Characterization of Multi-Walled Carbon Nanotubes/Natural Rubber Nanocomposite by Wet Mixing Method

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Keywords: Multi-walled carbon nanotubes, natural rubber composite, tensile strength.

Abstract. Multi-walled carbon nanotubes/natural rubber (MWCNTs/NR) nanocomposites is formed by incorporating nanotubes in a polymer solution and subsequently evaporating the solvent. Using this technique, nanotubes will be dispersed homogeneously in the NR matrix in an attempt to increase the mechanical properties of these nanocomposites. Mechanical test results show an increase in the tensile strength for up to 19 times in relation to pure NR. In addition to mechanical testing, the morphology of the MWNTs into NR was studied by Field Emission Scanning Electron Microscopy (FESEM) in order to understand the morphology of the resulting system. Slight shift noted from FTIR and Raman analyses from each different wt. % of MWCNTs with the NR due to the stress transfer that indicates reinforcement of the nanotubes.

Introduction

Natural rubber (NR) is considered one of the most important biosynthesized polymers which have excellent chemical and physical properties, such as outstanding elasticity, flexibility, antivirus permeation, and good formability and biodegradability [1]. Apart from that, NR is widely used in various areas such as tyres, gloves, sport inner liner, sealing materials and dairy rubber item [2, 3]. The raw NR is generally reinforced with fillers before being manufactured to products as the mechanical properties of raw NR including tensile strength and tear resistance in most cases cannot meet the requirements of applications. However, the reinforcement is not so effective for NR latex due to large dimension and agglomeration of these traditional reinforcing materials. Therefore, it is essential to exploit a new way to enhance the mechanical properties of rubber products. Reinforcement of rubber compounds dates back to 1904 when carbon black was used as nano-fillers. Also in present days carbon black is the principal reinforcement element for natural rubber, along with silica [4-7] and clay nanoparticles [8-11]. A huge amount of data is available on the topic, especially on the influence of surface treatment and morphology of the fillers on the reinforcing efficiency. Short fibers of various types have also been studied as reinforcing elements for elastomers [12-14]. The advantage of elongated, fibrous structures over the spherical ones has been emphasized, and the networking ability of natural fibers is particularly interesting for increasing the modulus at low filler content [15-17].

MWCNTs have long been recognized as the stiffest and strongest man-made material known to date. In addition, their high electrical conductivity has roused interest in the area of electrical appliances and communication related applications. However, due to their miniscule size, the excellent properties of these nanostructures can only be exploited if they are homogeneously embedded into light-weight matrices as those offered by a whole series of engineering polymers. MWCNTs have become a potential candidate for a wide range of application such as electronics, nanocomposite fabrication and gas storage [18-20] ever since the discovery by Iijima [21].

Compared with other nano-fillers, MWCNTs as an ideal reinforcing filler that are expected to provide a better enhancement effect in polymer nanocomposites, due to their inherent superior properties [22]. Consequently, MWCNTs have been widely exploited in different polymers. Due to very good intrinsic mechanical properties, high aspect ratio, low density, and high surface area, MWCNTs seem to be ideal candidate for the application as fillers in polymer matrices [23].

Most efforts have dealt with glassy matrices, such as polyvinyl alcohol, polymethyl methacrylate, epoxy, etc, where significant level of reinforcement has been achieved [23]. By contrast, there are few reports on using MWCNTs as reinforcing fillers in rubber matrices, although the first attempted showed that MWCNTs are very promising for this application [24].Little work has been done in the field of rubber reinforcement with MWCNTs due to their poor compatibility with NR phase. However, the improvement of MWCNTs dispersion in the polymeric matrix by forming oxygen functional groups on nanotubes surface via chemical modification plays an important role in reinforcing polymers [25-27].

