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Effect of Orientation and Content of Carbon Based Fillers on Thermal Conductivity of Ethylene-Propylene-Diene/Filler Composites

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ABSTRACT: In this study, synthetic graphite, carbon fiber, and carbon nanotube were used as thermal conductive fillers and ethylene-propylene-diene (EPDM) as matrix. Oriented EPDM/filler composites were prepared with two-roll mill, and the effects of orientation and content of carbon based fillers on thermal conductivity and tensile strength of the composites were investigated. Parallel thermal conductivity of the oriented composites is significantly higher than normal thermal conductivity of the oriented composites. Especially, at 31.6% graphite content, parallel thermal conductivity of oriented composites is 7.14 W/mK. Very high thermal conductivity was achieved for oriented EPDM/graphite composites. Orientation of the fillers using two-roll mill significantly improves the thermal conductivity in the orientation direction. For all the EPDM/filler composites, tensile strength of orientation direction is higher than that of normal direction. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41000.

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INTRODUCTION

Elastomers are used in many applications such as tires, hoses, and belts. Because thermal conductivity of elastomers is very low, heat build-up occurs in the elastomers in use. Increased temperature due to heat build-up is harmful to elastomers, because elastomers are susceptible to thermal degradation. To enhance the intrinsically low thermal conductivity of elastomers, thermal conductive fillers such as ceramic or metal fillers have been mixed with elastomers.[1–6] Also, significant studies[7–14] have been done for the composites with carbon-based fillers such as carbon black, carbon fiber, and graphite due to their chemical stability, light weight, and high thermal conductivity. Compared with metal fillers, carbon-based fillers have better corrosion resistance and lower density. Thermally conductive composites can be used in the electronics, aerospace, and energy storage industries.

It has been known that thermal conductivity of composites can be improved if the fillers in the matrix orient preferably along the heat flow direction.[14,15] Also, the orientation can provide the desired directional thermal conductivity. However, it is not always easy to obtain filler orientation with the common polymer processing methods such as extrusion molding. Even though the fillers in the elastomer matrix can be oriented with two-roll mill, there have been few detailed studies about the effect of orientation of various carbon-based fillers using two-roll mill on the thermal conductivity of the composites.

In this study, synthetic graphite, carbon fiber, and carbon nanotube (CNT) were used as thermal conductive carbon-based fillers ethylene-propylene-diene (EPDM) was used as a matrix because EPDM is widely used in the elastomer industry. Oriented EPDM/filler composites were prepared with two-roll mill, and the effects of orientation and content of carbon based fillers on thermal conductivity and tensile strength of the composites were investigated.

EXPERIMENTAL

Materials and Composite Preparation

Important characteristics of the materials used in this study are summarized in Table I. Carbon fiber is a polyacrylonitrile-based, 6 mm chopped carbon fiber. CNT is multiwalled CNT (MWCNT) and were synthesized by thermal CVD. MWCNTs (purity: 95%) were used as received. The thermal conductivity of graphite, carbon fiber and MWCNT are generally known to be ∼600, 175–200, and ∼3000 W/mK, respectively.[16,17]

EPDM and fillers were melt-mixed in a bench kneader (Irie Shokai Ltd., Japan) at 20 rpm for 10 min. Mixing temperature was fixed at 110°C. To study the effect of filler orientation on the thermal conductivity of the composites, the composites were oriented for 10 min with two-roll mill, after mixing in the kneader. Extensive shear force at the gap of the two rolls makes fillers align along the orientation direction. Then, the obtained composites were compression molded at 150°C for 5 min.

Table I. Important Characteristics of the Materials Used in this Study

Materials	Supplier	Characteristics
EPDM	Kumho Polychem., Korea	Specific gravity: 0.87, C2 content: 70 wt %, ML_{1+4}(125°C): 53
Graphite	TIMCAL, Canada	Specific gravity: 2.25, Particle size: 6.5 μm, Specific BET surface area: 20 m^2/g
Carbon Fiber	Bluestar, United Kingdom	Specific gravity: 0.36, Fiber length: 6 mm, Diameter: 40 μm
MWCNT	CNT Co., Korea	Bulk density: 0.06 g/cc, Length: 1–25 μm, Diameter: 20 nm, Specific BET surface area: 200 m^2/g

Sample Preparation and Testing

Thermal diffusivity of the composites was measured at room temperature by laser flash method using a Netzsch Nanoflash (LAF 447, German) according to ASTM E 1461. For the thermal diffusivity measurement, disk-shaped samples with diameter of 14 mm and a thickness of 1 mm were prepared. Thermal diffusivity was measured in the direction perpendicular to the flat plane of disk samples coated with graphite.

