Sains Malaysiana 42(4)(2013): 503–507

Properties Enhancement of TPNR-MWNTs-OMMT Hybrid Nanocomposites by Using Ultrasonic Treatment

(Peningkatan Sifat Nanokomposit Hibrid TPNR-MWNTs-OMMT
Menggunakan Kaedah Ultrasonik)

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ABSTRACT

The main goal of this paper was to study the effect of ultrasonic treatment time on the mechanical properties of thermoplastic natural rubber (TPNR) reinforced with hybrid MWNTs-OMMT. The intercalation of TPNR enhancement into layers of clay by increasing the d-spacing was found using X-ray diffraction. The tensile properties of nanocomposites treated with ultrasonic increased when compared with untreated nanocomposites. The optimum ultrasonic treatment time was obtained at 3 h. The transmission electron microscope micrograph showed a combination of intercalated-exfoliated structure of the TPNR composites with organic clay and dispersion of MWNTs. The ultrasonic treatment can promote the dispersion of MWNTs-OMMT in TPNR and also improved the compatibility of hybrid filler and the TPNR matrix.

Keywords: Carbon nanotubes; hybrid nanocomposites; mechanical properties; polymer nanocomposites; thermoplastic natural rubber

ABSTRAK

Matlamat utama kertas ini adalah untuk mengkaji kesan masa rawatan ultrasonik ke atas sifat mekanik termoplastik getah asli (TPNR) diperkukuh dengan hibrid MWNTs-OMMT. Melalui pembelauan sinar-X, terdapat penambahan dalam jarak antara lapisan di dalam nanozarah tanah liat menunjukkan kehadiran struktur saling selit di dalam TPNR sifat tegangan dan hentaman nanokomposit dengan rawatan ultrasonik menunjukkan peningkatan berbanding nanokomposit tidak terawat. Masa rawatan ultrasonik selama tiga jam merupakan tempoh optimum dalam kajian ini. Mikrograf mikroskop elektron penghantaran menunjukkan terdapat kombinasi struktur terkupas dan saling selit di dalam komposit TPNR dengan penyerakan nanozarah tanah liat organik dan MWNT. Rawatan ultrasonik dapat membantu penyerakan MWNT-OMMT di dalam TPNR dan juga memperbaiki keserasian antara hibrid pengisi dan matriks TPNR.

Kata kunci: Hibrid nanokomposit; karbon nanotiub; polimer nanokomposit; sifat mekanik; termoplastik getah asli

INTRODUCTION

The recent advent of nanoparticles research has attracted much attention in manufacturing polymeric nanocomposites using various nanoparticles as reinforcement. Experimental results on polymeric nanocomposites have revealed a wide range of variation in their properties. Nanoclay, as a new type of nanofiller, has generated great interest in the polymer industry because of its superior properties, such as enhanced mechanical properties when compared with the pure polymer or composites having conventional fillers. The excellent mechanical properties of carbon nanotubes (CNTs) make them ideally suited as filler for reinforcing polymer composites and also ideal reinforcing fibers for the manufacture of the next generation of fiber-matrix composite materials. The efficiency of reinforcement depends on different factors such as the filler aspect ratio, the filler mechanical properties and the adhesion between the matrix and the filler (Haggenmueller et al. 2006).

Hybrid composites are usually used when a combination of properties of different types of fibers or when longitudinal as well as lateral mechanical performance is needed. Another driving force in the area of hybrid materials is the possibility of creating multifunctional materials. In general, the properties of hybrid composites are mainly controlled by the fiber content, length of the individual fibers, orientation, arrangement of the fibers, nature of the matrix, extent of intermingling of the fibers, fiber-matrix interface and hybrid design (Leong et al. 2004; Mishra et al. 2003). Hybrid composites have long held the attention of researchers as a way to enhance the properties of composites. Most of the research focused on improving the mechanical properties and thermal properties such as nanoclay/glass fiber/epoxy hybrid (Li-Yu et al. 2006), epoxy/CNT/Graphite Nanoplatelets hybrid composites (Jing et al. 2008) and polyamide12/ MWNTs/Carbon Black hybrid composites (Robert et al. 2011).

In spite of these studies, which concern with the preparation, characterization and properties, no reports have been found in the literature on the processing of TPNR-OMMT-MWNTs hybrid nanocomposites using a continuous ultrasonic effect. In this paper, we reported the continuous ultrasonic effect of different times on the mechanical properties of TPNR- MWNTs-OMMT hybrid nanocomposites.

