

Effect of multi-walled carbon nanotube on mechanical and rheological properties of silane modified EPDM rubber

Fateme Khademeh Molavi^{1*}, Sedigeh Soltani¹, Ghasem Naderi¹, Rohollah Bagheri²

¹Iran Polymer and Petrochemical Institute, P.O. Box 14185/458, Tehran, Iran

²Departments of Chemical Engineering, Isfahan University of Technology, P.O.Box8415683111, Isfahan, Iran

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ABSTRACT

A novel approach for achieving a good dispersion of multi-walled carbon nanotubes (MWCNTs) within the ethylene-propylene diene monomer (EPDM) matrix has been investigated. In this approach, EPDM was modified with vinyltrimethoxysilane (VTMS) through a melt mixing process. In addition, the effect of MWCNTs concentration on the mechanical and rheological properties of the modified EPDM has been studied. The formulated composites exhibited significantly enhanced physical properties even at very low nanotube concentrations. The occurrence of the grafting reaction was confirmed by the Fourier transform infrared spectroscopy (FTIR) peaks at 1070 and 1250 cm^{-1} according to the Si-O and Si-C vibrations. The state of dispersion of the fillers in the polymer matrix was evaluated through transmission electron microscopy (TEM) and scanning electron microscopy (SEM), in addition surface topology was studied by atomic force microscopy (AFM). The results showed that the VTMS grafted on the EPDM surface improved the dispersion of MWCNTs in the matrix. The rheological characteristics have been studied by rubber process analyzer (RPA). At the low frequencies, the effect of increasing the MWCNT content was significantly high so that the storage modulus (G') and complex viscosity (η^*) increased but the difference in storage modulus and complex viscosity values reduced as the frequency was increased. It was found that at concentration of 1.5 wt% of MWCNT, the nanocomposites exhibited remarkable improvements in the mechanical properties such as modulus and tensile strength. **Polyolefins J (2016) 3: 69-77**

Keywords: EPDM; multi-walled carbon nanotube; rheological characteristic; mechanical properties

INTRODUCTION

Rubbers are desired in many industries because of some especial properties such as high and reversible deformability [1]. Rubbers are generally compounded with reinforcing fillers because of their low elastic modulus. Thus, the reinforcement is one of the most important processes in rubber industry [2]. The reinforcing characteristics of conventional fillers such as carbon black (CB) and silica have been widely demonstrated in the

literature [3-6]. Generally, it is desirable that the reinforced rubbers show an increase in modulus, hardness, tensile strength, abrasion and tear resistance as well as resistance to fatigue and cracking [1, 2]. But, only some of these properties are significantly improved by the reinforcing fillers since the discovery of carbon nanotubes (CNTs) by Iijima [7-9].

CNTs have good physical and mechanical properties and are widely used as the reinforcing materials in polymer matrices [10, 11] to obtain ultra-light structural

* Corresponding Author - E-mail: f.molavali@ippi.ac.ir

materials with enhanced electrical, thermal and optical characteristics. There are two main types of nanotubes: Single-walled carbon nanotubes (SWCNTs), individual cylinders of 1-2 nm in diameter, which are actually a single molecule, and multi-walled carbon nanotubes (MWCNTs), which are a collection of several concentric graphene cylinders [11].

Improvement of physical-mechanical properties of polymer nanocomposites by introduction of CNT depends on the dispersion of CNT in the matrix and interfacial interactions between them. In order to be compatible with the non-polar polymers, CNT modification with surfactants or compatibilizers is essential [8, 11].

Agglomeration of CNTs and weak interfacial interactions between the CNTs and matrix are the main problems in the fabrication of CNT-reinforced composites [12-15]. Non-polar rubbers and CNTs are incompatible due to differences in their chemical nature and polarity, thus, it is hardly possible to obtain a uniform dispersion of CNTs. Poor adhesion between CNTs and rubber matrix prevents the break-up of CNT aggregates resulting in poor dispersion of CNTs and insufficient reinforcement [8].

Coupling agents are suitable modifiers improving the interfacial interaction between filler and matrix in order to obtain composite materials with desirable properties. They provide a chemical bond between inorganic and organic materials. In rubber composites, the interaction between rubber and filler leads to increasing modulus and tensile strength properties [12, 13]. Compatibilization of rubber/CNT composites using a suitable coupling agent is a well-established method for changing the surface energy of the CNTs and improving their wetting or adhesion characteristics. In addition, it reduces the tendency to agglomerate in the polymer matrix [8, 12].