Because the thickness of a sheet of the oriented composites prepared with two roll mill is too small for the measurement of thermal diffusivity of orient direction, four or five of the sheets were stacked in parallel and compressed to produce the samples with 14-mm thickness as shown in Figure 1. The disk-shaped samples used for measuring thermal diffusivity of orientation direction were prepared in such a way that orientation direction is perpendicular to the flat plane of the samples using a circular iron punch. Therefore, orientation direction of the composites is parallel to the direction of heat flow during measurement of thermal diffusivity of orient direction.

Also, the samples used for measuring thermal diffusivity of normal direction were prepared in such a way that normal direction is perpendicular to the flat plane of the samples using a circular iron punch. Therefore, normal direction of the composites is parallel to the direction of heat flow during measurement of thermal diffusivity of normal direction.

Specific heat capacity was determined by differential scanning calorimeter (Perkin-Elmer DSC 8000, USA). Sapphire was chosen as reference material. The density of composites was measured by the Archimedean buoyancy method using a gravimeter (Ueshima MS-2150, JAPAN). Thermal conductivity (k) was then calculated from the thermal diffusivity (α), density (ρ), and specific heat capacity (C_p) by the following equation:

$$k=\alpha\rho C_p \tag{1}$$

Thermal conductivity calculated using the thermal diffusivity of orientation direction and normal direction was referred as parallel thermal conductivity and normal thermal conductivity, respectively.

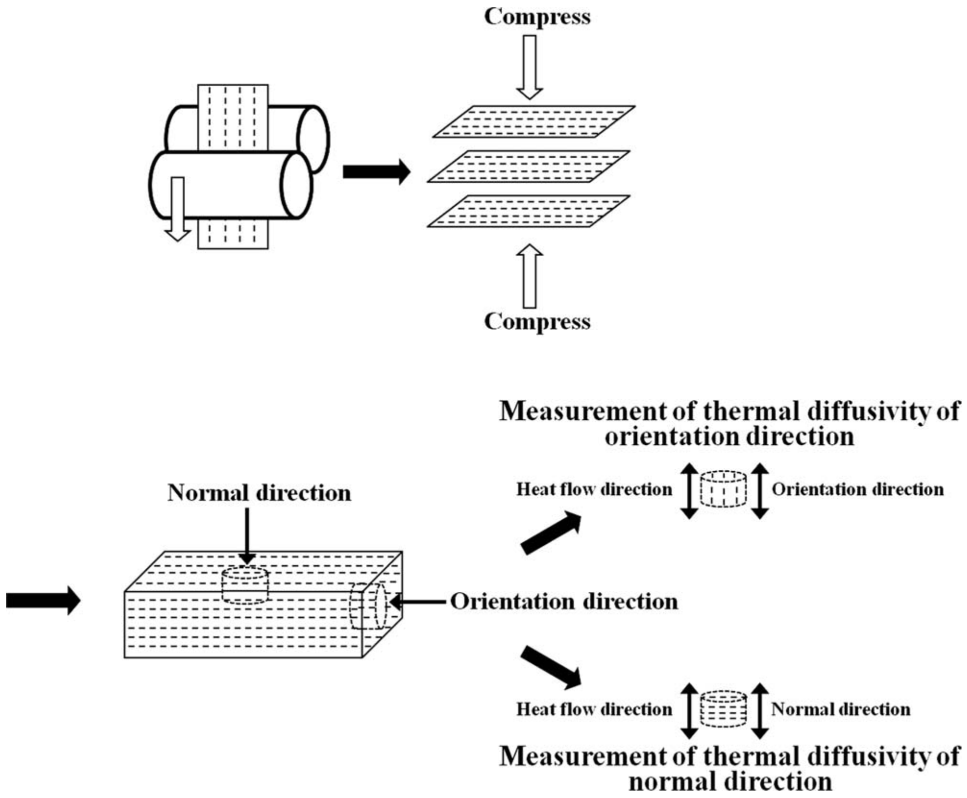

Figure 1. Schematics for sample preparation.