In our previous work, we developed a novel process that incorporates the latex compounding and self-assembly techniques to prepare carboxylated MWCNTs with NR dispersed with sodium dodecyl sulfate [28]. It was found that the chemical and physical properties of these nanocomposites, compared with the polymer host, were significantly enhanced. In the present work, MWCNTs/NR nanocomposites will be formed by incorporating MWCNTs in a polymer solution and subsequently evaporating the solvent leading to the successful introduction of a novel self-assembly process for the preparation of MWCNTs/NRnanocomposites. The self-assembly mechanism between MWCNTs will be dispersed homogeneously in the NR matrix in an attempt to increase the mechanical properties of these nanocomposites. The impacts of MWCNTs/NR nanocomposite on the morphology and mechanical properties of the composites such as tensile strength were investigated.

Methodology

Materials. As produced MWCNTs were purchased from Shenzen Nanotech (China). The samples were synthesized by thermal chemical vapor decomposition of hydrocarbon gases and were advertised as having 10-20 nm diameter, 5-15 μm length, and 95% purity.Standard Malaysian Rubberlatex grade(SMR L)was used as the NR. The technical specification [29, 30] of the NR is given in Table 1.

Table 1. Technical specifications of SMR L

Dirt content (max. %wt)	0.03
Ash content (max. %wt)	0.50
Nitrogen (max. %wt)	0.60
Volatile matter (max. %wt)	0.80
Plasticity retention index (min. %)	30
Mooney viscosity, ML,1+4 (100°C)	78

The molecular structure of SMR L was given in Fig. 1. It is a repeating unit of isoprene monomer to form cis-1,4polyisoprene.
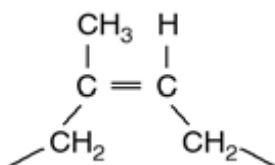

Fig. 1. Structure of SMR L

Purification of MWCNTs. Commercial MWCNTs produced by Chemical Vapor Deposition (CVD) technique may contain amorphous carbon and metallic nanoparticles (used as catalyst during synthesis) as impurities. Metal nanoparticles were removed by treating the raw nanotubes with nitric acid at 80 ^{o}C. For removal of amorphous carbon, MWCNTs were heated at 500 ^{o}C for 24 h.

Preparation of MWCNTs/NR nanocomposites. The nanocomposite (MWCNTs/NR = 1:99 w/w) was prepared according to the followingprocedures.For the preparation of composites containing 1, 3, 5, 7 and 10% of MWCNTs were dispersed in 10 ml of toluene by sonicating using a mechanical probe sonicator in order to induce an efficient dispersion of nanotubes. In order to dissolve the rubber, 10g of SMRL was added with 500 ml of toluene. This mixture was stirred and kept for certain duration of time until the rubber became uniformly dissolved in the solvent. The is the final step in the melt preparation process and basically involves thorough mixing and sonification of the solutions prepared in the first and second stages, resulting in a solution that consists of a good blend of MWCNTs in the rubber. Finally, the mixture was cast on glass plates and dried at 60°C to obtain MWCNTs/NR nanocomposite films and the films were used for further characterization studies.