MATERIALS AND METHODS

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. Liquid natural rubber (LNR) was synthesized using the photochemical oxidation technique on natural rubber in our laboratory. The MWNTs used in this paper were manufactured by catalytic chemical vapor deposition (CCVD), CVD process and supplied from Arkema (Graphistrength™ C100). The specification of MWNTs is as follows: purity >90%, length 0.1-10 µm, diameter 10-15 nm. The organoclay (Nanomer I.30P-OMMT) was supplied by Nanocor Inc., USA. It is a white powder containing montmorillonite (70 wt %) intercalated by octadecylamine (30 wt %) with a cation-exchange capacity of 110 meq/100g.

The indirect technique (IDT) was used to prepare the nanocomposites; this involved mixing 2wt%MWNTs-2wt% Nanomer I.30P with LNR (10wt%) assisted by ultrasonic bath (70Watts, 42 KHz) at different times (1, 3 and 5) h, before it was melt blended with PP (70wt%) and NR (20wt%) in the internal mixer. Using the melt blending technique the TPNR-1.30P-MWNTs hybrid composite was compounded using the internal mixer. The optimum processing parameters used were a temperature 180°C, 100 rpm screw rotation and 12 min processing time.

The X-ray diffraction equipment (XRD-model D8 advance) was used with a radiation source from CuK$_\alpha$, which generates energy of 40 KV and a current of 30 mA that emits a wavelength of 15.4 nm. The X-ray diffraction was done at small angles of 2°-10° to determine the degree of clay intercalation. Tensile properties were measured using 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 of 50 mm min^{-1}. At least, five samples were tested for each composition and the average value was reported. The sample dimension was 63 × 12 × 3 mm^3. The morphological examination was carried out using a Philips STEM CM12 transmission electron microscope with an acceleration voltage of 100 kV. An ultrathin section was prepared by using a Leica ultracut E with cryo FC4E attachment at -100°C.

RESULTS AND DISCUSSION

The XRD pattern shows the state of OMMT in the hybrid nanocomposites, as shown in Figure 1. In this hybrid system, after ultrasonic treatment of OMMT-MWNTs, the OMMT has a better dispersion inside the TPNR. The peak of hybrid system shifted to a low value of 2ϴ, where 3 h treatment time is the best as compared with 1 h and 5 h. At 3 h the distance between the layers of OMMT increases. Therefore, the rate of diffusion of polymer chains was increases, which allows the homogeneous dispersion of OMMT inside the matrix. This was revealed by a decrease in the intensity of the diffraction peak, the intercalated inside the layers as the space layers available for the intercalation between the OMMT gallery led to the disordering of the layered silicate structure, which is related to the presence of a delaminated configuration. It was also found that the intensity of the peak was increased at 5 h. This means that the d-spacing of the OMMT decreased with the increase in the ultrasonic time treatment. The latter is a direct evidence of the tendency of the OMMT to agglomerate inside the matrix. Consequently, the polymer chains experience more difficulty diffusing into the agglomerates and the OMMT interlayer, which means a decrease in the interaction between the polymer chain and the OMMT.

