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Thermal conductivity of cross-linked polyethylene composites contained nitride based ceramics

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Thermally conductivity of silane cross-liked polyethylene (PEX) composites combined with nitride based ceramic fillers investigated. Hexagonal boron nitride (hBN) and aluminum nitride (AlN) fillers were melt-mixed with PEX matrix by using internal mixer. Synergistic effects on thermal conductivity found, by hybridization of ceramic fillers and cross-linking of matrix. Highest thermal conductivity of these ceramic based composites reached to 6.01 W/m·K for PEX/AlN/hBN-PT180: 40/50/10 vol% composites meanwhile for non-cross-linked it was 5.2 W/m·K.

Besides, the effects of addition of low volume contents of copper particles to PEX/AlN/hBN compositions studied. The thermal conductivity of these electrical insulative composites, enhanced up to 7.55 W/m·K which contained 5 vol% of metal particles. Hybridization of electrical insulative ceramics, lower costs electrical conductive metals and matrix cross-linking can offer new generation of thermal conductive polymeric composites.

Keywords: Thermal conductivity, polymer composites, silane cross-liked polyethylene, boron nitride

INTRODUCTION

One of the recent challenges in electronic instruments is heat dissipation which forced scientists to find new approaches to overcome. Many applications would gain from the use of polymers with enhanced thermal conductivity. Electronic industry is one of the main targets for thermal management systems, while in some cases, preservation of their electrical insulation should be considered. For instance, thermally conductive plastics are applicable for heat sink applications, such as lighting ballasts and transformer housings [1, 2]. Incorporation of thermally-conductive but electrically-nonconductive ceramics in powder form such as silicon carbide [3], aluminum nitride (AlN), boron nitride (BN) to polymeric matrix, can offer electrically-insulative composites combined with appropriate thermal conductivity [4-7].Wide varieties of these nitride base ceramics have the potential using as a heat conductive component in polymeric matrix. AlN, with high thermal conductivity combined with relatively low price could be an appropriate candidate for wide variety of engineering applications. LLDPE/AlN electrically insulative composites with the thermal conductivity about 1.25 W/m·K and surface resistivity around $3.1\times10^{13}\Omega/\square$ reported by Zhou [5]. Incorporation of hBN into the polymers can improve their thermal conductivity without sacrificing insulating properties. Lee et al. [8] reported TC value of 3.66 W/m·K for high density polyethylene (HDPE) filled with 50 vol% BN and 2.42 W/m·K at 60 vol% of AlN as a filler. In one the recent reports, Sun et al. [7] reported the highest thermal conductivity (~30 W/m·K) for Epoxy/BN nanosheets nanocomposites. In another publication, Lau et al. [4] improved the thermal conductivity of PBT composites up to 1.1 W/m·K with addition of 22 vol% of hBN.

Cross-linking of different types of PE can enhance the thermal conductivity and thermal stability of resin by introduction new heat paths and directly contributes enhancement in abovementioned [9]. The major application of thermally conductive XLPE is in geothermal heat exchanger pipes [10]. Higher thermal conductivity led to length reduction of heat exchanger pipes and higher efficiency of heat pumps.

Chrissafis et al. [11] improved the thermal conductivity of cross-linked high density PE (XHDPE) by addition of carbon nanotubes (CNT) from 0.17 $W\cdot m^{-1}K^{-1}$up to 0.51 $W\cdot m^{-1}K^{-1}$ at 5 wt% of CNT. In other attempt, Roumeli et al [12] improved the thermal conductivity of XHDPE by introduction of low contents of nanodiamonds (NDs) and NDs/CNT hybrids. They improved the thermal conductivity of Si-XHDPE/NDs (0.5 wt%) from 0.17 $W\cdot m^{-1}K^{-1}$up to 0.5 $W\cdot m^{-1}K^{-1}$ and in the case of Si-XLDPE /NDs (3 wt%) /CNT (5 wt%) nanocomposites thermal conductivity enhanced up to 0.45 $W\cdot m^{-1}k^{-1}$. Azizi et al.[13] enhanced the thermal conductivity of XLDPE composites by addition of carbon fiber and Al particles up to 3.81 $W\cdot m^{-1}k^{-1}$. There are limited scientific reports on enhancement of thermal conductivity of silane crosslinked polyethylene by addition of micro fillers.