Coupling agents containing alkoxy silane functionalities are effective in improving physical properties of composites. The interaction between functional groups of a coupling agent and carboxyl or amine groups of CNTs can establish a well-dispersed morphology. It can improve the interfacial interaction between CNT and polymer matrix [8]. One of the most promising candidates to improve the composite properties, especially the nanotube composites, is vinyl trimethoxysilane (VTMS) [12, 16]. Kumar et al. synthesized a new copolymer of vinyloxyaminosilane grafted EPDM using dicumyl peroxide (DCP) initia-

tor. The mechanical, thermal and electrical properties of the copolymer were determined for some engineering applications [17].

Desai and Haque did a review on the mechanics of the interface for carbon nanotube-polymer composites. As a result, the strength of the interface and the nature of interaction between the polymer and CNT are the most important factors governing the ability of nanotubes to improve the performance of the composite [18]. Kim et al. fabricated aligned CNT-based EPDM sheets in a controllable direction. The selective alignment of CNTs led to enhancements in the elastic modulus, thermal and electrical conductivity and electromagnetic shielding property compared to those of pure rubber sheet [19]. Lorenz dispersed MWCNT in ethanol as a dispersion agent by sonication, then the paste was mixed with EPDM matrix using an internal mixer. The electrical properties were found to decrease by using solvent, compared to dry mixing [20].

In the present study, the influence of MWCNT on the mechanical and rheological properties of VTMS-g-EPDM/MWCNT is investigated at various concentrations. EPDM, an unsaturated polyolefin rubber, has attracted much attention for outdoor applications. This is due to its remarkable ability to accept high loading of fillers [15, 21]. The morphologies of modified and un-modified EPDM matrices were studied by SEM, TEM and AFM techniques. The main aim of this work is to improve these properties of EPDM/MWCNT composites by grafting VTMS onto the polymer during melt mixing using a special procedure at various amounts of nanotubes.

EXPERIMENTAL

Material

Commercial grade of EPDM rubber used in this study (KEP 270), containing 57% ethylene, 4.5% ethylenedene norbornene (ENB) with a moony viscosity ML (1+4) of 71 at 125°C, was supplied by Kumho Petroleum Chemical Co. Ltd., Korea. Functional MWCNT (functionalized with carboxylic acid groups, f-MWCNT) was purchased from Neutrino Co. China (average diameter 8-15 nm, length ~ 50µm and 98.9% purity). Vinyltrimethoxysilane (VTMS) was purchased from Merck Co. Dicumyl peroxide (DCP, $t_{1/2}$ (175°C) = 1 min) was commercially available. All other compounding ingredients such as stearic acid, trimethyl-

quinoline (TMQ), zinc oxide (ZnO), sulfur (S), tetramethylthiuram disulfide (TMTD) and 2-mercapto benzothiazole (MBT) were all supplied by Bayer Co., Germany.

Preparation of the sample compounds

The melt mixing process was carried out at two separate stages using an internal mixer (Haake- Buchler Rheomix 750, Germany) and a laboratory-sized (160mm×320mm) two roll-mill machine model Polymix 200L. In the first stage, EPDM was placed in the internal chamber at 125°C with rotor speed of 60 rpm. It was performed for 5 min, then the mixture of VTMS and DCP was added into the internal mixer. The obtained mixture was mixed at 175°C for another 10 min. During the process, the grafting reaction of VTMS on EPDM could occur under the initiation of DCP. After reaching a temperature of approximately 180-185°C, the functionalized MWCNT (f-MWCNT) was added. The composite product was finally removed from the mixer after 17 min mixing time and cooled down to room temperature. In the second stage, all other ingredients such as zinc oxide, stearic acid, sulfur, TMTD and MBT were added on a laboratory-sized two-roll mill at roll speed 50 rpm and temperature 40±5°C for 10 min. The nip gap, mill-roll speed ratio, mixing time, temperature and sequence of mixing were kept constant for all the compounds. Rubber mix was then removed and cooled down to room temperature. The sheeted rubber compound was conditioned at room temperature (25°C) for 24 h before vulcanization. The curing characteristic of the compounds were determined by using a Moving Die Rheometer (MDR 2000), then vulcanized at 160°C with a hot press. The sample formulations employed in this study are given in Table 1.

