

# Mechanical Spectroscopy of Multiwalled Carbon Nanotube-filled Polyurethane Nanocomposites

Shahrul Azam Abdullah\*

School of Mechanical Engineering, College of Engineering,  
Universiti Teknologi MARA  
40450 Shah Alam, Selangor, Malaysia  
\*shahrulazam@uitm.edu.my

Lars Frommann

Gesellschaft für Innovationsentwicklung mbH  
Olbrichtstraße 4c, 04157 Leipzig, Germany

## ABSTRACT

*Reinforced polyurethane composites provide possibility for tailoring material stiffness and combine the mechanical properties of fillers with behavior of matrix. This research work focuses on analyzing the mechanical behavior of polyurethanes filled with carbon nanotubes. Multi-walled carbon nanotube-filled polyurethane nanocomposites containing 7.8 to 30.5 vol%-MWNTs have been formulated by mixing and injection molding and their mechanical spectroscopy has been investigated. Tests including Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA) were conducted at a frequency range of 1-50 Hz and the attributes were measured as a function of the intensity of the filler. With the concentration of the fillers, the storage modulus of nanocomposites increased, which also implies an increase in stiffness, inferring a good adherence between fillers and the matrix of polyurethane. The addition of more MWNTs to the nanocomposites broadened and lowered  $\tan \delta$  peak specifies that the polyurethane nanocomposite is more elastic as the fillers and the matrix are well adhered to. The reliance of the storage modulus is more pronounced in initial glassy region of the polymer. The presence of MWNTs has also improved the activation energy of the polymer. In addition, thermogravimetric analysis shows that the inclusion of MWNTs fillers enhances the thermal stability of the nanocomposites. This work has suggested that the incorporation of MWNTs into polyurethanes matrix can improved the mechanical properties well as their thermal stability.*

**Keywords:** Polyurethane; Nanocomposite; Carbon Nanotubes; DMA, TGA

## Introduction

Thermoplastic polyurethane (PU), as any other thermoplastic elastomer, has the advantage of comprising both thermoplastic and elastomeric attributes. PU are segmented multiblock copolymers with such a general repeat arrangement of hard and soft units [1]-[4]. PU are known as having high resilience, toughness, and exceptional abrasion tolerance attributable to these unique hard and soft section architectures. Furthermore, PU characteristics enable them to be melt-processed through techniques such as extrusion, injection or blow molding, as well as the possibility of manipulating their structure with a transition temperature range of  $T_g$  which make them preferred in many industries. They are also biocompatible relative to other polymers [5]. However, the potential application of polyurethanes was constrained due to inadequate heat resistance and low stiffness. For ideal stipulation of smart applications, PU with a longer relaxation time, high ratio of glassy to rubbery modulus as well as sharp transition from glassy to rubbery state properties are necessary. The introduction of filler particles is generally favored to enhance the rubber modulus and to acquire the desired enhancement capabilities [6]-[13].

Carbon nanotubes (CNTs) have a great potential to be used in polymer nanocomposites as a reinforcing agent as they have excellent thermal stability and high strength as well as good thermal conductivity. The incredible properties of CNTs suggest that they are a great candidate to be integrated into the polymer matrix. Hypothetically, although when relatively small concentrations are being used, CNTs have the potential to enhance the thermal and mechanical properties of the polymers. Small percentages of presence of CNTs in the polymer matrix offer the possibility of improving the properties of the polymer nanocomposites while maintaining their process capabilities.

In order to enhance the properties of polyurethane, multiwalled carbon nanotubes (MWNTs) were used in the polymer matrix in this report. The processing and analysis of polyurethane nanocomposites incorporated with CNTs has been the focus of this report. A series of polyurethane composites with different MWNTs content were formulated and the influence of carbon length, structure, as well as composition on thermal and mechanical properties of the nanocomposites were investigated. Dynamic mechanical analysis, thermogravimetric and scanning electron microscopy have been used to analyze the samples of the nanocomposites.