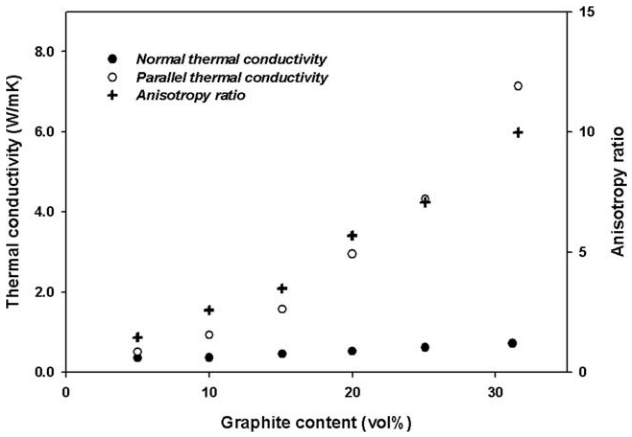

Figure 2. Effect of graphite content on thermal conductivity of oriented EPDM/graphite composites.

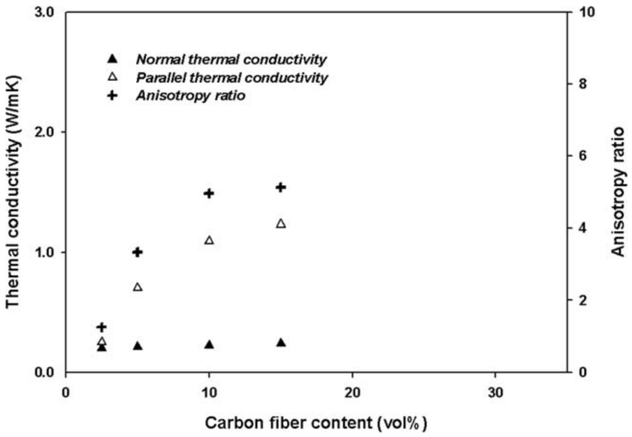

Figure 3. Effect of carbon fiber content on thermal conductivity of oriented EPDM/carbon fiber composites.

To investigate the orientation of carbon fiber and graphite in EPDM matrix, the samples were mounted in epoxy and then polished smooth using silicon carbide paper. The polished sections of the EPDM/carbon fiber and EPDM/graphite composites were examined with field emission scanning electron microscope (SEM, Hitachi S-4200, JAPAN).

RESULTS AND DISCUSSION

Figure 2 shows thermal conductivity of oriented EPDM/graphite composites. Parallel thermal conductivity was measured parallel to orientation direction of the samples. Normal thermal conductivity was measured perpendicular to the orientation direction of the samples. Because high thermal conductivity is required for the commercial use, the maximum amounts of fillers that can be melt-mixed with kneader were used. At the same content of graphite, parallel thermal conductivity of oriented EPDM/graphite composites is higher than normal thermal conductivity of oriented EPDM/graphite composites.

At 5% graphite content, a thermal conductivity anisotropy ratio (parallel thermal conductivity/normal thermal conductivity) is about 1.4. With increase of content of graphite, the difference between parallel and normal thermal conductivity of the oriented composites becomes bigger. At 31.6% graphite content, parallel and normal thermal conductivity of the oriented composites is 7.14 and 0.72 W/mK, respectively, which corresponds to a thermal conductivity anisotropy ratio of about 10. Considering that the commercial grade of thermally conductive silicon grease only has thermal conductivity about 2 W/mK, parallel thermal conductivity of oriented EPDM/graphite composites at 31.6% graphite is very high. Therefore, orientation of graphite with two-roll mill is a very effective method for the enhancement of parallel thermal conductivity of EPDM/graphite composites.

Figures 3 and 4 show thermal conductivity of oriented EPDM/carbon fiber and oriented EPDM/MWCNT composites, respectively. Both the composites display the similar behavior to oriented EPDM/graphite composites. Parallel thermal conductivity of the oriented composites is significantly higher than normal thermal conductivity of the oriented composites. At 2.5% carbon fiber content, a thermal conductivity anisotropy ratio is about 1.3. With increase of content of graphite, the anisotropy of the oriented composites becomes bigger. At 15% carbon fiber content, parallel and normal thermal conductivity of the oriented composites is 1.23 and 0.24 W/mK, respectively, which corresponds to a thermal conductivity anisotropy ratio of about 5.1.

