



# Improvement of dielectric properties and thermal conductivity of TPU with alumina-encapsulated rGO

Eyob Wondu<sup>a</sup>, Zelalem Chernet Lule<sup>b</sup>, Jooheon Kim<sup>a,b,c,\*</sup>

<sup>a</sup> Graduate School of Intelligence Energy and Industry, Chung-Ang University, Seoul, 06974, South Korea

<sup>b</sup> School of Chemical Engineering and Material Science, Chung-Ang University, Seoul, 06974, South Korea

<sup>c</sup> Department of Advanced Materials Engineering, Chung-Ang University, Anseong-si, Gyeonggi-do, 17546, South Korea

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## ABSTRACT

This study focuses on the fabrication of thermoplastic polyurethane (TPU) composites with high thermal conductivity and dielectric constants, which can be used in electronic devices that are able to store charge and dissipate heat. To fabricate the samples, GO was reduced via sonication, and alumina-encapsulated GO particles were prepared with sonication and high-temperature magnetic stirring for 24 h. The TPU composites were fabricated through the melt extrusion process after removing the moistures via oven drying. The storage of charge is enabled by the high dielectric constant obtained from the APTES-treated alumina-encapsulated GO-TPU composites; the heat dissipation characteristics are found from the high thermal conductivity and thermal image camera of the sample. Surprisingly, the tensile and ductile properties of the composite are promising. The thermal conductivity of the APTES treated alumina encapsulated TPU composite is 3.2 times higher than that of the neat TPU. The dielectric property of the GO containing alumina composites is promisingly higher as compared to all other composites investigated.

## 1. Introduction

Improved working capacity has been required for modern-day electronic devices. In addition, they are on moving to slim, small, multi-functional, light devices. This property is inherited by miniaturizing to dissipate excess heat more easily, they further require high dielectric constants. When electronic materials have poor dissipation and energy storage characteristics, they cannot cope up with today's cannot compensate for the excess heat generation by users in different applications and this in turn requires a higher energy. Thermal dissipation materials, energy storage devices, require thermally conductive, high-dielectric-constant materials with resilient mechanical properties. The dielectric constant is a measure of the capacity of a material to store energy; the thermal conductivity represents the ability of a material to withstand excess heat by dissipation. There are different routes for preparing this kind of materials in modern technology. For example, polymer materials modified with a certain filler or fillers for the preparation of thermally conductive, high-dielectric-constant composites are promising candidates [1]. Polymer-based composites with high thermal conductivity and dielectric constants are easy to use; they provide high power densities and good insulation characteristics, which make them

promising candidates for energy storage devices.

Many researchers have investigated thermally conductive polymer composites [1–26] and their dielectric properties; they have devoted much effort to improving the thermal conductivity and dielectric properties of polymer composites. In Ref. [14], we have investigated the thermal conductivity of thermoplastic polyurethane (TPU) composites was improved with alumina as a filler; the thermal conductivity was improved without negatively affecting the mechanical properties. Guo et al. [20] studied the thermal conductivity of polymer composites upon coating the multiwalled carbon nanotubes with multi-layered silica. In their work the silica coating improved the thermal conductivity of the composite. Zhang et al. [27] studied the thermal conductivity and mechanical properties of Al<sub>2</sub>O<sub>3</sub>- and graphene-containing polyurethane composites. The thermal conductivity was improved without significantly affecting the mechanical properties of the composites. Bonardd et al. [1] investigated the a biobased composites with an improved dielectric constants upon usage of nanocrystals of cellulose modified with nitrile and chitosan. The resulting flexible and homogeneous material had a higher dielectric constant because of the generation of high dipole moments. Mirkhani et al. fabricated MXene-based nanocomposites of poly (vinyl alcohol) to improve the dielectric constant and

\* Corresponding author. Graduate School of Intelligence Energy and Industry, Chung-Ang University, Seoul, 06974, South Korea.

E-mail address: [jooheonkim@cau.ac.kr](mailto:jooheonkim@cau.ac.kr) (J. Kim).

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minimize dielectric loss. The MXene provided good mechanical and dielectric characteristics. The researchers used a solution casting method to fabricate the composite, which had a high dielectric constant and low dielectric loss.

However, very rare researchers have tried to obtain a highly thermally conductive device with a high dielectric constant. This study focuses on the preparation of highly thermally conductive TPU composites with high dielectric constants. Alumina particles were used to circumvent high electrical conductivity development while retaining the mechanical properties of the composite; in addition, reduced graphene oxide (rGO) was applied to obtain a composite with a higher dielectric constant and thermal conductivity. The rGO was encapsulated with alumina particles by treating the alumina particle surfaces with aminopropyltriethoxysilane (APTES). The aim was to obtain a highly thermally conductive TPU composite with good dissipative nature and a high dielectric constant due to the APTES-treated alumina-encapsulated GO particles as fillers without affecting the mechanical properties of the composite. The fabricated composites thermal conductivity, morphological appearance, tensile properties, dielectric properties, thermal degradation properties were investigated.