Results and Discussion

Surface Morphology of MWCNTs/NR nanocomposites. The surface morphology of MWCNTs in the NR was characterized by using Field Emission Scanning Electron Microscopy (FESEM). Fig. 2 showed the lower magnification images whereas Fig. 3 showed the higher magnification images of FESEM. Fig. 2 and 3 (a) showed the images of NR without any MWCNTs used as a control for comparison with other samples at low and high magnification. Overall observed from Fig. 2 and 3, short and long MWCNTs can be seen. The MWCNTs were also homogenously distributed in the NR matrix without any obvious agglomeration.
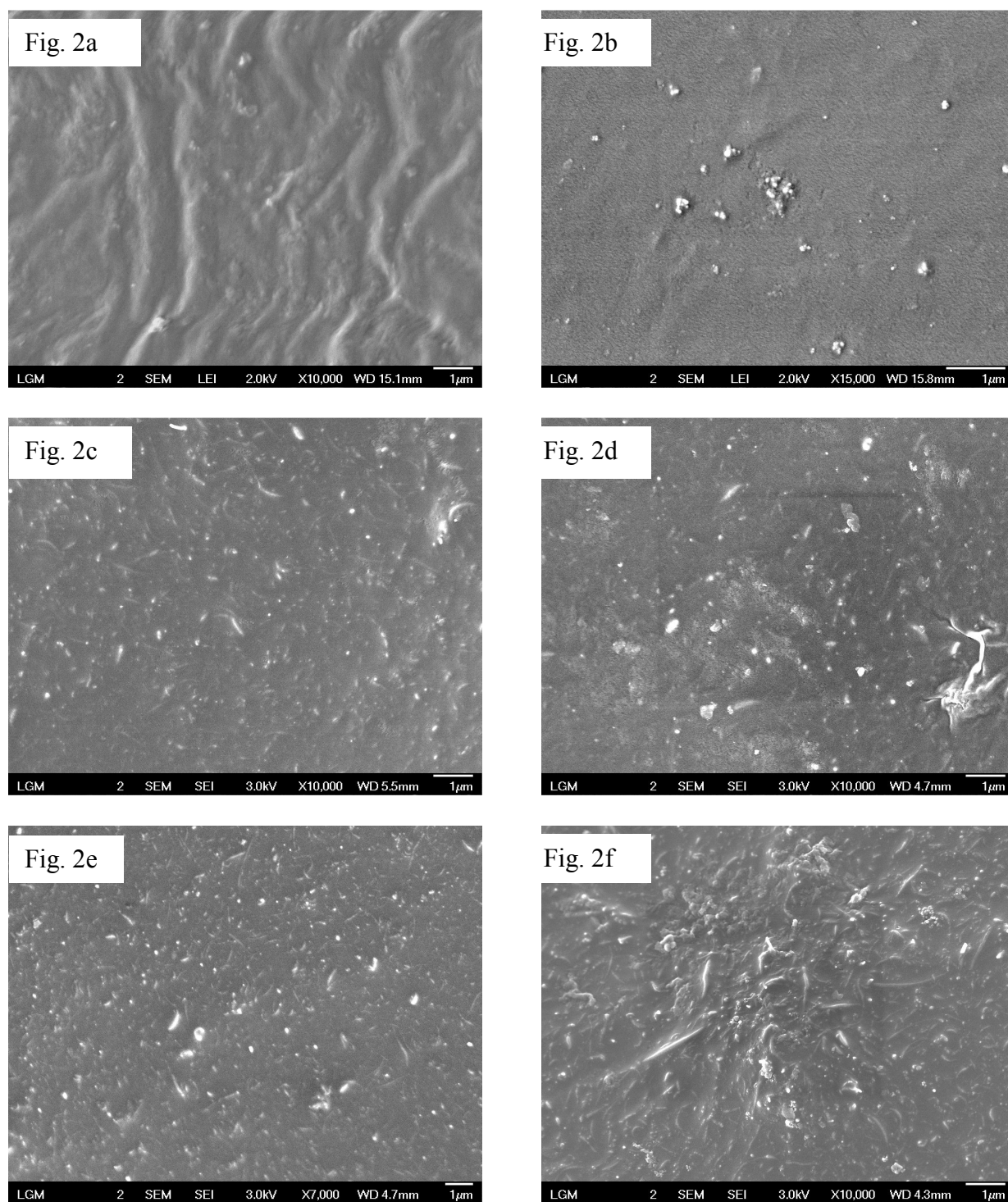
Fig. 2. FESEM images at low magnification on surfaces of MWCNTs/NR nanocomposites (a) 0%

(b) 1%, (c) 3%, (d) 5%, (e) 7% and (f) 10%.

