SCIENTIFIC
RESEARCH
JOURNAL **SRJ**
ISSN: 1675-7009
e-ISSN: 2289-649X

Fabrication and Characterization of Polyurethane/ Graphene Composite: Study on Conductivity and Thermal Properties

Sharifah Nafisah Syed Ismail[1*], Muhammad Iskandar Zulkarnain Mohd Raffee[2], Zuliahani Ahmad[1], Ahmad Faiza Mohd[3,4], Khuzaimah Nazir[1], Nor Mazlina Abdul Wahab[1], Siti Noorashikin Jamal[1], Salamiah Zakaria[1]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA Cawangan Perlis, Kampus Arau, 02600 Arau, Perlis, Malaysia
[2]IFFCO (Malaysia) Sdn. Bhd., PLO 406, Jalan Emas, 81700 Pasir Gudang, Johor, Malaysia
[3]Centre for Chemical Synthesis and Polymer Technology, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[4]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

*Corresponding author's E-mail: sharifahnafisah@uitm.edu.my

ABSTRACT

This study investigated the potential of graphene for improvement of properties of thermoplastic polyurethane (PU) composites in sight of thermal property, electrical conductivity, hardness, gel content and bonding spectra (FTIR). Polyurethane/graphene (PU/G) composites were synthesized by exfoliating graphene with DMF and then blending it with PEG and IPDI via in-situ addition polymerization with varying graphene concentrations (0–0.18 wt %), resulting in uniform dispersion and partial exfoliation of graphene-sheets in PU matrix. The PU/G synthesis was analyzed by IR spectra analysis, which revealed apparent urethane connections and hydrogen bonding. Glass transition temperature (Tg) property of PU exceeded by around 55 % with the addition of graphene, and it improved steadily as graphene concentration increased. 7B pencil hardness replicated the hardness of the PU/G2, indicating an improvement in hardness. The inclusion of graphene had less of an influence on the gel content of PU, with a proof showing that all of the results gel content was between 80 – 90 %. With the addition of 0.088 % graphene to PU, the electric conductivity

PENERBIT PRESS
UNIVERSITI TEKNOLOGI MARA

improved to 76 %. The composite's conductivity was improved due to graphene's capacity to conduct electricity and the covalent link between PU and graphene.

Keywords: Graphene; polyurethane; conductivity; exfoliation

INTRODUCTION

Carbon is classified into numerous types, including graphite, charcoal, diamond, and carbon black. The carbon arrangement could be altered, resulting in diverse properties that serve as real-life capabilities. Graphite is an allotrope of carbon with a distinct structural type. Graphene's unique physical, chemical, and structural features have made it a popular study material [1]. Graphene was composed of an atomic-size layer of sp2 carbon atoms [2]. The hexagon structure of graphene reflects the honeycomb form as graphene is made up of two comparable sub-lattices that are bound together by a pie bond [1].

Polyurethane (PU) is a versatile polymer that is polymerized via polyaddition that required polyol, isocyanate, and a chain extender as starting materials [3]. PU has a wide range of uses, including medical devices, primers, and so on. They have excellent anti-corrosion capabilities, however they have a low electrical conductivity. The incorporation of graphene into the polymer matrix affected the ability of electric charges to flow. Chemical sensors, anti-static materials, and fuel cells have all benefited from the use of enabled-conduction polymer products. As a result, the combination of graphene oxide and polyurethane in the form of a composite is capable of being applied to cells or any sort of semiconductor. Hence, the fabrication of the composite open a path for the application of electrical energy storage (EES).

Every now and then, EES converted the power or energy obtained from sources such as power plants into storage energy [4]. The EES applications ranged from small to huge in terms of energy production as needed. Portable batteries are classified as EES low. Hydroelectric pump storage is a large scale EES where the charges are immense and the output is distributed throughout a country. Tong et al. worked on PU/graphene

in-situ polymerization [4].