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Synergistic effect of hybrid fillers on thermal conductivity of composites was reported in several research studies. For instance, thermal conductivity of polystyrene/silicon carbide whisker (SiC_w)/silicon carbide particle (SiC_p) (volume fraction, 3:1, 40 vol %) [14] composites enhanced up to 1.29 W/m·K compare to ~ 1.1 W/m·K and 1 W/m·K for SiC_w and SiC_p. Xu et al. [15] incorporated the AlN whiskers combined with AlN particles to poly vinylidene difluoride and enhanced the thermal conductivity up to 11.5 W/m·K. Recently, Hong et al. [6] investigated the effect of bimodal hybrid hBN/AlN ceramics on thermal conductivity of epoxy and enhanced the thermal conductivity as high as 8.0 W/m·K, which found at a relative composition of AlN to hBN of 1:1 by analogous particle sizes. In other report, Kuo et al. prepared flexible thermal conductivity PI substrate (2.3 W/m·K) with addition of 60 vol% of hBN/AlN fillers [16] without finding any kind of synergistic effects.

Metal filled (Cu, Al,…) polymeric composites have been of interests not only in terms of cost saving [17] but also enhancement of thermal, electrical[14] and mechanical properties [15]. Addition of low-volume contents of metal particles (Cu <10 vol%) as single fillers didn't significantly affect the thermal and electrical conductivity [18-20]of composites. The motivation of this work is enhancement the through-plane thermal conductivity of the composites by introducing nitride base ceramics and matrix cross-linking in the same time. AlN (particles) hybridized with two different types of hBN (large agglomerates & agglomerates/flakes) at 60 vol%. Measured thermal conductivity results were investigated in terms of filler type, relative filler concentrations and cross linked density. Synergistic effect found in terms of combination hybrid fillers and cross-linking. Besides, in our study we investigated the effect of hybridization of ceramics with low volume contents of copper particles (5 and 10 vol %) on thermal and electrical properties of composites. In the same way the synergistic effect on thermal conductive XLDPE/AlN/hBN/Cu found without sacrificing the insulated properties.

EXPERIMENTAL

2.1. Materials

PE-g-Si was chosen as a matrix in thermal conductive. Two types of electrical insulative fillers (hBN and a grade of AlN) and cupper (Cu) used as an electrical conductive filler were used for composite preparation. Properties of used materials are summarized in Table 1.

Table1. General properties of PEX and fillers

Material	Grade	ρ [g/cm^3]	Thermal conductivity [W/m·K]	Size [µm]	Shape
AlN[a]	A500-150	3.26	70-180	14-23	Polygonal-shape particles
hBN[b]	PT371	2.28	266-284	250-300	Irregular-shaped agglomerates
	PT180			5-11	Flakes & agglomerates
Cu[c]	-	8.96	380	250-350	Sphere
LDPE-g-Si [d]	Hyundai Eng. Plastics	0.952	0.24	-	Pellet

*Data provided by Producer: a) Surmet Material, b) Momentive performance materials Inc, c) Sigma Aldrich, d) Radichi group.

2.2. Sample preparation

PE-g-Si and fillers were dry mixed and the composites were prepared by melt mixing method in batch-type mixer (W50EH, Brabender, Duisburg, Germany) at 60 rpm for 10 min at the 190°C. After melt mixing, the discharged composites were cooled at RT and hot pressed (15MPa) for 15 min at 280°C. Moisture curing (90°C for 24 hours) was done for producing PEX base composites at 90°C water bath. Abrasive paper was used to make a disc samples with10 mm diameter and 1 mm thickness in order to measure the thermal diffusivity. 5 disks were prepared for each composite. Table 2 shows the listing of all single and hybrid filler compositions.

2.3. Field emission scanning electron microscopy (FE-SEM) & X-ray energy dispersive spectrometry (EDS)

A field emission scanning electron microscope (S–4500, JEOL, Japan) at an acceleration voltage of 10 kV was used to observe morphological features of the fillers and fractured surface of the composites. The composites were cryogenically fractured in liquid nitrogen. The samples were Pt coated using a sputter coater (108, Cressington Scientific, UK) for 2 min before imaging to avoid charging during observation. Beside s the chemical composition of composites contained metal particles characterized by EDS at low magnification in order to find copper distribution in composites.