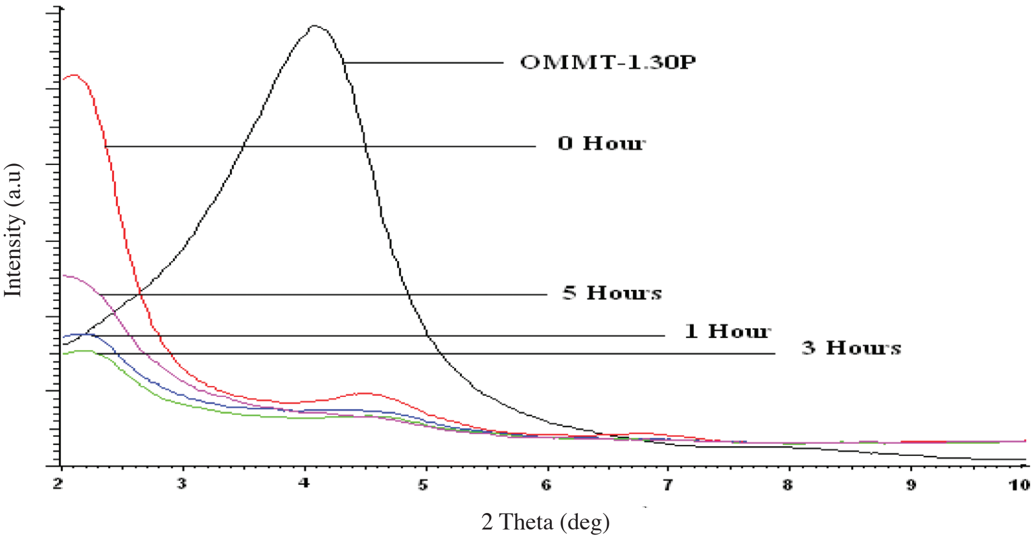

FIGURE 1. XRD patterns of TPNR reinforced with hybrid OMMT-MWNTs

The mechanical properties of TPNR nanocomposites are measured and summarized in Figure 2. It can be seen that the mechanical properties of TPNR hybrid nanocomposites with ultrasonic treatment improved in stiffness and tensile strength. The maximum tensile strength and Young's modulus for the new hybrid nanocomposites was obtained at 3 h, it can be seen that the tensile strength and Young's modulus increased about 57% and 88%, respectively, compared with TPNR. Furthermore, for the same 3 h ultrasonic treatment compared with 0 h, the tensile strength and Young's modulus increased about 27% and 55%, respectively. The maximum results of tensile strength and Young's modulus at 3 h is due to the stronger interfacial interaction between the matrix and hybrid filler OMMT-MWNTs as a result of the vast surface exposed for OMMT-MWNTs.

The improvement in the mechanical properties of new hybrid nanocomposites may be caused by the strong interactions between the TPNR matrix and the hybrid filler which leads to a good dispersion of the hybrid filler in the natural rubber and polypropylene as evidenced by the TEM images (Figure 3). The probability that hybrid nano-particles form a network depends on the interaction between the particles, on their shape (aspect ratio) and on their inter-particle distance. Through this particle-bridging mechanism, the applied stress can be easily transferred to the hybrid filler (Kim et al. 2001). As a consequence, the stiffness of the hybrid composite is improved and can also accommodate more applied stress.

The elongation at the break of TPNR-OMMT-MWNTs decreased as shown in Figure 2(c). It can be deduced that the ultrasonic effect of OMMT-MWNTs is very marked. This is because of the presence of OMMT-MWNTs in the TPNR matrix, which behaves like physical cross-linking points and restricts the movement of polymer chains, which limits their ability to adapt to the deformation (Avella et al. 2006). This is an indicator of the materials flexibility, which shows that the inclusion of OMMT-MWNTs makes the TPNR stronger but more brittle.

It can also be seen that the longer time of ultrasonic treatment has led a reduction in the tensile properties; which possibly contributed to an increase in the agglomeration effect of OMMT-MWNTs. Therefore, it yields a reduction of the aspect ratio of OMMT-MWNTs; which means a reduction of the contact surface between the hybrid filler and the TPNR matrix (Ahmad et al. 2007; Liu & Wu 2001). The agglomeration of the particles is the site of stress concentration and can act as a micro-crack initiator. Also, because the long-chain polymer molecules can be ruptured by high intensity ultrasonic during preparation, it may be