## **Materials and Methods**

The polymer used as the matrix was shape memory polyurethanes (MM 3520-Ether type) acquired from Diaplex SMP Technologies Inc., Japan. The polymer is of granulate form and is packaged in bags of 20 kg. It is an ether-based polyurethane SMP formulated from diphenylmethane-4, 4'-diisocyanate, 1, 2-butanediol, and bisphenol A. The glass transition temperature  $T_g$  for MM3520 is at around 35 °C. As compared to other types, it also has relatively good elongation (>600%) and strength. Moreover, the multi-walled carbon nanotubes (MWNTs), Baytubes C150P supplied by Bayer Materialscience AG, Germany were used as filler. It has a low outer diameter, a narrow distribution of diameter and an exceptionally high aspect ratio (length-to-diameter ratio). The average outer diameters are 13-16 nm, and the purity of synthesis is >95%. The MWNTs were used as synthesized.

Samples with 7.8 to 30.5 vol%-MWNTs were prepared at 260 rpm to optimize processing rotation. Before compounding, PU was first grounded into powder form. The powder was then dried in a vacuum oven for 2 hours at a temperature of 80 °C. The MWNTs were also vacuum-dried for 3 hours at a temperature of 200 °C prior to mixing. The polymer and MWNTs were first premixed manually in formulations range of 7.8 to 30.5 vol%-MWNTs after the drying process upon being loaded into Coperion ZSK 18 MEGALab (Coperion, Stuttgart, Germany) co-rotating twin screw extruder for the second mixing stage. Post mixing, the MWNT-filled PU nanocomposite granulates from extruder were injected into samples using Krauss Maffei KM 50-55 cx injection molding machine. Temperature profile for unfilled PU for different screw zones are in range of 200 to 220 °C. As with the extrusion process, when the MWNTs content was elevated, the end temperature was also progressively decreased. The processed temperature is slightly tailored with the presence of filler percentage due to thermal and electrical conductivity of fillers. In addition to the temperature setting, the pressure and time during plasticizing as well as holding pressure were also regulated during the preparation of samples.

Dynamic Mechanical Analyzer (DMA) 242 C/1G NETZSCH-Gerätebau GmbH, Selb Germany) was used to determine the dynamic mechanical properties using tension as the deformation mode. Samples obtained from the injection molding system with dimensions of 10 mm × 6 mm × 1 mm were used. A dynamic force of 0.4–4 N, amplitude of 160 μm as well as four different frequencies; 1 Hz, 5 Hz, 10 Hz and 50 Hz have been used in this analysis. The instrument was calibrated for temperature by using a standard mass and probe position. The data acquired in this work were at temperatures range of -90 to 100 °C and the scanning rate was 1 °C/min while the samples have been tested for each scan and the error was less than 2%. Dynamic mechanical analysis (DMA) findings were discussed as storage modulus and tan  $\delta$ .

Additionally, thermogravimetric analysis (TGA) was used to analyze thermal stability and decomposition behavior of unfilled PU and MWNTs-filled PU nanocomposites using TA Instruments, Thermal Analysis and Rheology TGA-2950 (TA Instruments, Alzenau, Germany). The instrument temperature calibration was performed using Curie temperature of various metals as per recommendation from manufacturer. In this experiment, samples of approximately 20 mg prepared from injection molding were heated at a constant heating rate of 10 °C/min from 0 to 800 °C. The sensitivity of the balance is 0.1 mg, and a constant nitrogen flow was used to purge the instrument, too. The result was documented as temperature dependence weight fraction.

Scanning Electron Microscopy (10 kV) with a Zeiss DSM 982 Gemini microscope (Carl Zeiss, Oberkochen, Germany) while the EDX-Detector is from ThermoFisher Scientific (NSS 7) were used to observed dispersion behavior of MWNTs in nanocomposites. The injection molding samples were extracted to a length of 5-7 mm and a width of 3 mm using a side cutter upon being glued to the carbon pad holder. Additionally, conducting carbon paste was put all around the samples to fix the samples. The material of the sample holder is Aluminum.

## Results and Discussion

Storage modulus and  $\tan \delta$  curves have been plotted against temperature for the analysis of DMA data and their response can be used to measure the glass transition temperature ( $T_g$ ) [14, 15]. The storage modulus is the measure of recoverable energy during deformation. Figure 1 displays the temperature dependence storage modulus for PU and PU/MWNT nanocomposites measured at 1 Hz. It shows the corresponding peak and point occurred at various temperatures, suggesting that the change occurred at a spectrum instead of at one sharp temperature [15].