To take a deeper look at the technique for this work, the polyurethane/ graphene composite was synthesized using the method previously used by [4] and [5] with minor alterations. The previous research by [4] concentrated on PU/graphene in-situ polymerization. Graphite with honeycomb-like elements has shown to be an excellent filler for improving the electrical properties of polymers. However, the amount of graphene filler must be carefully considered since there is a critical concentration limit over which exceeding the limit may cause fast deterioration.

Although there are several techniques for synthesizing PU/G composite, including solvent dispersion and chemical hybridization, this process is not preferred due to a negative impact on the result from residual solvent. Indeed, it has been demonstrated that sonication of in-situ polymerization at the microscale promotes greater dispersion, resulting in superior uniformity and compatibility. The chemical modified the graphene significantly, improve in PU composite due to the addition cross-link initiated by new chain which could lead to exhibition of some hard and soft segment [6].

Therefore, this research was proposed to modify PU with two distinct loads of graphene using sonication technique followed by polyaddition reaction. The significance creation of this research paper was about the interaction of graphene with dimethyl formamide under sonication to improve the dispersion of graphene before being infused into polyaddition process. The physical and thermal properties of PU/G composites were examined using differential scanning calorimetry (DSC), gel content, pencil hardness as well as their electrical conductivity using electrochemical impedance spectroscopy (EIS).

METHODOLOGY

Materials

Graphene powder (900561 grade) with electrical conductivity (>103

S/m); N, N- dimethyl formamide ($HCON(CH_3)_2$), poly(ethylene glycol), PEG 600 with average Mn= 400 and isophorone diisocyanate ($C_{12}H_{18}N_2O_2$) with molecular weight of 222.29 g/mol were supplied by Sigma Aldrich, United States.

Synthesization of Polyurethane/Graphene Composites

All components used in the methods were first dehydrated in an oven at 80 °C for 12 hours [7-10]. Sonicator was used to softly agitate the suspension of 5.0 mg of graphene and 50 mg of dimethyl formamide (DMF) at 27 °C [5]. The soft-agitation activity was run for one hour [11]. A three-necked reaction flask with a condenser and a mechanical stirrer was set up for polymerization process. The suspension was further homogenized in the reaction flask with 25.6 g of PEG for half an hour at 50 °C. 20 g of IPDI was added into the swirling mixture dropwise for around 45 minutes. The stirring process was repeated until viscous PU was formed. The homogenized solution was transferred to a petri dish and cured in an oven at 60 °C for 48 hours. The formulations were given in Table 1.

Table 1: Table Formulation of PU/G Composites with Different Graphene Loading

Composites	Graphene %	Graphene (g)	IPDI (g)	PEG (g)	DMF (g)
PU	0	0	20	25.6	0.2
PU/G1	0.088	0.04	20	25.6	0.2
PU/G2	0.18	0.08	20	25.6	0.2

CHARACTERIZATION AND TESTING

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical vibration of the PU/G composite materials was measured using a Shimadzu IR Affinity Fourier transformed infrared (FTIR) spectrometer with wavenumbers ranging from 4000 cm^{-1} to 400 cm^{-1} at 32 scans with a spectral solution of 4 cm^{-1}.

Thermal Stability of PU/Graphene

Differential Scanning Calorimetry (DSC) by Perkin Elmer Jade was used to measure the thermal stability of PU/G composite. About 5 mg to 10 mg was used in this analysis. The sample was held for 5 ^{0}C for 5 mins, heated at 0 ^{0}C/min to 180 0C at on a single run, subsequently held for 5 mins to erase the thermal history [12].