At 2.5% MWCNT content, a thermal conductivity anisotropy ratio is about 1.7. At 15% MWCNT content, parallel and normal thermal conductivity of the oriented composites is 1.15 and 0.66 W/mK, respectively, which corresponds to a thermal conductivity anisotropy ratio of about 1.7. Filler orientation makes fillers have more chance to contact with each other for the orientation direction. As a result, orientation of the fillers significantly improves the thermal conductivity in the orientation direction. In this study, the maximum content of fillers that can be melt-mixed with kneader is only 15% for both EPDM/carbon fiber and EPDM/MWCNT composites due to their high viscosity.

Figure 5 shows parallel thermal conductivity of oriented EPDM/filler composites. Parallel thermal conductivity of oriented EPDM/graphite composites continuously increases with

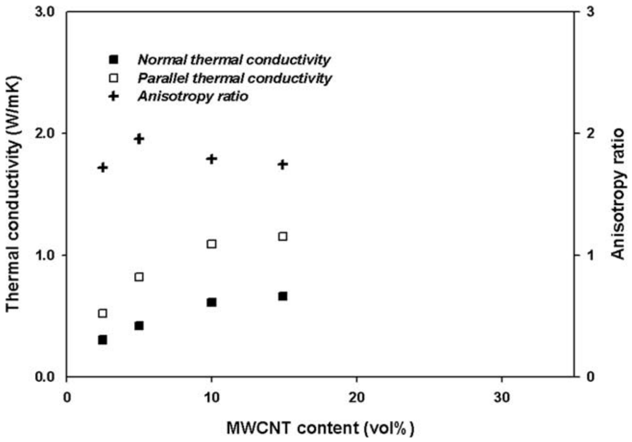

Figure 4. Effect of MWCNT content on thermal conductivity of oriented EPDM/MWCNT composites.

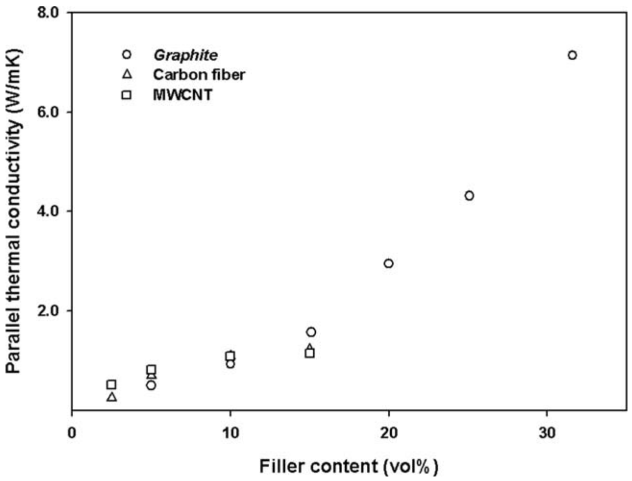

Figure 5. Effect of filler content on parallel thermal conductivity of oriented EPDM/filler composites.

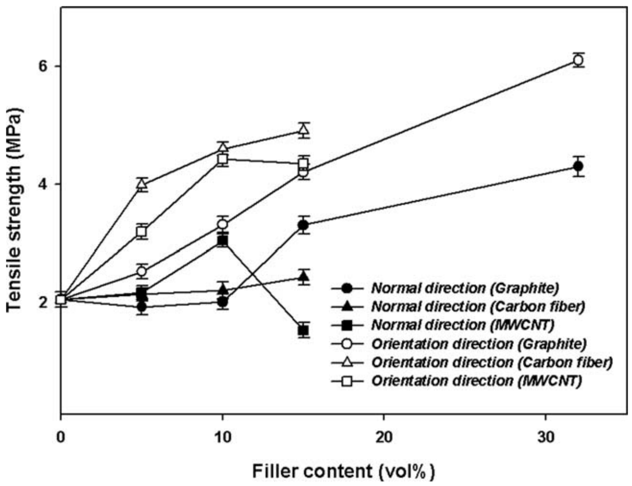

Figure 7. Effect of filler content on tensile strength of oriented EPDM/filler composites.

increasing content of graphite. But a leveling off in the thermal conductivity for EPDM/carbon fiber and EPDM/MWCNT composites is observed at 15% filler content. At 15% filler content, parallel thermal conductivity of EPDM/graphite composites is higher than that of EPDM/carbon fiber and EPDM MWCNT composites. At low content of fillers, EPDM/MWCNT composites display the highest parallel thermal conductivity in Figure 5. However, at 15% filler content, EPDM/MWCNT composites display the lowest parallel thermal conductivity. This might be related to poor dispersion of MWCNTs in the EPDM matrix with high content of MWCNT.

