

Melt Mixing of Carbon Fibers and Carbon Nanotubes Incorporated Polyurethanes

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ABSTRACT: Polyurethane composites filled with carbon fibers (CF) and carbon nanotubes (CNT) were prepared by mixing and injection molding, and its mechanical as well as their thermal properties were investigated. Dynamic mechanical analysis (DMA), thermogravimetry analysis (TGA), and thermal conductivity tests were done, and the properties were evaluated as a function of the filler concentration. The storage modulus of the composites increased with fillers concentration, which also mean the increase of the stiffness, suggest a good adhesion between the polyurethane matrix and the fillers. Addition of more CF and CNT to the composites broadened and lowered

the peak of $\tan \delta$ specifies that the polyurethane composite became more elastic because there is a good adhesion between the fillers and the matrix. The addition of carbon fillers improves the thermal stability of the polyurethane. The inclusions of CNT show a better thermal stability when compared with CF. The addition of carbon fillers also increased the thermal conductivity of the polyurethane composites. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 196–202, 2008

Key words: polyurethane; composite; carbon fibers; carbon nanotubes; carbon filler

INTRODUCTION

Thermoplastic elastomer is a class of polymers, which encompass both thermoplastic and elastomeric properties. Like any other thermoplastic elastomers, thermoplastic polyurethane has the advantage of elastic ability and can be melt processed with equipment such as extruders and injection-molding machines.¹

Polyurethanes are segmented multiblock copolymers, having general repeat unit structure of hard and soft segments.^{2,3} Usually, the soft segments have lower thermal transition and enables the formation of temporary shape, whereas the hard segment gave higher thermal transition and responsible for the permanent shape.³ Because of these unique hard and soft segment structures, polyurethanes are known for having a high resilience, tough, and excellent resistance to abrasion. Furthermore, they have properties of both elastomer and thermoplastics, which make them preferred in many industries.¹

Nevertheless, the pure polyurethanes demonstrate a low stiffness and poor resistance to heat, which makes its application limited.^{4,5} Incorporation of the fillers into polymer matrix is one of most favored methods to acquire the desired enhance properties.^{6–19}

In this study, carbon fillers were used in polymer matrix to enhance the polyurethane properties, especially mechanical and thermal conductivity. Carbon has a great potential to be used as a reinforcing agent in the polymer composites, because they possess a good thermal conductivity, thermal stability, and high strength. This study focused on the preparation and characterization of polyurethane composites incorporated with two carbon fillers: carbon fibers (CF) and carbon nanotubes (CNT).

A series of polyurethane composites with different carbon loading were prepared, and the effect of carbon structure, length, and concentration on the mechanical and thermal properties of carbon-filled polyurethane composites was investigated. The samples of the composites were studied with thermal conductivity, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA).

MATERIALS AND METHODS

The polymer used as the matrix was a thermoplastic polyurethane elastomer Elastollan supplied from Elastogran GmbH, Germany. The thermal conductiv-

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ity of the polymer is in the range of 0.19–0.25 W/mK, while specific heat is between 1.5 and 1.8 J/gK (room temperature) and 1.7–2.3 J/gK (melt temperature). The materials used as fillers were CF, obtained from Tenax Fibers, Germany, with an average length of 3 mm and CNT, which are multiwalled CNT provided by FutureCarbon GmbH, Germany. The average dimensions for CNT are 15 nm, and the synthesized purity is >98%.

The polyurethane pellets were ground to form powder and then dried in a vacuum oven at temperature of 80°C for at least 2 h to remove the moisture because the polymer was moisture sensitive. The CNT were also dried in vacuum at temperature of 200°C for 3 h prior mixing, whereas CF was used as received. The dispersion of the fillers in the polymer matrix is a key issue in preparing polymer composites with enhanced properties. The compounding of polymers and the fillers were done in two steps to improve the mixing quality between the polymer matrix and the carbon fillers. First, the polymers were premixed with the fillers manually at different composition before being fed into extruder. The compositions of 5 and 10 wt % for CF and 1 and 3 wt % for CNT were used.