The polymer transitions from glassy to rubbery phase as the temperature increases from below to above  $T_g$  and the changes can be observed from a rapid decrease in the value of the storage modulus. At temperatures below  $T_g$  region, the storage modulus of polymer is high since the polymer chains are less mobile that they are unable to resonate with the oscillatory loads and therefore remain stiff. The polymer is said to be in a glassy or energy elastic state at this temperature.

As the polymer was further heated after  $T_g$  region, there is an attenuation in the capacity of the storage modulus because the polymer chains become active and have no issues in resonating with the load. The polymer is said to be in rubber in entropy elastic state at this elevated temperature.

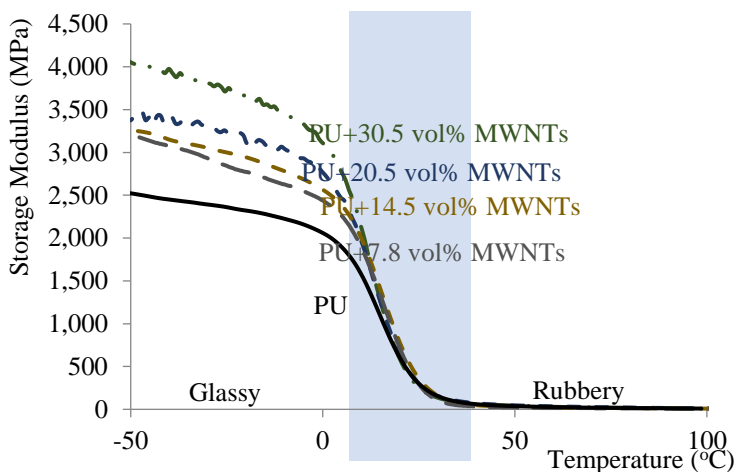


Figure 1: Temperature dependence of storage modulus for unfilled PU and PU/MWNTs nanocomposites at 1 Hz

Moreover, the temperature dependence storage modulus could provide details on the stiffness of the material as a function of temperature and was stated to be susceptible to structural changes such as fiber-matrix bonding [15,16]. The storage modulus of the nanocomposites increases with the fraction of MWNTs in the whole investigated temperature spectrum. However, in the initial glassy region of the polymer, the dependency of the storage modulus is more pronounced. Higher initial storage modulus in MWNTs reinforced PU nanocomposites can also be attributed to good fiber/matrix bonding as suggested by [15]. The improvement in storage modulus with the inclusion of a very low carbon concentration indicates the efficient transfer of the load and the reinforcement of the polymer due to the smaller diameter and the high aspect ratio of the fillers. Other researchers also documented an improved effect of storage modulus with the incorporation of CNTs in polymers [17].

Tan  $\delta$  is the ratio of loss to storage modulus, which combines the viscous and elastic components into a single term and measures material damping. Tan  $\delta$  or the damping modulus of PU/MWNTs nanocomposites as a function of temperature is shown in Figure 2. The higher value of tan  $\delta$  implies that the substance is less elastic. Tan  $\delta$  curves and peaks of the nanocomposites show a significant change relative to unfilled PU. Additionally, a decreased peak height can be associated with an increased MWNTs fraction in the polymer nanocomposites. Decreased tan  $\delta$  peak reflects the higher rigidity of the nanocomposites and demonstrates the constraint effect of the filler [20,21].

Furthermore, Figure 2 demonstrates expanded and flattened damping peaks through increasing the content of MWNTs content. A broader damping peak with the inclusion of MWNTs into the polymer matrix indicates the distribution of relaxation times and therefore further relaxation modes might be initiated [13]. The decline in  $\tan \delta$  peaks can also be attributed to the reduction in the number of materials participating in the transition [22]. A similar behavior has been documented for magnetite-filled shape memory polymers [13]. The results shown suggest that the mechanical properties of PU can be enhanced with the incorporation of MWNTs.

