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Reinforced Thermoplastic Natural Rubber (TPNR) Composites with Different Types of Carbon Nanotubes (MWNTS)

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1. Introduction

The emergence of thermoplastic elastomers (TPEs) is one of the most important developments in the area of polymer science and technology. TPEs are a new class of material that combine the properties of vulcanized rubbers with the ease of processability of thermoplastics (Abdullah & Dahlan, 1998). Thermoplastic elastomers can be prepared by blending thermoplastic and elastomers at high shear rate. Thermoplastics, for example, polypropylene (PP), polyethylene (PE) and polystyrene (PS), and elastomers, such as ethylene propylene diene monomer (EPDM), natural rubber (NR) and butyl rubber (BR), are among the materials used in thermoplastic elastomer blends.

Blends of natural rubber (NR) and polypropylene (PP) have been reported widely by previous researchers (Abdullah & Dahlan, 1998; Ismail & Suryadiansyah, 2002). According to Abdullah and Dahlan (1998), polypropylene is the best choice for blending with natural rubber due to its high softening temperature (150°C) and low glass transition temperature (-60°C, is T_g for NR), which makes it versatile in a wide range of temperatures. Even though NR and PP are immiscible, their chemical structure is nearly the same. Thus, stable dispersion of NR and PP is possible. Incompatibility between NR and PP can be overcome by the introduction of a compatibilizer that can induce interactions during blending. Compatibility is important as it may affect the morphology, mechanical and thermal properties of the blends. Among the commonly used compatibilizers are dicumyl peroxide (DCP), m-phenylene bismaleimide (HVA-2) and liquid natural rubber (LNR). Apart from compatibility, mixing torque and curing are interrelated in determining the homogeneity of the TPNR blend (Abdullah & Dahlan, 1998).

A pioneer group of researchers in UKM has studied extensively the utilization of liquid natural rubber (LNR) as a compatibilizer on various natural rubber/polyolefin blends (Ibrahim Abdullah & Sahrim Ahmad, 1999). Liquid natural rubber was produced by photodegradation of natural rubber (NR) in toluene and exposure to ultraviolet for 6 hours (Dahlan, 1998). The LNR has the same microstructure with NR but with a short chain of polyisoprene (different in molecular weight, M_w) (Ibrahim, 2002). The M_w for LNR is around

50 000 whereas for NR it is 900 000, new functional new groups such as –OH, C-O and C=O have been formed via oxidation of photochemical sensitization of NR. The LNR with some active terminals like –OH is expected to react with the plastic particles and thereby bond the plastic particles to the NR matrix. There are also successful studies on the NR and various PE with LNR as a compatibilizer (Abdullah et al., 1995; Che Som et al., 1994).

One of the most important aspects to be considered in the thermoplastic elastomer blend is the components ratio. In addition, the processing parameters involving temperature, rotor speed of the mixer and mixing time, play a significant role in producing good blend properties (Abdullah &Dahlan, 1998; Yang et al., 1995). The processing is normally done at a temperature above the melting point of the thermoplastic. The quality of blend reflects its miscibility, where it exhibits better mechanical and thermal properties, as well as homogeneity. The properties obtained can be further enhanced by introducing a variety of additives, such as compatibilizer agents, interfacial agents, cross-linking agentsor fillers to promote miscibility by reducing interfacial tension.

Mechanical blending of PP and NR with the addition of LNR as a compatibilizer was reported to be optimal at a temperature of 175-185oC and a rotor speed of 30-60rpm (Abdullah &Dahlan, 1998). The percentage of LNR used depends on the ratio of NR to PP. For a NR:PP ratio of 30:70 the best physical properties are obtained at 10% LNR (Abdullah & Ahmad, 1992). The compatibilizer helps to induce the interaction between the rubber and plastic interphase and thereby increases the homogeneity of the blend.

Nanometer scale reinforcing particles have attracted considerable attention from polymer scientists. Due to their high aspect ratio (surface/area ratio) and low density, they may be used as substitutes for traditional fibers as fillers in polymer matrices. The excitement that followed the discovery of the possibility of preparing multiwall carbon nanotubes (CNTs) and other carbon nano-structured materials via a catalyst-free process (Ijima S, 1991) inspired scientists regarding a range of potential applications. Depending on the synthesis conditions, nanotubes can be single-walled (a single tubule of 1 nm) or multi-walled (2–50 tubules of 2–50 nm positioned concentrically). The measurements have determined that carbon nanotubes possess excellent mechanical properties (tensile modulus ≈1 TPa (Yu F et al, 2002), tensile strength ≈11–63 MPa (Wagner D et al., 1998)and compressive strength ≈150 GPa (Lourie O et al., 1998)in the direction of the tubule axis. This compressive strength is one order of magnitude higher than that of any other known material. This makes them ideal reinforcing fibers for the manufacture of the next generation of fiber-matrix composite materials (Sinnott B et al., 1998). Conventional microfillers including mica, talc, glass fiber, carbon black, etc. are incorporated in polymer to further improve its mechanical performances. However, additions of a large volume content of microfillers (20–30 wt %) are needed to achieve the desired mechanical properties. The thermal properties of CNT/polymer composites are of particular interest in many applications such as the development of conductive polymer films and electronic components. Because of the high thermal conductivity of CNTs (for SWNTs and MWNTs are 6000 W/m K and 3000 W/m K, respectively) and their extremely high aspect ratio (>1000), the thermal conductivity of CNT-related composites is expected to be very high. This also implies that using only a small amount of CNTs should be able to significantly improve the thermal conductivity properties of polymer-based materials. Compared with SWNTs, MWNTs are more predominantly used as conductive fillers due to their lower cost, better availability and easier dispersability. The addition of a large volume content of microfillers is detrimental to

the processability of the composites. However, only very small amounts of CNTs are required to improve the properties of the polymer. Nanophased matrices based on polymers and carbon nanotubes have attracted great interest because they frequently include superior mechanical, electronic, and flameretardant properties. Different polymer/CNT nanocomposites have been synthesized by incorporating carbon nanotubes (CNTs) into various polymer matrices, such as polyurethane (H.C.Kuan et al., 2005), epoxy (Liao et al., 2004), polypropylene (Li et al., 2004), polyimides (Cai et al., 2004), and polyurethane (Koerner et al., 2005; Kuan et al., 2005).

Currently, the use of composites has primarily been limited to high performance applications like the automotive, aerospace and sporting goods because of low properties. There has been much debate in the literature as to whether this interface region is important in composites and what effect it has on the properties of composites. As far as mechanical and thermal properties are concerned, the main target is to strike a balance of stiffness, strength, toughness, thermal conductivity, specific heat, melting temperature and glass transition temperature. However, with the explosion of the information age and higher demand for materials with superior properties, composites such as TPNR are now making their way into more common applications. Therefore, the most important aspect in the development of reinforced TPNR by carbon nanotubes isto achieve a good combination by incorporating carbon nanotubes into TPNR based composites.Synergistic effects may be achieved in the form of higher mechanical and thermal properties, therefore, making use of this potential will lead to new high performance products and technology that was hitherto not possible.

Despite the considerable number of studies concerning the preparation, characterization and properties of polymer/CNT nanocomposites, no adequate information has been reported on the phenomena behind the property changes resulting from the addition of MWNTsto thermoplastic natural rubber.

In this chapter, thermoplastic natural rubber TPNR reinforced with two types of multi-walled carbon nanotube (MWNTs) nanocomposites were prepared by the melt blending method. Using this method, MWNTs will be dispersed homogeneously in the TPNR matrix in an attempt to increase the mechanical properties of these nanocomposites. The effect of MWNTs on the mechanical properties of TPNR nanocomposites is reported in this chapter.

2. Experiment details

Polypropylene, with a density of 0.905 g cm-3, was supplied by Propilinas (M) Sdn. Bhd, natural rubber was supplied by Guthrie (M) Sdn. Bhd, and polypropylene (PP) with a density of 0.905 g/cm3 was supplied by Polipropilinas (M) Sdn. Bhd were used in this research. Maleic anhydride–grafted–polypropylene (MAPP) with a density of 0.95 g/cm3 was supplied from Aldrich Chemical Co., USA. The maleic anhydride content in MAPP was about 0.57%. The chemicals used were sodium hydroxide and sulfuric acid (95-97) % supplied by MERCK, Germany. Liquid natural rubber (LNR) was prepared by the photochemical degradation technique.

In this study two types of MWNTs were used. The first one, MWNTs 1, was supplied by the Chinese academy of science. The second one, MWNTs 2, and was provided by Arkema (GraphistrengthTM C100). Table 1 shows the properties of the two types of multi-walled carbon nanotubes (MWNTs).

Mixing was performed by an internal mixer (Haake Rheomix 600P). The mixing temperature was 180° C, with a rotor speed of 100 rpm and 13 min mixing time. The indirect technique (IDT) was used to prepare nanocomposites, this involved mixing the MWNTs with LNR separately, before it was melt blended with PP and NR in the internal mixer. TPNR nanocomposits were prepared by melt blending of PP, NR and LNR with MWNTs in a ratio of 70 wt% PP, 20 wt% NR and 10wt% LNR as a compatibilizer and 1,3,5 and 7% MWNTs.

MWNTs	Purity	Length	Diameter	Manufactured
MWNTs 1	>% 95	10-30 μm	8< nm	Catalytic Chemical Vapor Deposition (CVD)
MWNTs2	>90%	0.1-10 μm	10-15 nm.	Catalytic Chemical Vapor Deposition (CVD)

MWNTs 1: Fist type of multi-walled carbon nanotubes.

MWNTs 2: Second type of multi-walled carbon nanotubes.

Table. 1 Properties of the two types of multi-walled carbon nanotubes (MWNTs)

The tensile properties were tested using a Testometric universal testing machine model M350-10CT with 5 kN load cell according to ASTM 412 standard procedure using test specimens of 1 mm thickness and a crosshead speed 50 mm min^{-1}. At least five samples were tested for each composition, and the average value was reported. The impact test was carried out using a Ray Ran Pendulum Impact System according to ASTM D 256-90b. The velocity and weight of the hammer were 3.5m/s and 0.898kg, respectively. Dynamic mechanical analysis for determining the glass transition temperature, storage and loss modulus was carried out using DMA 8000 (PerkinElmer Instrument), operating in single cantilever mode from -100 to 150 oC at a constant frequency of 1 Hz, with a heating rate of 5 oC/min. The dimensions of the samples were 30 x 12.5 x 3 mm.

The thermal conductivity was measured by a laser flash method. Disk-type samples (12.7 mm in diameter and 1mm in thickness) were set in an electric furnace. Specific heat capacities were measured with a differential scanning calorimeter DSC. Thermal diffusivity (λ, Wm$_{-1}$ K$_{-1}$) was calculated from thermal diffusivity (α, m^2 s$_{-1}$), density (ρ, g cm$_{-3}$) and specific heat capacity (C_p, J g$_{-1}$ K$_{-1}$) at each temperature using the following:

$$\lambda = \alpha. \rho. C \qquad\qquad (1)$$

The reference used for the heat capacity calculation was a 12.7mm thick specimen of pyroceram. The reference sample was coated with a thin layer of graphite before the measurement was performed. The thermal conductivity of MWNTs reinforced TPNR matrix composites of all volume fractions was studied from 30°C to 150°C. The morphology of the MWNTs and the composite were examined using a scanning electron microscope (Philips XL 30). The samples were coated with a thin layer of gold to avoid electrostatic charging during examination.

3. Results and discussion

3.1 Tensile properties
3.1.1 Tensile strength
The tensile strength of TPNR reinforced with two types of MWNTs of different percentages (1%, 3%, 5% and 7%) is shown in Figure 1. Generally, both MWNTs exhibited an increasing trend up to 3wt% content. Further increments in MWNTs content decreased the tensile strength compared to the optimum filler loading.
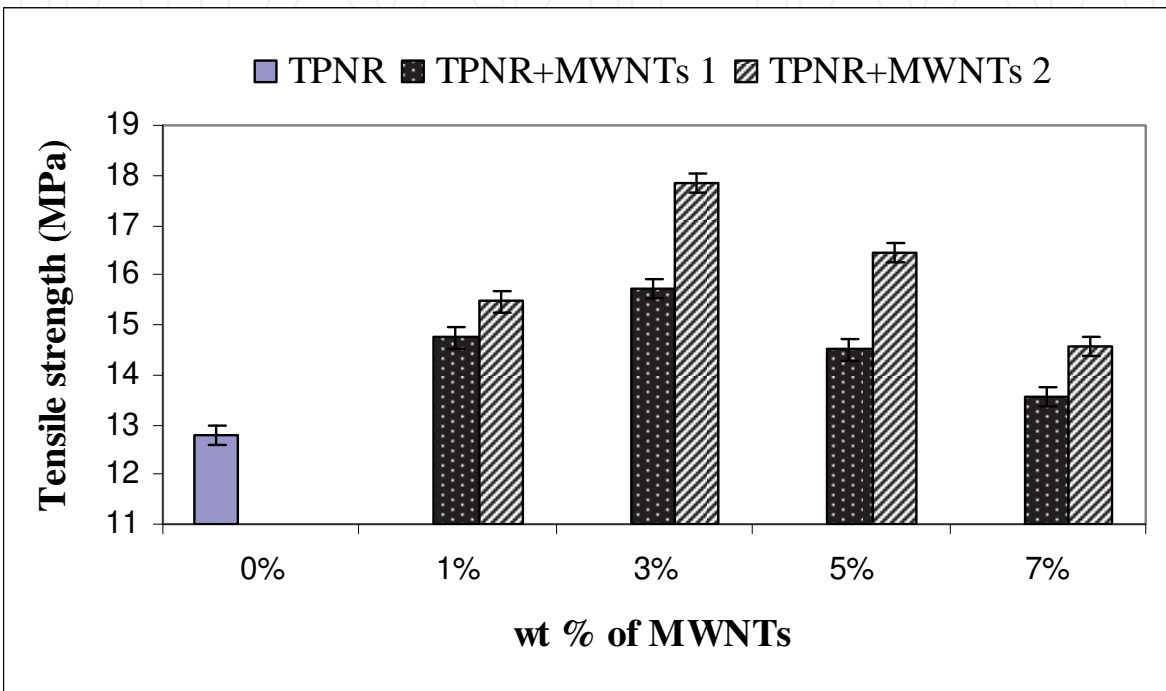

Fig. 1. Tensile strength of TPNR reinforced with two types of MWNTs

From Figure 1,TPNR with MWNTs 1 and MWNTs 2 have optimum results at 3 % wt, which, compared with TPNR, increased by 23% and 39%, respectively. The tensile strength increased radically as the amount of MWNTs concentration increased. The mechanical performance, such as tensile properties, strongly depends on several factors such as the properties of the filler reinforcement and matrix, filler content, filler length, filler orientation, and processing method and condition. The improvement in the tensile strength may be caused by the good dispersion of MWNTs in the TPNR matrix, which leads to a strong interaction between the TPNR matrix and MWNTs. These well-dispersed MWNTs may have the effect of physically crosslinking points, thus, increasing the tensile strength (Bin et al., 2006).

