

Thermal conductivity of silane cross-linked polyethylene composites

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Silane cross-linked polyethylene (XLDPE) composites contained aluminum (Al) particles and carbon fiber (CF) prepared via melt mixing. The effect of filler loading and cross-linking on thermal properties of composites were investigated. Thermal conductivity was calculated from thermal diffusivity multiplying by specific heat capacity by density. Thermal stability was investigated by thermogravimetric analysis (TGA) and morphology of composites studied by scanning electron microscopy (SEM). Thermal stability of composites didn't affected by cross-linking. Thermal conductivity increased with enhancement of degree of cross-linking and reached to 3.81 and 0.9 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ for composites contained 60 vol% Al and 15 vol% CF, respectively. With increasing filler content the filler- filler interaction would be enhance and three dimensional thermal conductive pathways formed in all compositions leading to increase of thermal conductivity of composites.

Keywords: Thermal conductivity, Polymer composites, Silane cross-linked polyethylene

INTRODUCTION

Thermal conductive polymers have wide applications in various fields such as electronics, solar cells, automotive, heat exchanger equipment and etc. There are several methods for enhancement of thermal conductivity of bulk polymers. Typical methods mainly focused on introduction of heat transport networks by addition of thermal conductive inorganic fillers into polymer matrix which can enhance the thermal conductivity of prepared composites. The enhanced thermal conductivity of such composites doesn't reach theoretical expectations as a result of high thermal contact resistance at polymer-filler interfaces [1]. The other way for controlling thermal conductivity of polymers is enhancement of intrinsic thermal conductivity by changing structural design [2], crystallinity [3] and introducing cross-link bonds (high density) [1] between polymer chains.

Polyethylene is the most widely used polymer which has a great potential in geothermal pipe applications but it suffered from low thermal conductivity and thermal stability. Highly Cross-linking of PE can improve the thermal conductivity and thermal stability of bulk resin by opening new heat paths and directly contributes to the increase in abovementioned [4]. The main application of thermally conductive XLPE is in piping systems in geothermal heat exchangers [5]. Higher heat dissipation in thermal conductive pipes led to length reduction of heat exchanger pipes and better efficiency of heat pumps.

Chrissafis et al [6] enhanced the thermal conductivity of cross-linked high density PE by addition of carbon nanotubes (CNT) from 0.17 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ up to 0.51 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ at 5 wt% of nano filler. In other attempt, Roumeli et al [7] enhanced the thermal conductivity of cross-linked high density PE by addition of low nano filler contents of nanodiamonds (NDs) and NDs/CNT hybrids. They enhanced the thermal conductivity of Si-XLDPE/NDs (0.5 wt%) from 0.17 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ up to 0.5 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$ and in the case of Si-XLDPE /NDs (3 wt%) /CNT (5 wt%) nanocomposites thermal conductivity enhanced up to 0.45 $\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$. There are limited scientific reports on enhancement of thermal conductivity of silane crosslinked polyethylene by addition of micro fillers.

In this work for the first time we attempt to investigate the effect of addition of Al and CF as micro fillers in order to enhance the thermal conductivity of XLDPE composites. We investigate the effect of crosslinking on thermal conductivity, thermal stability and morphological properties of XLDPE composites.

EXPERIMENTAL

Materials

PE-g-Si was chosen as a matrix in thermal conductive composites CF and Al powder considered as effective and commercialized thermal conductive fillers in this study. Table 1 summarizes the characteristics of used materials.

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Table 1. Material properties

Material	Size [μm]	Density [$\text{g}\cdot\text{cm}^{-3}$]	Thermal conductivity [$\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$]	MFI 190°C/5 kg [g/10 min]	Manufacturer
LDPE-g-Si	-	0.952	0.31	1.1	Hyundai Eng. Plastics
CF (COAL TAR PITCH)	Chop length: 3600 Filament diameter: 11	2.12	140	-	DIALEAD
Al	<180	2.7	205	-	K.P.M

Sample preparation

PE-g-Si and fillers (Al & CF) were first dry mixed on desired volume percentages. Formulations were designed at three different filler volume content.

The composites were prepared by W50EH internal mixer (Brabender GmbH & Co., Duisburg, Germany) at 60 rpm for 10 min at the temperature 190°C. After the melt mixing step, prepared composites were cooled down at the room temperature and hot pressed at 30 MPa at 195°C for 5 min in a press machine Ttoyoseiki, Japan). Abrasive paper was used to make a disc sample manually with 10 mm diameter and 1 mm thickness to measure the thermal diffusivity by the laser flash method.