## 2. Materials and methods

### 2.1. Materials

Thermoplastic polyurethane (TPU), polyester based which is to be used as a matrix were procured from Dongsung Chemical, Ulsan, Korea. An aluminum oxide ( $\text{Al}_2\text{O}_3$ ) sample with an average size of 15  $\mu\text{m}$  and aminopropyltriethoxysilane (APTES) were obtained from Sigma Aldrich, St. Louis, MI, USA. Moreover, ethanol was purchased from Daejung Chemical and Metal Co. Ltd. (Seoul, Korea). The graphene oxide (GO) was procured from GrapheneAll, Siheung-si, Gyeonggi-do, Korea.

### 2.2. Methods

#### 2.2.1. Preparation of filler particles

The alumina particles surface were treated with APTES according to the method in Ref. [14]. The alumina particles were first dried in an oven at 60 °C before the attachment of hydroxyl groups with KOH pellets. The OH attachment was realized with 3 M KOH solution in 100 mL deionized water (DI) at 80 °C under stirring in an oil bath for 36 h. After the OH-attachment, vacuum filtration was performed to neutralize the basic solution with DI water. The solution was treated with DI water until it became neutral. The neutralized alumina particles with attached OH were dried in a vacuum drier for 24 h at 80 °C and then dispersed in ethanol at 80 °C; 5% APTES (weight percentage) was poured into the solution, upon stirring. The APTES attachment took 24 h under stirring. Afterward, the solution was filtered with vacuum filtration washing with ethanol. The filter cake was dried in an oven drier for 24 h. Moreover, GO particles were reduced with probe sonication; 2 mg GO was dispersed in DI water and sonicated at an amplitude of 20% for 2 h. The sonicated GO was weighed for centrifugation at an equal weight and centrifuged to separate the DI water from the rGO. The centrifuged rGO was dried in a vacuum drier at 80 °C for 24 h prior. In the next step, the rGO particles were encapsulated with alumina via probe sonication; 5 wt % rGO, with respect to the alumina weight was sonicated in KOH solution with a pH value of 4.5. The APTES-treated alumina was weighed and dispersed in a solution of HCl to prepare a solution with a pH of 4.5. The acidic medium APTES-treated alumina particles were poured into the rGO solution under sonication and sonicated for 2 h. The solution was transferred to magnetic stirring medium at 80 °C for 24 h to cover the rGO surfaces with alumina particles. The alumina-encapsulated GO solution was separated from the solvent via centrifugation. Moreover, the centrifuged alumina-encapsulated GO particles were oven-dried for 24 h.

The TPU matrix was dried in an oven at 60 °C before fabricating the

**Table 1**

Properties of the TPU-GO-Alumina composites.

Specimen	Tensile strength (MPa)	Elongation at break (%)	Dielectric constant	Thermal conductivity (W/m.K)
Neat TPU	11.8	381	0.8	0.21
GO-TPU	6.4	170	1.8	0.62
TPU-Al <sub>2</sub> O <sub>3</sub>	11.2	420	2.0	0.43
TPU-TAl <sub>2</sub> O <sub>3</sub> -GO	9.6	335	21.2	0.63

composite to prevent the creation of voids in the final product. The dried alumina-encapsulated rGO particles and TPU had a ratio of 40/60. Furthermore, to create a 5% GO/TPU sample for comparison, an untreated alumina-encapsulated rGO composite with 40/60 ratio was fabricated via twin extrusion (model BA-11, L/D ratio = 40, Bau Technology, Seoul, Republic of Korea) at an extrusion speed of 83 rpm at 210 °C.

## 3. Characterization

The surfaces of the rGO and GO particles were compared via field emission scanning electron microscopy (FE-SEM; Sigma, Carl Zeiss, Oberkochen, Germany). In addition, the improved thermal stability of the rGO particles with respect to that of the GO particles was analyzed with FE-SEM. The recording of the reduced GO crystal structures at 40 kV and 40 mA was studied with X-ray diffraction (XRD, New D8-Advance/Bruker-AXS) a scan rate of 1°/s and Cu-K $\alpha$  radiation ( $\lambda = 0.154056$  nm). The APTES attachment results after the hydroxyl treatment of the alumina particles was studied with Fourier transform infrared spectroscopy (FTIR; Nicolet, is5, Thermo Fisher Scientific, Seoul, Korea), and the amount of APTES attached to the surfaces of the alumina particles was determined with TGA. The surfaces of the APTES-treated alumina particles were studied with FE-SEM after having coated the surface-treated alumina particles with platinum (Pt) to circumvent the charge accumulation during analysis.