Table 2. Formulation of composites at 40 vol% of PEX

<table>
<tr><td colspan="2">Compositions</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td></tr>
<tr><td colspan="2">AlN [vol%]</td><td>60</td><td>0</td><td>50</td><td>40</td><td>30</td><td>20</td><td>10</td><td>50</td><td>50</td></tr>
<tr><td rowspan="2">hBN[vol%]</td><td>PT180</td><td rowspan="2">0</td><td rowspan="2">60</td><td rowspan="2">10</td><td rowspan="2">20</td><td rowspan="2">30</td><td rowspan="2">40</td><td rowspan="2">50</td><td rowspan="2">5</td><td rowspan="2">0</td></tr>
<tr><td>PT371</td></tr>
<tr><td colspan="2">Cu[vol%]</td><td colspan="7">0</td><td>5</td><td>10</td></tr>
</table>

2.4. Thermal conductivity

The thermal conductivity (W/m·K) was given by the product of the thermal diffusivity (mm^2/s), specific heat (J/g·K) and density (g/cm^3). The thermal diffusivity of the composites was measured by a laser flash method (TC-7000, ULVAC Co. Japan) at 30°C. The laser flash technique was introduced in 1961 by Parker [21]. Laser heat pulses irradiated on the front side of the disc sample; the heat was transmitted through the sample thickness direction and was measured by an infrared camera. The time to reach the half of the maximum temperature ($t_{½}$) at the back side of the sample was chosen to calculate the heat diffusivity calculated by following equation:

$$\alpha = 1.38\, L^2 / \pi^2 \cdot t_{1/2}$$

α is thermal diffusivity and L is the thickness of the samples. Then thermal conductivity was calculated from thermal diffusivity by the following equation:

$$K = \alpha \times \rho \times C_p$$

2.5. Electrical insulation properties

The surface resistivity (R_s) was determined by measuring the DC resistance on a disc sample (diameter, 50 mm; thickness up to 3 mm). An Agilent 4339B high resistance meter equipped with a resistivity cell (Agilent, 16008B) was used to measure the surface resistivity of each sample. This equipment allows the resistivity measurement up to $4\times10^{17}\ \Omega$. The source voltage was set at 500 V for all the samples. The reported values represent the mean value of five measurements.

RESULTS AND DISCUSSIONS

3.1. Morphological characteristics

FE-SEM micrographs of AlN and two types of hBN fillers are shown in Fig. 1. AlN particulates with polygonal-shape are shown in Fig. 1(a). Fig. 1(b) shows the large size hBN agglomerates of PT371, which comprised of many hBN platelets (10-15 µm) packed in the bulky shapes. Unlike typical thin hBN platelets, these high bulk density agglomerates can facilitate higher loading during batch mixing. The PT180 contains thin flakes and agglomerates shown in Fig. 1(c) and it has surface area of ca. 16 m2/g [4]**.** The difference of these two hBN fillers can affect the composite morphology and properties especially at high filler loadings. Large size copper agglomerates selected as high thermal conductive metallic filler. As shown in Fig. 1(d), the agglomerates were comprised of small particles.

Fractured images of PEX/AlN (60 vol %), PEX/hBN (60 vol%), PEX/AlN (50 vol%) /PT180(10 vol%) and PEX/AlN (50 vol%)/PT371(10 vol%) composites were shown in Fig. 2. At that high filler loading (60 vol%) (Fig. 2 (a-b), PEX/AlN) the inter-particle distances was short and most of the AlN particles were touched each other and consequently, the filler contact area would increase [22]. In addition, the formation of porosity or defects is almost unavoidable in these types of single filler composites [16] specifically at high filler contents hBN filled composites showed different morphologies compared to AlN filled composites with their 2D structure. The FE-SEM micrographs show particle size reduction of hBN agglomerates specifically in the case of large particles size. The size of hBN agglomerates could not preserve [23] at high shear stress during the melt mixing or applied pressure during the hot pressing. This particle size reduction was much more severe for PT371 compare to PT180. In addition, for all of composites containing hBN as single filler, alignment of platelets is fairly random, specifically in the case of composites contained PT180 (Fig. 2c and Fig. 2d).