CHARACTERIZATION

Scanning electron microscopy

A field emission scanning electron microscope [(FE-SEM), S-4500, JEOL Co.LTD, Tokyo Japan] at an accelerated voltage of 10 kV was used to observe the morphology 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 (Sputter Coater 108 auto, Cressington Scientific, Watford, UK) for 2 min before imaging to avoid charging during observation.

Thermal stability

Thermal gravimetric analysis (STA 625 from Rheometric Scientific) used in order to investigate thermal stability of different samples under N_2 atmosphere. The heating rate considered at 20°C/min. A mass of about 100 mg of samples was heated at temperatures ranging from 30 to 700°C. TGA analysis gives an idea of the thermal stability of samples

Gel content

The gel content of cross-linked samples was determined according to ASTM D 2765. Xylene used as solvent in the gel content analysis.

Thermal conductivity

Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\text{k}^{-1}$) was given by the product of the thermal diffusivity (mm^2/s), multiplying by specific heat capacity ($\text{J}\cdot\text{g}^{-1}\text{K}^{-1}$) and density ($\text{g}\cdot\text{cm}^{-3}$). 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 Park et al.[8]. 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 ($t_{1/2}$) at the back side of the sample was chosen to calculate the heat diffusivity calculated by Equation 1:

$$\alpha = 1.38 L^2 / \pi^2 \cdot t_{1/2} \quad (1)$$

The parameter α is thermal diffusivity and L is the thickness of the samples. DSC N-650 instrument equipped with specific heat capacity calculation software was used for measuring the specific heat. For this purpose, a three-curve analysis method was used including obtained DSC sample curve, baseline and reference material data. Sapphire was selected as a reference material. Then thermal conductivity was calculated from thermal diffusivity by Equation 2:

$$K = \alpha \times \rho \times C_p \quad (2)$$

RESULTS AND DISCUSSION

Morphological characteristics

The morphology of Al, CF and composites were observed by SEM. As shown in Figure 1, Al particulates (Figure 1a-c) have irregular shapes meanwhile CF (Figure 1d-f) has perfectly straight

shape and smooth surface. The aspect ratio of CF is about 330.

The morphological structure of the prepared composites was also investigated. SEM micrographs of cryogenically fractured disk shaped samples, shown in Figure 2. Composites (Figure 2d-i), has rough surface compared to virgin PEX (Figure 2a-c). With enhancement of Al content, the roughness of composites surfaces will be more pronounced. Al powder content enhancement led to decrement of average inter-particle space and formation of more agglomerates. As it can be seen at high magnifications, there is a great interaction between Al surface and XLDPE. The surface of all Al particles has well coated with the matrix. It could be as result of condensation reaction of Si-OH groups in silane grafted PE and OH groups on the surface of Al particles [9]. Formation of 3-dimensional pathways inside the matrix is seen clearly at high filler concentrations.

In the case of XLDPE/CF composites, at low filler contents (5 Vol%, Figure 3a-c), the inter-particle space between the fibers are high and CFs are mostly separated without any contacting each other. Comparing to Al particles, there isn't any reaction possibility between XLDPE and CF surfaces. It would be as result of different surface chemistry of CF and XLDPE. Attendance of

several cylindrical holes on the fractured surface is completely clear for all composites.

By increasing the volume content of CF (15 % vol., Figure 3d-f), the average inter-particle space become smaller and local networks would be form.

Thermal stability

The different behavior of the LDPE-g-Si, XLDPE and their composites showed that the influence of thermal conductive fillers on the thermos-oxidation process resulted in a superior thermos-oxidative stability in composites. Thermal stability of samples investigated by TGA and presented on Figure 4. Under a nitrogen atmosphere LDPE-g-Si and XLDPE degrade in a single step and reached near zero at the last. Addition of thermal conductive fillers led to improving of overall thermal stability and enhancement of onset temperature thermal degradation in XLDPE/Al and XLDPE/CF composites about 8-9°C. However, the thermal degradation behavior of composite samples is completely different with non-filled XLDPE. From Figure 4 it can be concluded that thermal stability of XLDPE didn't change significantly in comparison with LDPE-g-Si. Attendance of silane cross-linked networks hardly affected the thermal properties of our materials.