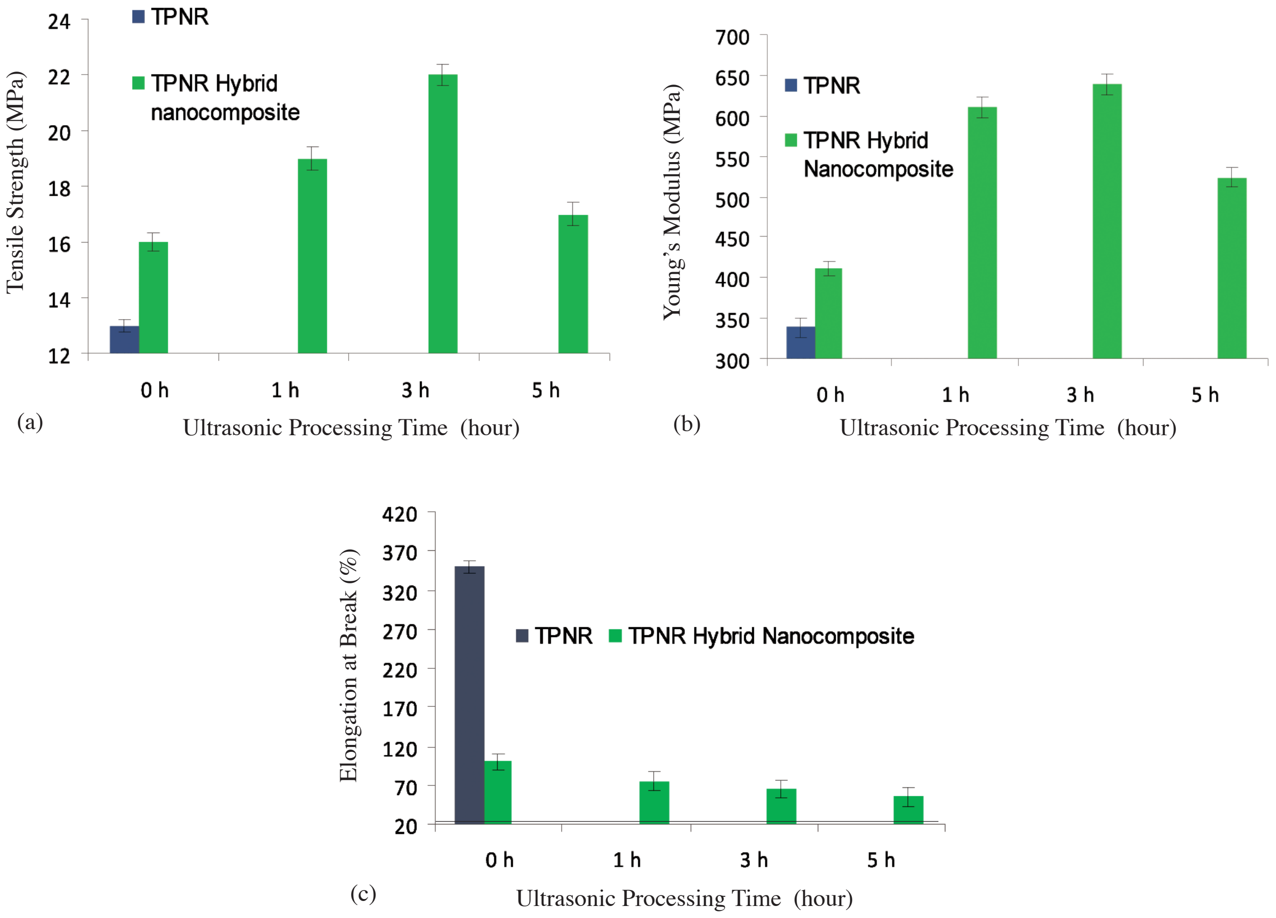

FIGURE 2. Tensile Strength (a), Young's modulus and (b) and Elongation at break (c) of TPNR reinforced with hybrid OMMT-MWNTs

that the polymer chains of LNR ruptured with the higher ultrasonic time due to the LNR being used as compatibilizer for the rubber and plastic interphase and thereby decreasing the homogeneity of the blend (Mou'ad et al. 2011). It might also be attributed to the immobilization of the macromolecular chains by the filler, which limits their ability to adapt to the deformation and cause the material to become more brittle (Avella et al. 2006).

The morphological characterization transmission electron micrographs of the hybrid nanocomposite samples treated with different ultrasonic times are shown in Figure 3. The TEM micrograph of TPNR is shown in Figure 3(a). This figure shows the TPNR without a filler inside it, the lighter area represents the PP phase and the darker area represents the rubber phase. Without ultrasonic treatment of the hybrid nanocomposites, the OMMT-MWNTs still maintain ordered stacks in the TPNR, the hybrid filler particles form big agglomerations and present the spatial-linked like structure as shown in Figure 3(b).

The TEM results provide additional support for the fact that nanofillers in the TPNR matrix have a good dispersion of OMMT-MWNTs in TPNR at 3 h, as shown in Figure 3(c). At this time, the size of the hybrid filler clusters is reduced when the optimum sonicating time is reached. The OMMT-MWNTs have a high surface area and are homogenous in the matrix (the OMMT and MWNTs are more homogenously dispersed in both PP phase and NR phase according to the swelling effect of OMMT-MWNTs inside LNR). Therefore, there is a strong interfacial interaction between the TPNR and OMMT-MWNTs. Strong interfacial adhesion is essential for the efficient stress transfer from the matrix to the hybrid filler; this supports our observation that the higher efficiency of ultrasonic treatment assisted in enhancing the mechanical properties of TPNR. By further increasing the sonicating time beyond the optimum value, the size of the OMMT-MWNTs clusters will start growing and therefore, the number of clusters will then decrease as shown in Figure 3(d). Thus, the surface area for the interaction between the clusters and the TPNR is reduced and the properties of the composites are adversely affected.