Combination of flaky type fillers such as hBN with polygonal-shape particles at different relative volume ratios can induce high filler packing [6] by considering their relative particle size properties.

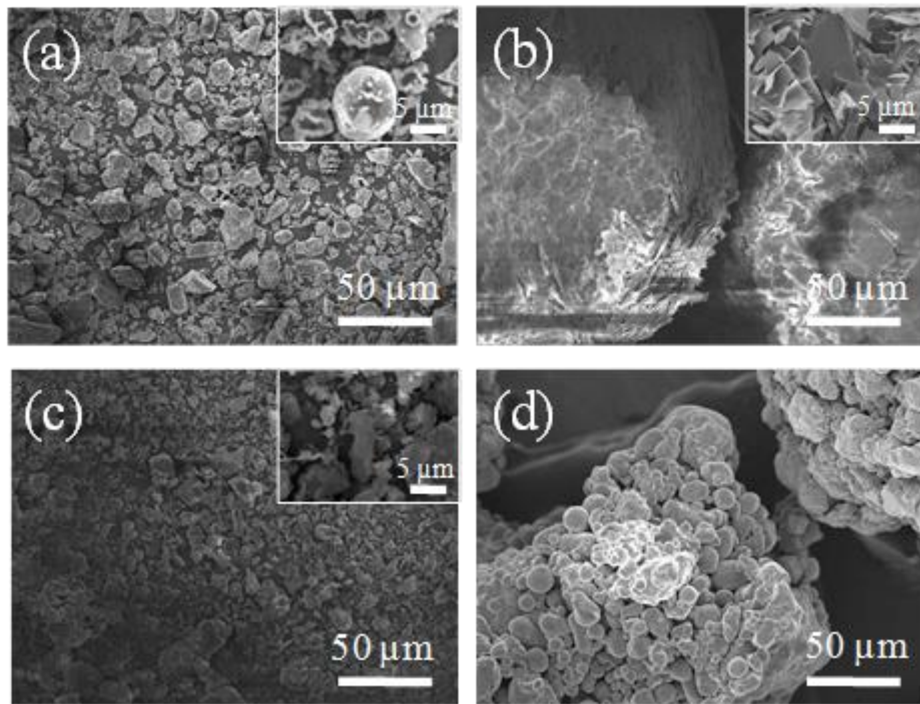

Fig 1. FE-SEM images of (a) AlN; (b) PT371; (c) PT180 (d) Cu at the same magnification (× 500). The inset figures magnification (× 5000).

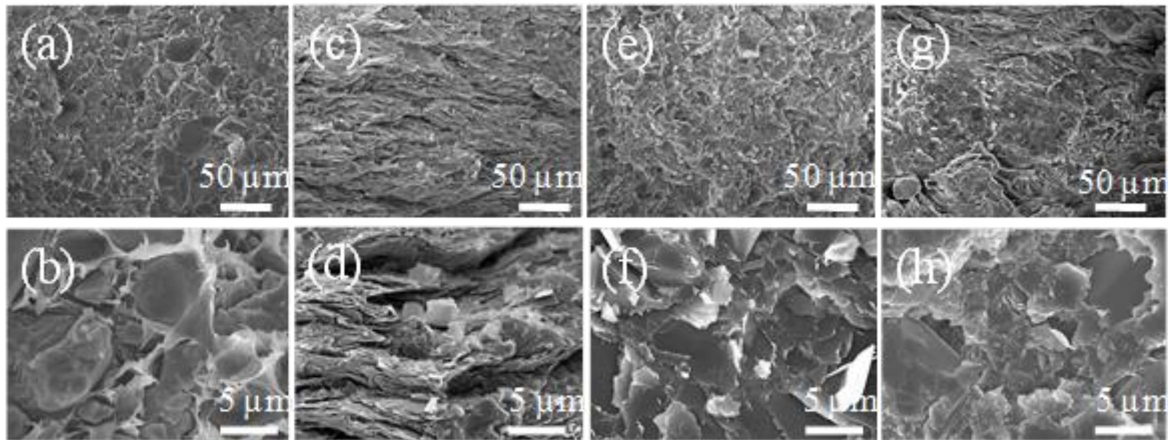

Fig 2. FE-SEM images of (a , b) PEX/AlN [40/60 vol%]; (c) PEX/PT180 [40/60vol%]; (d) PEX/PT371 [40/60vol%]; (e , f) PEX/AlN/PT180 [40/50/10 vol%] and (g , h) PEX/AlN/PT371 [40/10/50 vol%] at two different magnifications (×500 & ×5000).