Furthermore, the thermal, mechanical, morphological, conductivity, and dielectric properties of the TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites were investigated. The thermal degradation of the TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites was investigated with TGA (TGA-2050, TA Instruments, New Castle, DE, USA) approximately 5–8 mg of the specimens was weighed and the thermogravimetry was taken place in a nitrogen gas atmosphere. A universal testing machine (UTM; model UTM-301, R&B Corp., Daejeon, Korea) was used to investigate the tensile characteristics of the TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites; two samples of each type were investigated at a crosshead speed of 15 mm/min and force load of 1000 MPa per millimeter; the specimens were prepared in accordance with the ASTM D412. The morphological behavior, adherence characteristics of the alumina-encapsulated GO particles on the TPU matrix as compared to those of the neat TPU, and the pristine alumina GO particles were explored with FE-SEM (Sigma, Carl Zeiss, Oberkochen, Germany). The thermal conductivity was assessed with laser flash analysis (LFA467 Hyper-Flash, Netzsch Instrument Co., Selb, Germany). In addition, an impedance analyzer (Agilent, 4294A) was used to investigate the dielectric properties of the TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites at 40–10<sup>6</sup> Hz at room temperature.

## 4. Results and discussions

The main objective of this research work was to fabricate thermally conductive TPU-alumina-GO composites with high dielectric constants and without a significant effect in thermo-mechanical properties. Highly thermally conductive thermo-mechanical composites with high dielectric constants are not easy to prepare. A good thermally conductive

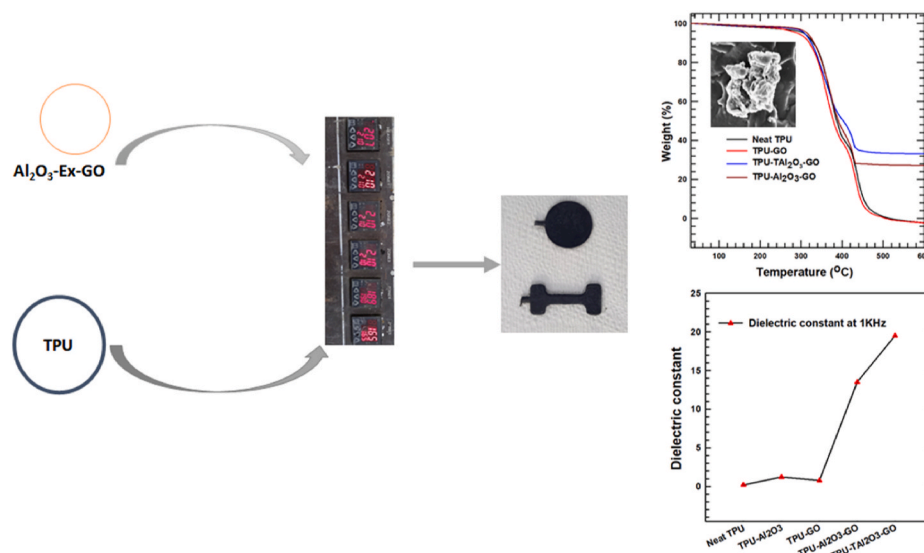


Fig. 1. Scheme for fabrication of TPU-Al<sub>2</sub>O<sub>3</sub> GO composites.

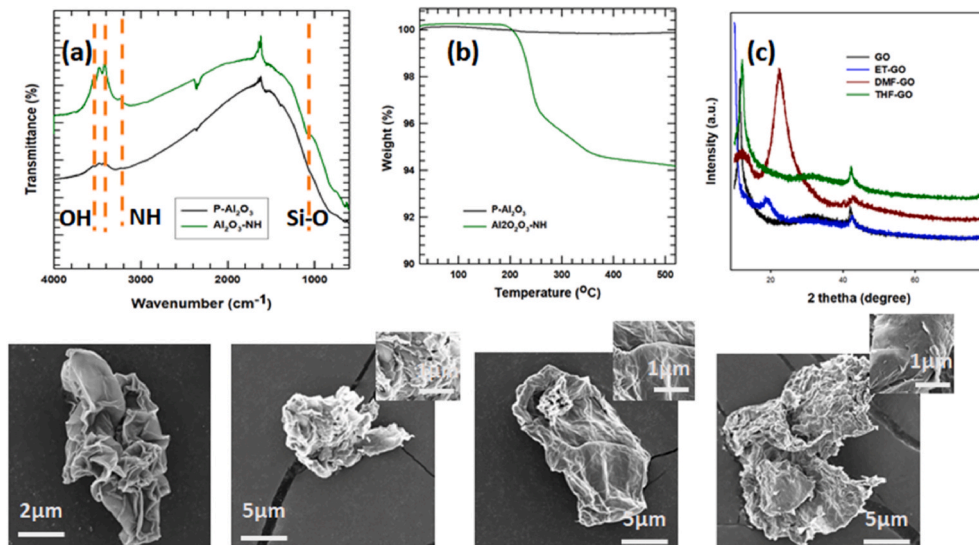


Fig. 2. Characterization of filler particles: (a) FTIR analysis of APTES treated alumina; (b) TGA analysis of APTES treated alumina particles; (c) XRD analysis results of exfoliation of GO with various solvents; FE-SEM analysis results of (d) Pristine GO; (e) THF-exfoliated GO; (f) Ethanol exfoliated GO; (g) DMF-exfoliated GO.

polymer composites with a filler having a good dielectric constant must be available (see Table 1). In this study, a composite with a high dielectric constant was prepared by reducing the high electrical conductivity of rGO with alumina encapsulation and by treating the surfaces of the alumina particles with APTES. The twin extrusion method was used to prepare the composites. Fig. 1 represents a scheme for fabrication of the composites, the temperature profile is taken from the twin extruder.