Table 1. Composition of the EPDM/MWCNT composites.

Composition (phr) ^(a)	ESM-0 ^(b)	ESM-1	ESM-1.5	ESM-2	UEM-1.5 ^(c)
EPDM	100	100	100	100	100
MWCNT	0	1	1.5	2	1.5
ZnO	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1
MBT	0.8	0.8	0.8	0.8	0.8
TMTD	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5

^(a) Parts per hundred of rubber

^(b) VTMS-modified EPDM

^(c) Unmodified EPDM

Characterization

Prior to the FTIR measurement, the grafted samples were under extraction in boiling xylene for 6 h and then the extracted fraction precipitated into methanol to remove the un-grafted VTMS monomers. Afterwards, the samples were pressed to get thin films for the FTIR analysis. The FTIR spectra were obtained using an FTIR spectrophotometer on Nicolet Magna 550 series II (Nicolet Instrument Corporation, Madison, WI, USA) in the absorbance range 4000- 400 cm⁻¹.

Tensile tests were performed using an Instron machine HIWA 200 at a cross-head speed 500 mm/min according to ASTM D 412. Data such as tensile modulus (M100 and M200), tensile strength and elongation-at-break (Eb) were obtained from the testes. In addition, the hardness was measured at room temperature using a Shore A hardness tester (Zwick Company, Germany), according to ASTM D2240.

Morphological characterization of fractured composite surfaces was investigated using a Cambridge Stereo Scan 360 scanning electron microscope (SEM) and an atomic force microscope (AFM) model DS-95-200E. The fractured pieces were coated with a thin layer of gold-palladium to avoid electrostatic charge build-up during examination. The AFM was also used to visualize the surface topology at room temperature. A nano-sensor cantilever with a typical static load of 10 nN and dynamic frequency of 190 kHz was used. The samples first were cut with a metal knife in cryogenic condition at -100°C to obtain a smooth surface before examining by AFM. In addition the samples for TEM analysis were prepared by ultracryo-microtomy using Leica Ultra cut UCT (Wein, Austria). Freshly sharpened glass knives with cutting edge of 451 were used to get cryosections of 50–70 nm thickness. The cryosections were collected and directly supported on a copper grid of 300 mesh size. The microscopy was performed latter using JEOL-2100 electron microscope (Japan), having Lab 6 filament, operating at an accelerating voltage of 200 kV.

The rheological characterization of the samples was carried out using a stress controlled rheometer (RPA 2000). Experiments were done at a temperature of 50°C and in the angular frequency range of 0.01-32 Hz at constant strain of 5% to assure that it was in the range of linear viscoelasticity. The elastic modulus (G') and complex viscosity (η^*) of the compounds were characterized.

RESULTS AND DISCUSSIONS

The mixing torque-time curves of the composites with various amounts of f-MWCNTs are shown in Figure 1. It can be seen that the curves show two sharp peaks. The first peak at a mixing time of approximately 1.3 min is related to the incorporation of un-melted rubber into the mixing chamber. A decrease in mixing torque is then observed due to the melting of rubber material and with a subsequent sharp increase at a mixing time of approximately 6.7-7.2 min. This is due to grafting reaction of VTMS on the EPDM matrix. Thereafter, the increase in torque, related to the incorporation of multi-walled carbon nanotubes into the mixing chamber, is observed up to the mixing time of approximately 11 min and the gradual decrease in torque is occurred and finally the curve becomes almost plateau. From Figure 1, it is also seen that the ESM-2 sample exhibits higher mixing torque compared to that of the others. This may be attributed to the higher chemical interaction between the functional groups present in the MWCNTs and EPDM-g-VTMS molecules [8, 23]. The possible chemical interaction between functional groups of MWCNT and EPDM-g-VTMS is shown in Figure 2. This interaction creates stronger links at the interfaces of EPDM and f-MWCNTs. This may cause an increasing trend of mixing torques. Furthermore, it can be seen that the mixing torque of the samples increases proportionally with increasing f-MWCNTs. Grafting of VTMS on EPDM in the presence of DCP was carried out through the melt process. Figure 3