In our study AlN and hBN at different relative concentrations, hybridized at fixed volume ratio (60 vol%). The fracture images of hybridized composites, 10 vol% of PT180 with 50 vol% of AlN and 50 vol% of PT371 with 10 vol% of AlN particles, at different magnifications demonstrates at Fig. 2 (e-h). Highly packed filler structures for all of hybrid composites is clear in images, especially at higher magnifications. Attendance of 2D type structure of PT180 in between 1D AlN particles would improve packing density and contact area among AlN particles as a main filler. It would be suggests that PT180 had better chance to fill the AlN interparticle distance rather than PT371, which thermal conductivity results can give us true idea about this assumption. In addition, through-plane alignment was reported [6] for the composites with similar particle size of AlN and hBN. In other embodiment the FE- SEM images of composites contained 10 vol% AlN and 50 vol% of large particle size PT371 investigated. In these compositions, smaller particle size AlN can enhance the contact area between the larger PT371 aggregates which already broken down during melt mixing. These types of filler combination would suggest high filler packing in hybrid composites contain PT371 as hBN filler.

By addition of hBN to PEX/AlN composites, highly packed three dimensional filler structure formed (Fig. 2-e & 2-gg)). At higher magnifications (Fig. 2-f &2-h), for PEX (40 vol%)/AlN (50 vol%) /hBN(10 vol%), the defects that observed in PEX/AlN (40/60), decreased to some extent. It would be suggested that PT180 has better chance to locate in the interstitial space of AlN particles [6, 24]compare to larger breaking down PT371agglomerates, specially at low hBN concentrations (i.e., 10 vol%).

3.3. Thermal and electrical conductivity

AlN and two types of hBN were used as basic hybrid fillers to increase the heat conductivity of composites. Variation of thermal conductivity of PEX/AlN/PT180 and PEX/AlN/PT371 at a total filler content of 60 vol% is shown in Fig. 3(a).