The successful attachment of hydroxyl and silane groups on the surface of alumina particle was confirmed with FTIR analysis. Fig. 2(a) represents the FTIR analysis results. The data were recorded at 400–4000  $\text{cm}^{-1}$  wavenumber with the attenuated total reflectance method. At approximately 3500–3200  $\text{cm}^{-1}$ , OH-groups were observed; they were due to the treatment of the alumina particles in 3 M KOH solution, which prepared their surfaces for the attachment of silanes. The amine groups (NH) due to the silane attachment were visible at the double wavelength (3300  $\text{cm}^{-1}$ ) of the OH-groups. Moreover, SiO-CH<sub>2</sub> groups were found at 1248  $\text{cm}^{-1}$ . In addition, the attached APTES amount was determined via TGA.

Fig. 2(d) shows the TGA thermograms of the pristine and APTES-treated alumina particles. The silane groups on the samples started to degrade at 180 °C. The final degradation temperature was 345 °C. Approximately 95% of the final residue remained after the final degradation temperature; thus, the degraded 5% corresponds to silane groups.

The reduction of GO was investigated with the XRD analysis. Fig. 2(c) reflects the crystalline structure of the GO and rGO with different solvents. GO's pattern of diffraction had a peak around 11.5° that arises due to the (001) plane. Because of the strong van Der Waals forces, GO was aggregated together after reduction is taken place [28]. A broad, peak for Ethanol exfoliated GO is observed which was due to restacking of GO's partially. Fig. 2(d–g) displays the FE-SEM analysis of GO, THF exfoliated-, Ethanol exfoliated-, DMF-exfoliated- GO's respectively taken at 5  $\mu\text{m}$  and 1  $\mu\text{m}$ . The exfoliation has resulted in reduced GO which has been stipulated in the XRD analysis. The results display a regular shape for ethanol exfoliated GO particles and almost the opposite for THF and DMF exfoliated GO.

Fig. 3 demonstrates the thermal degradation characteristics of the neat TPU, TPU-Al<sub>2</sub>O<sub>3</sub>, TPU-GO, TPU-Al<sub>2</sub>O<sub>3</sub>-GO, and TPU-TAl<sub>2</sub>O<sub>3</sub>

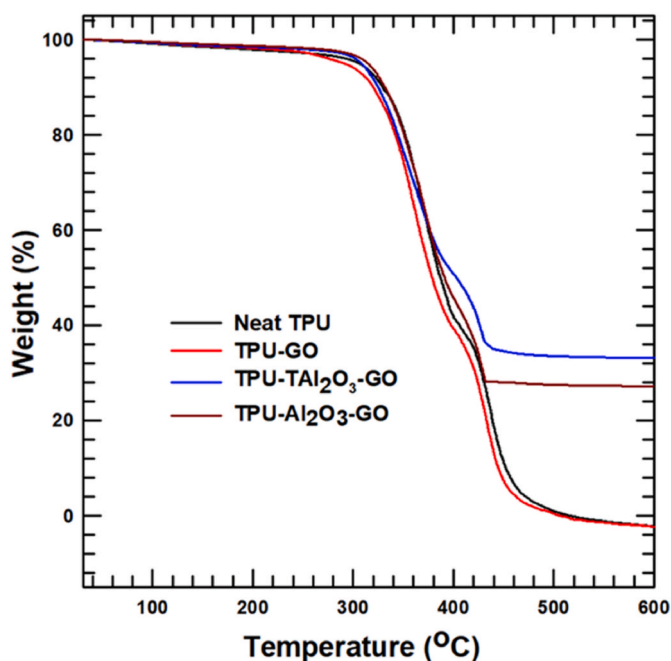


Fig. 3. Thermal degradation features of TPU and its corresponding, GO and alumina composites.

particles as a function of temperature. We analyzed the thermal degradation features at 25–600 °C at 20 °C/min heating rate in a nitrogen gas atmosphere. The thermal stability of the neat TPU was very good; the application of filler particles did not significantly impact its stability. However, the deposition of GO particles onto the TPU matrix has slightly affected its thermal stability (hence, the TPU-GO composite is less thermally stable). Fortunately, the addition of alumina particles and GO to the matrix has improved the thermal stability of the composite. Neat TPU starts degrading at 260–310 °C; it degrades at an approximately infinite slope up to 385 °C when the third degradation stage begins. It continues degrading with an increasing negative slope until the final degradation stage begins at 425 °C; in this stage, it degrades continuously until it reaches the residue stage at 475 °C. Thus, the thermal degradation process of TPU has five stages including the residual stage.