Figure 6 shows normal thermal conductivity of oriented EPDM/filler composites. The thermal conductivity of graphite, carbon fiber and MWCNT are generally known to be ~600, 175–200, and ~3000 W/mK, respectively.[16,17] Normal thermal conductivity of the composites in this study may depend on the thermal conductivity of fillers. Normal thermal conductivity of oriented EPDM/MWCNT composites is the highest, and that of oriented EPDM/carbon fiber composites is the lowest at the same content of fillers.

Figure 7 shows tensile strength of orientation and normal direction of oriented EPDM/filler composites. For all the EPDM/filler composites in this study, tensile strength of orientation direction is higher than that of normal direction. Tensile strength of orientation direction for EPDM/carbon fiber and EPDM/graphite composites increases with increasing content of fillers. Also, tensile strength of orientation direction of EPDM/MWCNT composites increases with increasing content of MWCNT from 0 to 10%. However, further increase of content of MWCNT leads to the decrease of tensile strength of EPDM/MWCNT composites. This might be related to deteriorated dispersion of MWCNTs in the EPDM matrix. The decrease of the tensile strength could be caused by the premature failure starting at the filler aggregates.[18] MWCNTs are very difficult to achieve uniform dispersion especially with their high content because MWCNTs are highly entangled with each other.

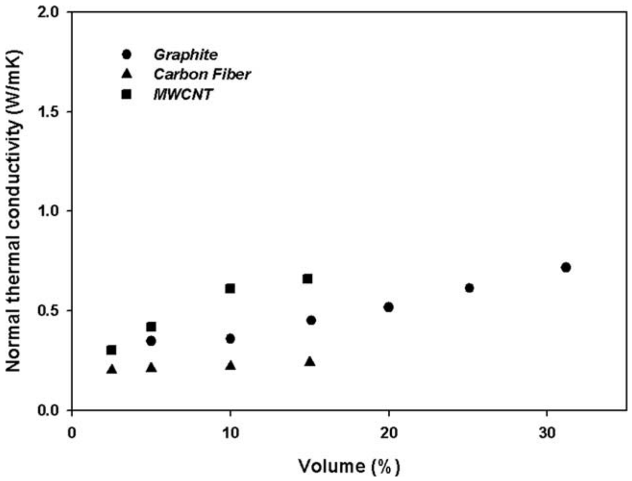

Figure 6. Effect of filler content on normal thermal conductivity of oriented EPDM/filler composites.

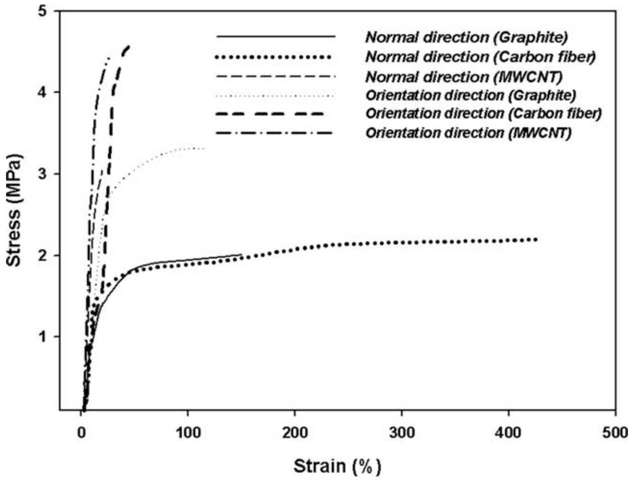

Figure 8. Original stress–strain curves for EPDM/filler composites at 10% filler content.