A good interface between the CNTs and the TPNR is very important for a material to stand the stress. Under load, the matrix distributes the force to the CNTs, which carry most of the applied load. When the content of MWNTs is higher, the MWNTs cannot disperse adequately in the TPNR matrix and agglomerate to form a big cluster. This is because of the huge surface energy of MWNTs as well as the weak interfacial interaction between MWNTs and TPNR, which leads to inhomogeneous dispersion in the polymer matrix and negative effects on the properties of the resulting composites that causes a decrease in the tensile strength (Sang et al., 2007).

3.1.2 Young's modulus

Figure 5.2 shows the effect of filler content on the tensile modulus of TPNR reinforced by two types of MWNTs. The same trend as for the tensile strength in Figure .1 was observed for the tensile modulus of MWNTs 2, however, for MWNTs 1 it was different. Figure 2 clearly shows that the presence of MWNTs has significantly improved the tensile modulus of the TPNR.
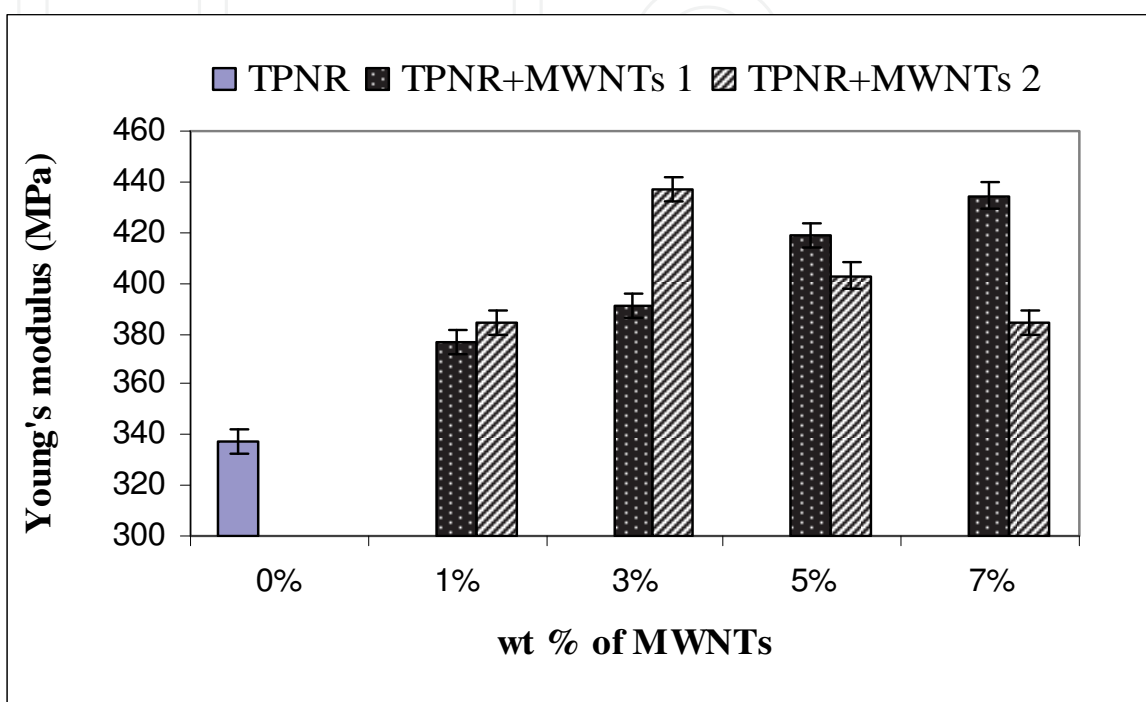

Fig. 2. Young's modulus of TPNR reinforced with two types of MWNTs.

The remarkable increase of Young's modulus with MWNTs 1 content shows a greater improvement than that seen in the tensile strength at high content, which indicates that the Young's modulus increases with an increase in the amount of the MWNTs 1. At 1 wt% of MWNTs the Young's modulus is increased by 11% compared to TPNR. At 3 wt% of MWNTs the increase in the Young's Modulus is about 16%. Further addition of MWNTs from 5 to 7 wt% increased the Young modulus by about 24% and 29%, respectively. The improvement of modulus is due to the high modulus of MWNTs (Treacy et al., 1996).

As depicted in Figure 2 the Young's modulus of MWNTs 2 increased with the increase in the amount of MWNTs. The maximum result was achieved at 3% wt, with an increase of about 30%, which was due to the good dispersion of nanotubes displaying perfect stress transfer (Potschke et al., 2002). As explained before, a reduction in performance occurred at higher filler contents. Initially it increases with filler content and then decreases when exceeding the filler loading limit due to the diminishing interfacial filler-polymer adhesion. It is assumed that aggregates of nanotube ropes effectively reduce the aspect/ratio (length/diameter) of the reinforcement (Lopez Manchado et al., 2005).

3.1.3 Elongation at break

The elongation at the break of TPNR with two types of MWNTs is shown in Figure 3. For MWNTs 1, the elongation at break increased with the increase in the amount of MWNTs, at

3% wt the result is the optimum, which increased 29% compared with TPNR. However, the elongation at break of MWNTs 2 decreased with the increase in the amount of MWNTs.

It can be deduced that the reinforcing effect of MWNTs is very marked. As the MWNTs content in the TPNR increases, the stress level gradually increases but at the same time the strain of the nanocomposites decreased. This is because the MWNTs included in the TPNR matrix behave like physical crosslinking points and restrict the movement of polymer chains (Sang et al., 2007). This shows that the inclusion of MWNTs makes the TPNR stronger but more brittle.
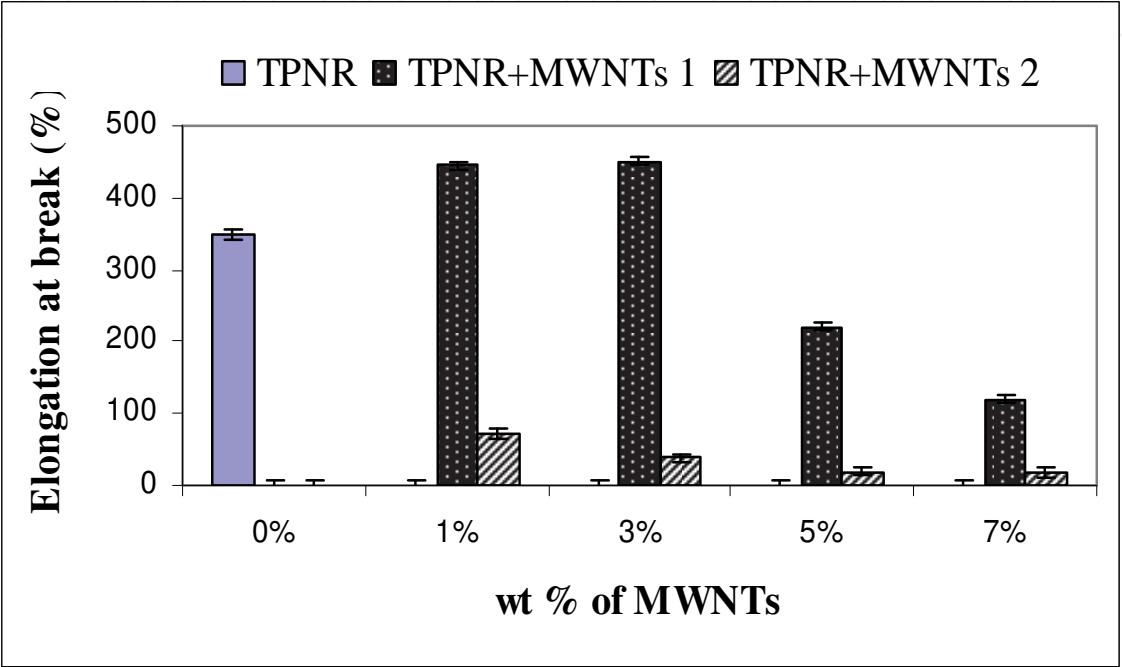
Fig. 3. Elongations at break of TPNR reinforced with two types of MWNTs.

3.2 Impact strength

The effect of filler loading on the impact strength of TPNR/MWNTs nanocomposites (MWNTs 1 and 2) is given in Figure 4. It shows that incorporation of MWNTs into TPNR considerably affects the impact strength of TPNR nanocomposites.

The results exhibited better impact strength for MWNT 1 and MWNT 2 at 5 wt% with an increase of almost 70 % and 74%, respectively. This is due to the better dispersion of carbon nanotubes in the matrix, which generated a significant toughening effect on the TPNR/MWNTs nanocomposite. However, when the load is transferred to the physical network between the matrix and the filler, the debonding of the chain segments from the filler surface facilitates the relaxation of the matrix entanglement structure, leading to higher impact toughness.

The low impact energy was attributed to the filler content. This will reduce the ability of reinforced composites to absorb energy during fracture propagation. However, in the case of elastomer-toughened polymer, the presence of the elastomer basically produces stress redistribution in the composite, which causes micro cracking or crazing at many sites, thereby resulting in a more efficient energy dissipation mechanism (Canche-Escamilla et al., 2002).
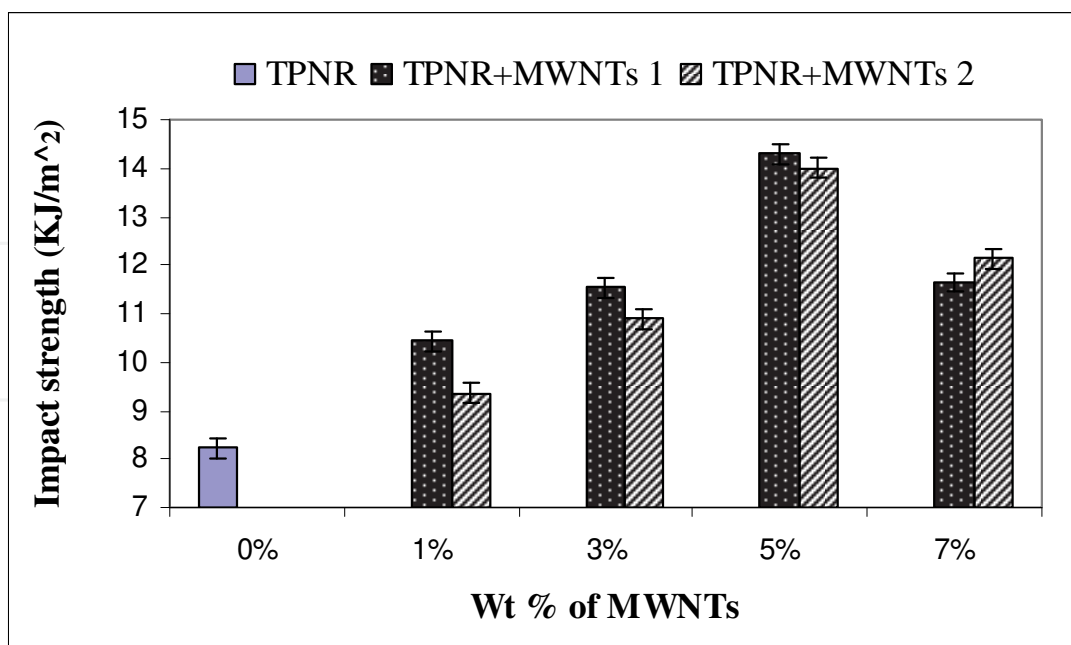
Fig. 4. Impact strength of TPNR reinforced with two types of MWNTs.

Consequently, because of their higher surface energy and large aspect ratio, it will be difficult for the nantubes to disperse in the TPNR when the MWNTs content is higher. This will lead to less energy dissipating in the system due to the poor interfacial bonding and induces micro spaces between the filler and polymer matrix. This causes micro-cracks when impact occurs, which induces easy crack propagation. Therefore, the higher agglomeration of MWNTs can cause the mechanical properties of the composites to deteriorate (Jianfeng Shen et al., 2007).