The TPU-GO composite (highlighted in red in Fig. (3)) is slightly less thermally stable than the other composites. It starts degrading with a linear slope at 265 °C and exhibits an approximately infinite slope between 360 and 389 °C. It shows the same degradation behavior as the other composites before reaching the final residual temperature of 470 °C; however, its final residual temperature is lower than that of the other composites.

The alumina-encapsulated GO composites of the TPU matrix degrade in a similar manner to the neat TPU; however, the final residual temperature is 440 °C. The final residue at the end of the degradation process constitutes approximately 35%, which is the exact amount of alumina that has been added to the TPU matrix together with 5% GO.

The adhesion characteristics of the liquid nitrogen-fractured neat TPU, TPU-GO, TPU-Al<sub>2</sub>O<sub>3</sub>, TPU-Al<sub>2</sub>O<sub>3</sub>-GO, and TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites were evaluated with FE-SEM; before the analysis, the specimens were coated with Pt to prevent charge accumulations during electron scanning. Fig. 4 illustrates the results of the morphological analysis of the composites. According to Fig. 4(a), the neat TPU has a rough, fractured, uniform surface that might be owing to its ductile nature. Fig. 4(c) shows the surface morphologies of the alumina TPU (TPU-Al<sub>2</sub>O<sub>3</sub>) composites, which seem more brittle than the neat TPU; the alumina particles only exist on the TPU surface, which may be due to the rigidity of the TPU surface and the untreated alumina particles. By contrast, the surfaces in Fig. 4(e) display good adherence properties to the TPU matrix; this may be due to the application of APTES-treated alumina particles to encapsulate GO; this resulted in good compatibility between the filler particles and TPU matrix. However, the surface with untreated-alumina-covered GO particles on the TPU matrix in Fig. 3(d) displays randomly distributed GO and alumina particles. Thus, the APTES-treated alumina-encapsulated GO-TPU composites have better adherence characteristics than the other investigated composites.

The spatial distribution of the filler particles over the surface of TPU matrix were displayed in Fig. 5 for the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO specimens. One can observe that the alumina encapsulated GO particles were dispersed over the surface of TPU. The arrows show the filler particles.

In this study, we prepared composites with good mechanical properties. We analyzed the tensile characteristics of the composites at room temperature with a UTM machine. The tensile strength was determined from the stress–strain diagrams of the respective specimens; it is defined as the stress at which the specimen breaks; the respective point on the abscissa (which corresponds to the strain) was considered the elongation

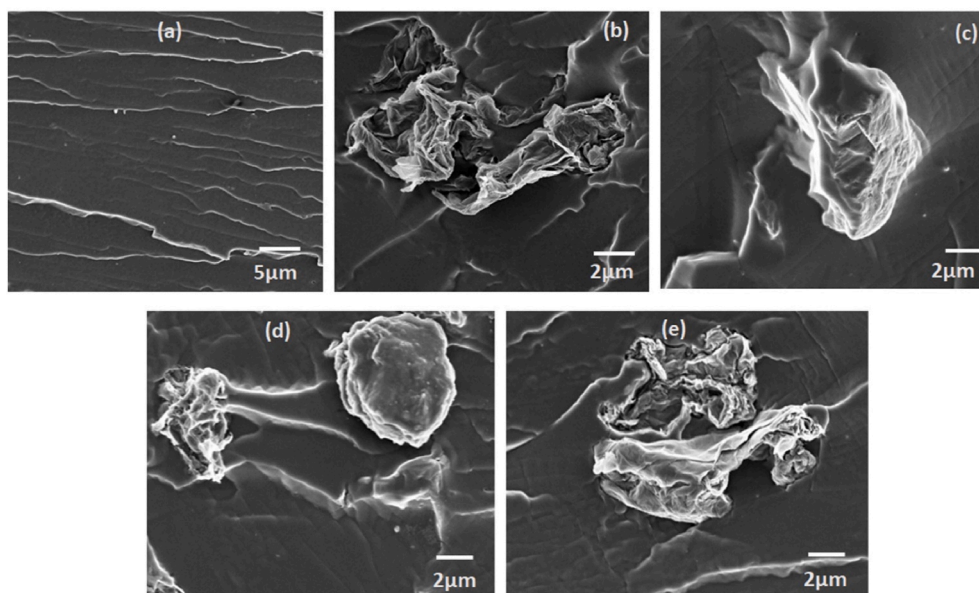


Fig. 4. The morphological and adhesion properties of TPU composites (a) Neat TPU; (b) TPU-GO; (c) TPU-Al<sub>2</sub>O<sub>3</sub>; (d) TPU-Al<sub>2</sub>O<sub>3</sub>-GO and (e) TPU-TAl<sub>2</sub>O<sub>3</sub>-GO.

