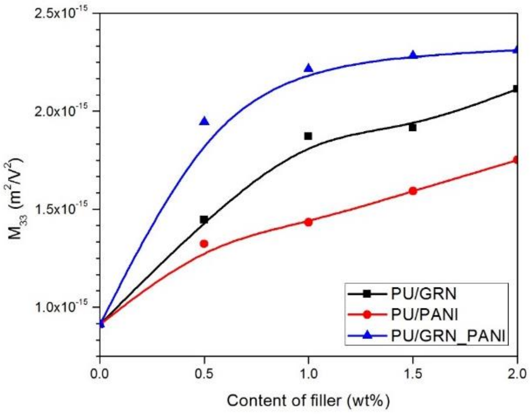

Fig. 11. Variation of the electrostrictive coefficient as a function of filler content at 1 Hz

Table 2 presents summaries of their dielectric constant and Young's modulus, while electrostrictive coefficient (M_{33}) with the Maxwell stress effect included for comparison. The electrostrictive coefficient (M_{33}) was taken from the slope of the transverse strain as a function of quadratic electric field, which can be given by $S_{33} = M_{33}E_3^2$, Where S_{33} is the transverse strain and E_3 is the electric field. In comparison with the Maxwell stress effect, the electrostrictive effect has higher value than the Maxwell stress effect. It can be comprehended that there is no electrostatic interaction beetwen the electrode with the PU composites, and hence the Maxwell stress effect can be minor influenced [31]. Therefore, in this case can be assumed that the tranverse strain in consequence of the electrostrictive effect.

Fig. 11 depicts percentage filler content dependence of the electrostrictive coefficient for PU two-phase composites and PU three-phase composites at E = 4 MV/m. the electrstrictive coefficient was highly enhanced with increased content of filler. The electrostrictive coefficient is depends on the dielectric constant and the Young's modulus by following the Eq. 2 [32]. In several works have been reported that the electrostrictive effect of PU can be enhanced with various conductive filler [9] [11] [8]. The interfacial charge of conducting fillers can contribute to the dielectric constant and lead to enhance the electrostrictive effect. In our case studies, the value of electrostrictive coefficient of PU/GRN composites is larger than value of PU/PANI composites. While comparing beetwen GRN and PANI, not only in term of the interfacial charge of consucting fillers but also in term of the shape and distribution in PU matrix, the nanosheets of GRN broader than PANI which contributes to the enhance the free electrons and leads to increase the dielectric constant, nevertheless somewhat the electrostrictive coefficient of PANI was occurred because of the agglomeration of PANI which affected to the increasing dielectric loss. Moreover, the electrostrictive coefficient of the PU three-phase composites is much higher than PU two-phase composites.

Table 1. The parameters obtained from the DSC thermograms of PU pure and PU three-phase composites

Sample	**Tg (˚C)**	**T_{MMT} (˚C)**	**Tm (˚C)**	**ΔH_m (J/g)**
PU Pure	-67.37	123.22	143.17	16.03
PU/GRN	-66.86	123.72	147.90	21.84
PU/PANI	-67.00	133.91	153.08	24.58
PU/GRN_PANI	-65.86	136.99	174.80	27.82

4. Conclusion

The PU two-phase composite and PU three-phases composite films were synthesized with GRN nanosheets and PANI as the conducting fillers in the PU matrix using solution casting method. The electrostrictive effect with the various fillers was observed using the electrostrictive setup with help from the photonic sensor. The morphological, structure, thermal behavior, electrical and mechanical properties were studied in deep discussion to support the knowledge. The PU three-phase composites presented the incredible electrostrictive effect, the PU three-phase composites showed a good dispersion which improved the interfacial charge. The increasing dielectric properties of the PU three-phase composites indicated that

the cooperative interaction between matrix and fillers. As larger free charge quantities, filler network formed and charge carrier effect has increased, a combined effect behavior is achieved. Compared to the two-phase composites, Young’s modulus of PU three-phase composites slightly increased. In the last experimental result, the electrostrictive effect of PU three-phase composites presented significantly better than separate composite.

Table 2. The comparison of the dielectric constant (ε_r), Young's modulus (Y), M_{33} coefficient, and the Maxwell stress effect for the synthesized PU two-phase composites and PU three-phase composites

Sample	**ε_r at 1 Hz**	**Y (Mpa)**	**M_{33} (m^2/V^2) at 1 Hz**	$\frac{\varepsilon_r \varepsilon_0}{Y}$
PU pure	10.89	2.94	0.91×10^{-15}	3.28×10^{-17}
PU/GRN 0.5wt%	17.19	4.27	1.45×10^{-15}	3.56×10^{-17}
PU/GRN 1wt%	21.08	4.55	1.87×10^{-15}	4.10×10^{-17}
PU/GRN 1.5wt%	24.86	4.66	1.92×10^{-15}	4.72×10^{-17}
PU/GRN 2wt%	29.41	5.26	2.11×10^{-15}	4.95×10^{-17}
PU/PANI 0.5wt%	14.52	3.52	1.32×10^{-15}	3.65×10^{-17}
PU/PANI 1wt%	17.31	3.66	1.43×10^{-15}	4.18×10^{-17}
PU/PANI 1.5wt%	20.39	3.88	1.59×10^{-15}	4.65×10^{-17}
PU/PANI 2wt%	28.09	4.79	1.75×10^{-15}	5.18×10^{-17}
PU/GRN_PANI 0.5wt%	29.63	4.43	1.95×10^{-15}	5.92×10^{-17}
PU/GRN_PANI 1wt%	35.82	4.87	2.22×10^{-15}	6.51×10^{-17}
PU/GRN_PANI 1.5wt%	39.44	4.85	2.28×10^{-15}	7.19×10^{-17}
PU/GRN_PANI 2wt%	57.24	5.77	2.31×10^{-15}	**$8.78\ 10^{-17}$**

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