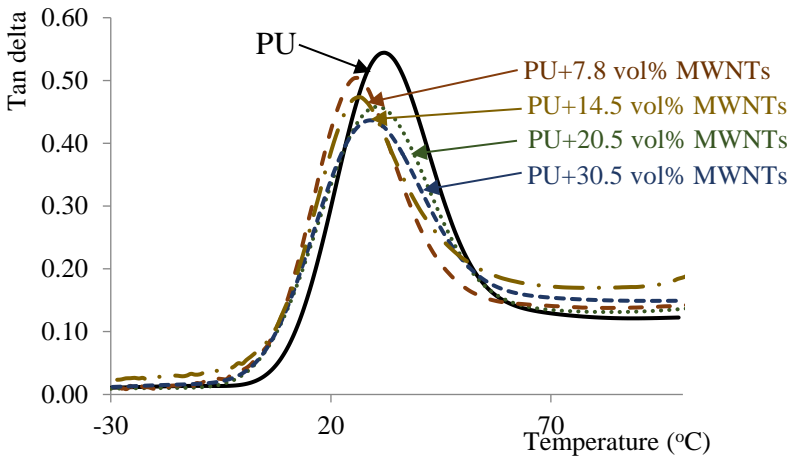


Figure 2: Temperature dependence of loss factor for pure PU and PU/MWNTs nanocomposites at 1 Hz

The test frequency may have an influence on  $T_g$  of the materials because glass transition is a kinetic transition. The effect of 4 different frequencies (1 Hz, 5 Hz, 10 Hz and 50 Hz) on the  $\tan \delta$  for pure PU is depicted in Figure 3. The result shows the peak temperatures of unfilled PU varies with the used frequencies and that  $T_g$  was shifted to higher temperature as the frequency was increased while the heating rate remains constant. Additionally, the peak height ascends while  $\tan \delta$  curves broadened with increasing test frequency. The position of  $T_g$  shifts to a higher temperature as the mechanical frequency is increased since there is a delay in relaxation movements of polymer segments or glass transition [18]. Therefore, molecular relaxations can only occur at elevated temperatures as the test frequency increases and hence increasing the  $T_g$  of material [18]. Similar findings of frequency effects were also recorded by other researchers [13, 18,19].

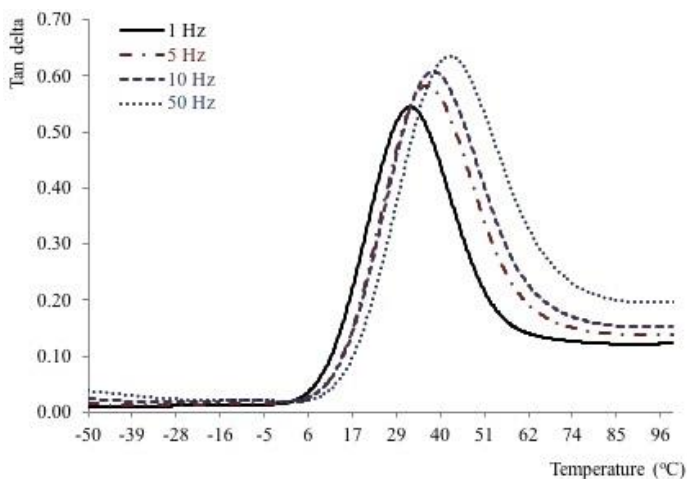


Figure 3: Temperature dependence of loss factor for pure PU at different frequencies

In addition, the Arrhenius law can be used to measure the activation energy of the glass transition [15, 23].  $\tan \delta$  peaks for different frequencies determined in DMA analysis were superimposed to calculate the activation energy [23]. Figure 4 displays a plot of  $\ln f$  against inverse temperature or also known as Arrhenius plot of the glass transition relaxation for PU nanocomposites with various MWNTs loading. To deduce thermally stimulated process, which is more susceptible to greater energy, Arrhenius plots in Figure 4 were then used to measure the activation of glass transition energies for PU/MWNTs nanocomposites.

The activation related to the glass transition can be accomplished by multiplying the slope of each line with negative gas constant. Table 1 summarized the glass transition activation energies for PU nanocomposites with various MWNT loads. PU matrix shows glass transition activation energy of 305.76 kJ/mol. The inclusion of MWNTs intensified the activation energy of the polymer nanocomposites. One reasonable interpretation is that the MWNT particles increase the effective viscosity of the PU, which hinders the rearrangement of the PU macromolecule fragments and hence increases the value of the activation energy [24]. Activation of PU/MWNTs nanocomposites tends to further increase with auxiliary addition of fillers content. Nevertheless, it was observed that the activation energy was decreased when the filler fraction higher than 14.5 vol%. Similar activation energy behavior for polymer nanocomposites also were documented by other researchers [24, 25].