Then, the preblend of polyurethane and CF were mixed using a ThermoHaake polylab extruder at temperature of 210°C and the screw speed of 60 rpm. Increasing the screw speed will cause the CF to break to smaller particle. After mixing, the polyurethane composites were injected using injection molding at temperature of 210°C into bone and round-shaped samples as shown in Figure 1. The polyurethane composites with weight fractions of 5 and 10 wt % CF were prepared in this way. The pure polyurethane was labeled as PU, whereas polyurethane composites with 5 and 10 wt % CF fractions were labeled as PU05CF and PU10CF, respectively.

Meanwhile, ThermoHaake minilab extruder was used for mixing the preblend of polyurethane and the CNT at temperature of 210°C and the screw speed of 260 rpm to optimize mixing properties. After mixing, the polyurethane composites were injected by using injection molding at temperature of 210°C into bone and round-shaped samples. The polyurethane composites with weight fractions of 1 and 3 wt % CNT were prepared in this way. The composites were labeled as PU01CNT and PU03CNT for polyurethanes composites with 1 and 3 wt % CNT fractions, respectively.

Thermal conductivity measurements were performed using Thermal Conductivity Analyzer (TCA-200LT-A, Netzsch, Germany). Different temperatures from 25 to 80°C were introduced to the samples in a controlled condition and the thermal conductivity of the polymer at different temperatures was gathered.

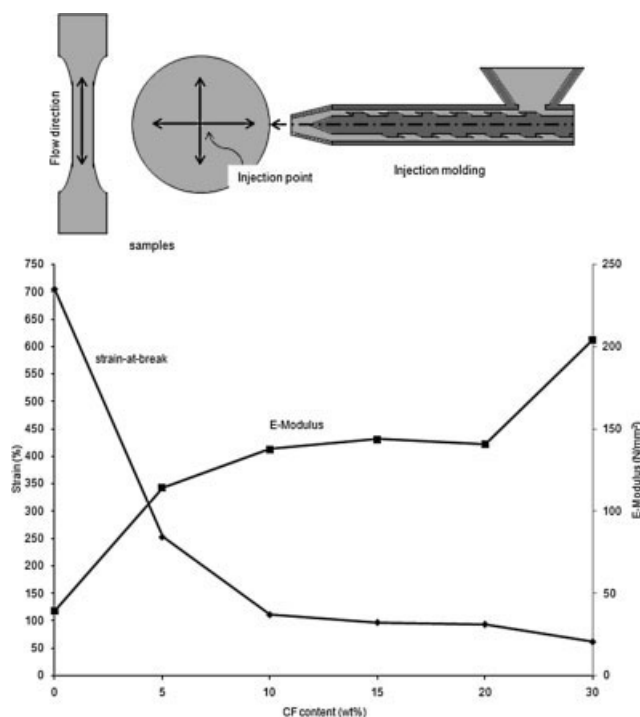


Figure 1 Preparation of bone and round-shaped samples with injection molding and the effect of carbon fiber fractions on strain-at-break and E modulus of polyurethanes composites.

The round-shaped samples were obtained from injection-molding process. Thermal conductivity was measured as a function of temperature.

Furthermore, the dynamic mechanical properties were determined using a TA Instruments DMA 2980 with the frequency of 1.0 Hz. A constant nitrogen flow was used to purge the instrument. Data were collected at temperature range from -60 to 100°C , and the scanning rate was $10^\circ\text{C}/\text{min}$. The samples were obtained from injection-molding process. This analysis determines the storage modulus, E' , loss modulus, E'' and damping coefficient, $\tan \delta$ as a function of temperature.

Additionally, the thermal stability of polyurethane composites was measured using the TGA using TA Instruments, thermal analysis, and rheology TGA-2950. The samples were heated at a constant heating rate of $10^\circ\text{C}/\text{min}$ from 0 to 800°C . A constant nitrogen flow was used to purge the instrument too. The result is recorded as temperature dependence weight fraction.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The storage modulus, often related to the Young's modulus, describes the stiffness of a material. Stor-