Gel Content Test

Each of the samples including the pristine PU and infused graphene PU was measured in weight to evaluate the changes occur on each of taken dimension. Each of the sample was immersed in toluene for 24 hours [13, 14]. The samples were being filtered and dried in an oven at 50 °C until a constant final weight is obtained. The gel content was calculated by using Equation 1.

$$Gel\ Content = \frac{Final\ weight}{Initial\ weight} \times 100\%$$ (1)

Pencil Hardness Test

The hardness test was performed in accordance with ASTM D3363-74 using a variety of graphite pencils ranging from 9B to 9H. B denotes blackness, which also denotes softness, whereas H denotes hardness. The greater the number of B indications, the softer it becomes, and the greater the number of H indications, the higher the level of hardness. To ensure the coating's hardness, the coating must be able to prevent any marks from being left by the pencil graphite. A coating capable of preventing any trace of graphite for a certain type of pencil having the hardness level for that specific type of pencil. The fabrication of sample was poured onto a clean petri dish to ensure that the graphite mark was clearly visible. Each pencil was pressed with a consistent force, slanted at 45 degrees, and scratched approximately 1 cm away.

Electrical Conductivity

An electrochemical impedance spectroscopy (EIS) Princeton Model VERSASTAT4 was used to determine electrical conductivity with applied frequency from 1 MHz to 0.01 Hz at 100 mV amplitude. Each sample

was cut into small pieces with their dimension such as thickness and area were recorded for mathematical reasoning of conductivity magnitude. The temperature was set up at ambient temperature (27 °C) to standardize and imitate the normal condition when in service. The outcome of the tested samples were indirect result- Z_r (real impedance) in the respect of Z_i (imaginary impedance). The curve and flattened line have been observed and ZR value was taken as well as area and thickness to obtain conductivity value.

$$\sigma = \frac{t}{(Rb)A} \tag{2}$$

Conductivity
A = Area
t = Thickness
Rb = Bulk Resistance

RESULTS AND DISCUSSION

Interaction of Graphene with Polyurethane

The chemical interactions between Gr and PU are shown in Figure 1. In this work, the graphene aqueous dispersion was dispersed in DMF at 40 °C for 1 hour using sonicator and intense sound agitation. The well-dispersed graphene particles in DMF reveal complete graphene exfoliation upon ultrasonic dispersion. This means that the graphene has been completely exfoliated [15]. The active site in exfoliated graphene is OH (hydroxyl group). The presence of OH in graphene, when combined with PEG, results in a prepolymer [16].
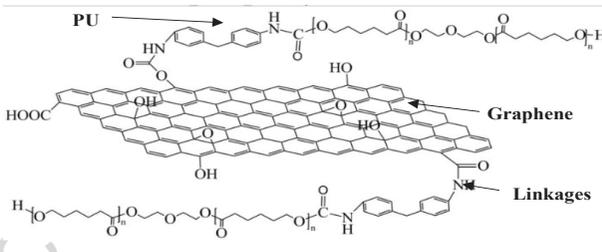

Figure 1: The Chemical Interaction between Graphene and PU [17]

Fourier Transfer Infrared (FTIR) Analysis

The pristine PU has shown a significant number of peaks within the range from 4000 cm^{-1} to 500 cm^{-1}. The basic functional group of PU has been confirmed by the peak between 2920 cm-1 and 2852 cm-1 meaning stretching bond of alkane C-H and a spike revealed in between 1699 cm^{-1} (PU) shifted to 1702 cm^{-1} (PU/G1) correlated to the stretching of C=O bond [18]. Significant peak 1017 cm^{-1} and 1077 cm^{-1} mean the resonance –OCO-NH- (urethane) group. The band located at 1700 cm^{-1} and 3319 cm^{-1} are serve as stretching vibration of hydrogen bonded C=O and –NH- group [19].