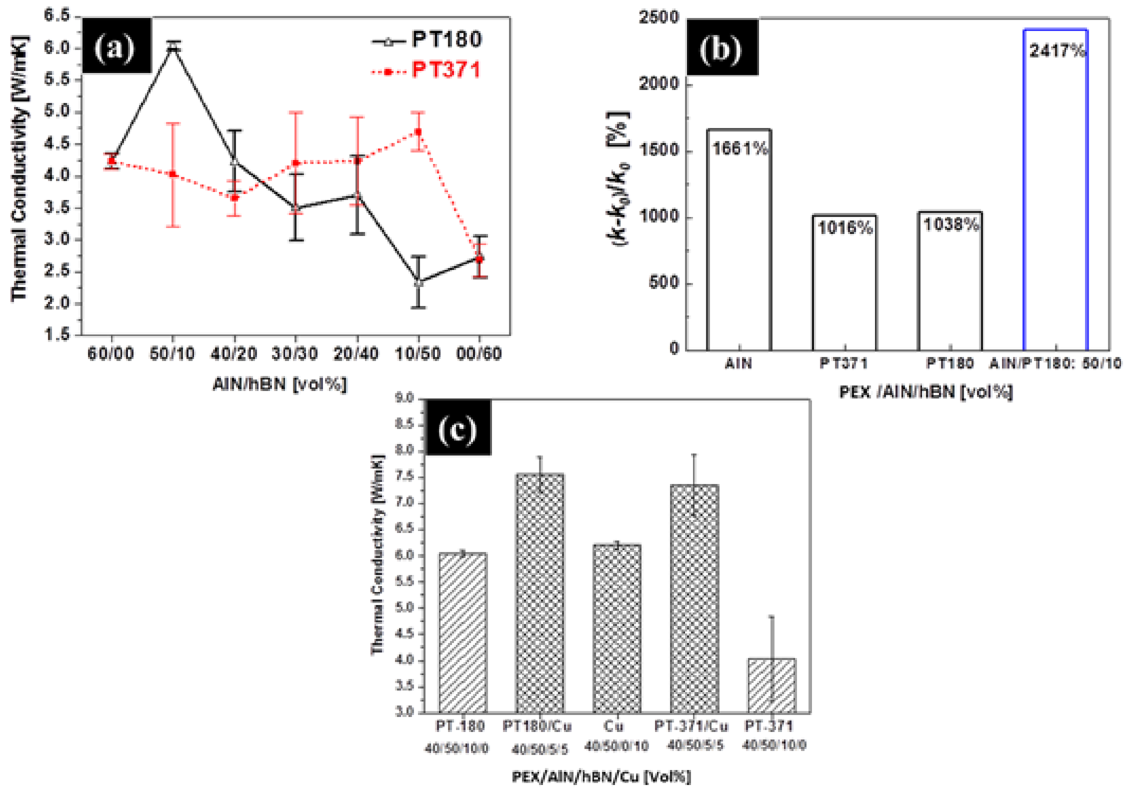

Fig 3. Thermal conductivity and thermal conductivity enhancement of PEX/AlN/hBN (a, b) and thermal conductivity PEX/AlN/hBN/Cu (c) at 60 vol% of filler

The thermal conductivity of PEX/AlN (60 vol %) was 4.23 W/m·K which is much higher than PEX/AlN (40 vol %) with 1.63 W/m·K. This increase may be attributed to the more formation of thermal conductive paths [5] at higher AlN concentrations. The thermal conductivity of PEX/AlN was higher than that of PEX/hBN composites at 60 vol% of filler content in the through plane direction. The large difference in thermal conductivity of BN crystal in basal plane (300 W/m·K) and in through-plane direction (3 W/m·K) [24] could be a reason. Due to the large difference in thermal conductivity of BN in basal and thickness direction, it is needed to align the hBN flakes in random direction to enhance the through-plane thermal conductivity. The addition AlN polygonal particles with isotropic thermal conductivity (70-180 W/m·K) into polymer matrix could lead the higher through-plane thermal conductivity, rather than the addition of hBN platelets which are randomly aligned to the heat flow direction.

The thermal conductivity of two types of hBN fillers with presence of AlN shows different behavior. Both hBN grades and AlN showed synergistic effects at certain compositions. The highest thermal conductivity was observed at PEX/AlN(50 vol%)/PT180(10 vol%), whereas for composites which contained PT371 the peak observed at PEX/AlN(10 vol%)/PT371(50 vol%) composition. The thermal conductivity of the epoxy/AlN/BN hybrid composites was depended on the filler particle size, as well as the relative composition of AlN to BN [6,24]. At hybrid filler loading of AlN (50 vol %) / PT180 (10 vol %), there is higher chance to align the hBN sheets in

normal plane direction and increase the thermal conductivity in through plane direction [6]. In PEX/AlN (10 vol%)/PT371(50vol%), the smaller particle size of AlN, 14-23µm, could fill the interstitial space between the larger hBN aggregates and provide the close contact between PT371 and AlN. At high PT371 loadings, the larger PT371 particles were broke down to the smaller aggregates and the heat conduction by the formation of structured networks improved [25].

In Fig. 3b, the thermal conductivity of virgin PEX (k_0, 0.26 W/m·K) and that of composites (k) were compared. Fig. 3b shows the significant enhancement of through plane thermal conductivity, $(k-k_0)/k_0$, for the hybrid filler composite of PEX/AlN (50 vol%)/ PT180(10 vol%) compared to the single filler composite. Thermal conductivity enhancement of PEX/AlN (50 vol %) / PT180 (10 vol%) was higher than 2000% compare to PEX. PEX/AlN composites showed the higher increase of through plane thermal conductivity than the PEX/hBN filler composites due to the isotropic thermal conductivity of AlN and their polygonal particles which make their thermal conductive effect insensitive to orientation.