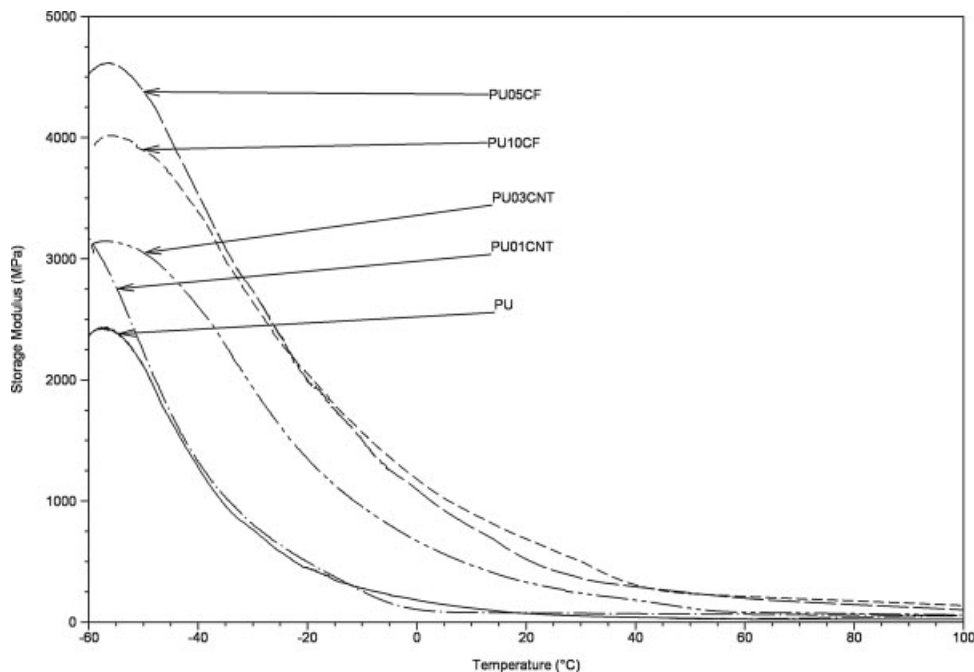


Figure 2 Storage modulus versus temperature for unfilled polyurethane and different concentration of carbon-filled polyurethane composites.

age moduli for polyurethane composites, measured at 10 Hz, are shown in Figure 2 as a function of temperature. Below the glass transition temperature (T_g), the storage modulus is high, because the polymer is in the glassy state. After the T_g , there is drop in the value of the storage modulus, because the polymer chains become mobile and the polymer is in the rubbery state.

The addition of carbon fillers to the polyurethane matrix has increased the storage modulus value, because the movements of the polymer chains were restricted by interactions between the carbon fillers and the polymer chains and increase the stiffness of the polyurethane matrix. As the percentage of the fillers increased, there are more carbon fillers that restrict the movement of the polymer chains, which further increases the stiffness of the polyurethane composite.

The polyurethane composite with only 3 wt % CNT show a higher storage modulus when compared with polyurethane with 5 wt % CF. The increase in storage modulus for polymer-filled CNT is better than the polymer with CF, because the reinforcement and the load transfer from the matrix to the fillers is more effective due to smaller diameter and a higher aspect ratio. The increases in storage modulus of polyurethane composites, which also mean the increase of the stiffness, suggest a good adhesion between the polyurethane matrix and the fillers. Another work cited also report similar improvement effect of storage modulus with the introduction of CNT in the polymer.²⁰

Tan δ is the ratio of loss modulus to storage modulus. Figure 3 shows tan δ of polyurethane compo-

sites as a function of temperature. The glass transition temperature (T_g) of the material can be observed from the peak in tan δ . For unfilled polyurethane, the value for peak of tan δ is at temperature around -24.67°C . Addition of carbon fillers change the tan δ peaks, thus change the T_g of the polymer. Polyurethanes with the addition of 1 wt % CNT and polyurethanes with 5 wt % CF show broadened and flattened tan δ peaks, which indicate better adhesion because less energy is absorbed. The presence of the fillers limits the relaxation and the motion of the polyurethane chains and decreased the peak intensity and cause the T_g to differ slightly.^{21,22}

The CNT-filled polyurethane show a significant change in T_g for concentration lower than 3 wt %, as shown in Figure 3. Addition of more CF or CNT to the composites broadened and lowered the peak of tan δ even more. A lower and broader tan δ peak specifies that the polyurethane composite became more elastic, because less energy was absorbed by the composite because there is a good adhesion between the fillers and the matrix. The decrease of tan δ peaks is also thought to be corresponding to a decrease in the amount of materials participating in the transition.¹

The tan δ peak of the polymer composites also shifts slightly to a higher temperature if the concentration of the fillers was increased, which reflect the increases in the glass transition temperature (T_g). The results above suggest that the mechanical properties of polyurethane can be improved by the addition of carbon fillers.