Both PU/G1 and PU/G2 showing the peaks with different transmittance. 0.088 wt% peak showed a narrower than 0.18 wt% with transmittance at 85 % and 90 % respectively. With the reduce of graphene content, the bonding magnitude of PU functional group tend to be higher because the less disturbance cause by carbon molecule of graphene. The C-N stretching has been identified in both PU/G1 and PU/G2 stating at 1302.25 cm^{-1} and 1302.70 cm^{-1} respectively. Next, N-H molecular bending sited at 1535.08 cm^{-1} in PU/G1 shifted to 1544.24 cm^{-1} in PU/G2. Both C-N and N-H molecular vibration indicated the graphene and isocyanate interaction [17]. It is noted that 0.088 % G and 0.18 % G exhibit a shifted peak from 3324 cm^{-1}(peak pure PU) to 3332 cm-1 (peak 0.88 %) and peak 0.18 % 3331 cm^{-1} of the N–H group. It verifies that the H-bonding interaction exists between the N–H groups of PU/Gr and the remaining oxygenated groups of graphene, showing an interaction between PU and graphene [15].
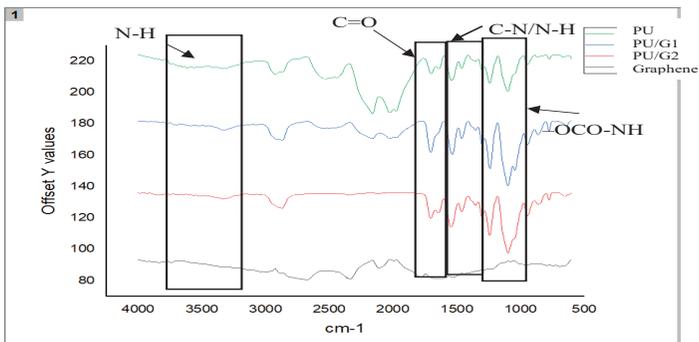

Figure 2: FTIR analysis of PU pristine, PU/G1 and PU/G2 and Graphene.

Differential Scanning Calorimeter (DSC)

Table 2 displays the Tg data for pristine PU, PU/G1 (0.088 %) and PU/G2 (0.18 %) obtained from DSC thermograms. Pristine PU start to become rubbery and less stiffen at 33.96 oC. The addition of 0.088 % graphene into PU has altered the composites to increase the Tg to 52.65 oC, allocated about 64 % increment. As for the influence of 0.18 % of graphene, it can be seen that the Tg keep increasing up to 75 % (69.86 °C).

According to [20], the increasing trend of Tg might be due to the thermally conductive properties of graphene as its two-dimensional structure, further offers a lower thermal resistance between the surface. Comparing the result with the outcome from the research by The Tg was identified as PU at 40 °C and PU-graphene reach at 47 °C. This too has shown that the graphene addition proved the increment of Tg. Another improvement of Tg can be referred to a previous paper by [15] that has conveyed Tg result where TPU at -31.99 °C increased to -29.41°C for TPU/G-0.8. Hence, the results from previous journals supported the fruition in this project regarding thermal characteristic.

The pattern here would be directly proportional to each other as the Tg has increased with the graphene loading. It has been identified that introduction of graphene into polyurethane has optimized the Tg for about 55 % which accounted of every addition of 1.2 x10-3 % of graphene has increase 1 % of Tg temperature. The difference of loading for about 0.092 % has increased the Tg temperature up to 32 %. Based on three sample the, 0.18 wt% (PU-G2) sample possessed highest thermal stability compared to the others while virgin PU has the lowest. For PU containing Gr, the peak shifted to slightly higher temperature, which might be due to a good interaction between graphene and PU indicated by the presence of hydrogen bonding, as analyzed by FTIR [21].

The increased in Tg by incorporation of graphene is because the inhibition of molecular mobility disallowing them to move within each other even they absorb a specific amount of heat. The reason beyond this is related with interphase adhesion among the graphene filler particle of carbon allotrope and group of hard segment or group of soft segment of TPU matrix [7]. Another theory is about H bonding is affecting the Tg of

the composites because of the graphene bonding with PU [15].

This too can be applied with the addition of the graphene filler 0.18 %, where much more graphene filled the volume spaces within the matrix which increase the connectivity between surfaces which allocate the hard segmented section has higher proportion than soft segment. Hard segment and soft segment contributed by IPDI and PEG, respectively. Another evidence is cause by crystallinity where graphene has disrupted the credibility of crosslinking chains to be in order [22]. Hence, the randomness lead to difficulty in disentangle of chain when heat flow. Thus, without incorporation of graphene, pristine PU able to gain mobility once receive low heat amount and eventually harder to slide within chains which result in need of higher amount of heat.