3.3 Dynamic mechanical analysis
3.3.1 Storage modulus
Figure 5 and Figure 6 illustrate the storage modulus of TPNR reinforced with MWNTs 1 and MWNTs 2. As illustrated in these Figures, the storage modulus of the nanocomposites mainly depends on the filler content in the composite. Two consistent variations of the E' with temperature are observed for all systems, which are a sharp drop around -50°C (±10°C) and a reduction in the E' drop rate with temperatures above 80°C. The first drop is related to the glass transition region of compatibilised TPNR blends. The reduction in E' is less severe until the softening point or when the melt region is reached.
The storage modulus of neat TPNR and its nanocomposites decreased with the increasing temperature, as expected. However the most characteristic difference is that the storage modulus E' of TPNR/MWNTs 1 nanocomposites tends to increase with the increase in the amount of MWNTs. This indicates the effectiveness of the MWNTs' reinforcing effect. The maximum values of storage modulus for the first type (MWNTs 1) were obtained at 1wt% and 3wt%, however, for the second type (MWNT 2) it was obtained at 3wt% and 5wt%.
At the same time the storage modulus of two types of MWNTs, below T_g, of TPNR/MWNTs is higher compared with composites above T_g. The stiffening effect is maximized at temperatures below T_g and becomes greatly reduced at temperatures above T_g. Such a phenomenon has also been observed in other well dispersed polymer composite systems
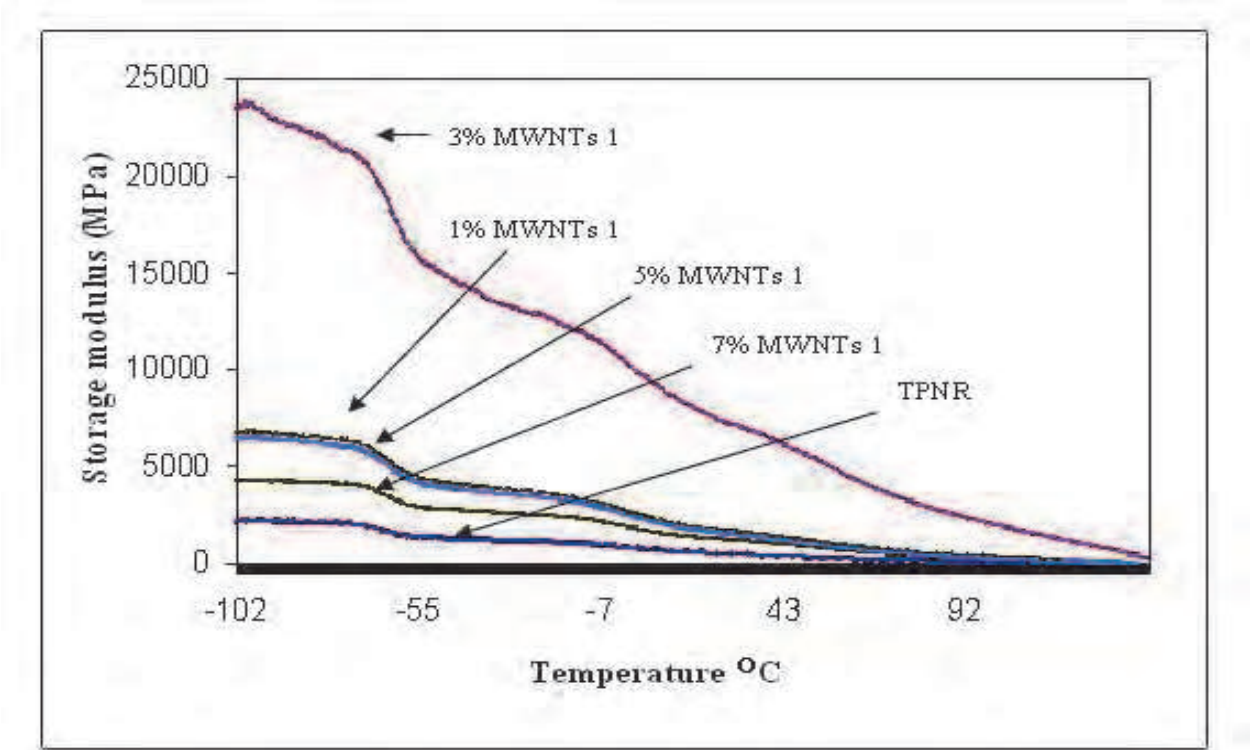
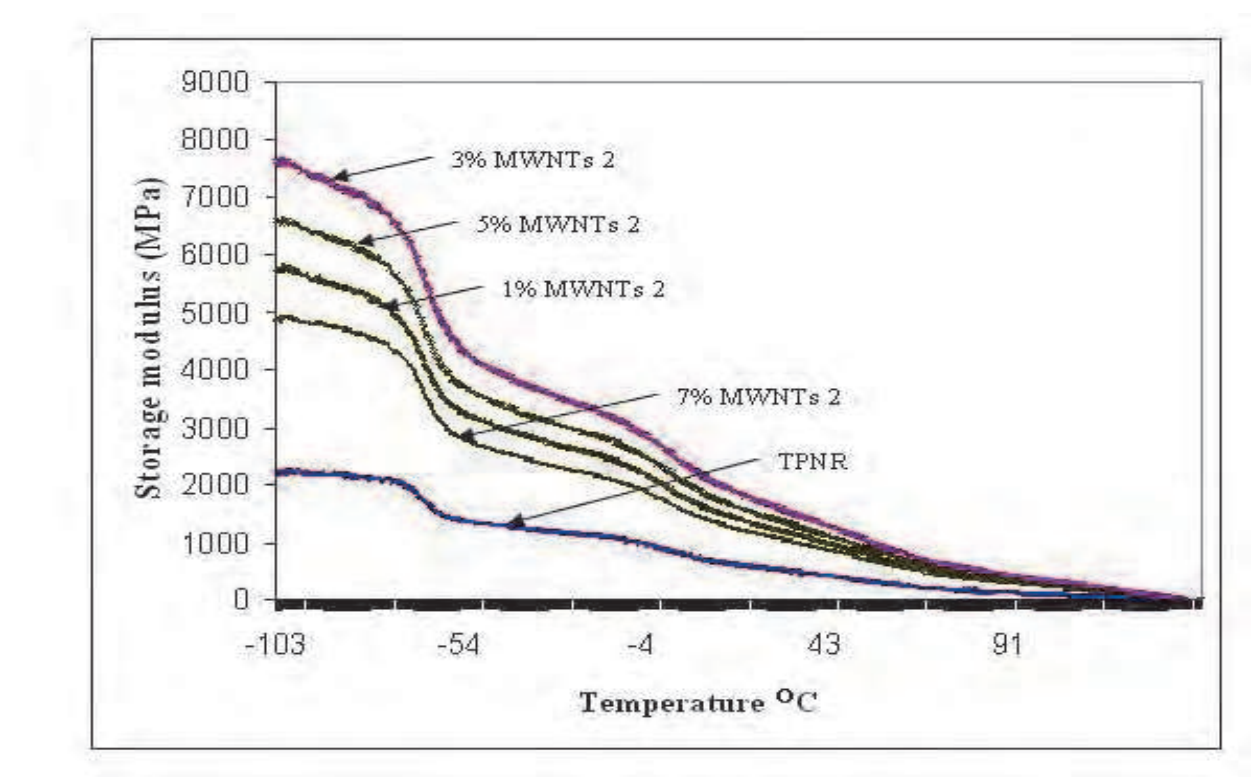Fig. 5. Storage modulus of TPNR and TPNR/MWNTs 1 nanocomposites.

Fig. 6. Storage modulus of TPNR and TPNR/MWNTs 2 nanocomposites.

(Sue et al., 2004). The carbon nanofibers are effective at increasing the stiffness of the prepared nanocomposites, even at relatively small nanofiber loadings. For 1% and 3% of MWNTs this increase should be attributed to the finer dispersion of these nanotubes in the TPNR matrix and the decreased size of the formed aggregates. After 3% of MWNTs 1 and after 5% of MWNTs 2 the storage modulus decreased due to the agglomeration of nanotubes inside the matrix.

3.3.2 Loss modulus
In addition, from Figure 7 and Figure 8, the loss modulus E'' of the composites is higher than TPNR at 1% and 3% of MWNTs 1, and 3% and 5% of MWNTs 2, which is because the nanotubes can be more uniformly dispersed in the matrix at this percentage of MWNTs. Therefore, the interfacial area is larger and the interaction between the matrix and nanotubes is stronger.
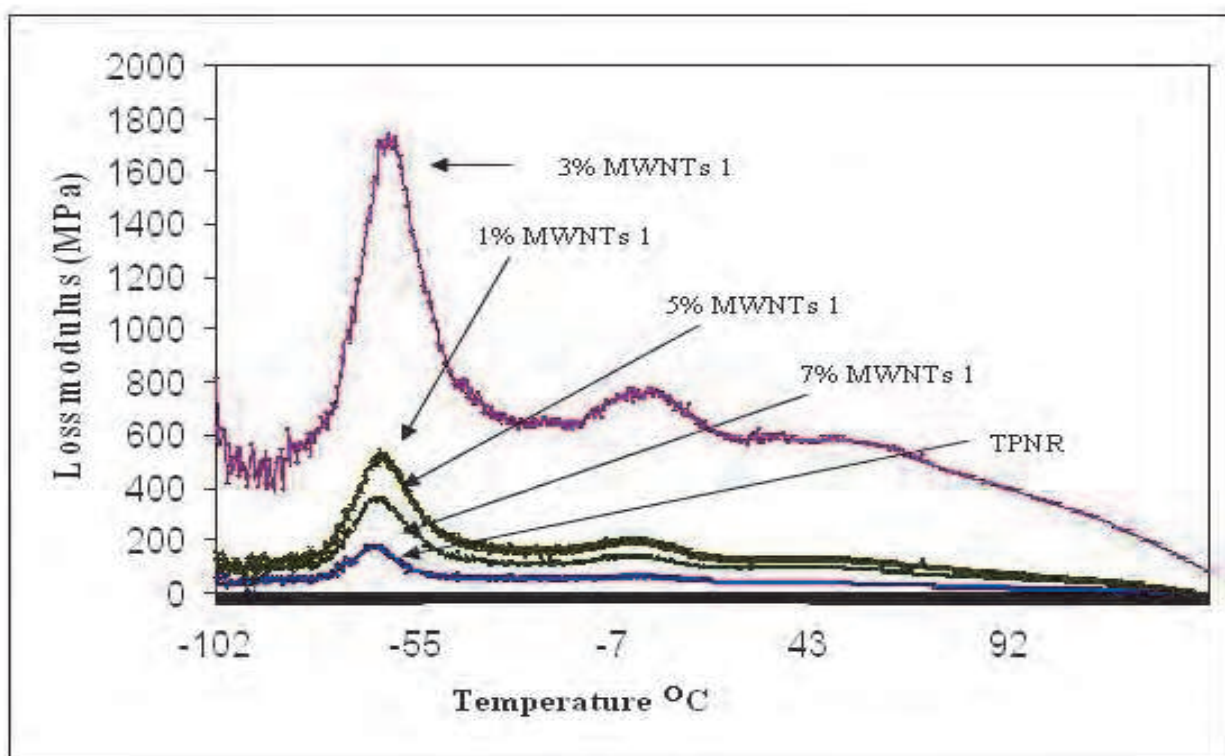
Fig. 7. Loss modulus of TPNR and TPNR/MWNTs 1 nanocomposites.

Since the value of E'' at lower temperatures has a great influence on the toughness of the matrix, it is obvious that MWNTs contribute to the improvement of the toughness of the composites. A mesophase is formed between the matrix and MWNTs. Therefore, when the composites were subjected to external stress, the external energy was dissipated by the friction between MWNTs-MWNTs and MWNTs-TPNR interaction through the mesophase. However, after 3% of MWNTs 1 and 5% of MWNTs 2 the loss modulus E'' had decreased due to agglomeration of MWNTs inside the matrix as mentioned before. Due to the polymer-filler interaction, the adsorption of the polymer chains on the filler's surface reduces the mobility of the macromolecular segments. This transition zone surrounding the nanoparticles exhibits a higher modulus, which gradually reduces with the increasing distance from the filler surface (Wang, 1998).
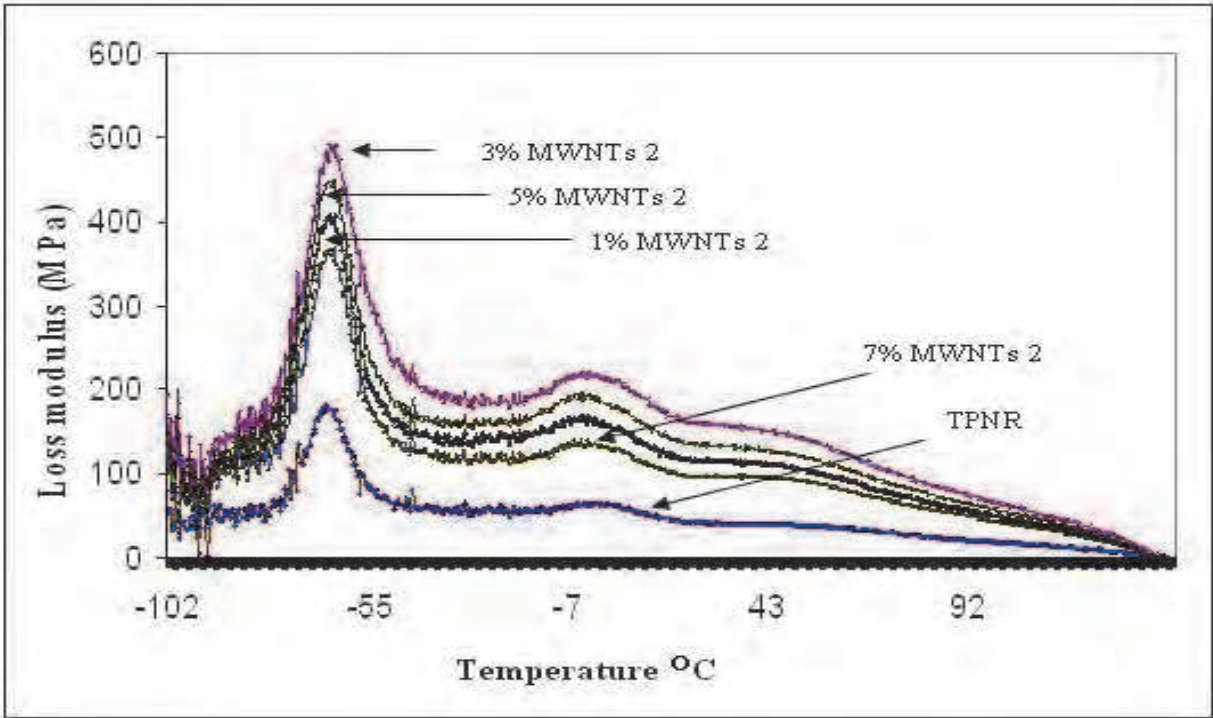
Fig. 8. Loss modulus of TPNR and TPNR/MWNTs 2 nanocomposites.