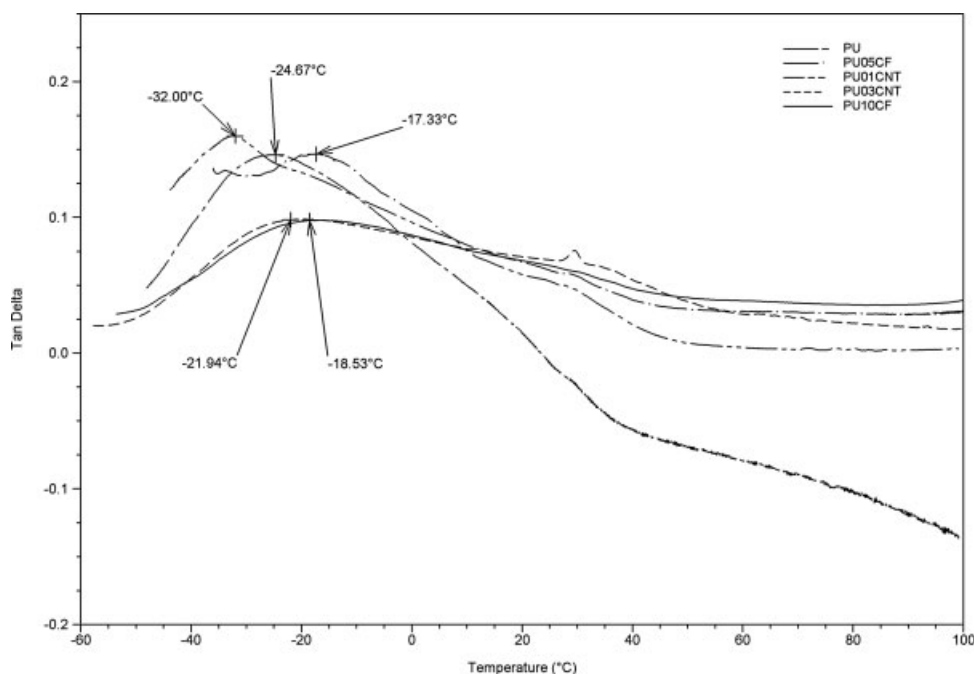


Figure 3 Temperature dependence of $\tan \delta$ for unfilled polyurethane and different concentration of carbon-filled polyurethane composites.

As shown in Figure 3, the curve for polyurethane composite with 10 wt % fiber is almost similar to polyurethane with 3 wt % nanotubes, which means that the properties of polyurethane can be improved with the incorporation of CNT at lower loadings when compared with CF due to higher aspect ratio, which result in more filler/matrix interface for load transfer.

Thermogravimetry analysis

Figure 4 presents the thermal decomposition behavior of polyurethane composites as a function of temperature. Because of the soft and hard segments,²³ thermal decomposition for polyurethane is observed to proceed in two steps. The first-decomposition step