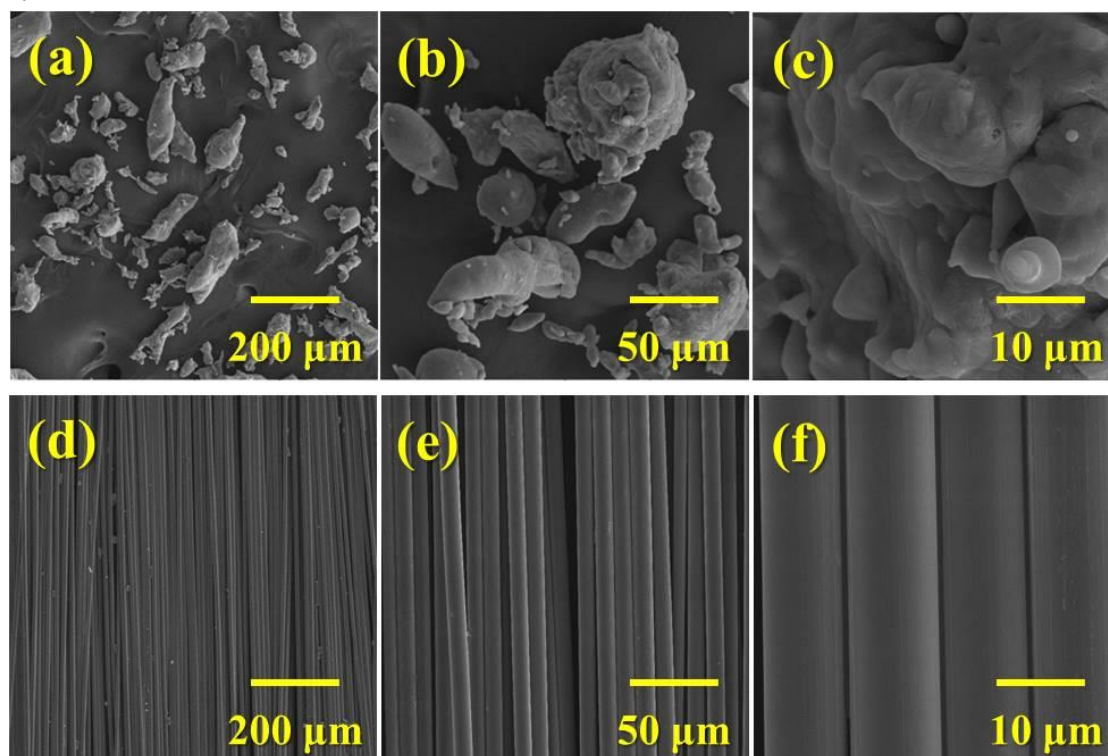


Fig. 1. SEM images of Al (a-c) and CF (d-f) at different magnifications X 250, X 1000 & X 5000 respectively.