All in all, all of those chains included in the hard segment effected the most by the introduction of heat energy [22]. Another matter that can be brought up is crosslinking density. Based on a writing by [3], fillers like graphene can disrupt the crosslinking ability due to tendency of particle aggregation and inhibition of ally group and in turn decreasing thermogram analysis. However, in this research, the crosslinking density is relatively high by referring the gel content test plus with positively increase Tg characteristic. Thus, the statement from them is negligible.

Table 2: Glass Transition Evaluation by DSC Constitute Sample of PU, PU/ G1 and PU/G2

Samples	Tg value (°C)
PU	33.96
PU/G1	52.65
PU/G2	69.86

Pencil Hardness Test

The results demonstrated that content of graphene allocated at 0.088 wt% (PU/G1) has the hardness level of a 5B pencil. However, with the increasing of graphene loading in the matrix, a significant result has been observed where the filler has reinforced the coating resulting the level hardness reached as high as 7H as tabulated in Table 3.
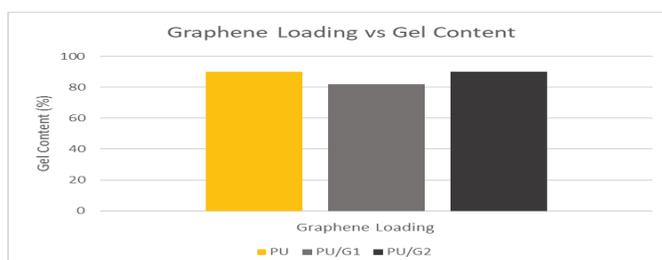
Table 3: Representative of Pencil Hardness Level in the Respective of Different Graphene Loading

Samples	Pencil Type
PU	5B
PU/G1	7H
PU/G2	6B

The differences of the result among the two coatings are affected by the interfacial cooperation between PU and graphene. Pristine PU hold a significant less in hardness due to the structure within. The crosslinking entangled inside matrix is lesser. When the chain unable to entangle with their neighbour chains, they have tendency to move or slide with each other even when a low magnitude of force is applied. As for this case, a hardness level (force) of 6B pencil able to leave graphite mark on pristine PU. Next, the incorporation of graphene volume into the matrix about 0.088 wt% has increased the hardness level up to 5B pencil crossing one level from the previous PU. Thus, this can be elaborate by chain entanglement boosting with the merger of the graphene, generating a less flexible composite than before.

Determination of Gel Content PU/G

Figure 3 shows result on gel content. The pristine PU showed a gel content accumulated at 90 % which is considered as a promising result. Even at none graphene filling, the crosslinking has shown a robust value whichever the crosslinking happened during the polymerization between the PEG and IPDI [23].

Figure 3: The Statistical Graph of Gel Content and Graphene Loading

Upon immersed in the toluene for about 24 hours, the weight of PU has decreased from the original and converted to percentage showing gel content at 90 %. At 0.088 % of graphene (40 mg) the calculated gel content was about 82 %, meaning an 8 % of gel content decrement has been notified. This information disclosed that the graphene has less significant effect on the cross-linked chain in the Polyurethane. Next, the crosslinking density has been increased about 10 % with the graphene content increase up to 0.088 % thus making it consists of 90 % accumulation of crosslinking density. Overall, Pristine PU and PU containing 0.18 % of graphene has the highest crosslinking density. In addition, the crosslinking density determination can be referred as swelling ratio. This is because both terms use the same formula and the concept of loss weight to the solvent.

Swelling ratio is brought up into discussion because the graphene content capable affecting the swelling property of PU. Upon increasing the graphene loading, the composite tends to inhibit the miscibility of solvent happened to less tendency for polyurethane to dissolve in the toluene [24], resulting in low differences of weight loss to the solvent. The present of crosslinking bonding section between graphene and PU has increased the tendency to increase the resistance toward of organic solvent and indicating high amount of crosslinking density [23].