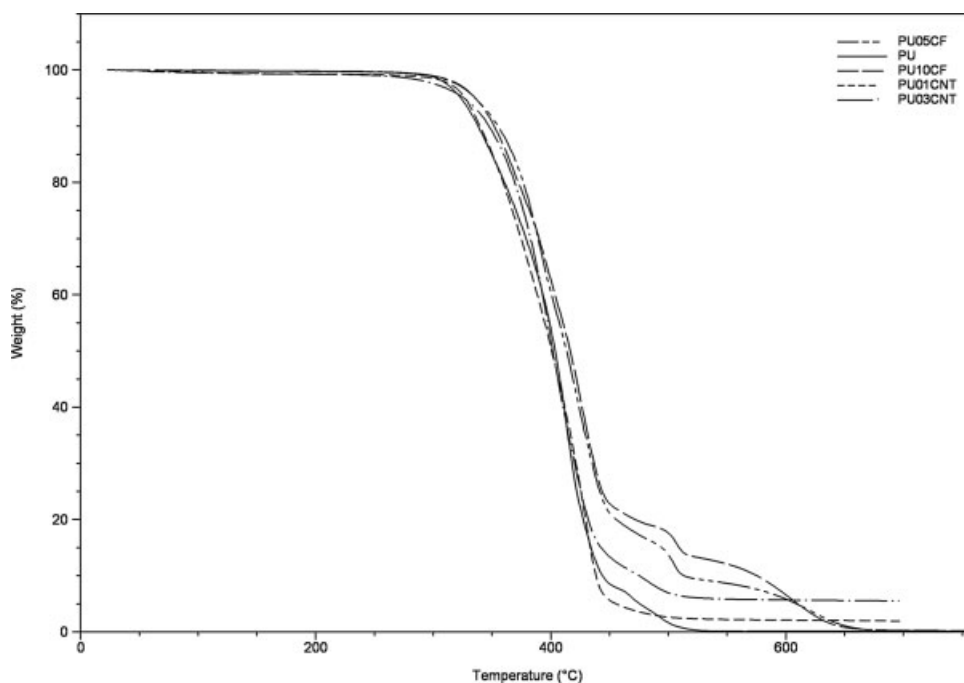


Figure 4 Thermogravimetry result of unfilled polyurethane and different weight fraction of carbon-filled polyurethane composites as a function of temperature.

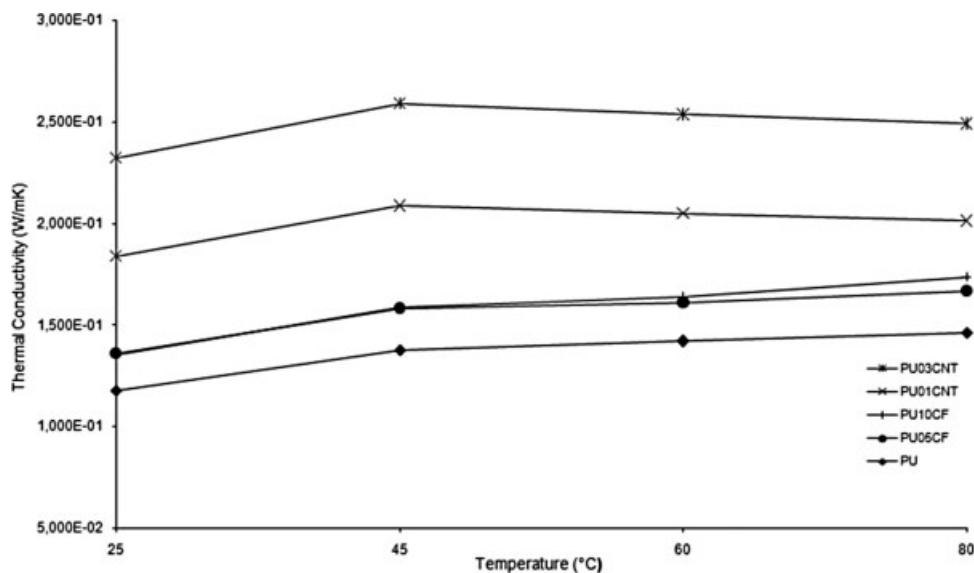


Figure 5 Thermal conductivity versus temperature unfilled polyurethane and different concentration of carbon-filled polyurethane composites.

of pristine polyurethane starts at about 295°C; meanwhile, the second step started at 460°C.

From Figure 4, with the addition of carbon fillers, the onset of decomposition temperature increases slightly and the full decomposition increases with higher temperature too. The thermal properties of the carbon fillers attributed to the increase in thermal-degradation temperature of the polyurethane composites. For polyurethane with 5 wt % of CF, the second-decomposition step starts at 494°C, and the maximum thermal decomposition was increased from 540°C for pristine polyurethane to 790°C.

The addition of 10 wt % fibers increased the second decomposition to 450°C and the maximum thermal decomposition to 800°C. At the temperature of 700°C, the polyurethane incorporated with 1 and 3 wt % was still not totally degraded, because the CNT is known to have high-thermal stability up to 2800°C (vacuum).²⁴

Because CNT has a high-thermal stability,²⁵ the CNT-filled polyurethane degrades at higher temperature when compared with pure polyurethane or CF-filled polyurethane. The heat applied to the polyurethane composite was absorbed by the CNT and eventually improved the thermal stability.²⁴ Better thermal stability of the CNT-filled polyurethane may also derive from better distribution of nanotubes.²¹ The results show that the addition of carbon fillers will raise the temperature of maximum thermal decomposition and eventually improve the thermal stability of the polyurethane. The inclusion of CNT shows a better thermal stability when compared with CF due to its high thermal stability.