The bright dots shown in Fig. 3 at higher magnification are the tips/ends of carbon nanotubes. The tips/ends of the MWCNTs were indicated with the black arrow as shown in the figures.
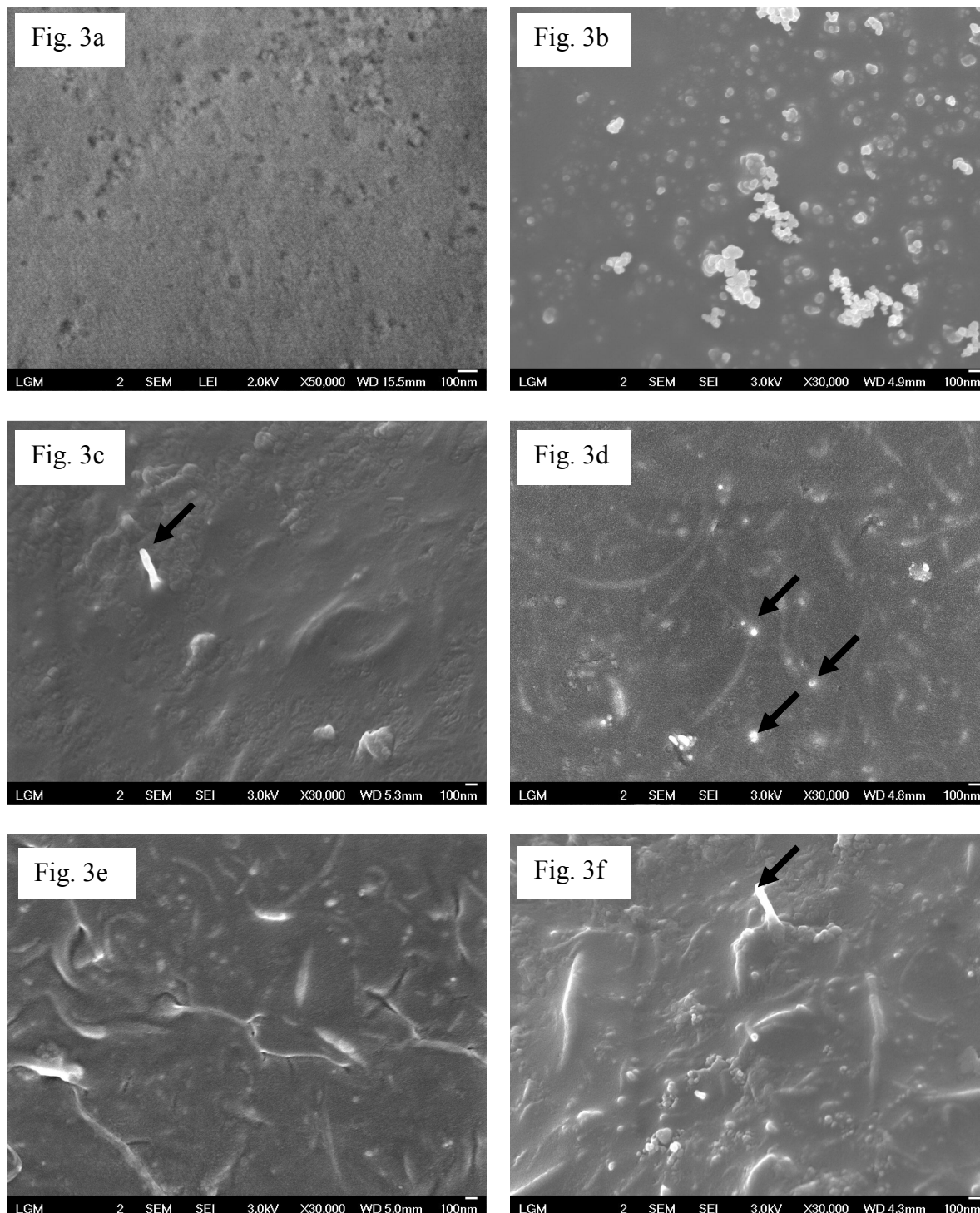

Fig. 3. FESEM images at high magnification on surfaces of MWCNTs/NR nanocomposites (a) 0% (b) 1%, (c) 3%, (d) 5%, (e) 7% and (f) 10%.