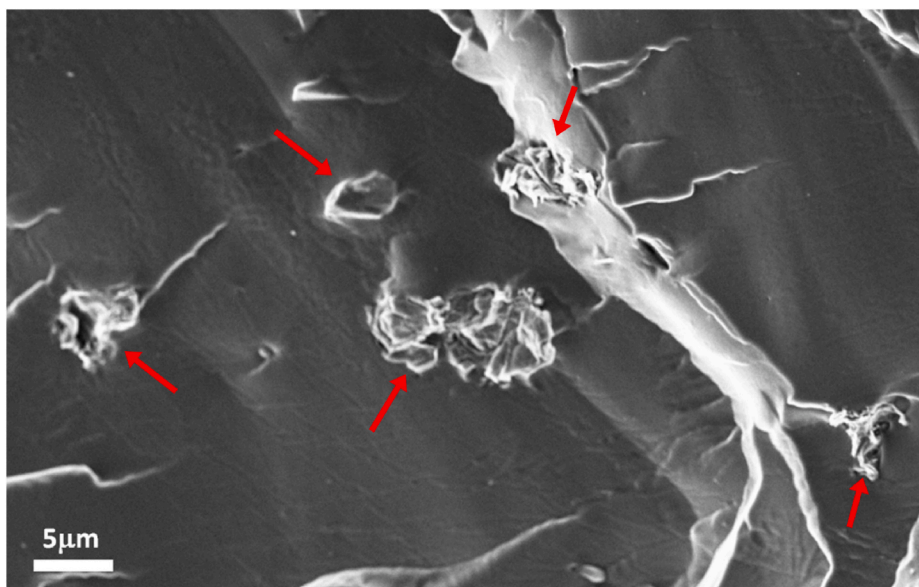


Fig. 5. The spatial distribution of the filler particles over the surface of TPU (TPU-TAl<sub>2</sub>O<sub>3</sub>-GO specimen).

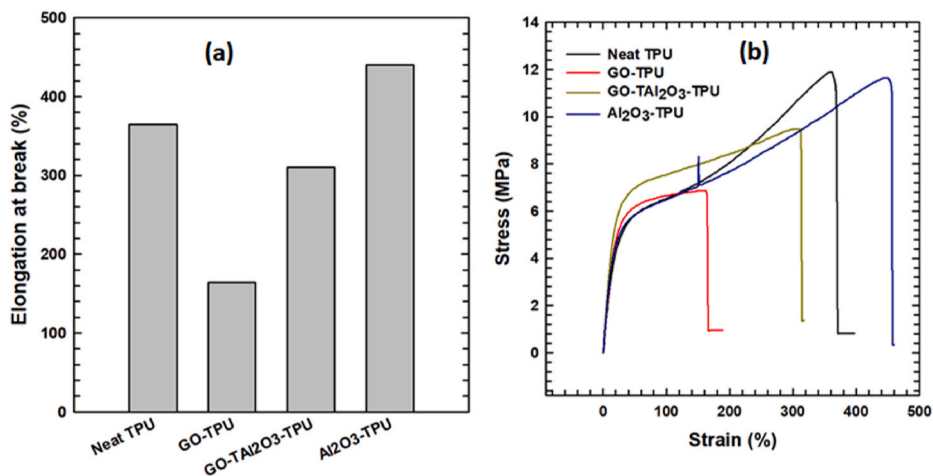


Fig. 6. Mechanical property of TPU and its corresponding, GO and alumina composites. (a) Elongation at break; (b) Tensile strength.

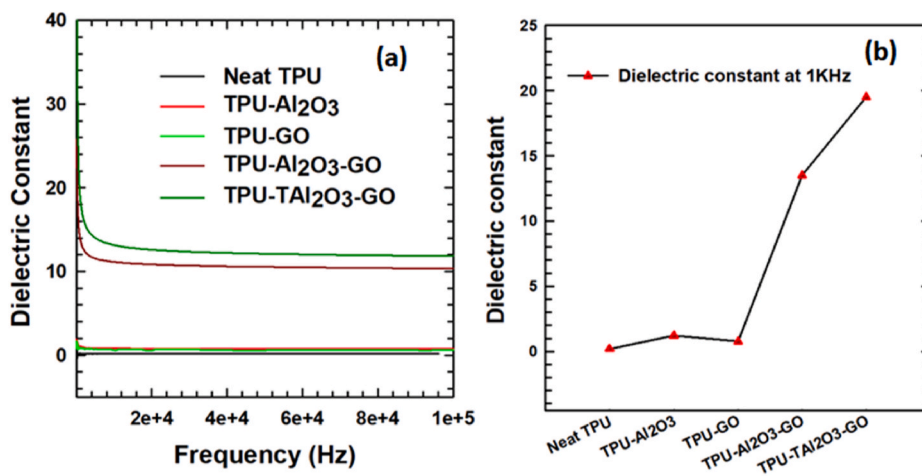


Fig. 7. Dielectric properties of the composite. (a) dielectric constant as a function of frequency, (b) dielectric constant as a function of filler difference at constant frequency (1 KHz).