3.3.3 Tan delta

The dynamic mechanical data shows that the glass transition temperature of the TPNR/MWCNTs is affected by the addition of the different amounts of two types of MWNTs, as depicted in Figure 9 and Figure 10.
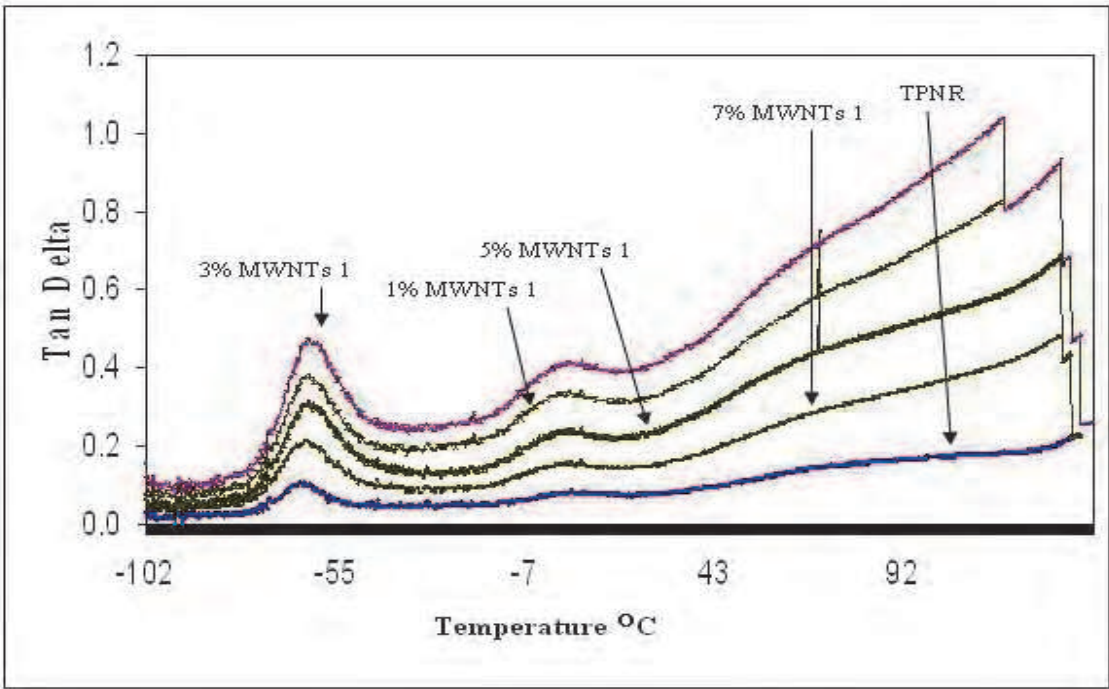

Fig. 9. Tan delta of TPNR and TPNR/MWNTs 1 nanocomposites.

From the figures, the tan δ peak of the nanocomposites is higher than the corresponding temperature of TPNR. As mentioned earlier, usually the T_g of a polymeric matrix tends to increase with the addition of carbon nanotubes. The rise in T_g in any polymeric system is associated with a restriction in molecular motion, reduction in free volume and/or a higher degree of crosslinking due to the interactions between the polymer chains and the nanoparticles, and the reduction of macromolecular chain mobility (Potschke et al., 2002). With the high amount of MWNTs (after 3% of MWNTs 1 and 5% of MWNTs 2) the T_g drops. This maybe due to the phase separation/agglomeration of MWNTs, which allows the macromolecules to move easily. When the content of MWNTs is higher, the MWNTs congregate, possibly because the intrinsic van der Waals forces occurs, which leads to bubbles and small aggregates. The conglomerations and matrix holes existing in the network of MWNTs may perform as defects, which make the macromolecules move easily, and the T_g of the matrix is decreased.
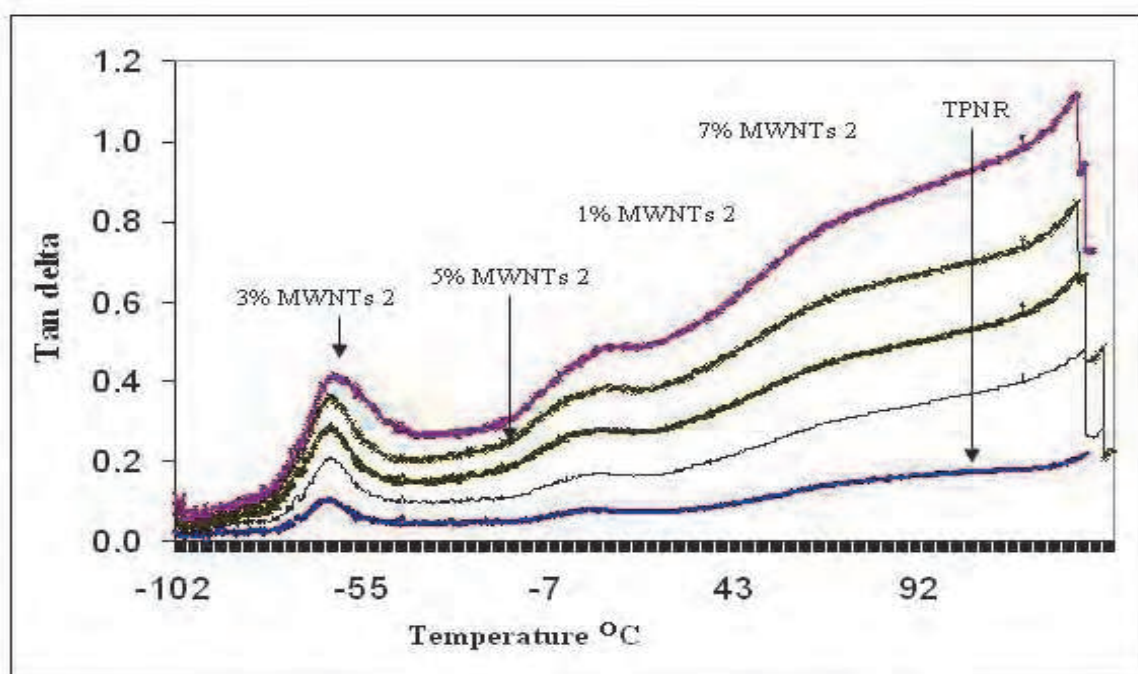
Fig. 10. Tan delta of TPNR and TPNR/MWNTs 2 nanocomposites.

3.4 Thermal behavior of TPNR/MWNTS (Two Types OF MWNTS)
3.4.1 Thermal conductivity
To study the effect of MWNTs filler on thermal conductivity, the temperature was varied from (30 – 150) □C. The temperature range was selected based on the melting point of polypropylene (PP), since PP melts above 178 °C (Mustaffa, 1991). The carbon filler loading was from 1%wt to 7%wt for two types of carbon nanotubes. Introducing MWNTs to TPNR can significantly enhance the thermal conductivity of the TPNR matrix, as shown in Figure 11 and Figure 12.
As shown from the figures at 30°C the thermal conductivity of TPNR/MWNTs 1 composites, Thermal conductivity increased 232%, 222%, 17.69% and 18.6% of 1%, 3%, 5% and 7%, respectively, and for TPNR/MWNTs 2, the thermal conductivity increased 80%, 94%, 125% and 108% of 1%, 3%, 5% and 7% respectively, as compared with TPNR at the

same temperature. Thermal transport in the CNT composites includes phonon diffusion in the matrix and ballistic transportation in the filler.
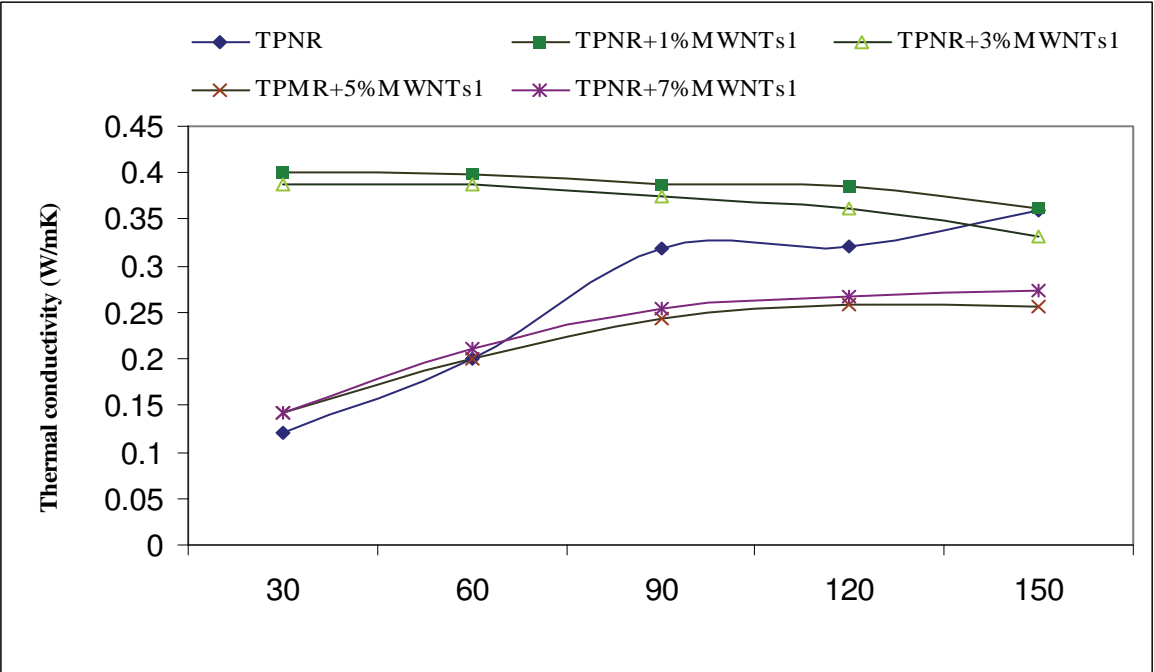