Electrical Conductivity

The testing of conductivity was conducted on the two samples- pristine PU and PU/G composite loading at 0.088 % with temperature was set up at ambient temperature. A semi-circle and flattened raw data graphs were obtained and evaluated in the respective of Z_i (imaginary impedance) and Z_r (real impedance) in order to calculate and tune to electric conductivity (S cm^{-1}). The semi-circle graph represents PU filler with 0.0066 % graphene while the flat line serves as PU pristine.
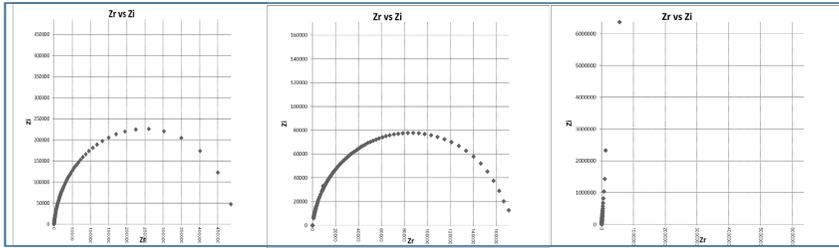
a   b   c

Figure 4: EIS Zr vs Zi Graph of PU (c), PU/G1 (b) and PU/G2 (a)

Based on calculation and Table 4, the pristine PU possessed 3.07×10^{-7} S cm^{-1} of conductivity while PU infused graphene able to increase the conductivity to 5.41×10^{-7} S cm^{-1}. This profound has made a comparative percentage for about 76 % of increment. The PU soft segment categorized as a polymer solvent that to solvate the cations allowing the mobility of the ions hence contribute to the conductivity of the PU [20]. The increase pattern in conductivity is that hydroxyl group bonded covalently between graphene and isocyanate of PU [20] and contact resistance and tunnelling resistance between graphene is low [4].

Table 4: The Conductivity Result OF PU/G

Samples	Thickness (cm)	Area (cm^2)	Bulk Resistance (Rb)	Conductivity (S cm^{-1}) (x10^{-7})
PU	0.378	1.97	625010	3.07
PU/G1	0.101	1.10	169719	5.41
PU/G2	0.115	1.15	477419	2.09

In many composites, the surface resistance plays an essential role in determining the performance of conductivity [25]. However, as for PU/G2 composites, the conductivity was decreased to 2.08×10^{-7} S cm^{-1}. This deduces a decrement for about 61 % of conductivity. Even though, the reduction is significant, the magnitude was still in a range of the previous journal.

A research study conducted by [20] had only managed to get 1.39×10^{-9} S cm^{-1} which is slightly lower conductivity value. This proved that the incorporation of graphene as filler in PU able to increase the conductivity

of composite compared to PU without graphene. Even the further increasing of graphene impacted lesser on the conductivity, the conductivity magnitude is still in range. The conductivity was definitely influenced by the electron mobility provided by graphene that formed network of chains within composites [20]. In addition, the conductivity results were still competence as previous journal that accumulate the conductivity in range 1.00×10^{-8} to 1.00×10^{-12} S cm^{-1} [26].
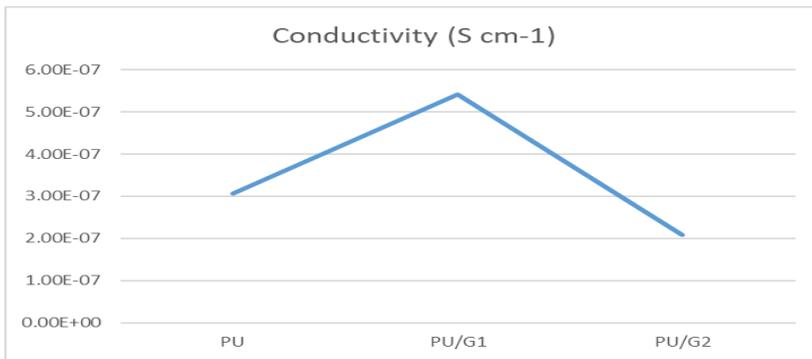

