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Mechanical Properties of Thermoplastic Natural Rubber (TPNR) Reinforced with Different Types of Carbon Nanotube

(Sifat Mekanik Termoplastk Getah Asli Diperkuat dengan Pelbagai Jenis Nanotiub Karbon)

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ABSTRACT

The effect of various multi-walled carbon nanotubes (MWNTs) on the tensile properties of thermoplastic natural rubber (TPNR) nanocomposite was investigated. The nanocomposite was prepared using melt blending method. MWNTs were added to improve the mechanical properties of MWNTs/TPNR composites in different compositions of 1, 3, 5, and 7 wt.%. The results showed that the mechanical properties of nanocomposites were affected significantly by the composition and the properties of MWNTs. SEM micrographs confirmed the homogenous dispersion of MWNTs in the TPNR matrix and promoted strong interfacial adhesion between MWNTs and the matrix which was improved mechanical properties significantly.

Keywords: Mechanical properties; multi-walled carbon nanotubes; thermoplastic natural rubber

ABSTRAK

Kesan beberapa jenis nanotiub karbon berbilang-lapisan (MWNTs) ke atas sifat tegangan getah asli termoplastik (TPNR) telah dikaji. Nanokomposit tersebut telah disediakan melalui kaedah pencampuran leburan MWNTs ditambahkan untuk meningkatkan sifat mekanik komposit MWNTs/TPNR, pada komposisi pengisi berbeza iaitu: 1, 3, 5 dan 7% berat. Hasil kajian mendapati sifat mekanik nanokomposit sangat dipengaruhi oleh komposisi pengisi dan sifat pengisi MWNTs. Sementara itu, mikrograf SEM mengesahkan penyerakan MWNTs yang homogen dalam matrik TPNR. Dengan demikian pelekatan antara muka yang bagus antara pengisi MWNTs dan matrik TPNR ini menjadi asas kepada peningkatan sifat mekanik yang ketara.

Kata kunci: Getah asli termoplastik; nanotiub karbon berbilang-lapisan; sifat mekanik

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs), nanocomposites of polymers with carbon nanotubes (CNTs) have been studied widely due to their extraordinary electrical and mechanical properties which make them potentially used for a wide range of applications (Lin et al.2003; Potschke et al. 2003). Two main types of CNTs exist: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). SWNTs consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. MWCNTs consist of many graphite layers concentrically nested like rings of a tree trunk. SWCNTs have a lower diameter (0.4 and 5.6 nm) compared with MWNTs, which is in the range of 20-100 nm. MWNTs are also more rigid because their section is much larger compared to that of SWNTs. MWNTs have been proven to be very effective fillers especially in tailored polymeric materials suited to prescribed applications at very low loadings. This is because neat multi-walled carbon nanotubes (MWNTs) exhibit excellent mechanical, thermal, and electrical properties (Schartel et al.2005). One of the advantages of MWNTs used as filler is their high aspect ratio, as high as 1000, which can induce better adhesion with the polymeric matrix, which is an important factor for effective enhancement of the nanocomposite's properties (Curran et al.1998). This enables percolation of the fillers at very low concentrations and makes them attractive for use in a broad spectrum of applications, especially as reinforcing fibers in nanocomposites.

Different polymer/CNT nanocomposites have been synthesized by incorporating CNTs into various polymer matrices, such as epoxy (Liao et al. 2004), polypropylene (Seo et al. 2005), polyimides (Cai et al. 2004) and polyurethane (Kuan et al. 2005) These polymer-based nanocomposites derive their high properties at low filler volume fractions due to the high aspect ratio and high surface area to volume ratio of the nano-sized particles. Despite the considerable number of studies concerning the preparation, characterization and properties of polymer/CNT nanocomposites, no report has been published regarding the processing of TPNR nanocomposites by using CNT. In this work, we reported the fabrication and mechanical studies of TPNR reinforced with two types of MWNTs.

MATERIALS AND METHODS

In this study we used two types of multi-walled carbon nanotubes (MWNTs). The first one (MWNTs1) was manufactured by CVD process and supplied by Chinese Academy of Science. The specifications of MWNTs 1 are as follow: purity <95%, length 10-30 µm, diameter >8 nm. The second one was MWNTs 2, produced by catalytic chemical vapor deposition (CCVD), provided by Arkema (Graphistrength™ C100) with purity >90%, length 0.1-10 µm, diameter 10-15 nm. Polypropylene (PP) with a density of 0.905 g cm^{-3} was supplied by Propilinas (M) Sdn. Bhd, and natural rubber was obtained from Guthrie (M) Sdn. Bhd. Liquid natural rubber (LNR) was produced by the photochemical degradation technique.