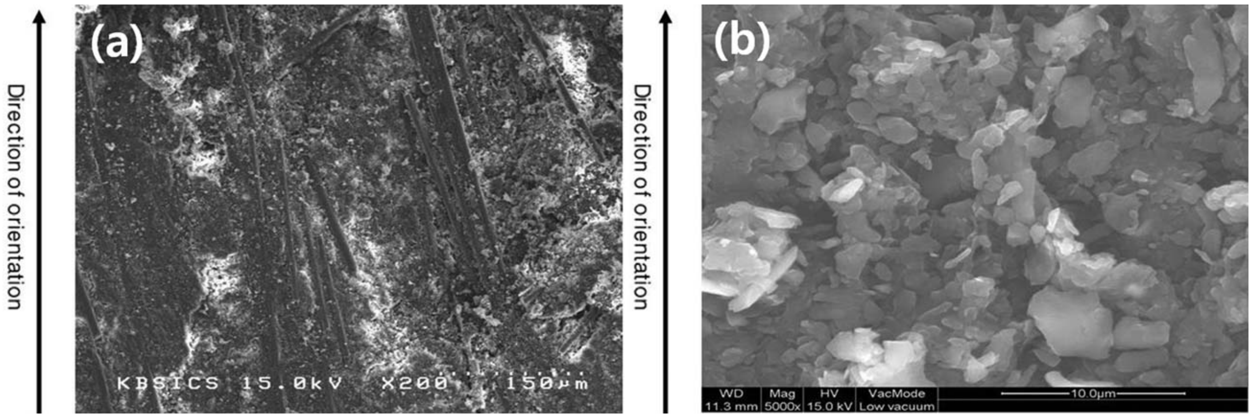

Figure 9. SEM images of (a) EPDM/carbon fiber composite containing 10 vol % carbon fiber and (b) EPDM/graphite composite containing 15 vol % graphite.

Original stress–strain curves for EPDM/filler composites at 10% filler content are shown in Figure 8 as an example.

Figure 9 shows SEM images of EPDM/carbon fiber composite containing 10% carbon fiber and EPDM/graphite composite containing 15% graphite. The arrow in Figure 9 indicates the orientation direction of two-roll mill process. Figure 9(a) indicates that carbon fibers primarily align in the orientation direction. Orientation direction is the same as the heat flow direction during parallel thermal conductivity measurement. Because the graphite sheets are broken during mixing in the kneader and two-roll mill process, it is difficult to investigate the orientation direction for EPDM/graphite composites. However, highly interconnected network of graphite along the orientation direction can be observed in Figure 9(b).

It has been reported that the use of a mixture of filler materials increases thermal conductivity of polymer/filler composites.[15,19,20] Therefore, in this study, the effect of graphite/carbon fiber, graphite/MWCNT, and carbon fiber/MWCNT mixtures on parallel thermal conductivity of the oriented composites is investigated as shown in Figure 10. Total content of fillers in Figure 10 is fixed at 10%. Compared with parallel thermal conductivity of EPDM/filler composites containing only single filler, a significant increase in the parallel thermal conductivity of the EPDM/filler composites containing mixtures of fillers is observed in Figure 8. Among the composites containing mixtures of fillers, the composite containing graphite/MWCNT mixture displays the highest parallel thermal conductivity.

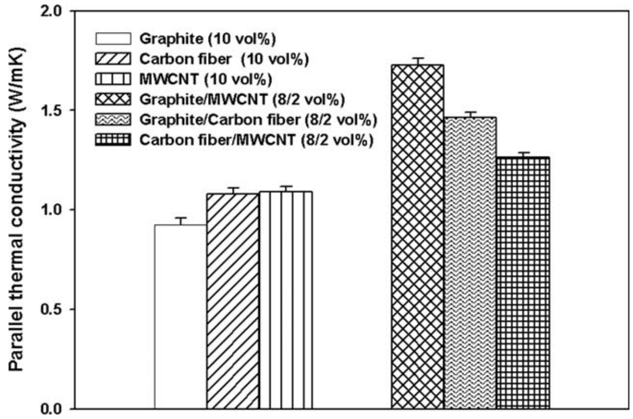

Figure 10. Parallel thermal conductivity of oriented EPDM/filler composites. Total content of fillers is fixed at 10 vol %.

CONCLUSIONS

From this study, it can be concluded that the desired filler orientation was successfully achieved in EPDM matrix with two-roll mill process, resulting in significant improvement in parallel thermal conductivity especially for graphite. At 31.6% graphite content, parallel thermal conductivity of oriented EPDM/graphite composites is 7.14 W/mK and its thermal conductivity anisotropy ratio is about 10, which is the highest anisotropy ratio in this study.

However, improvement of parallel thermal conductivity of EPDM/MWCNT composite is not effective compared with EPDM/graphite composites due to poor dispersion of MWCNTs in the EPDM matrix with high content of MWCNT. MWCNTs are irregularly curved along the length, and are highly entangled with each other. At 10% filler content, the parallel thermal conductivity of the EPDM/filler composites containing mixtures of fillers is higher than that of the EPDM/filler composites containing only single filler, and the composite containing graphite/MWCNT mixtures displays the highest parallel thermal conductivity. For all the EPDM/filler composites, tensile strength of orientation direction is higher than that of normal direction.

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