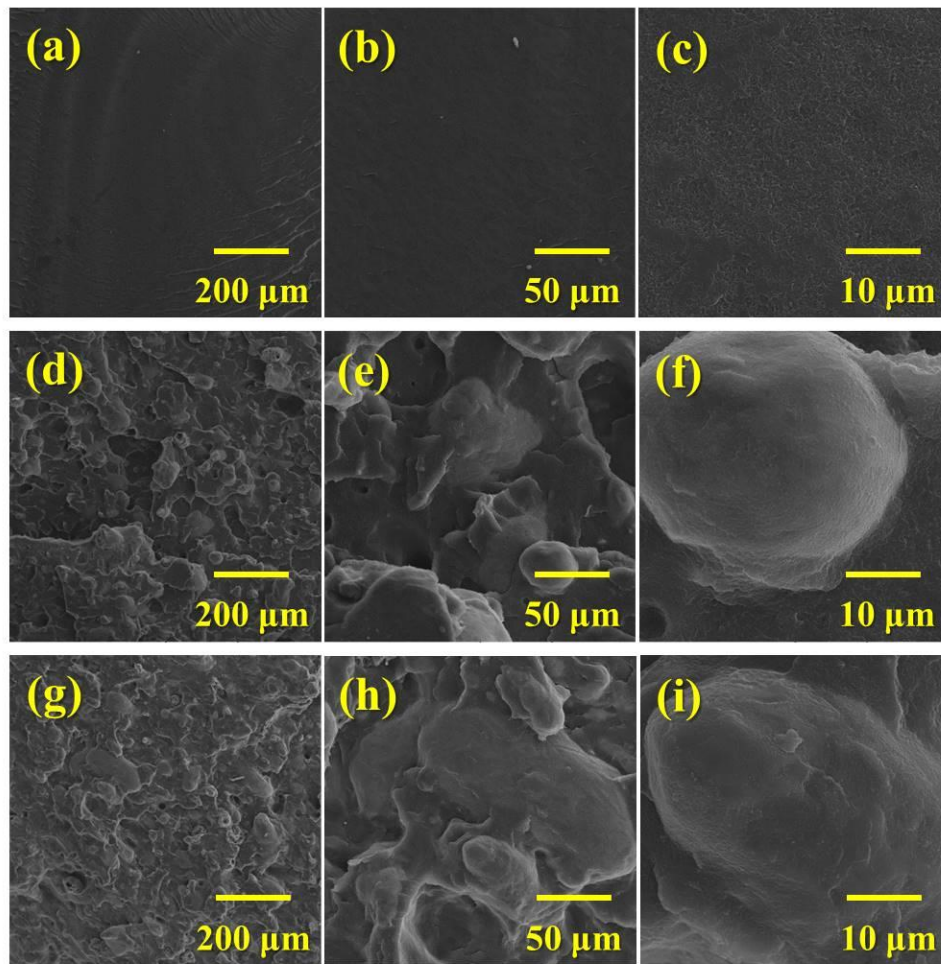


Fig.2. SEM images of XLDPE (a-c) and XLDPE/Al composites at different volume concentrations (vol%): XLDPE/Al (d-f, 40 vol%), XLDPE/Al (g-i, 60 vol%).

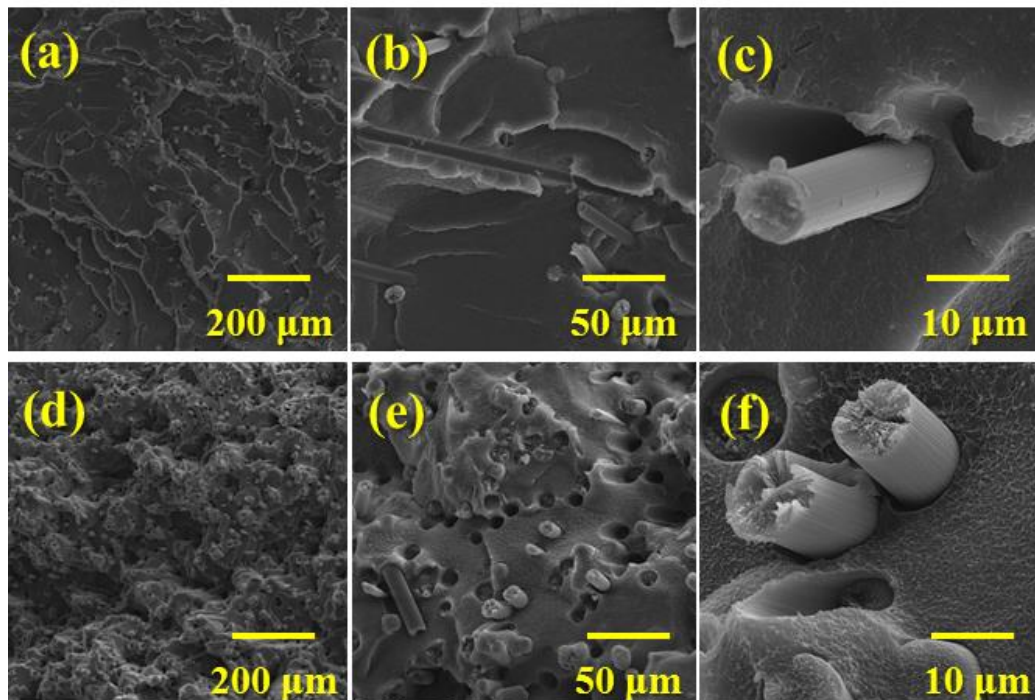


Fig. 3. SEM images of and XLDPE/CF composites at different volume concentrations (vol%): XLDPE/CF (a-c, 5 vol%) & XLDPE/CF (d-f, 15 vol%).