The dispersion of the MWCNTs into the toluene was carried out by using ultrasonic frequency vibration and mixing of MWCNTs in the NR matrix by mechanical stirring. The distance between the MWCNTs in the matrix was wide and that makes them well oriented with little interface interaction between them. The size of the MWCNTs in the FESEM shows variationin terms of length, which can be either short or long. Fig. 3 (b and c) shows the images of 1 and 3 wt. % where the orientations of the MWCNTs in the rubber matrix had become less oriented and more random. As a comparison from Fig. 3(d, e and f) shows the higher loading of MWCNTs in the rubber matrix at 5, 7, and 10 wt. % respectively; indicated that the orientation of the MWCNTs lesser even though the concentration of MWNTs were higher. It was also revealed from Fig. 2(d and f) that the MWNTswere forming percolating networks at 5 and 10 wt. %. However, with smaller magnification (Fig. 3d and f), the distribution of the MWCNTs were less homogeneous compared to others. Besides areas with agglomerated parts one can also observe finely distributed tubes. The arrangement of MWNTs in the rubber matrix is vital because it plays a very important role in the stress and strain of the matrix. Apart from that, it will also affect the mechanical properties.

Spectroscopic investigations. Since the mechanical properties of the nanocomposites are intimately related to the filler structure and especially to the tube surface, techniques able to bring information at a molecular level are required for a further insight into the structure or property correlation. Interactions between the nanotube bundles and the matrix were required for an efficient stress transfer from the NR matrix to the MWCNTs.

Effect of Tensile Stress on MWCNTs/NR nanocomposites. The tensile stress curve of different percentages of MWCNTs (0, 1, 3, 5, 7 and 10 wt. % of MWNTs) with NR was presented in Fig. 4. The tensile strength radically increases as the amount of MWCNTs concentration increases. From the figure,the maximum stress of pure NR was 0.32 MPa. When 1 wt % of MWNTs were added to

the rubber the stress level for the nanocomposite material increased to 3.16 MPa. Addition of the wt.

% CNTs to the natural rubber increased the stress level gradually as shown in the figure. At 3 wt %

of CNTs the stress value obtained reached 6.17 MPa which was 19 times higher than pure NR. This

is probably due to less agglomeration of MWCNTs networking in the rubber matrix compared to

other concentration. The general tendency was that the stress level increased by the addition of

MWCNTs which plays the role of reinforcement. However, at 5, 7 and 10 wt. % of MWNTs, the

tensile stress decreased upon higher loading of MWCNTs which probably due to high agglomeration

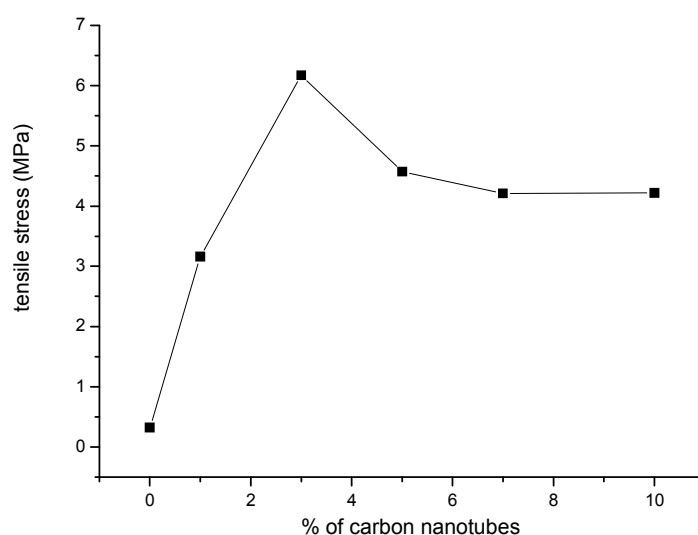of MWCNTs bundles in the polymeric matrix as observed from the FESEM images.

Fig. 4. Tensile stress of MWCNTs/NRnanocompositeswith different percentage of MWCNTs.

Generally, the increased level of tensile was due to the interaction between the MWCNTs and the

rubber. A good interface between the MWCNTs and the rubber is very important for a material to

withstand the stress. As described above MWCNTs are extremely strong materials compared to other

types of fillers, thus making them good candidates as nanofillers. Under load, the matrix distributes

the force to the MWCNTs which carry most of the applied load.

Fig. 5 illustrated the sketch diagram of NR/MWNTs with optimal dispersion in composites made by mixture where MWCNTs discretely embedded in the polymer matrix. It has been speculated that the waviness of the tubes could also be mitigated owning to the restriction of nearby framework. One key determining the mechanical performance of such composites is the strengths of MWCNTs network's junctions. In this study, the MWNTs have self-assembled into continuous networks through the dispersion of nanotubes bundles of. Under the assistance of MWCNTs-affinitied solvent, the natural rubber molecules were intercalated into the interspaces of MWCNTs network in their high viscosity in liquid state.