Fig. 11. Thermal conductivity of the composites with different volume fractions of MWNTs 1 (first type) at different temperatures
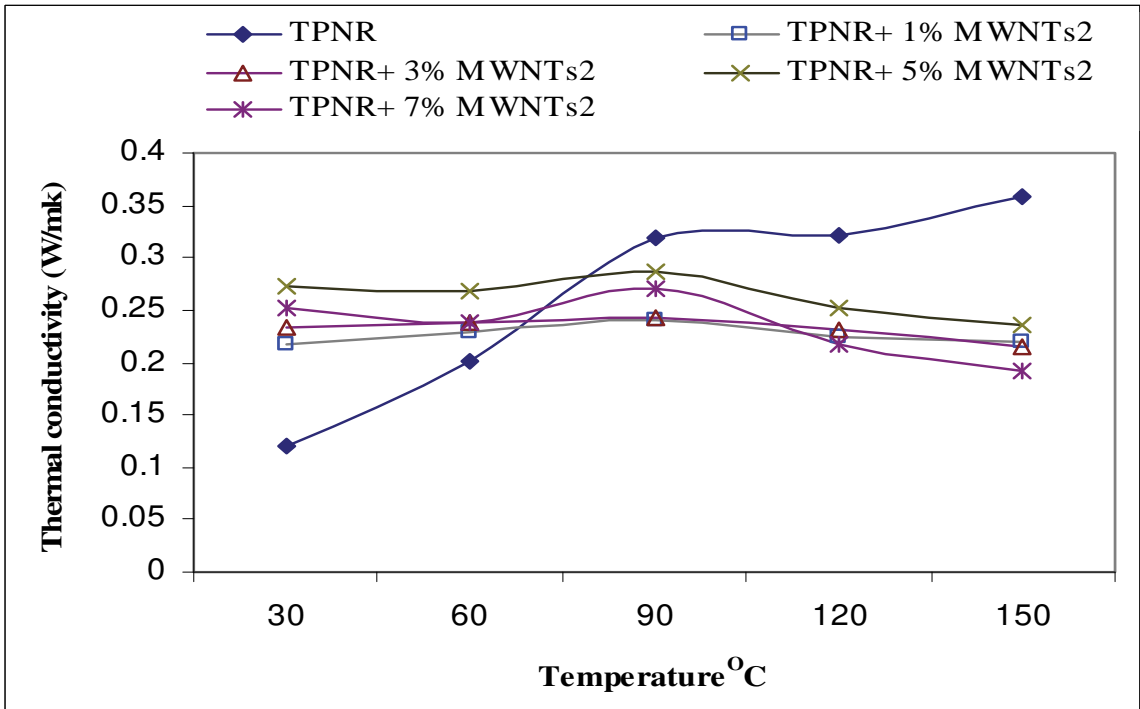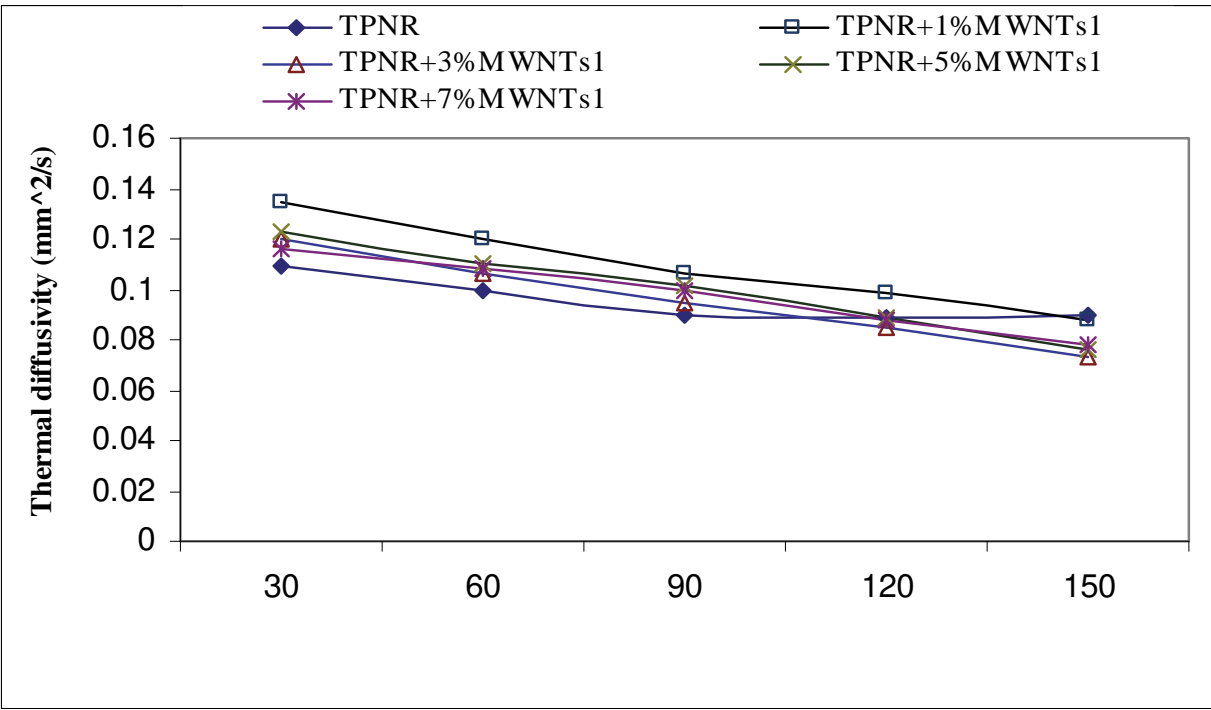

Fig. 12. Thermal conductivity of the composites with different volume fractions of MWNTs 2 (second type) at different temperatures

The improvement in thermal conductivity in MWNTs/TPNR may stem from the improved percolation because of the better dispersion and formation of a network (Kumar et al., 2007). The dispersion of 1wt% and 3wt% MWNTs is better than 5wt% and 7wt% in TPNR for the first type (MWNTs 1), at 5% and 7% the MWNTs 1 agglomerated inside TPNR. Therefore, the large amounts of junctions among the carbon nanotubes form a single conducting path, which is believed to be the reason why the measured thermal conductivity is low. For the second type (MWNT 2) the conductivity at 5wt% and 7wt% is better than 1% and 3%, respectively.

The significant enhancement in the thermal conductivity of CNT nanocomposites is possibly attributed to the kinks or twists of MWNTs. When the phonon travels along the nanotubes, if it meets the kinks or twists it would be blocked at those sites. The existence of such kinks or twists in CNTs would lead to a decrease in the effective aspect ratio of the nanotubes (Nan et al., 2003) when the amount of MWNTs increases, and, thus, the thermal conductivity of MWNTs-TPNR nanocomposites would be reduced. Therefore, the low amount of MWNTs in TPNR could reduce these kinks or twists of MWNTs due to the good dispersion of MWNTs in TPNR, causing the thermal conductivity of the nanocomposites to increase.

As shown in Figure 11 and Figure 12, the thermal conductivity of MWNTs 1 reinforced TPNR matrix composites for all volume fractions studied from 30°C to 150°C is better than MWNTs 2. The effect of temperature on the thermal conductivity is clear from 30°C to 90°C, as shown in the Figures. This is because of the opposing effect of temperature on the specific heat and thermal diffusivity. Eventually, at high temperatures, as the phonon mean free path is lowered, the thermal conductivity of the matrix approaches the lowest limit and the corresponding thermal resistivity approaches the highest limit.

The resistance to phonon movement from one nanotube to another through the junction will hinder phonon movement and, hence, limit the thermal conductivity. The low thermal conductivity could be partly due to the non-uniform diameter and size, the defects in and the nano-scale dimension of MWNTs. However, the numerous junctions between carbon nanotubes involved in forming a conductive path and the exceptionally low thermal conductance at the interface (Yunsheng et al., 2006) are believed to be the main reason for the low thermal conductivity.

The effect of reducing the thermal conductivity is the transfer of phonons from nanotube to nanotube. This transition occurs by direct coupling between CNTs, in the case of the improper impregnated ropes, CNT-junctions and agglomerates, or via the matrix. In all these cases, the transition occurs via an interface and, thus, the coupling losses can be attributed to an intense phonon boundary scattering. At the same time the thermal conductivity decreases with the increase in temperature (if the temperature is near the melting point of the matrix). This indicates that the thermal conductivity of the composites is dominated by the interface thermal transport between the nanotube/matrix or nanotube/nanotube interface. Thus, it is believed that the decreased effective thermal conductivity of the studied composites could be due to the high interface thermal resistance across the nanotube/matrix or nanotube/nanotube interfaces (Ramasamy et al., 2007).

3.4.2 Thermal diffusivity

The thermal diffusivity of the TPNR/MWNTs were measured at various temperature points in the range of 30°C-150°C, it decreased with increasing temperature. In addition, the results

obtained indicate that the MWNTs content influences the thermal diffusivity values of two types of multi-walled carbon nanotubes, as shown in Figure 13 and Figure 14.

As shown in Figure 13 and Figure 14, as the temperature increased from 30 °C to 150 °C, there is a decrease in the thermal diffusivity. The maximum thermal diffusivity was obtained at 30 °C. However, after 30 °C, there is a sudden drop in diffusivity. The thermal diffusivity of MWNTs 1 dropped as did MWNTs 2 by increasing the test temperature.

The thermal diffusivity of the TPNR/MWNTs decreases with fiber content due to the density of the nanocomposites, which decrease with the increase in the amount of MWNTs (the density of MWNTs less the TPNR density), hence, the density of the samples affects the thermal diffusivity (Kumari et al., 2008). This means that the TPNR containing MWNTs fiber will require a shorter time to be heated or cooled than the TPNR. Above 150 °C, the temperature at which the TPNR starts to melt, a slight variation of the thermal diffusivity with temperature is observed. The thermal diffusivity depends mainly on the mean free path length of the phonons as mentioned before.

As the test temperature goes up, the phonon vibration frequency will be quickened raising the possibility of an increase in collisions. Therefore, the mean free path decreases rapidly, which leads to the rapid decrease of the thermal diffusivity (Ruiying et al., 2004). The decrease in the thermal diffusivity is attributed to the different thermal properties of the individual nanotubes and CNT ropes in the matrix. Therefore, its thermal diffusivity and thermal conductivity are very high under the same temperature.

Fig. 13. Thermal diffusivity of the composites with different volume fractions of MWNTs 1 (first type) at different temperatures
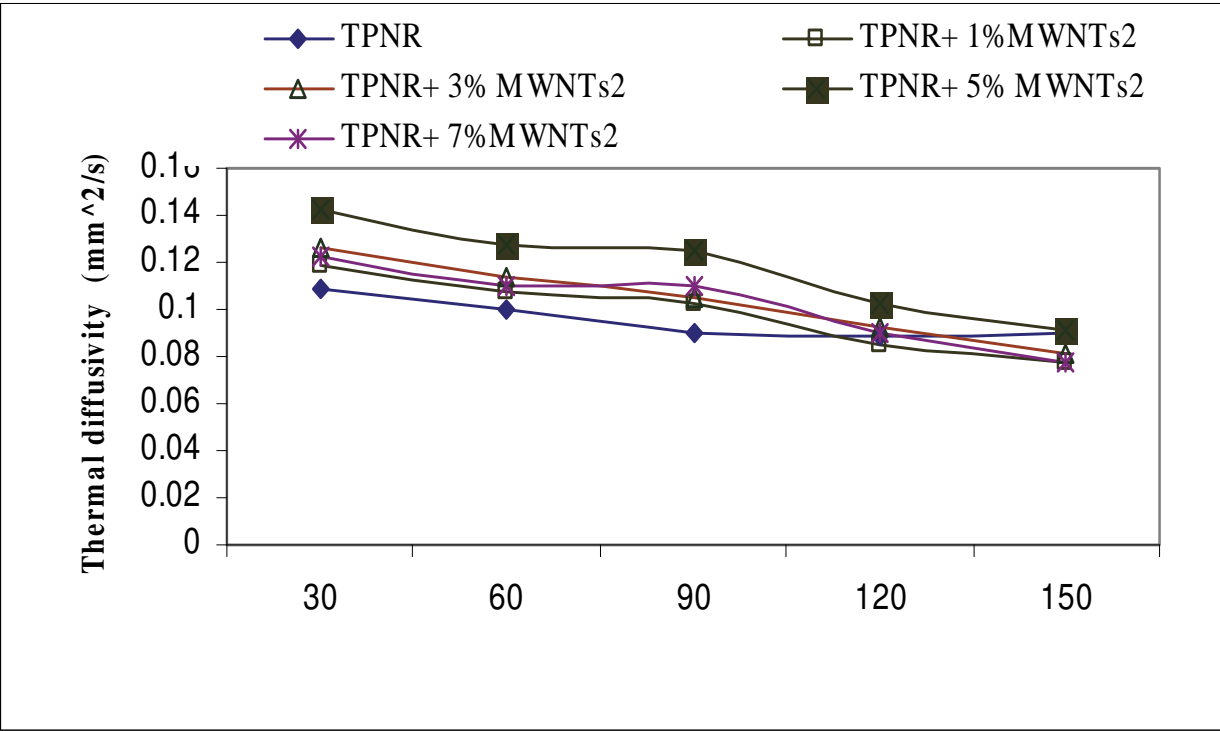
Fig. 14. Thermal diffusivity of the composites with different volume fractions of MWNTs 2 (second type) at different temperature

3.4.3 Specific heat

The temperature dependence behavior of the specific heat of the composites is different from that of their thermal diffusivity, which decreased with the temperature. The specific heat of all the measured samples increases linearly with the measured temperature from 30 °C to 150 °C. The addition of MWNTs 1 decreased the specific heat, as expected, from the relatively high specific heat of the matrix, as shown in Figure 15. The specific heat capacity of the composites was influenced by the filler content. It decreased with the increasing filler content, 1% and 3 % have shown high specific heat capacity compared with 5% and 7%. The phonon mean free path is determined by both the phonon-phonon and the phonon-defect interactions. However, its specific heat increases a little with an increase in temperature, while the phonon mean free path decreases, which makes its thermal conductivity first increase and then decrease with temperature.

From Figure 16, the specific heat increased by increasing the MWNTs 2, with a sharp peak at 90°C. This means that the maximum energy is required to change the temperature of material one degree at this temperature. This is clear from the figure of thermal conductivity of MWNTs 2. The most important factor affecting the specific heat is the lattice vibrations or phonons, which means the vibration at this temperature is the maximum, as mentioned before, also the structure of the material. Thus, change in dislocation density, grain size, or vacancies have little effect.