The effect of cross-linking on thermal conductivity of composites investigated for AlN (50 vol%)/ PT180(10 vol%) composites. In order to investigate abovementioned effect, thermal conductivity of LDPE-g-Si/ AlN (50 vol%)/ PT180(10 vol%) composites compared with PEX/ AlN (50 vol%)/ PT180(10 vol%). The thermal conductivity of PEX composites enhanced up to 0.81 W/m·K compare to LDPE-g-Si. Combination of high density cross-linking and formation of 3D conductive filler pathways provided such a high thermal conductivity [13].

In order to Fig out the effect of hybridization between ceramics and metal fillers, limited amount of copper particulates added to the ceramic fillers and the results are shown in Fig. 2c. The large Cu aggregates were broken down into smaller spherical particles or aggregates (< 90 µm, Fig. 4a and Fig. 4b) as a result of high shear stress during melt processing. Copper particles can be distinguishable with green color in EDS images of fractured surface. The synergistic effects between hBN and copper was found in PEX/AlN (50 vol%)/hBN(5 vol%)/Cu(5vol%) composites compared to PEX/AlN(50 vol%)/hBN(10 vol%) and PEX/AlN(50 vol%)/Cu(10 vol%). The addition of isotropic conductive metal particles into the anisotropic ceramic hBN resulted in significant improvement in through plane thermal conductivity of composites. The thermal conductivity of PEX/AlN(50 vol%)/PT180 (5 vol%)/Cu(5vol%) and PEX/AlN(50 vol%)/PT371 (5 vol%)/Cu (5 vol%) enhanced up to 7.55 and 7.35 W/m·K respectively. The effective thermal path formation in through plane direction with the broken isotropic Cu particles may be a reason for the higher thermal conductivity. Fig 4 (c & d) show the FE-SEM images of PEX/AlN/hBN/Cu composites after burning out the PEX matrix. It clearly shows the particle size reduction of PT180 and PT371 after melt mixing process. The higher thermal conductivity was obtained, might due to the larger hBN breakdown to the thinner hBN plates/or smaller aggregates during melt mixing. These smaller hBNs may provide higher filler contact area and consequently higher thermal conductivity. The enhancement was higher for PT371 than PT180. Another reason for great enhancement of thermal conductivity may come from, higher effectiveness of 2D structure hBN fillers compare to 1D structure of copper particles in PEX/AlN (50 vol%)/ Cu (10 vol%) for enhancement interconnectivity [26] between the fillers. The 2D structure can provide larger interconnectivity between the fillers.

Fig 6 shows the sheet resistance of composites. Ceramic filler contained composites showed the sheet resistance of 8.6E14 ~ 2.8 E15 Ω/sq which decreased to the range between 2.97E13 ~ 2E14 Ω/sq. by addition of Cu particles. It indicates that PEX/AlN/hBN/Cu composites are thermally conductive and electrically insulative. Based on investigation of different types of polymer/Cu composites, 5 vol% of Cu particulate contents would be far below the electrical percolation threshold for composites containing Cu as single filler [13]. The R_s of PEX/AlN/PT371/Cu resulted in the lower R_s compared to that of PEX/AlN/PT180/Cu composites as shown in Fig. 5a. The large size PT371broken down aggregates might be used to explaining this contrast (Fig. 4a & 4b).

Those large size agglomerates could decrease the possibility of connecting the Cu particles more than PT180 flakes. The limited size reduction and filler connection of the PT371 agglomerates after melt processing might resulted in the R_s difference between PT180 and PT 371. The thinner PT180 flakes can be more favorable than the broken down PT371 for heat transfer (Fig 5b). With the addition of 5 vol% of Cu particles, the composites were electrically insulative and they could be used in thermally conductive, electrically insulating applications.