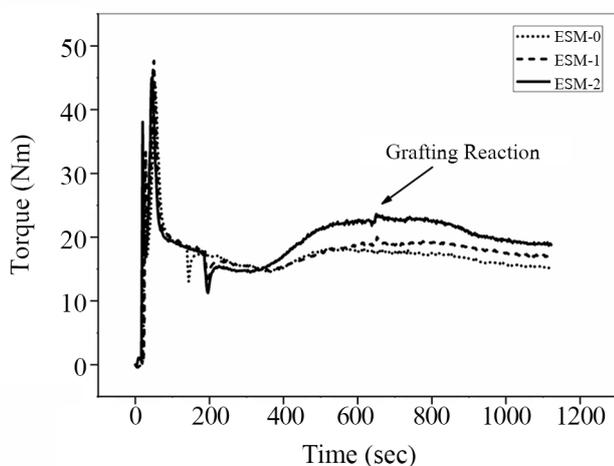


Figure 1. Relationship between mixing torque-time of VTMS-g-EPDM/MWCNT composites with various amounts of MWCNT.

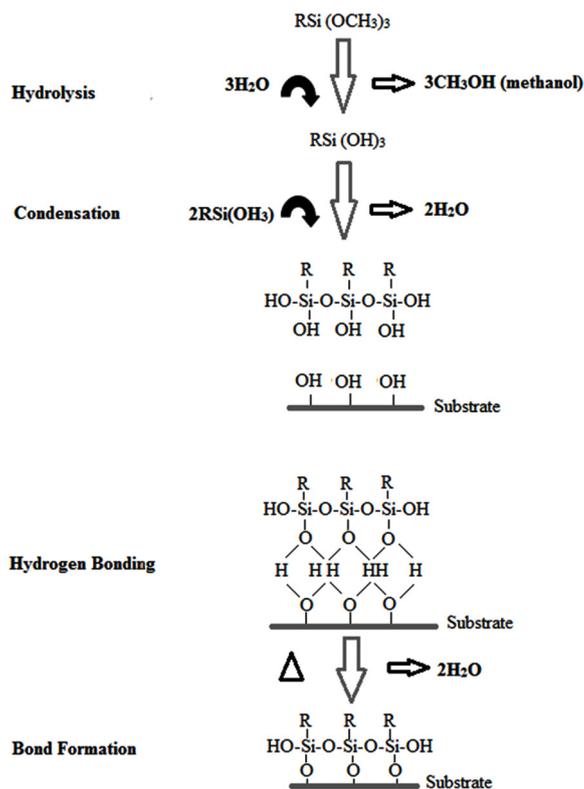


Figure 2. Schematics of the possible interaction between functional groups of MWCNT and EPDM-g-VTMS.

shows the FTIR spectra of EPDM and VTMS-grafted EPDM. The IR spectra of EPDM (Figure 3a) shows the C-H stretching vibration at 2926 cm^{-1} , -CH_2 rocking vibration at 1457 cm^{-1} , CH_3 symmetric bending vibration at 1370 cm^{-1} due to the presence of propylene group, $\text{-(CH}_2\text{)}$ wagging vibration at 730 cm^{-1} due to the presence of polyethylene chain, C-C stretching vibra-

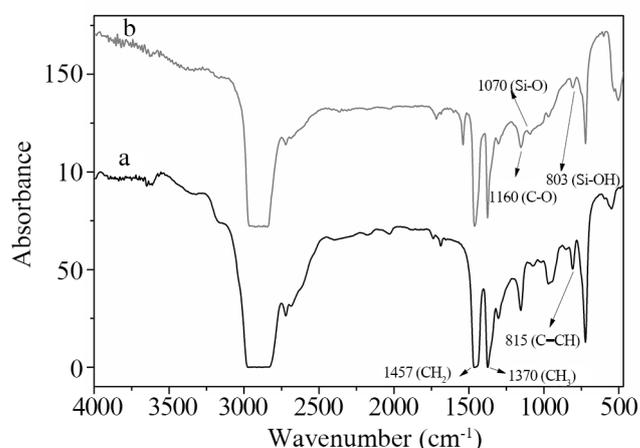


Figure 3. FTIR spectra of (a) pure EPDM, (b) Extracted EPDM-g-VTMS.

tion at 2854 cm^{-1} and the unsaturation band ($\text{C}=\text{CH}$) at 815 cm^{-1} due to the presence of ENB content.