Fig. 5. Schematic illustration of MWCNTs/NRnanocomposites.

ATR-FTIR Spectroscopy. Carbon-filled polymers are optically opaque and consequently difficult to analyze by the transmission technique unless measurements are carried out through thin sample. Attenuated total reflectance method has been shown to yield useful information on these systems. ATR spectra carried out on samples around 200 mm thick of pure natural rubber and with different wt. %of MWCNTs contents was displayed in Fig. 6.
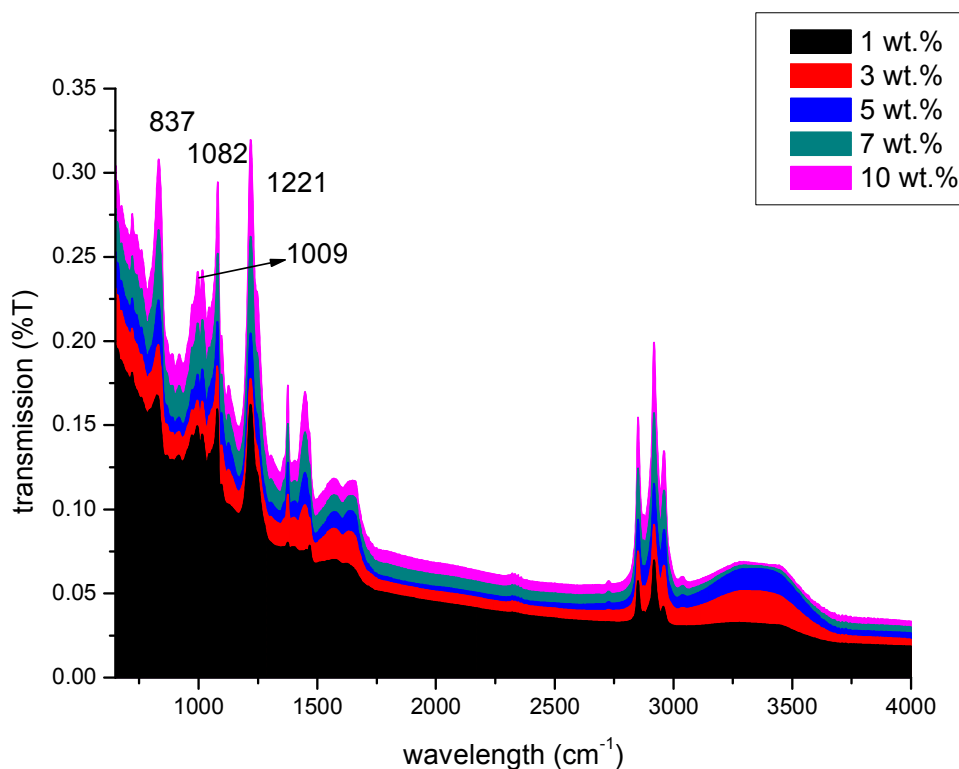
Fig.6. ATR-FTIR spectra of (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.%, (d) 7 wt.% and (e) 10 wt.% of

MWCNTs/NR nanocomposites.

Because of its microstructure, NR displays a unique important characteristic, which is the capability

to distinguish the characteristic of natural rubber polymeric chains and MWCNTs. The peaks

observed from 1009, 1082 and 1212 cm^{-1} contributed from the solvent residual used in the

preparation of the MWCNTs/NRnanocomposites. The peaks at 1378 cm^{-1} attributed to C-H

stretching. Features at 1569 and 1658 cm^{-1} attributed to vibrational modes (C=C) which due to

carbon skeleton of MWCNTs [31] that further confirmed the presences of MWNTs in the

nanocomposite.The presences of NR polymeric chain can be detected by infrared spectroscopy since

the band associated with the C–H out of- plane bending mode of the cis-isoprene unit, located at 837

cm^{-1} [32-34]. ATR measurements were made possible on thin films (thickness around 80 mm) and

polymer containing low filler content. The change in wavenumber upon stretching occurs at a lower

extension ratio for the MWNTs/NRnanocomposites. It is most likely attributed to the fact that the polymer chains in the nanocomposites are more oriented than in the unfilled sample, the orientation being induced by the uniformity of the MWCNTs.