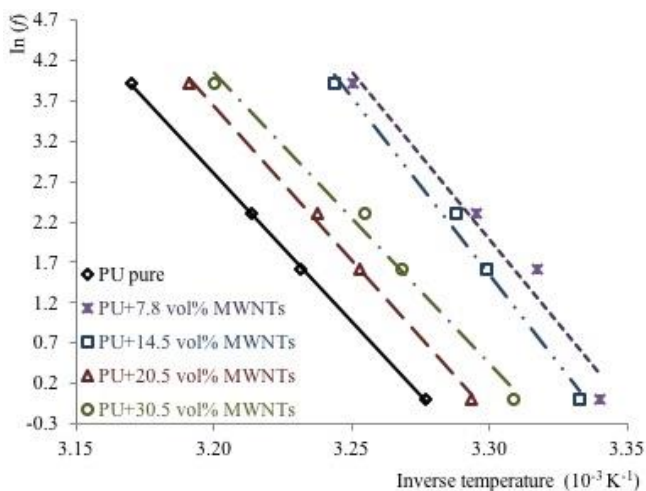


Figure 4: Arrhenius plot for unfilled PU and PU/MWNTs nanocomposites

Table 1: Activation energy for glass transition relaxation of unfilled PU and PU/MWNTs nanocomposites calculated from Arrhenius plot (Figure 4)

Filler fraction (vol%)	Activation energy (kJ/mol)
0	305.76
7.8	347.61
14.5	364.47
20.5	317.94
30.5	299.13

Figure 5 demonstrates the thermal decomposition behavior of MWNTs-filled PU nanocomposites. With regards to their soft and hard parts, unfilled PU was found to undergo two stages of thermal decomposition [26]. The first phase of PU decomposition begins at about 346°C, while the second phase starts at about 497°C. In the case of unfilled PU, this first step has already shown a 94.81% weight loss. It was also observed that the second degradation was at a lower rate as compared to the first.

The incorporation of MWNTs was found to decrease the first and second decomposition weight loss, but no substantial difference was observed in the temperature where the degradation commenced. A subtle percentage of residue (0.13%) was recorded for unfilled PU at 600°C, although at this temperature the polymer was anticipated to be fully degraded. Similar behavior was observed for nanocomposites of PU/MWNTs where the residue was greater at 600°C as compared to the percentage of MWNTs used. The presence of platinum (Pt) in the polymer matrix is shown by EDX analysis, which may



clarify the residue at 600°C. Another hypothesis is that due to the dispersion and formation of the fillers, certain polymer chains may be embedded within the MWNTs network, providing a greater residue than anticipated at 600°C [27, 28, 29].