The major mechanism of the specific heat enhancement induced by the CNTs addition is not well understood. It may be related to the multi-walled structure of MWNTs in which the weak interlayer coupling can exhibit anything from 1D to 3D behavior, depending on the detailed value of the radius and number of wall (Benedict et al., 1996). However, the

interface between the boundaries of the matrices or CNTs and matrices, or nanotube-nanotube will also affect the heat capacity.
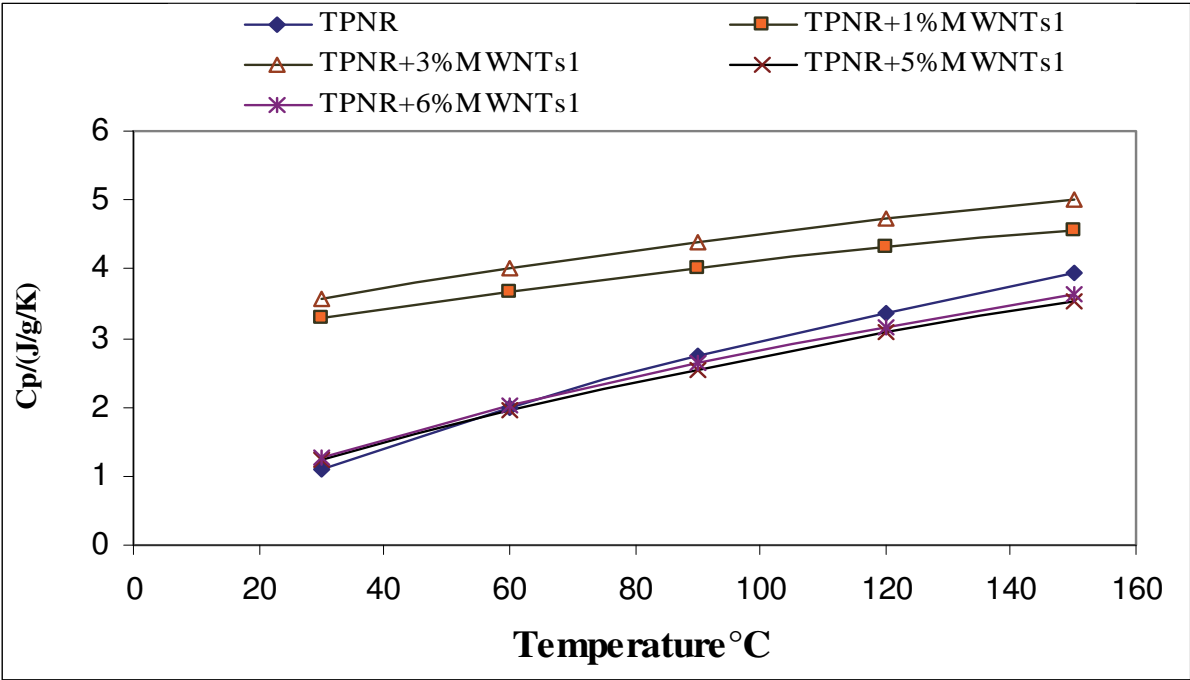

Fig. 15. Specific heat of the composites with different volume fractions of MWNTs 1 (first type) at different temperatures
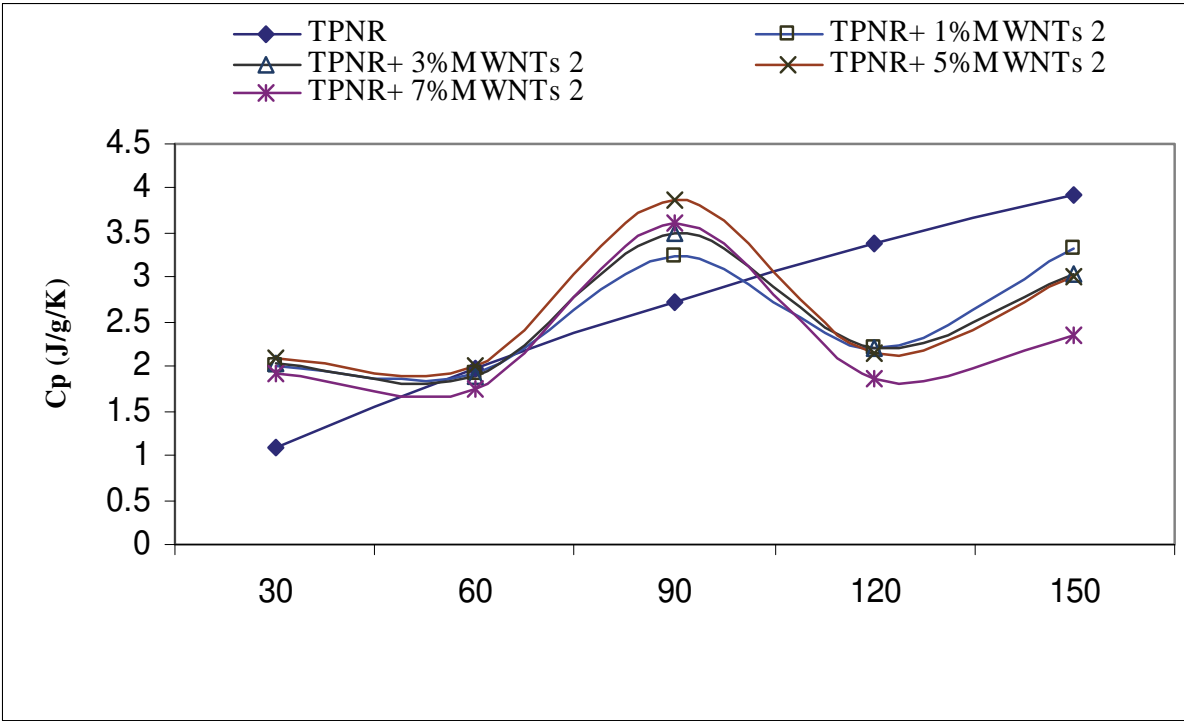

Fig. 16. Specific heat of the composites with different volume fractions of MWNTs 2 (second type) at different temperatures

3.4 Morphological examination

Figure 17 and Figure 18 show MWNTs (first and second type) as-received, with a large agglomeration of bundles of MWNTs, the carbon nanotubes tend to aggregate to form bundles because of the strong van der Waals forces (many graphene layers wrapped onto themselves). In addition, the Figures show the diameter of the walls of the MWNTs (the diameter of the first type is from 4-7nm, and the diameter of the second type is from 7-15nm). The SEM micrograph of TPNR is shown in Figure 19. This figure shows the TPNR without a filler inside it, and so the surface is smooth.
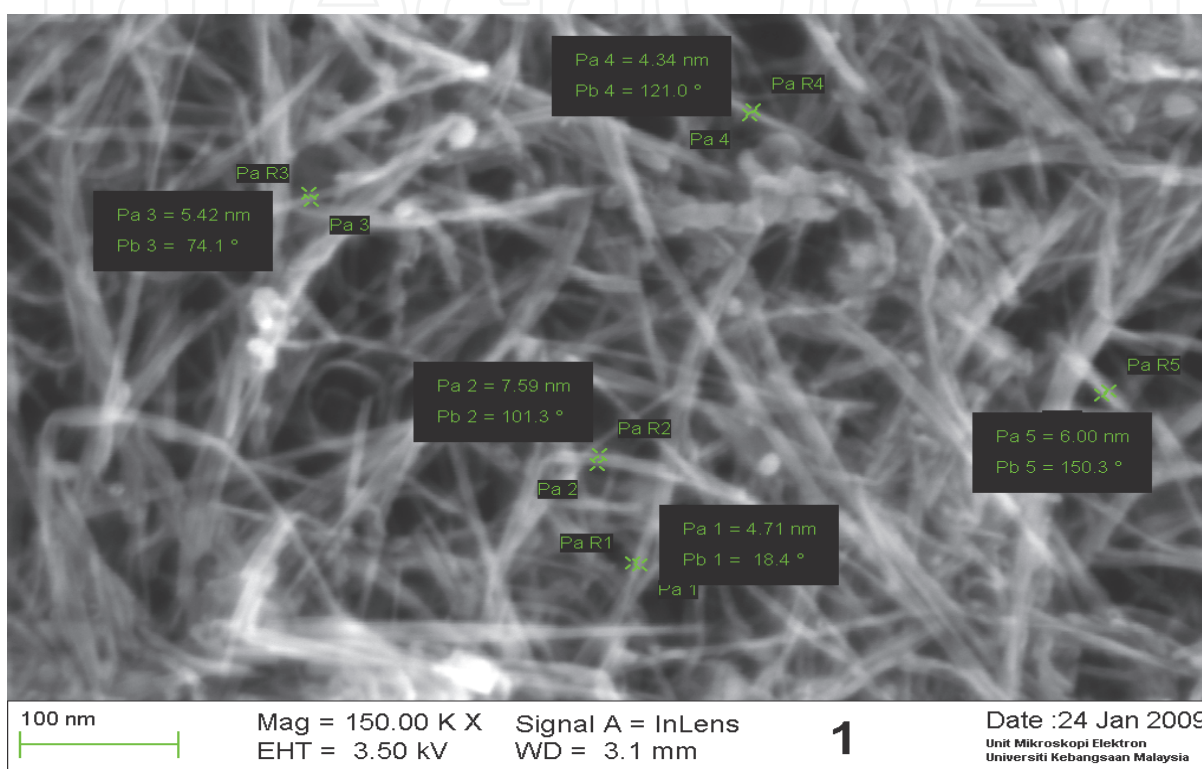
Fig. 17. SEM micrograph of MWNT 1 (first type).

The homogenous dispersion of MWNTs in the composites is confirmed by scanning electron microscopy (SEM). Figure20, Figure 21, Figure 24 and Figure 25, show 1wt% and 3wt% of MWNTs 1 and MWNTs 2, respectively, they are well dispersed as individual tubes in the matrix (the bright dots are the ends of broken MWNTs, indicated by arrows), they also show that the nanotubes that had pulled out from the matrix were still coated with polymer. In addition, the bright spots inside the TPNR, suggestion a strong polymer nanotubes interfacial. The key parameter to improve the composites containing the nanotubes is their uniform dispersion (Sandler et al., 1999; Yoshino et al., 1999). This is often conducted in two steps. One is to reduce the aggregate (the tangled MWNTs) size. The second is to homogenize the individual nanotubes and the aggregates in the matrix. Therefore, strong interfacial adhesion is essential for efficient stress transfer from the matrix to the nanotubes. This supports our observation of the higher efficiency of carbon nanotubes in enhancing the properties of TPNR nanocomposites. Figure 22 and Figure 26 show the SEM image of TPNR with 5wt% of MWNTs 1 and MWNTs 2. They depict an aggregate in TPNR, which observes a large amount of MWNTs that are self-organized in bundles. Low magnification was necessary in Figure 23 (7wt% MWNTs 1) and Figure 27 (7wt% MWNTs 2) to observe the

poor dispersion of nanotubes in the TPNR. The small circles in the figures clearly show a large number of unbroken carbon nanotubes, (many zones with very high local MWNTs concentrations), indicating a poor polymer/nanotube adhesion, which contributes to a reduction in the properties of TPNR/MWNTs nanocompsites.
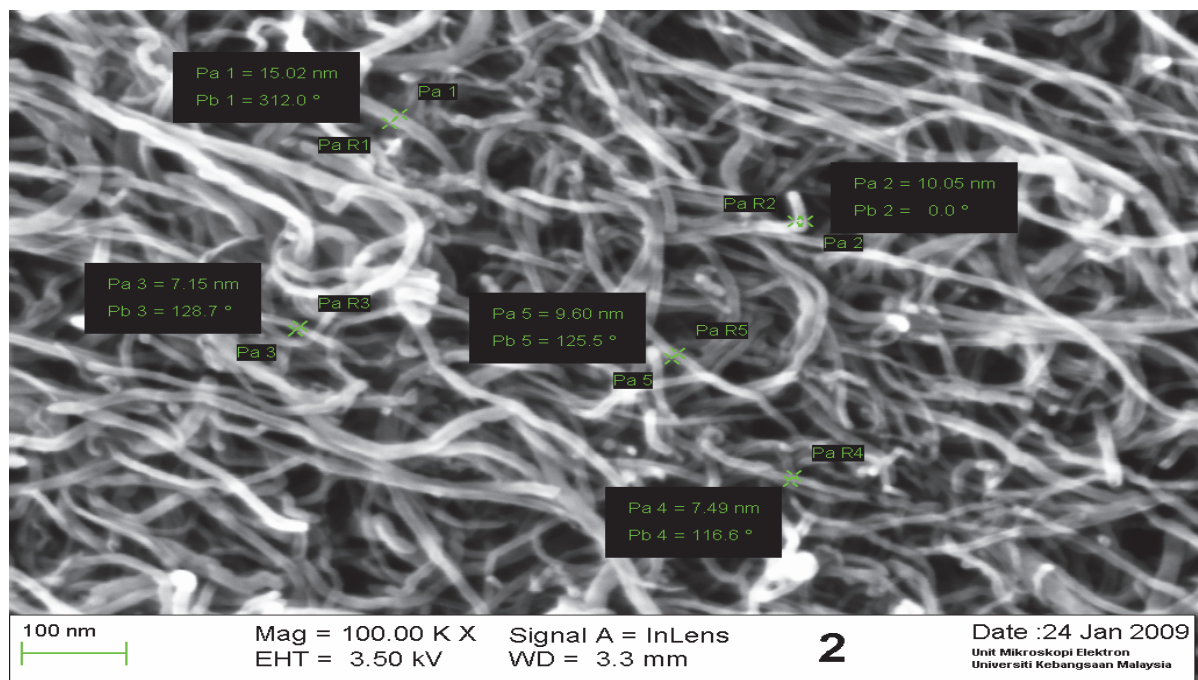