The samples were prepared by using an internal mixer (Haake Rheomix 600P). The mixing temperature was 180°C, with a rotor speed and stirring time of 80 rpm for 11 min, respectively. The indirect technique (IDT) was used to prepare the nanocomposites, which involved mixing the MWNTs with LNR separately, before melt blended with PP and NR in an internal mixer. TPNR nanocomposites were prepared by melt blending of PP, NR and LNR with MWNTs in a ratio of 70 wt%, 20 wt% and 10wt%, respectively as compatibilizers and MWNTs varied from 1wt% to 7wt%.

Tensile properties were measured using Testometric 350 according to ASTM D638-91a at crosshead speed of 50 mm/min. The gauge length was kept at 70 mm. At least 10 samples were tested for each compositions and a mean of 10 samples were taken for stress and strain calculations. Morphology of the MWNTs and the composite were examined by scanning electron microscope (Philips XL 30). The samples were coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

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. From Figure 1 TPNR with MWNTs 1 and MWNTs 2 showed optimum results obtained at 3 % wt, which compared with TPNR increased 23% and 39%, respectively. The tensile strength radically increased 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 homogeneous dispersion of MWNTs in the TPNR matrix, which led 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. 2006).

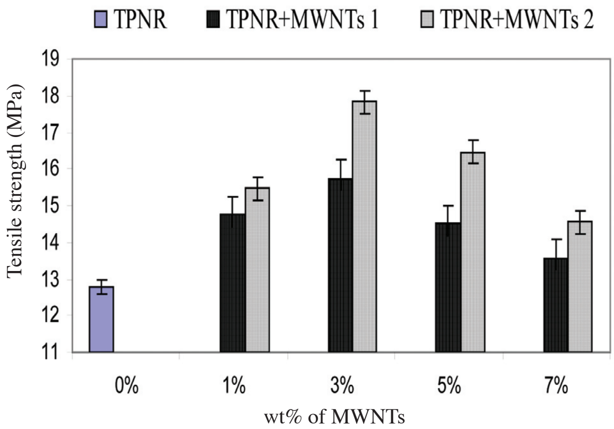

FIGURE 1. Tensile strength of TPNR reinforced with two types of MWNTs

Figure 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 but for MWNTs 1 it was different. Figure 2 clearly shows that the presence of MWNTs has significantly improved the tensile modulus of the TPNR. The remarkable increase of Young's modulus with MWNTs 1 content shows a greater improvement than that seen in tensile strength at high content, which indicates that the Young's modulus increased with an increase in the amount of the MWNTs 1. At 1 wt% of MWNTs the Young's modulus was increased by 11% compared to TPNR. At 3 wt% of MWNTs the increase in the Young's modulus was 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. 2006).

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).

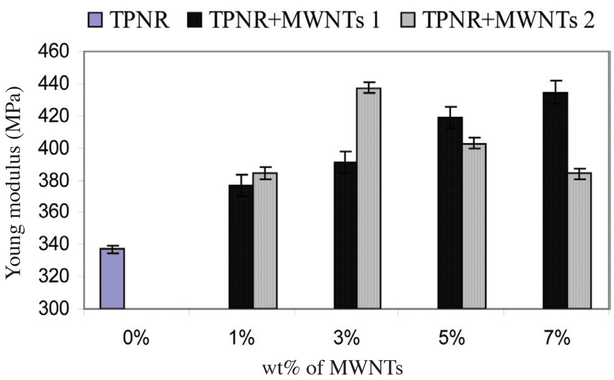

FIGURE 2. Young's modulus of TPNR reinforced with two types of MWNTs

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.

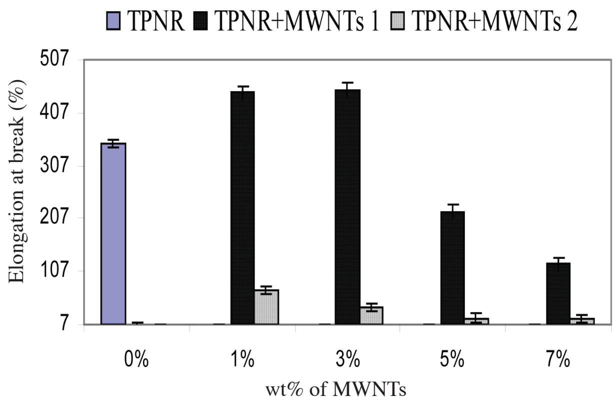

FIGURE 3. Elongation at break of TPNR reinforced with two types of MWNTs

It can be deduced that the reinforcing effect of MWNTs was very effective. 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.