Figure 5: The generated line graph of the conductivity from Table 4
Conclusion

The PU infused with graphene by polyaddition polymerization has been successfully synthesized. Glass transition properties has been improved in which placement of graphene content in PU at 0.18 % increase 105 % of temperature. The hardness for the coating application reached high level of hardness pencil-7H, giving that PU coating compounded with graphene 0.18 wt% creating a near-level of anti-scratch property. The addition of the graphene has less significant effect towards PU crosslinking and apparently the graphene infusion decreased 5 % - 7 % of gel content however upon increasing them help recover the gel content of PU. Lastly, electrical conductivity fluctuated 76 % with the addition of graphene at 0.088 % which respecting the theories and findings of previous journals.

ACKNOWLEDGEMENT

REFERENCES

[1]   B. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, (2010). Graphene and graphene oxide : Synthesis , properties and applications. *Advanced Materials*, 22 (35), 3906–3924.

[2]   D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev and J. M. Tour (2010). Improved synthesis of graphene oxide. *ACS Nano 4* (8), 4806-4814.

[3]   J. T. Kim, B. K. Kim, E. Y. Kim, H. C. Park, and H. M. Jeong, (2014). Reactive & functional polymers synthesis and shape memory performance of polyurethane / graphene nanocomposites. *Reactive and Functional Polymers,* 74, 16–21.

[4]   Y. Tong, S. Bohm, and M. Song, (2017). The capability of graphene on improving the electrical conductivity and anti- corrosion properties of Polyurethane coatings Applied Surface Science The capability of graphene on improving the electrical conductivity and anti-corrosion properties of Polyurethane. *Applied Surface Science,* 424, 72–81.

[5]   N. Yousefi, M. M. Gudarzi, Q. Zheng, X. Lin, X. Shen, J. Jia, and J. K. Kim, (2013). Highly aligned, ultralarge-size reduced graphene oxide/ polyurethane nanocomposites: Mechanical properties and moisture permeability. *Composites Part A: Applied Science and Manufacturing,* 49, 42–50.

[6]   Z. Yang, H. Peng, W. Wang, and T. Liu, (2010). Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites. *Journal of Applied Polymer Science,* 116(5), 2658–2667.

[7]   J. Bian, H. L. Lin, F. X. He, X. W. Wei, I. T. Chang, and E. Sancaktar, (2013). Fabrication of microwave exfoliated graphite oxide reinforced thermoplastic polyurethane nanocomposites: Effects of filler on morphology, mechanical, thermal and conductive properties. *Composites Part A: Applied Science and Manufacturing,* 47(1), 72–82.

[8]   J. Bian, X. W. Wei, H. L. Lin, L. Wang, and Z. P. Guan, (2011). Comparative study on the exfoliated expanded graphite nanosheet-PES composites prepared via different compounding method. *Journal of Applied Polymer Science, 1*24 (5),3547-3557.

[9]   J. Bian, X. W. Wei, H. L. Lin, S. J. Gong, H. Zhang, and Z. P. Guan, (2011). Preparation and characterization of modified graphite oxide/ poly (propylene carbonate) composites by solution intercalation. *Polymer Degradation and Stability,* 96(10), 1833–1840.

[10]   J. Bian, M. Xiao, S. J. Wang, Y. X. Lu, and Y. Z. Meng, (2009). Novel application of thermally expanded graphite as the support of catalysts for direct synthesis of DMC from CH_3OH and CO_2. *Journal of Colloid And Interface Science,* 334(1), 50–57.

[11]   J. T. Choi, D. H. Kim, K. S. Ryu, Lee, L. Hyung-il, H. M. Jeong, C. M. Shin, J. H. Kim and , B. K. Kim, (2011). Functionalized graphene sheet/polyurethane nanocomposites: Effect of particle size on physical properties. *Macromolecular Research*, 19(8), 809–814.