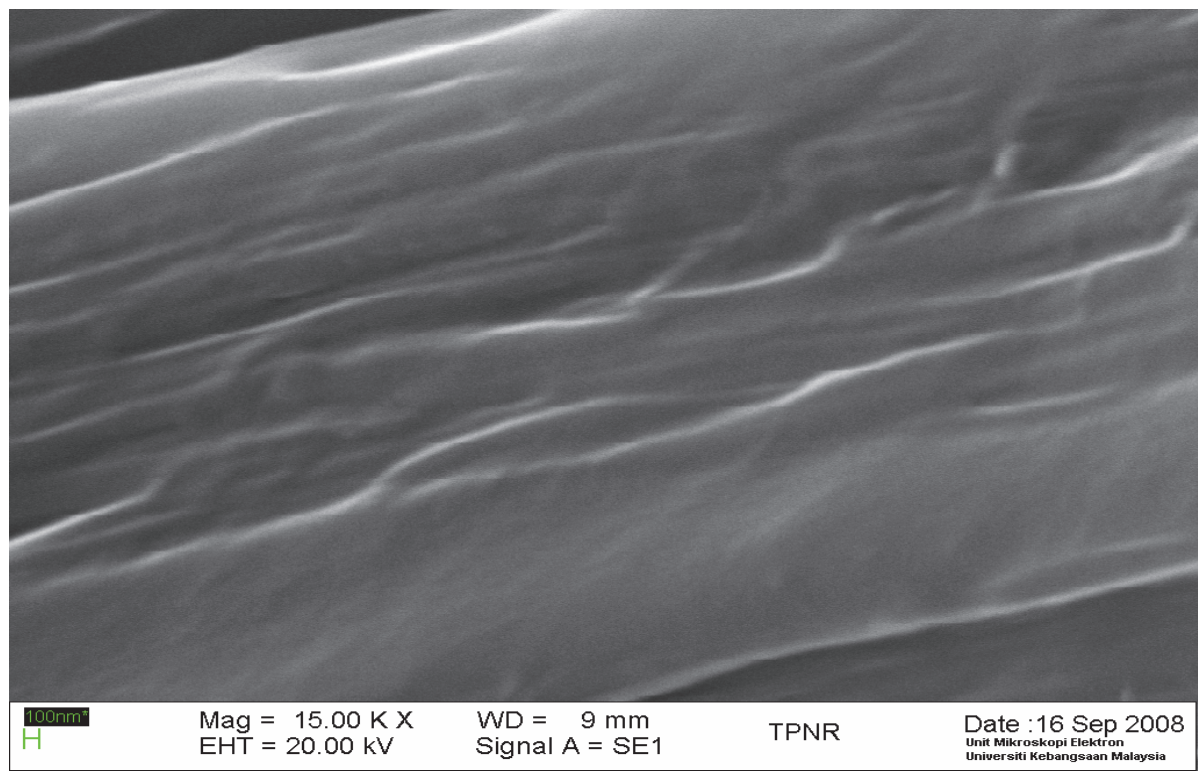Fig. 18. SEM micrograph of MWNT 2 (second type).
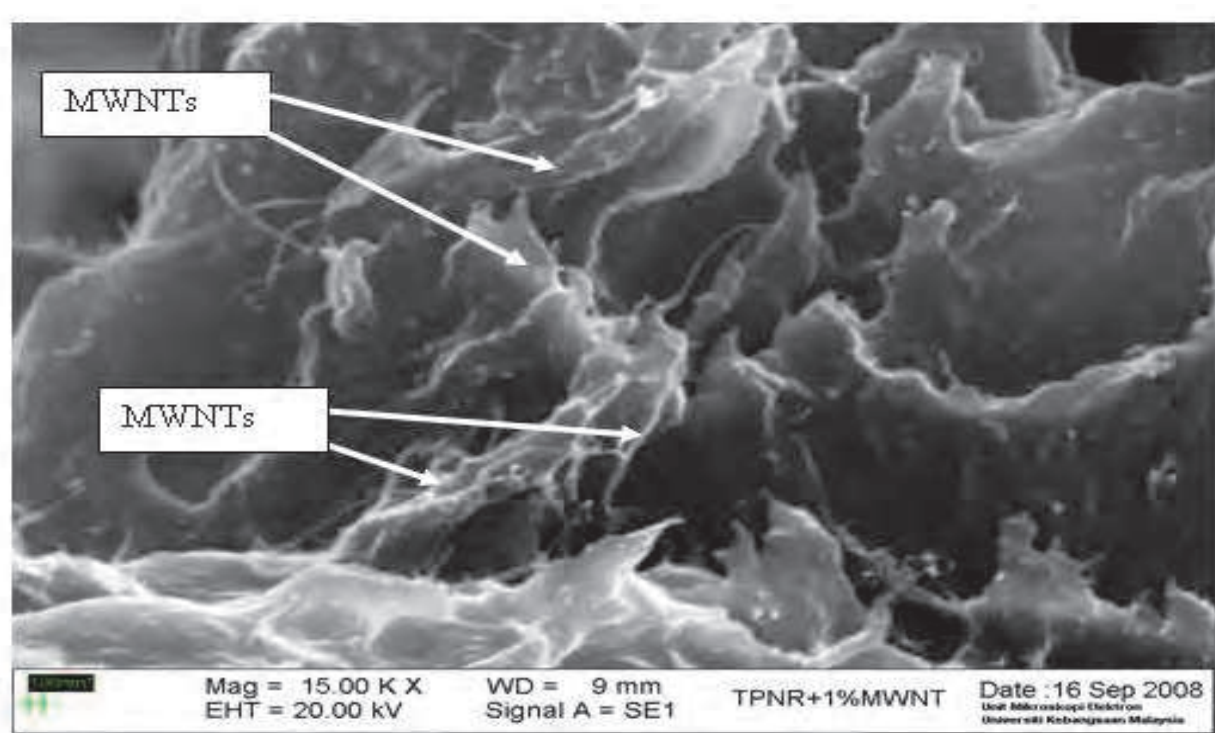

Fig. 19. SEM micrograph of TPNR.
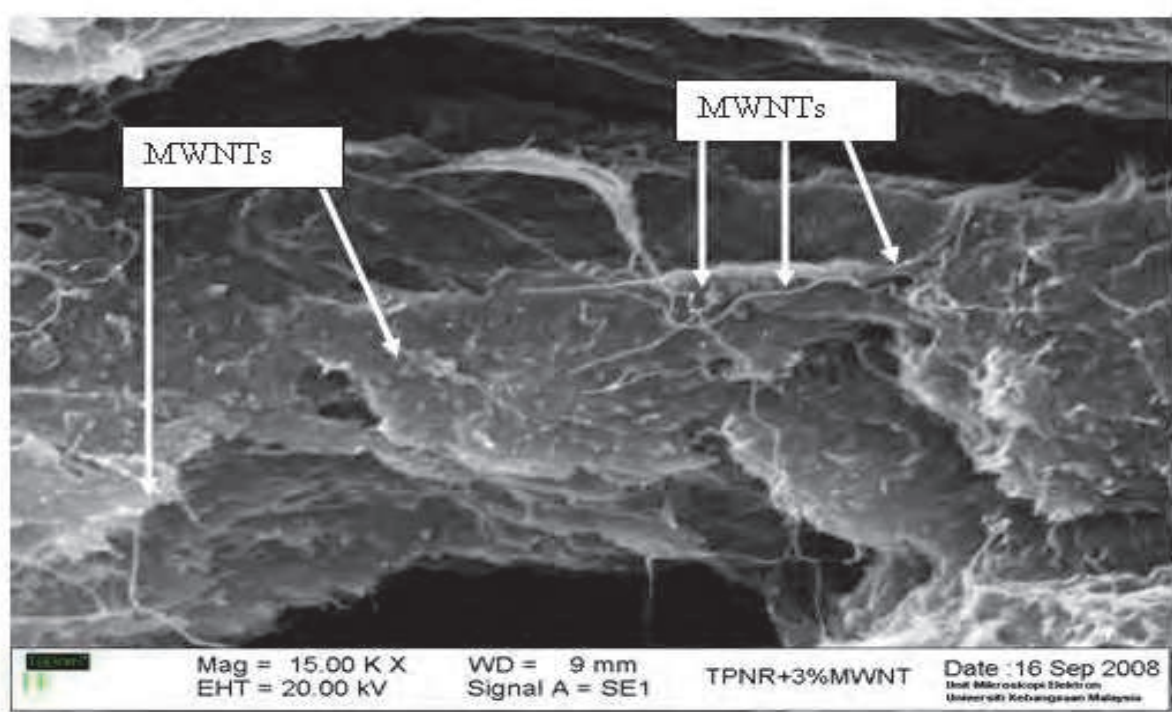
Fig. 20. SEM micrograph of TPNR with 1% MWNTs 1.