The homogenous dispersion of MWNTs in the composites is confirmed by scanning electron microscopy (SEM). Figure 4(a) and 4(b), show 1 wt% of MWNTs 1 and MWNTs 2, they are well dispersed as individual tubes in

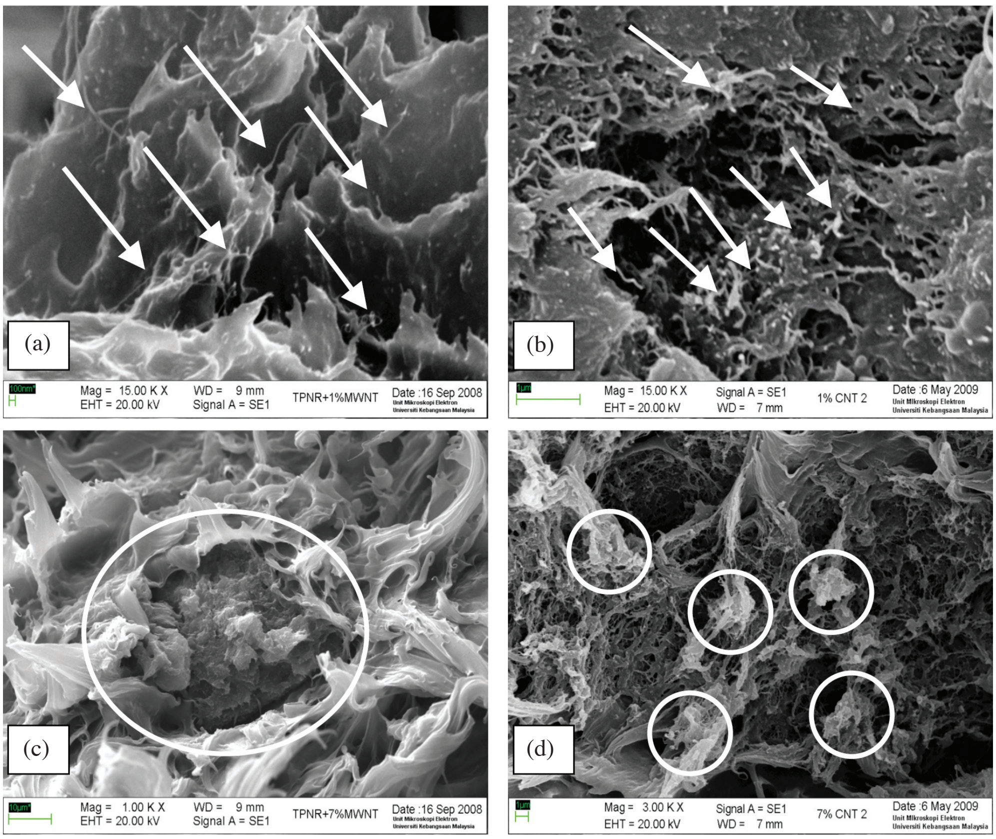

FIGURE 4. SEM micrographs of TPNR with two types of MWNTs (a) TPNR+1% MWNTs 1 (b) TPNR+1% MWNTs 2 (c) TPNR+7% MWNTs 1 (d) TPNR+7% MWNTs 2

the matrix (the bright dots are the ends of broken MWNTs, indicated by arrows), they also show that the nanotubes that were pulled out from the matrix were coated with polymer. In addition, the bright spots inside the TPNR, suggested a strong polymer nanotubes interfacial. Figure 4 (c) (7 wt% MWNTs 1) and Figure 4 (d) (7 wt% MWNTs 2) with low magnification was necessary 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.

Conclusion

In this work, MWNTs 1 and 2/TPNR nanocomposites were fabricated and the tensile properties were measured. The addition of MWNTs in the TPNR matrix improved the mechanical properties. At 3 wt% the tensile strength and elongation at break of MWNTs 1 increased by 23%, 28.9%, respectively. Young's modulus increased with increasing the content of MWNTs. For MWNTs 2 the optimum result of tensile strength and Young's modulus recorded at 3% which increased 39%, 30%, respectively. However, elongation at break decreased with increasing the amount of MWNTs. SEM micrographs confirmed a good dispersion of MWNTs in TPNR at 1% MWNTs. However, at higher content of MWNTs the dispersion was low due to the agglomeration of nanotube inside the matrix for both MWNTs.

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