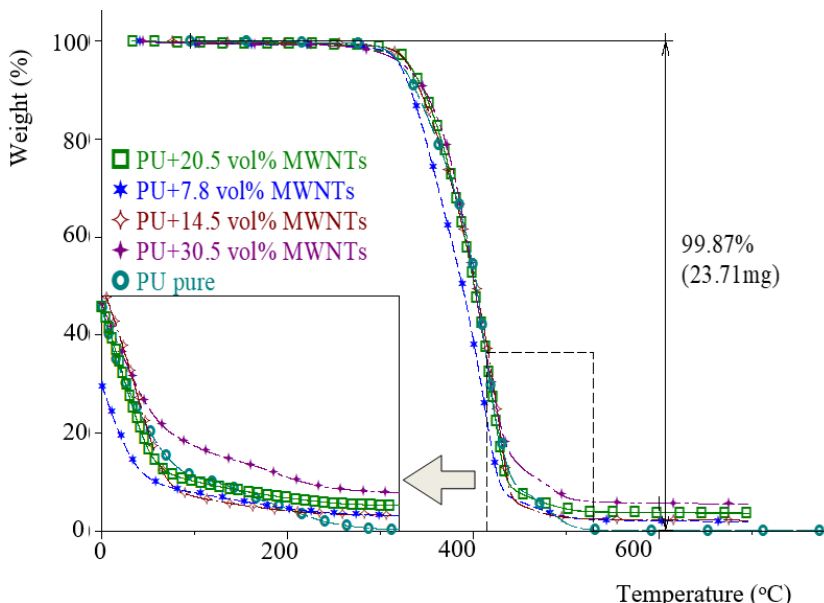


Figure 5: Thermogravimetry result of unfilled PU and PU/MWNTs nanocomposites

In Figure 6, SEM micrographs of injection molded nanocomposites indicate that the fillers are dispersed in the polymer matrix. A good filler dispersion as well as filler/matrix interface may also contributed to enhanced thermal conductivity through mitigating the scattering of phonons at the interface [30, 31].

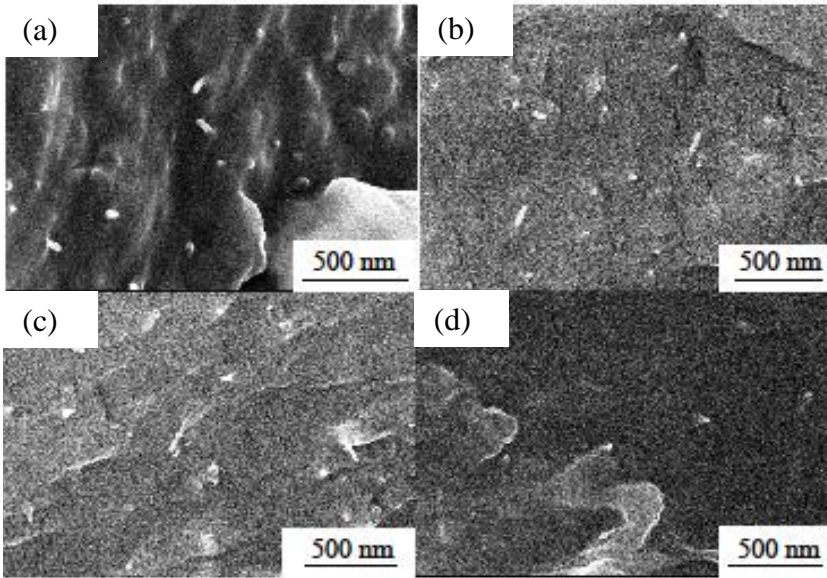


Figure 6: SEM micrograph of injection molded samples of PU/MWNTs nanocomposites. (a) 30.5 vol% MWNTs, (b) 20.5 vol% MWNTs, (c) 14.5 vol% MWNTs, and (d) 7.8 vol% MWNTs

## Conclusions

Mechanical behavior of polyurethanes filled with carbon nanotubes at different concentrations were analyzed to accommodate future requirements for advanced applications polymer composites. DMA analyses revealed that the storage modulus of nanocomposites improves with the fraction of MWNTs. Good fiber/matrix bonding can also be attributed to greater initial storage modulus in MWNTs reinforced PU nanocomposites. Furthermore, the improvement in the storage modulus with the incorporation of a of MWNTs indicates an efficient transfer of load and polymer reinforcement due to the smaller diameter and high aspect ratio of the filler particles. In addition, the analysis reveals that the peak temperatures are dependent on the test frequency. The peak height rises as the  $\tan \delta$  curves widen with increasing test frequency. In addition, with an expanded proportion of MWNTs in the polymer nanocomposites, a reduced peak height can be observed which suggests the restrain effect of the filler as well as increasing nanocomposites rigidity. Furthermore, Arrhenius law was used to calculate glass transition activation energy where the presence of MWNTs has improved the activation energy of

polymer. The value of activation energy increases due to improvement of effective viscosity of composites with the presence of MWNTs and hinders the rearrangement of macromolecule segments. Moreover, the TGA findings reveals that unfilled PU undergoes two stages of thermal decomposition. With the inclusion of MWNTs, the onset of degradation temperature and the total decomposition of the polymer shifted to a higher temperature. The increase in thermal degradation temperature of the nanocomposite can also be associated to the high thermal stability of MWNTs. It was shown that MWNTs as the reinforcing agent for the nanocomposites have a significant effect on the mechanical spectroscopy of the materials.

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