Fig. 21. SEM micrograph of TPNR with 3% MWNTs 1.
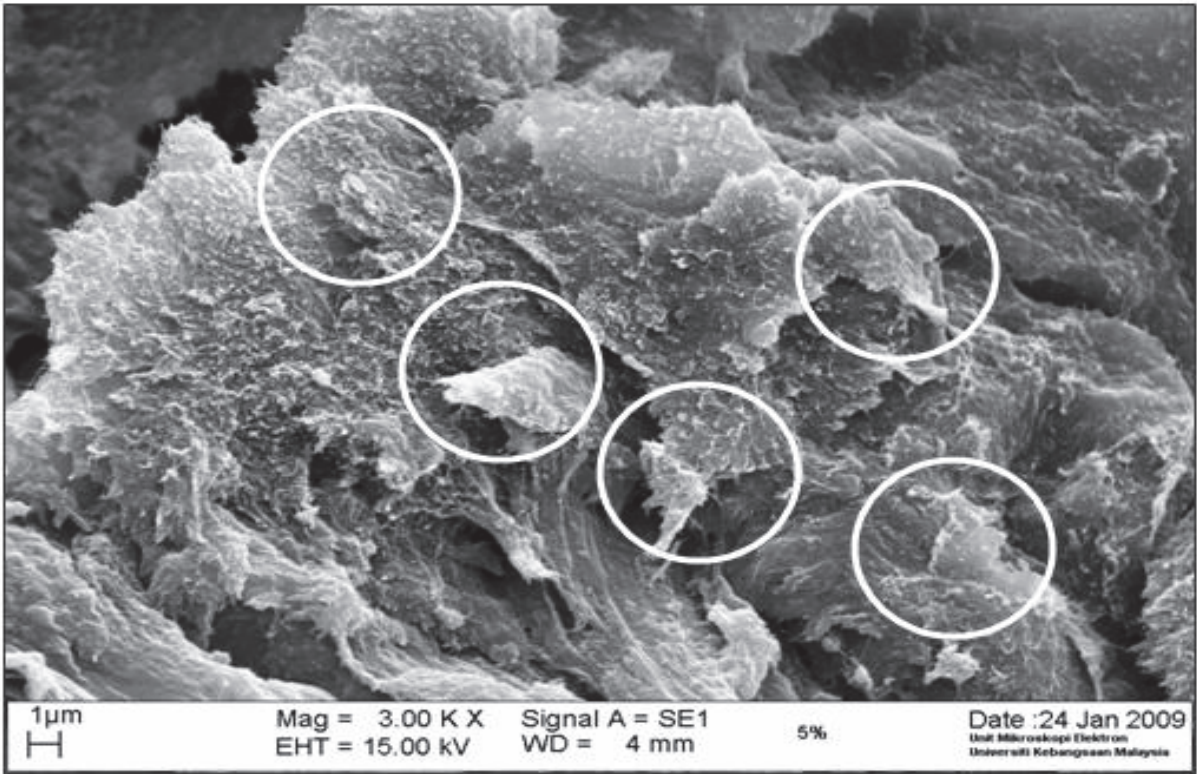
Fig. 22. SEM micrograph of TPNR with 5% MWNTs 1.
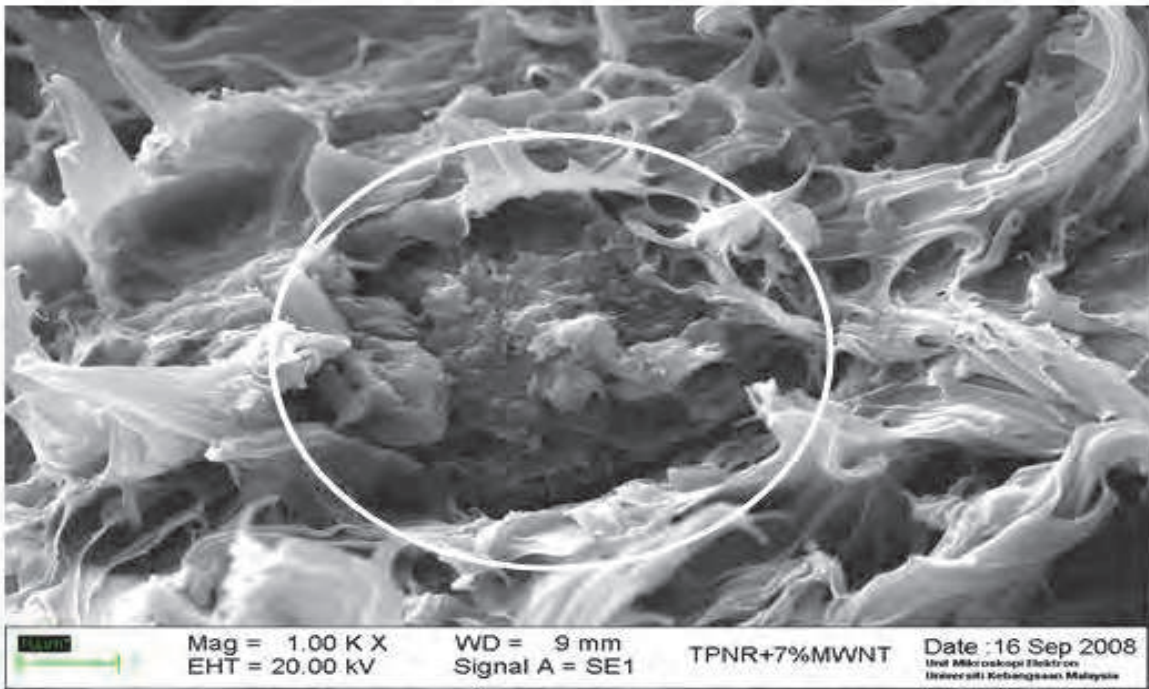
Fig. 23. SEM micrograph of TPNR with 7% MWNTs 1.
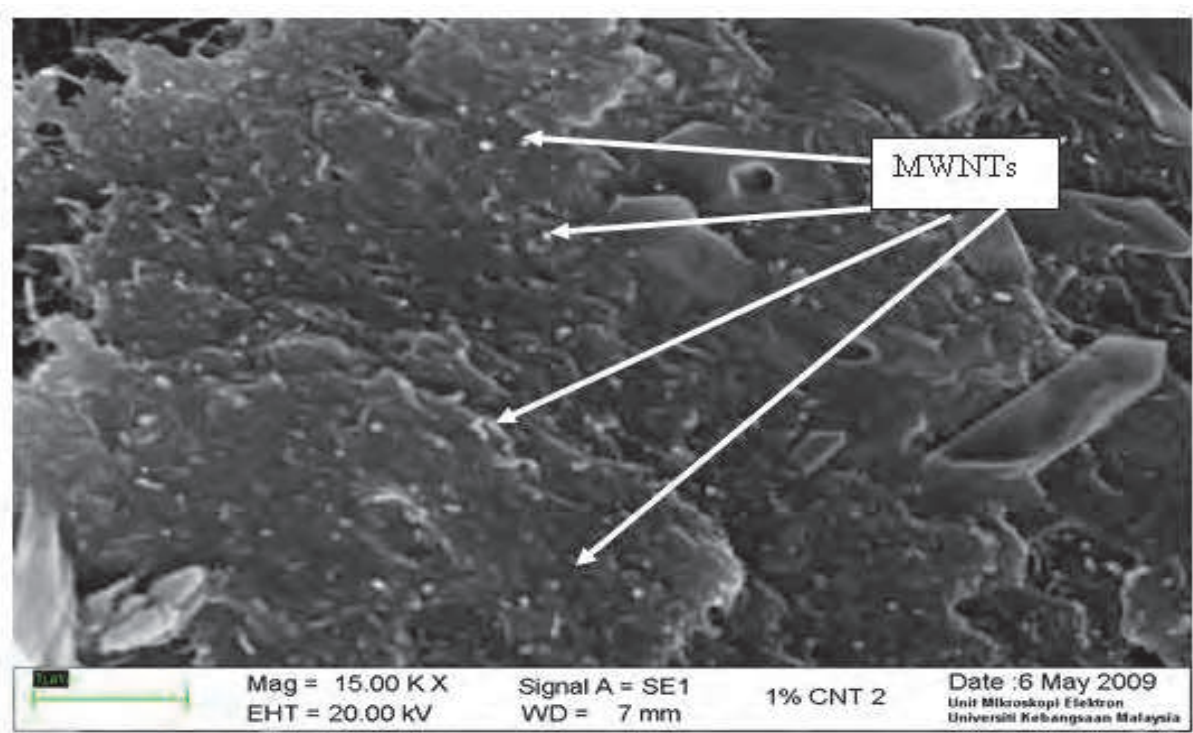
Fig. 24. SEM micrograph of TPNR with 1% MWNTs 2.
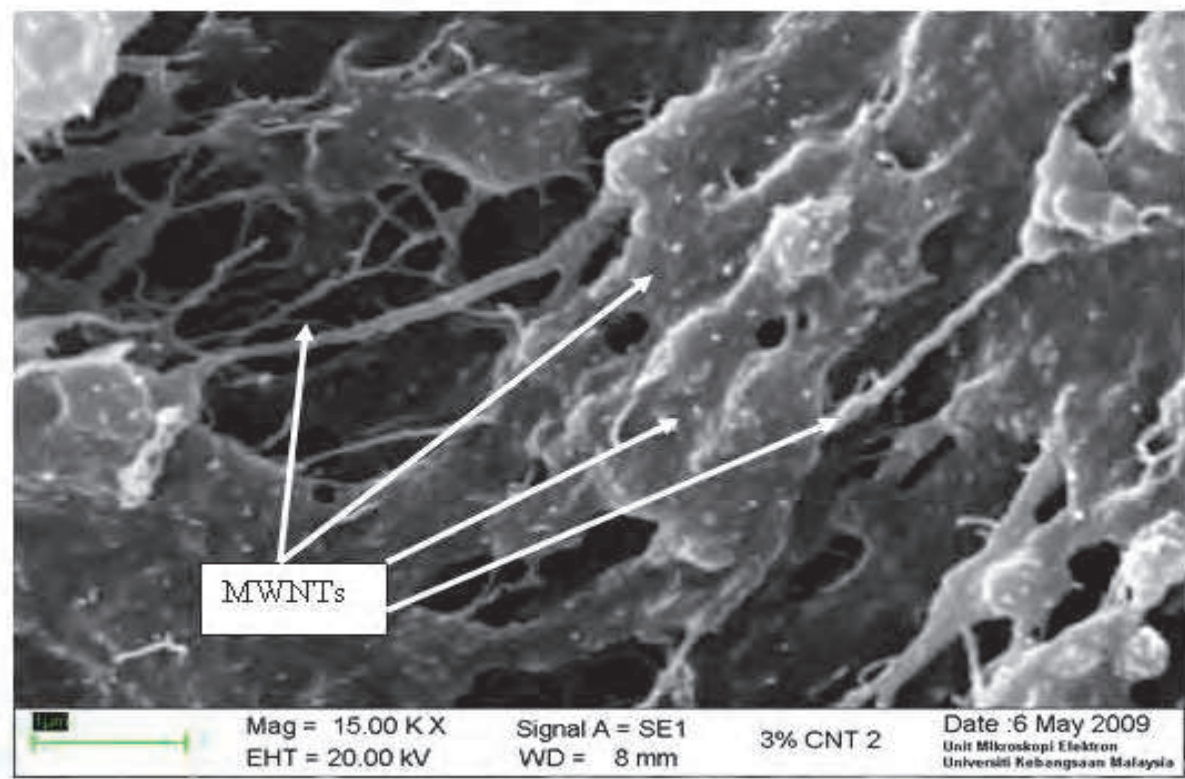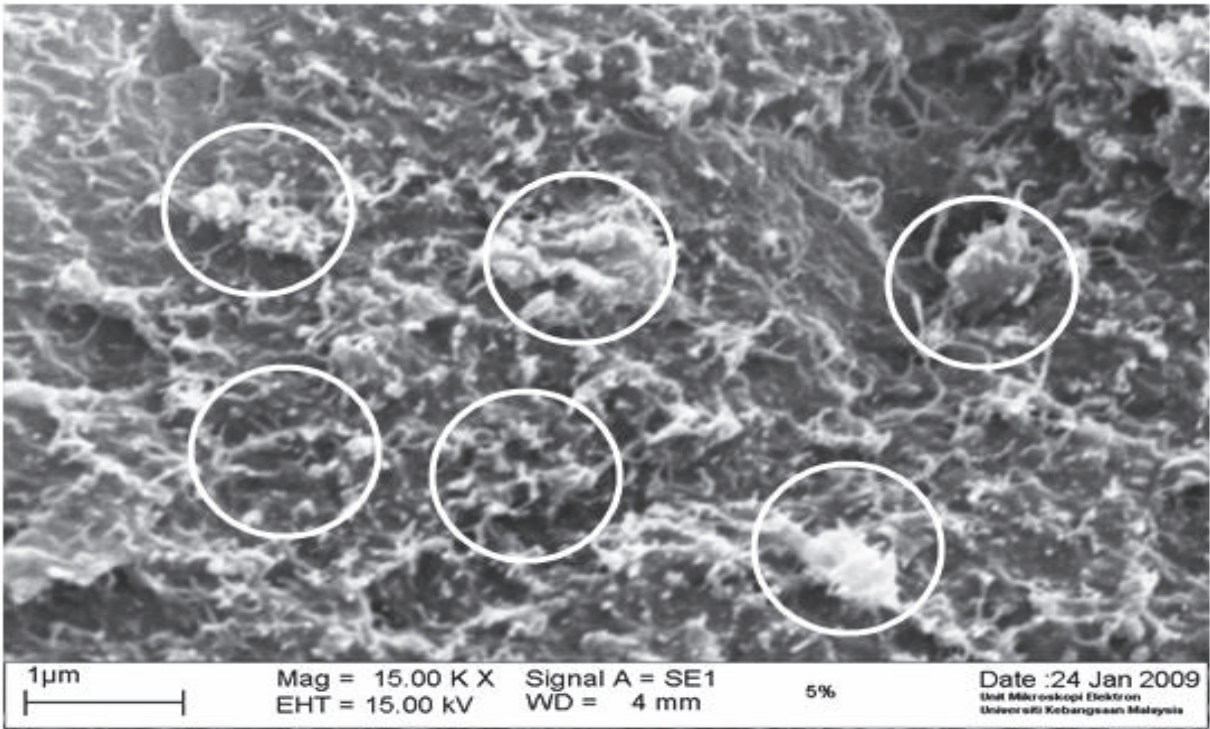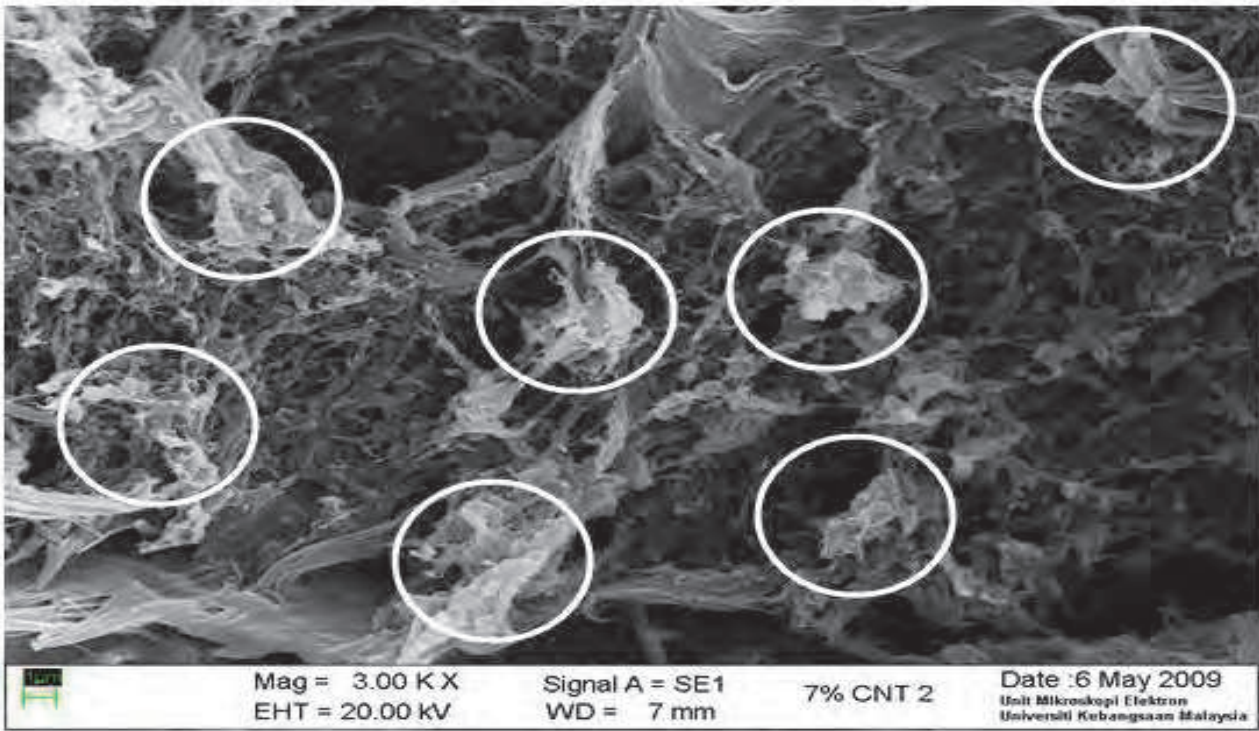

Fig. 25. SEM micrograph of TPNR with 3% MWNTs 2.

Fig. 26. SEM micrograph of TPNR with 5% MWNTs 2.

Fig. 27. SEM micrograph of TPNR with 7% MWNTs 2.

4. Conclusion

In this work, the MWNTs 1 and 2/TPNR nanocomposites were fabricated and the tensile and properties were measured. The addition of MWNTs in the TPNR matrix improved the mechanical properties. At this percent the tensile strength and elongation at break of MWNTs 1 increased by 23%, and 29%, respectively. The Young's modulus had increased by increasing the content of MWNTs. For MWNTs 2 the optimum result of tensile strength and Young's modulus was recorded at 3% which increased 39%, and 30%, respectively. However, elongation of break decreased by increasing the amount of MWNTs. The results exhibited better impact strength for MWNT 1 and MWNT 2 at 5 wt% with an increase of almost 70 % and 74%, respectively. The reinforcing effect of two types of MWNTs was also confirmed by dynamic mechanical analysis where the addition of nanotubes have increased in the storage modulus E', and the loss modulus E" also the glass transition temperature (Tg) increased with an increase in the amount of MWNTs. The laser flash technique was used to measure the thermal conductivity, thermal diffusivity and specific heat, from the results obtained. The high thermal conductivity was achieved at 1 wt% and 3 wt% of MWNTs compared with TPNR after 3 wt% it decreased, also the improvement of thermal diffusivity and specific heat was achieved at the same percentage. The homogeneous dispersion of the MWNTs throughout the TPNR matrix and strong interfacial adhesion between MWNTs and matrix as confirmed by the SEM images are considered responsible for the significant mechanical enhancement.

5. Acknowledgment

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Carbon Nanotubes - Synthesis, Characterization, Applications
Edited by Dr. Siva Yellampalli

Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

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