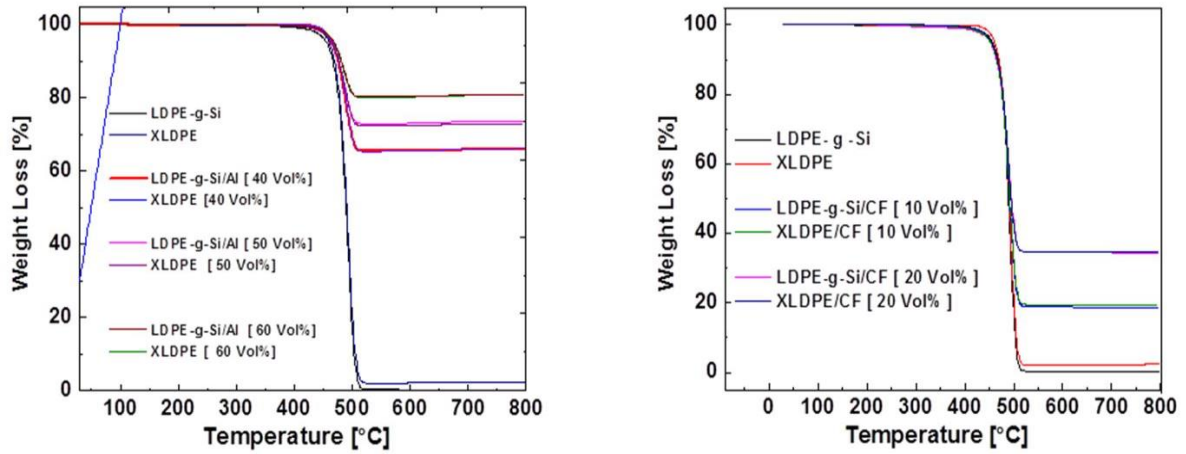


Fig. 4. TGA curves of XLDPE, LDPE-g-Si and their composites with (a) Al and (b) CF.

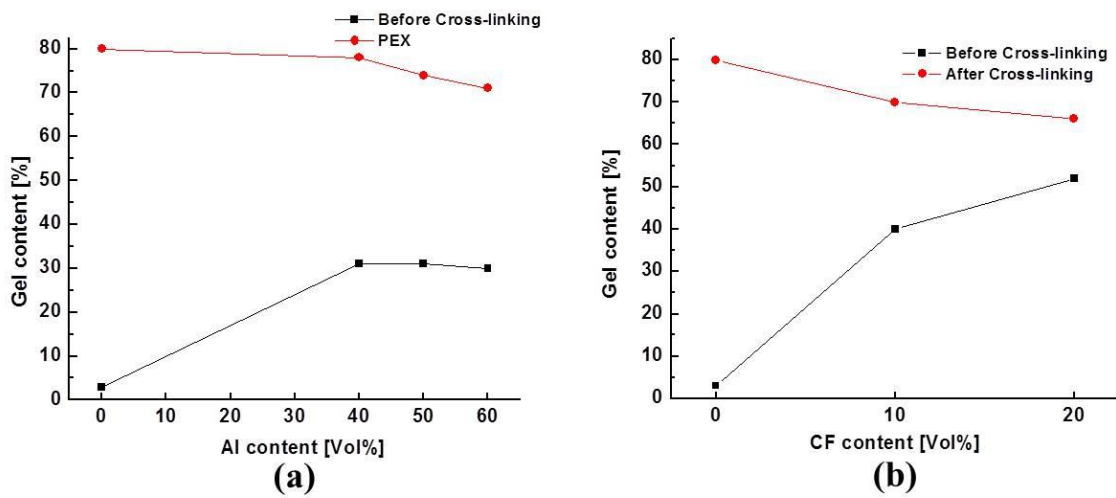


Fig. 5. Effect of filler volume fraction on gel contents of composites containing (a) Al and (b) CF as a filler.