Thermal conductivity

The thermal conductivity for polyurethane composites plotted as a function of temperature is shown in Figure 5. In general, the addition of carbon fillers increased the thermal conductivity of the polyurethane composites.

At 45°C, the thermal conductivity of pristine polyurethane is 0.1424 W/mK. By the addition of 5 wt % of CF, the thermal conductivity has increased to 0.1614 W/mK. The thermal conductivity is related to the network formation of the fillers in the polymer composites, and so the formation of thermally conductive networks is very important to ensure that the composite shows a good thermal conductivity. Interconnected structures of the fillers were formed, and the thermal was conducted through the matrix and the network along the polymer composite. The more easily the fillers form conductive network in the matrix, the more thermal conductivity of the composite will be improved. Higher fillers concentration shows better thermal conductivity, because the fillers are better connected in the polymer matrix.

The increased is more prevailing for polyurethane with 3 wt % CNT where thermal conductivity value becomes 0.2589 W/mK. Another report on thermal conductivity of CNT-filled polymer also found similar result where the thermal conductivity increases with an increase in the amount of CNT.²⁶ The thermal conductivity in CNT-filled polyurethane is more significant when compared with CF filled polyurethane, because the CNT has a higher thermal conductivity up to 3000 W/mk for multiwalled CNT.²⁷

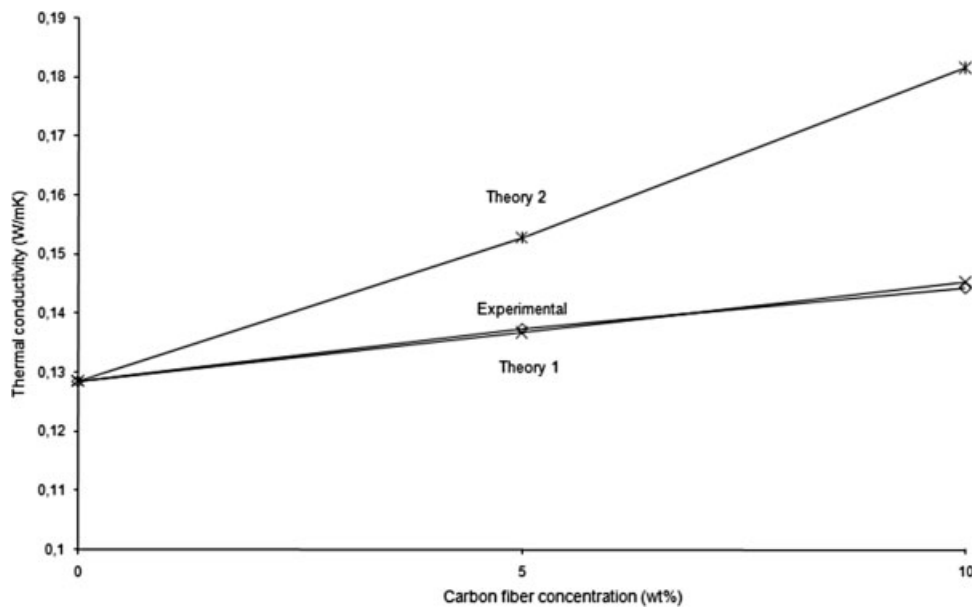


Figure 6 Comparison of experimental and theoretical results for the thermal conductivity for carbon fiber-filled polyurethane at 25°C.

Agari and Uno²⁸ proposed thermal conductivity model for particle-filled composite.

$$\log k_c = \phi C_2 \log k_f + (1 - \phi) \log(C_1 k_m) \quad (1)$$

k_c , k_m , k_f , and ϕ are thermal conductivity of composite, thermal conductivity of the matrix, thermal conductivity of the fillers, and volume fraction of fillers, respectively. C_1 measures the influence of the particles on the secondary structure of the polymer, whereas C_2 describes the easiness to form conductive chains.