Raman Spectroscopy. Interactions between the nanotube bundles and the matrix are required for an efficient stress transfer from the matrix to the nanotubes. Raman spectroscopy has proved to be very sensitive for an evaluation of the strength of the between the polymer and filler interface. In fact, carbon nanotubes exhibit well-defined Raman peaks located for our MWCNTs at 1376-1513, 1617-1744 and small but noticeable peaks at 2732-2841 cm^{-1}, respectively, assigned to the disordered graphite structure (D band), tangential stretching mode of carbon-carbon bonds (G band) and to the overtone of the D band (G' band) as shown in Fig. 7.
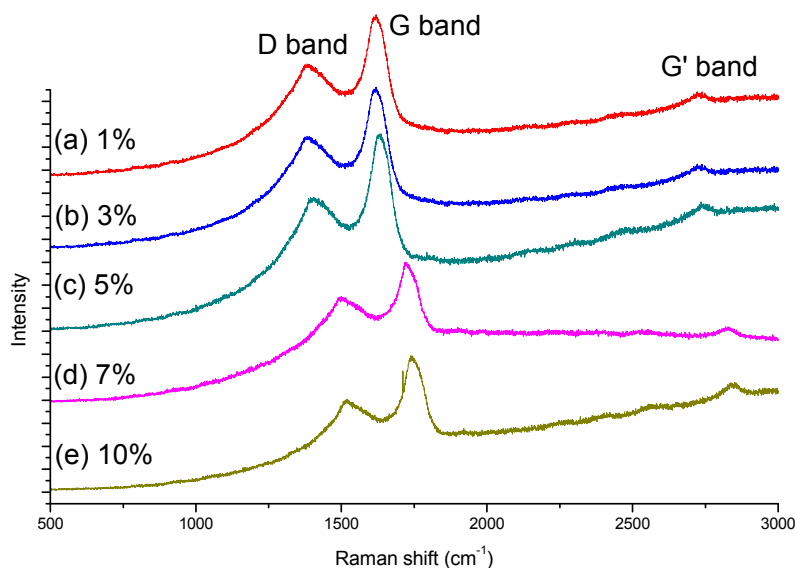

Fig.7. Raman spectra of (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.%, (d) 7 wt.% and (e) 10 wt.% of MWCNTs/NR nanocomposites.

Slight shift noted from each different wt. % of MWCNTs with the NR. The shift shows the stress transfer from the matrix to the nanotubes and hence indicates reinforcement of the MWCNTs in the rubber matrix. The G' band will shifts to a lower wavenumber upon application of a tensile stress on composites based on epoxy resins and single or MWCNTs [35]. Nevertheless, the rates of band shift were found to differ for all the samples probably due to poor dispersion and lower aspect ratio were invoked to account for smaller shift rate.

Summary

In this paper, results obtained on MWNTs reinforced in NR are presented. The MWNTs/NR nanocomposites have been prepared by wet mixing method. The strong self-aggregation of MWCNTs has been greatly depressed and MWCNTs are homogenously distributed throughout the NR matrix as individual nanotubes, due to an excellent interfacial adhesion of MWCNTs with NR phase. The nanocomposites showed a very high degree of increase in tensile stress in the rubbery region at room temperature. The result indicates that, by increasing the amount of MWCNTs added into the rubber the ductility decreased and the material become stronger and tougher but at the same time more brittle. Slight shift noted from each different wt. % of MWCNTs with the NR. The shift observed in Raman analyses due to the stress transfer from the rubber matrix to the nanotubes which indicates reinforcement of the MWCNTs.The MWCNTs/NR nanocomposites have great potential to manufacture products with high mechanical performances and for smart material applications.

Acknowledgement

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