CONCLUSION

New hybrid nanofiller (2wt%MWNTs-2wt%OMMT) reinforced TPNR composites have been fabricated by ultrasonic treatment. Ultrasonic treatment achieved a rapid interaction of OMMT-MWNTs inside a matrix. This is supported by a TEM study showing a homogenous dispersion of OMMT-MWNTs and XRD study indicating an increase of d-spacing of OMMT. The tensile properties of thermoplastic natural rubber nanocomposites were substantially improved after ultrasonic treatment and the optimum results were achieved at 3 h. However, prolonging the time of ultrasonic treatment for more than 3 h resulted in particle aggregation and caused a significant reduction in tensile properties.

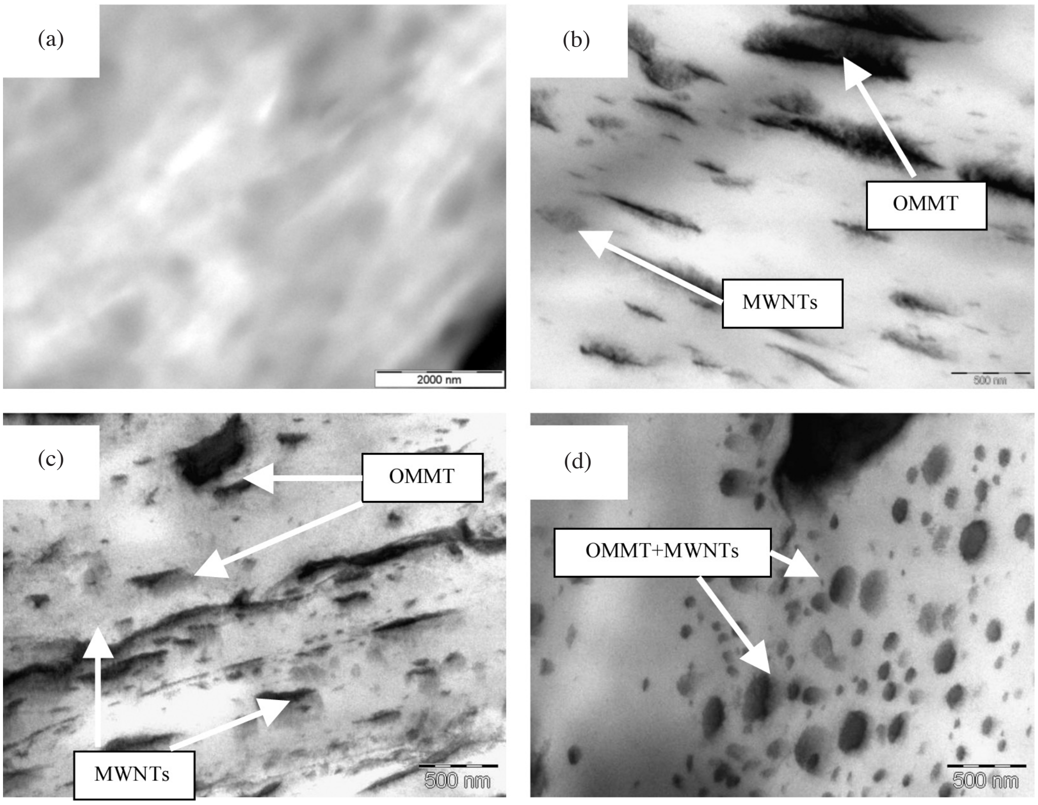

FIGURE 3. (a) TEM micrographs of TPNR and TPNR-OMMT-MWNTs hybrid nanocomposites at (b) zero h, (c) 3 h and (d) 5 h

ACKNOWLEDGMENTS

The authors would like to thank the Malaysian Government and Universiti Kebangsaan Malaysia (UKM) under Science Fund Grant UKM-OUP-NBT-29-142/2011 and UKM-OUP-2012-135 for financial support.

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Received: 21 June 2011
Accepted: 19 May 2012