[12]   J. Zhang, C. Zhang, and S. A. Madbouly, (2015). In situ polymerization of bio-based thermosetting polyurethane/graphene oxide nanocomposites. *Journal of Applied Polymer Science,* 132(13), 1–8.

[13]   S. Practices, (2001). Standard Practices for Evaluating the Resistance of Plastics to Chemical. 95(Reapproved), 4–10.

[14]   V. V. Gite, P. P. Mahulikar, D. G. Hundiwale, and U. R. Kapadi, (2004). Polyurethane coatings using trimer of isophorone diisocyanate. *Journal of Scientific and Industrial Research,* 63, 348–354.

[15] H. Liu, Y. Li, K. Dai, G. Zheng, C. Liu, C. Shen, X. Yan, J. Guo and Z. Guo, (2016). Electrically Conductive Thermoplastic Elastomer Nanocomposites at Ultralow Graphene Loading Levels for Strain Sensor Applications. *Journal of Materials Chemistry C*, 4, 157-166.

[16] U. Khan, A. O. Neill, M. Lotya, S. De, and J. N. Coleman, (2010). High-concentration solvent exfoliation of graphene. *Small* ,6 (7), 864–871.

[17] Q. Jing, W. Liu, Y. Pan, V. V. Silberschmidt, L. Li, and Z. L. Dong, (2015). Chemical functionalization of graphene oxide for improving mechanical and thermal properties of polyurethane composites. *Materials and Design,* 85, 808–814.

[18] N. Yousefi, M. M. Gudarzi, Q. Zheng, X. Lin, X. Shen, J. Jia, and J. K. Kim, (2013). Highly aligned, ultralarge-size reduced graphene oxide/ polyurethane nanocomposites: Mechanical properties and moisture permeability. *Composites Part A: Applied Science and Manufacturing,* 49, 42–50.

[19] D. Cai, J. Jin, K. Yusoh, R. Rafiq, and M. Song, (2012). High performance polyurethane/functionalized graphene nanocomposites with improved mechanical and thermal properties. *Composites Science and Technology,* 72(6), 702–707.

[20] F. Jasmi, N. U. R. H. Azeman, A. A. A. Bakar, S. Member, M. Saiful, and D. Zan, (2018). Ionic conductive polyurethane-graphene nanocomposite for performance enhancement of optical fiber Bragg grating temperature sensor. *IEEE Access,* 6, 47355–47363.

[21] B. Adak, M. Joshi, and B. S. Butola, (2019). Polyurethane/ functionalized-graphene nanocomposite films with enhanced weather resistance and gas barrier properties. *Composites Part B*, 176, 107303.

[22] D. A.Nguyen, Y. R. Lee, A. V. Raghu, H. M. Jeong, C. M. Shin, and B. K. Kim, (2009). Morphological and physical properties of a thermoplastic polyurethane reinforced with functionalized graphene sheet. *Polymer International,* 58(4), 412–417.

[23] C. Oh, S. Lee, J. Park, and D. Lee, (2019). Thermally self-healing graphene-nanoplate/polyurethane nanocomposites via diels – Alder reaction through a one-shot process. *Nanomaterials,* 9 (3), 434.

[24] H. Kang, H. Zuo, K. Wang, Z. Zhang, L. Liu, and B. Guo, (2014). Using a green method to develop graphene oxide/elastomers nanocomposites with combination of high barrier and mechanical performance. *Composites Science and Technology,* 92, 1–8.

[25] G. S. Marlow, and M. B. Das, (1982). The effects of contact size and non-zero metal resistance on the determination of specific contact resistance. *Solid State Electronics*, 25(2), 91–94.

[26] I. S. Fahim, (2013). A nanoscale investigation of mechanical, thermal stability and electrical conductivity properties of reinforced thermoplastic polyurethane/graphene nanocomposite. American *Journal of Nanoscience and Nanotechnology,* 1(1), 31.