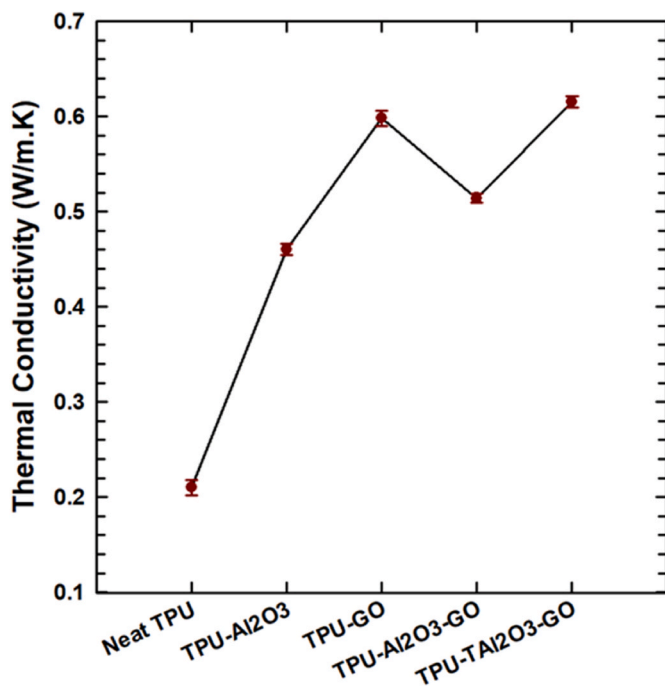


Fig. 8. Thermal conductivity of TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites measure at room temperature.

at break of the sample. The resulting stress–strain diagram in Fig. 6(b) shows that the neat TPU sample has a tensile strength of approximately 11.8 MPa, which is the highest value among all investigated composites; the sample has the second longest elongation at break after the TPU-Al<sub>2</sub>O<sub>3</sub> composites. Fig. 6(a) illustrates the elongation at break values of the TPU-alumina-GO composites with respect to the filler loading percentage (refer to Table 1 for more). The filler loadings for TPU-GO, TPU-Al<sub>2</sub>O<sub>3</sub>, and TPU-TAl<sub>2</sub>O<sub>3</sub>-GO were as follows: 5% GO, 40% alumina, and 35% alumina and 5% GO, respectively. The results display great variation in the elongation at break. The TPU-GO sample has the lowest elongation at break (approximately 170%); thus, the ductility characteristics of TPU were negatively affected; in contrast to the other composites, it can break when a weak loading force is applied. The TPU-Al<sub>2</sub>O<sub>3</sub> composites has the highest of all specimen's elongation at break values; this may be due to the alumina application, which has made the polymer composite more compatible with the filler particles and improved the ductile properties of the composite. The strain at which the tensile strength of the TPU-Al<sub>2</sub>O<sub>3</sub> composite occurs is approximately

420% (elongation at break); it is more than two times that of the TPU-GO composites and approximately 40% higher than that of the neat TPU sample.

To apply polymer composites in dielectric devices, the composite must have a high dielectric constant. The capacity of a composite to store charge is reflected with higher dielectric constant. The dielectric constant of a material is calculated using equation (1). The dielectric constant of the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites are shown in Fig. 7 (a) as a function of the frequency (40–10<sup>5</sup> Hz). We have also analyzed the dielectric constant of the composites at 1 kHz, as shown in Fig. 7(b) (see also Table 1). Evidently, the dielectric constant of the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composite is higher than that of the neat TPU sample. In particular, at lower frequencies, the dielectric constant is much higher than that of the neat TPU. At the percolation threshold, the dielectric constants of the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO and TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites are high and stable. This might be backed by the systems of heterogenous composites as stipulated by Maxwell-Wagner [29].

$$k = \frac{E}{E_0} \quad (1)$$

where  $k$  is the dielectric constant,  $E$  is permittivity of substance and  $E_0$  is permittivity of vacuum (free space).

At constant frequency, the dielectric constant of TPU-TAl<sub>2</sub>O<sub>3</sub> is approximately 20 times that of the neat TPU sample. The higher dielectric constant may be due to the surface treatment of the alumina particles with APTES and the use of ethanol for the exfoliation of GO; these aspects have improved the interfacial interaction between the two fillers and their compatibility with TPU.