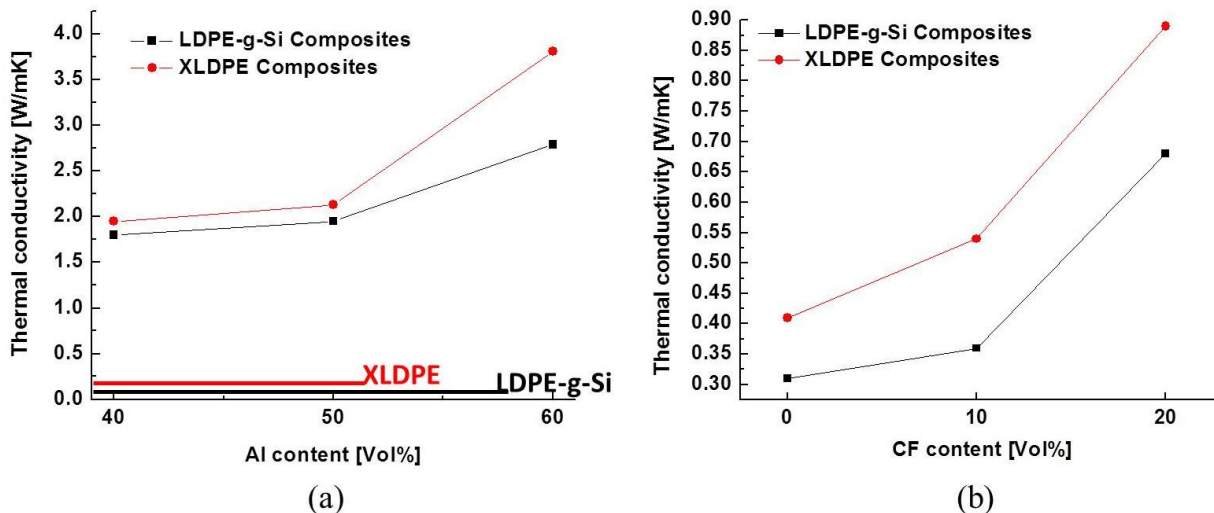


Fig. 6. Thermal conductivity of composites contain (a) Al and (b) CF as a filler.

Gel content

The effect of Presence of thermal conductive fillers on the gel content of samples investigated before and after crosslinking and results are

depicted in Figure 5. Cross-linking would be happened even before moisture curing as a result of unavoidable atmospheric moisture during raw material storage and melt blending. Existing of

filler affected the cross-linking level before and after moisture curing of composites. Before moisture curing and crosslinking process, addition of filler enhanced the gel contents meanwhile after moisture curing, the reverse trend was found. Before moisture curing step, gel content enhanced from 2% up to 30 % and 50% for LDPE-g-Si/Al and LDPE-g-Si/CF composites at the highest filler contents, respectively. For XLDPE composites presence of fillers would be hinders of condensation of silanols to form Si-O-Si crosslinks which negatively influence the gel content. By introduction of different type of fillers in the polymer matrix, the possibility of formation of bridges between the chains during moisture curing would be decrease. The gel content decreased from 80 for XLDPE to about 70 at highest concentrations of fillers.

Thermal conductivity

There are limited investigations on thermal conductivity of XLDPE composites. Thermal conductivity of composites before and after moisture curing investigated and results depicted in Figure. 6. Thermal conductivity of Al and CF contained composites enhanced with increment of filler loading as result of formation thermal conductive pathways through the matrix especially at high filler loadings. The thermal conductivity of LDPE-g-Si/Al (Figure 6a) and LDPE-g-Si/CF (Figure 6b) composites increased from $0.31 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ up to $2.79 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ at (Al-60 % vol.) and $0.68 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ (CF-20 vol %) of fillers respectively. Moisture curing of LDPE-g-Si led to enhancement of thermal conductivity of matrix (XLDPE) as a result of introduction heat pathways and these paths directly contributes to increment in thermal conductivity [4]. In our study, thermal conductivity of XLDPE reached to $0.41 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$. The similar results found for XLDPE composites. Thermal conductivity of XLDPE/Al and XLDPE/CF composites rose up to $3.81 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ and $0.9 \text{ W}\cdot\text{m}^{-1}\text{K}^{-1}$ at highest filler contents. Combination of high density cross-linking and formation of 3D conductive filler pathways provided such a high thermal conductivity. In the case of XLDPE/Al composites, there is a great interaction between the XLDPE and Al surface which can reduce the amount of defects in composites and subsequently decrease the Umklapp-scattering. In the case of

XLDPE/CF composites, there isn't any interaction between the CF surface and XLDPE due to different surface chemistry of CF sizing and matrix. Based on above results, thermal conductivity of composites is closely related to performance of filler and matrix. These results can open up application of such thermal conductive fillers in production of heat exchanger pipes and similar applications.

CONCLUSION

XLDPE composites successfully prepared by melt mixing of LDPE-g-Si in presence of Al and CF at different loadings and thermal conductivity, gel content and morphology of prepared composites were investigated. Thermal conductivity of composites was calculated after measurement of the thermal diffusivity, specific heat and density of samples. By introducing high density cross-linking and increasing of filler content, thermal conductivity of nanocomposites enhanced. The highest thermal conductivity was surprisingly more than 12 times superior than LDPE-g-Si. With considering our results, these types of composites can be applied as a thermal conductive pipes in thermal management applications, semi-conductive products and so on.

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