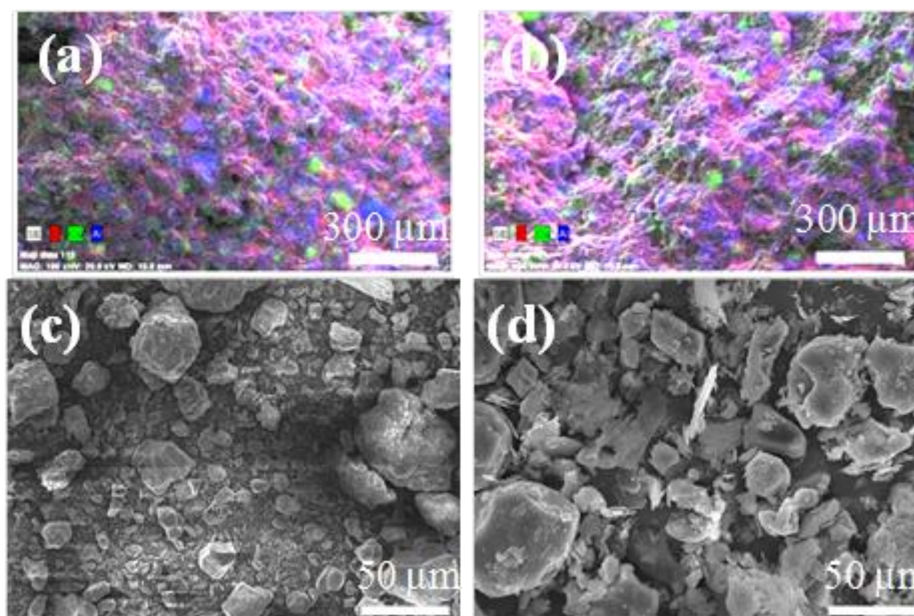

Fig 4. Energy dispersive X-ray (EDX) of the fractured surface of PEX/AlN/hBN/Cu:40/50/5/5 (a) PT180 (b) PT371 and FE-SEM of fillers in PEX/AlN/hBN/Cu:40/50/5/5 composites after processing (c) AlN/PT371/Cu, (d) AlN/PT180/Cu (The PEX removed before taking FE-SEM images)

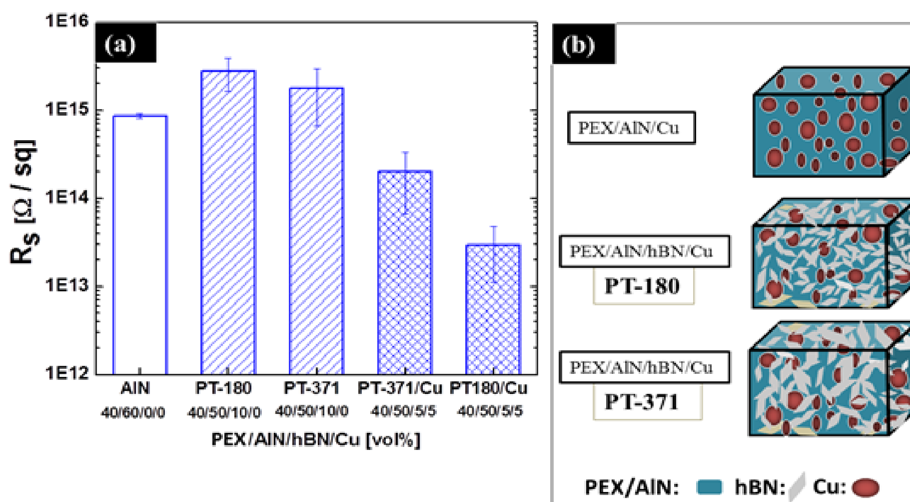

Fig 5. Sheet resistance of PEX composites with and without attendance of copper (a) and related graphical scheme for PEX/AlN/hBN/Cu composites (b).

CONCLUSION

AlN, hBN and Cu were added as thermally conductive fillers into PEX. Synergistic improvement in the thermal conductivity of the PEX/AlN/hBN composites was observed and alignment of hBN sheets was a critical function for through plane thermal conductivity increment. Matrix cross-linking can enhance the thermal conductivity of composites. Attendance of Hybridization of metal particles with insulative ceramic fillers resulted in thermal conductivity enhancement. Replacement of 5 vol% of Cu particles by hBN in PEX/AlN(50 vol%)/hBN (10vol%) composites improved the thermal conductivity while maintaining the electrical insulation properties. Thermal conductivity of ceramic/metal based filler composites, enhanced up to 7.55 and 7.35 for composites contained 5 vol% of Cu particles. Hybridization of electrical insulative ceramics and low costs electrical conductive metals can offer new approaches for polymeric composites with great potential for using as cost-effective geothermal pipes and heat sink based materials.

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