The thermal conductivity of the TPU composites were examined using the LFA analysis. Five samples were investigated to compare the thermal dissipation nature of the fabricated composites. Fig. 8 demonstrates the thermal conductive nature of the fabricated TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites. Fortunately, one can get aware that the thermal conductivity has increased highly as compared to the neat TPU, almost about 3.2 times that of neat TPU upon application of APTES treated alumina encapsulated GO particles. As compared to the pristine alumina GO-TPU composites, the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites has higher thermal conductivity value which might be due the interfacial adhesion of filler particles to the TPU matrix. The higher thermal conductivity value for the alumina-GO composites were gained from the conducting nature of GO particles and poor conductivity of alumina particles as compared to GO has led TPU-alumina composites to have a lower thermal conductivity almost 28% lower than that of the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites. The thermal conductivity of each specimen prepared were tabulated in Table 1

Furthermore, a thermal imaging camera was used to examine the

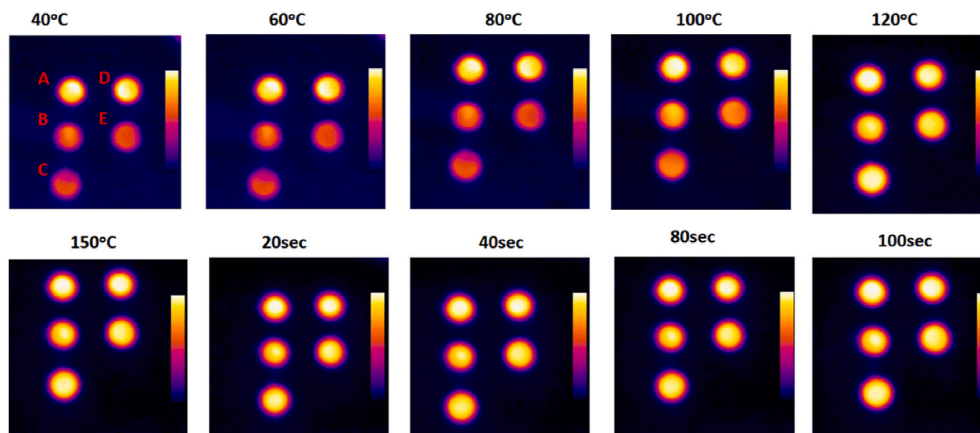


Fig. 9. Thermal image results of the composites at various temperatures and keeping the temperature constant once it reaches at 150 °C. A represents neat TPU, B-TPU-GO, C- TPU-Al<sub>2</sub>O<sub>3</sub>, D- TPU-Al<sub>2</sub>O<sub>3</sub>-GO and E- TPU-TAl<sub>2</sub>O<sub>3</sub>-GO.

heat dissipation characteristics of the TPU-Al<sub>2</sub>O<sub>3</sub>-GO composites; the temperature was controlled with a hotplate, and the images were taken at a desired temperatures using IR camera. Circular specimens with 13 mm diameter were prepared for this analysis and placed on the hot plate, which was heated to 150 °C; this corresponds to the maximal temperature that can occur while electronic materials are operating. The thermal imaging results, Fig. 9, show that the specimens have different properties. The neat TPU and untreated alumina-GO-TPU composites dissipate the heat earlier (even at 40 °C), whereas the other composites start dissipating at higher temperatures.

However, the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composite can resist temperatures of up to 120 °C and starts dissipating once the temperature has reached the maximal operation temperature (i.e., 150 °C). Once this temperature had been reached, it was kept constant, and thermal images were recorded every 20 s. During this process, all composites dissipated more heat. Thus, the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites are taken as heat resistive specimens that can withstand up to 120 °C and dissipates easily any heat higher than this temperature.

## 5. Conclusion

We fabricated TPU composites with high dielectric constants and good thermal conductivity and dissipation properties. The twin extrusion method was used to fabricate composites consisting of TPU matrices and Al<sub>2</sub>O<sub>3</sub>-GO particles. The rGO particles were encapsulated with Al<sub>2</sub>O<sub>3</sub>, which was treated with APTES. The successful attachment of APTES onto the alumina particles was confirmed with FTIR, FE-SEM, and TGA. The thermal degradation results of the composites show a slight improvement in the thermal stability of the TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites, whereas the TPU-GO composites are slightly less stable. The FE-SEM results of the composite morphology reveal good interfacial interactions in the APTES-treated alumina-exfoliated GO-TPU composites. The thermal conductivity of TPU-TAl<sub>2</sub>O<sub>3</sub>-GO composites were 3.2 times (320%) higher than that of the neat TPU. The dielectric constants at different frequencies show that the APTES-treated alumina-exfoliated GO-TPU composites have improved properties. Moreover, the tensile properties of the composites have not been significantly affected by the application of alumina and GO to the TPU matrix; only the TPU-GO composites exhibit lower tensile strength and a highly brittle nature compared to the neat TPU sample.

## Author statement

**Eyob Wondu:** Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Roles/Writing - original draft; Writing - review & editing. **Zelalem Chernet Lule:** Resources; Software; Visualization; Roles/Writing - original draft. **Jooheon Kim:** Project administration; Supervision; Validation; Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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