However, because CNT has a very high aspect ratio, and k_c of CNT is also much larger when compared with k_m of the polymer matrix, the thermal conductivity model above is not suitable to calculate the thermal conductivity of CNT-filled polyurethanes. A new thermal conductivity model for CNT composite has been proposed based on an effective medium approach.²⁷

$$k_c = k_m + \frac{k_f L}{2R_i k_f + L} \langle \cos^2 \theta \rangle \phi \quad (2)$$

L is the length of the CNT, and R_i is interface thermal resistance or Kapitza resistance (about $8.0 \times 10^{-8} \text{ m}^2/\text{KW}$).^{29,30} In this study, $\cos^2 \theta$ is 1/3 as CNT are randomly dispersed in the polymer matrix.^{29,30}

Substituting all the properties in eqs. (1) and (2), the thermal conductivity of the polyurethane composites is found to be in the range of 0.1367–0.1528 W/mK for the case of 5 wt % CF and 0.1454–0.1815 W/mK for the case of 10 wt % CF while for CNT-filled

polyurethane, it is in the range of 0.19024–0.25024 for 1 wt % CNT and 0.19072–0.25072 W/mK for 3 wt % CNT. Figures 6 and 7 show the comparison between theoretical and experimental measurement of the thermal conductivity. Theory 1 is calculated using k_m value of 0.19 W/mK, while k_m value of 1.25 W/mK is used in theory 2 because the thermal conductivity of pure polyurethane is in the range from 0.19 to 1.25 W/mK. These theoretical thermal conductivity ranges approximately agree with the experimental measurements for the composites studied.

CONCLUSIONS

This work has suggested that the mechanical properties of polyurethane as well as their thermal properties can be improved by the addition of carbon fillers. The higher storage moduli of the polyurethane composites were found with the addition of carbon fillers, which also means the increase in stiffness of the polyurethane composites. The CNT-filled polyurethane shows a higher storage modulus when compared with polyurethane with CF, because the reinforcement and the load transfer from the matrix to the fillers in the former is more effective due to smaller diameter and higher aspect ratio.

Addition of carbon fillers to the composites also broadened and lowered the $\tan \delta$ peak of polyurethane composites specifies that the polyurethane composite became more elastic because there is a good adhesion between the fillers and the matrix. The CNT-filled polyurethane at lower concentration shows similar $\tan \delta$ curve with CF-filled polyurethane at higher fillers content due to higher aspect

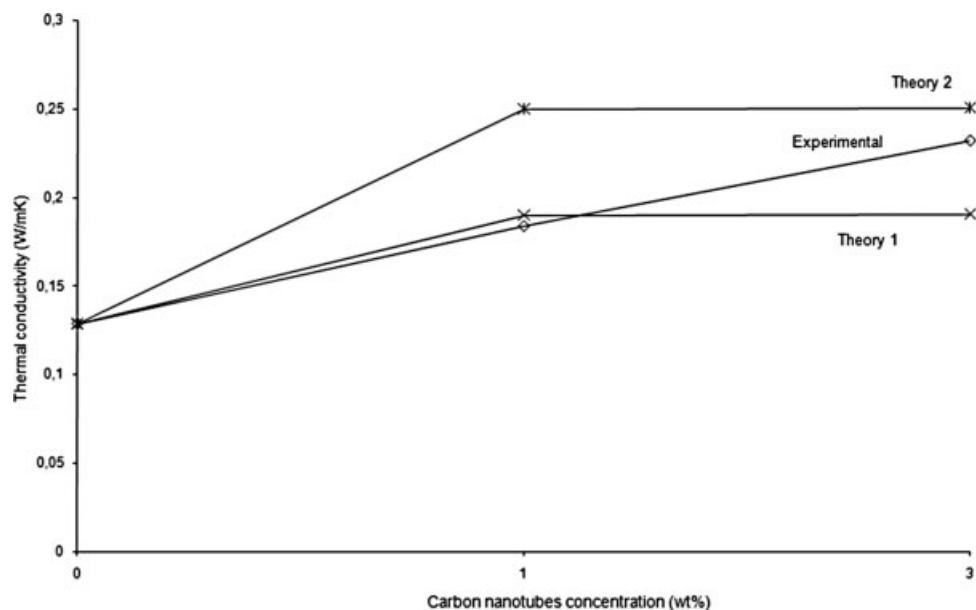


Figure 7 Comparison of experimental and theoretical results for the thermal conductivity for carbon nanotubes-filled polyurethane at 25°C.

ratio, which results in more filler/matrix interface for load transfer. Thermal stability of the polyurethane was increased with the addition of CF. The inclusion of CNT shows a better thermal stability when compared with CF. Thermal conductivity of the polyurethane increased with the introduction of carbon fillers. Thermal conductivity in CNT-filled polyurethane is more significant when compared with CF-filled polyurethane, because the CNT has a higher thermal conductivity.

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