Figure 3b presents the IR spectra of VTMS-grafted EPDM: C-H stretching vibration at 2926 cm^{-1} , $-\text{CH}_2$ rocking vibration at 1460 cm^{-1} and $-\text{CH}_3$ symmetric bending vibration at 1365 cm^{-1} . However, C-H stretching vibration at 3265 cm^{-1} , C=C stretching vibration at 1663 cm^{-1} , $-\text{CH}_2$ wagging vibration of $\text{Si}-\text{CH}=\text{CH}_2$ at 930 cm^{-1} and Si-OH vibration at 803 cm^{-1} appeared due to grafting of VTMS with the unsaturated group in the side chain of ENB termonomer at 815 cm^{-1} without affecting the Si-O stretching vibration at 1070 cm^{-1} . The results show that a new chemical bond is formed with VTMS. On the other hand, the presence of absorption peaks at 1070 and 803 cm^{-1} are due to the Si-O and Si-OH vibration, indicates that the grafting reaction of VTMS on EPDM chain is done successfully [8,9].

The effect of nanotubes on the mechanical properties of EPDM/MWCNT is illustrated in Figures 4-6. In Figure 4, the tensile strength of the composites increases gradually with increasing of MWCNTs. Comparing with pure EPDM, the tensile strength of the composite filled with 2 phr MWCNTs is increased by 182%. It was expected that the tensile strength values would increase with the increase of MWCNT concentration, which would be due to the strong and stable Si-O-Si networks formed by VTMS-g-EPDM and functional groups of MWCNT. It is well known that the properties of a rubber are controlled by the nature and the degree of crosslink in the network and filler-polymer interactions [6]. In this case, the main factors that influence the strength of rubber composites are the chemical interactions between the nanotubes and rubber chains.

The VTMS introduced on the surface of EPDM

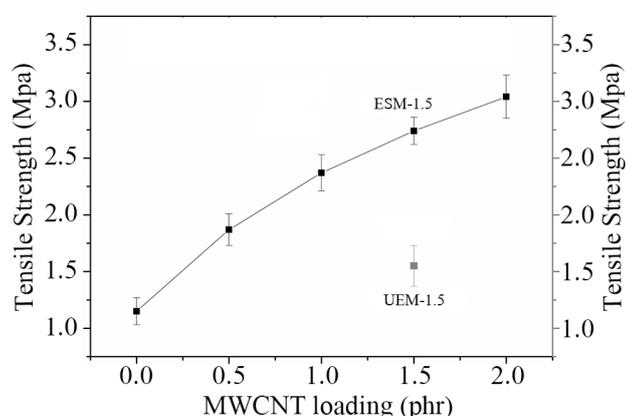


Figure 4. Tensile strength results for EPDM/MWCNT composites as a function of MWCNT concentration.

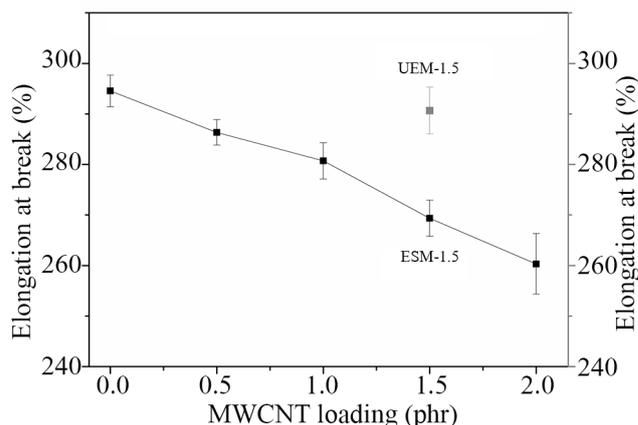


Figure 5. Elongation-at-break results for EPDM/MWCNT composites as a function of MWCNT concentration.

could result in physical adsorption and chemical interaction between the CNTs and rubber chains and cause a restriction in the mobility of the rubber molecules. On the other hand, the functionalized CNTs with high aspect ratio may also provide some physical crosslinks in the vulcanized filled EPDM, which provide a higher modulus compared to that of unfilled EPDM [6, 24].

Effect of additives on the physical and chemical crosslinks of the chains plays an important role at the beginning of the deformation and compared to unfilled EPDM the presence of additives leads to a higher modulus.

The elongation-at-break (E_b) of the EPDM/MWCNT composites at different MWCNT concentrations is shown in Figure 5. It can be seen that, as the MWCNTs content increases, stiffening effect of MWCNTs becomes more apparent, which, consequently, leads to a reduction in elongation-at-break. It is probably due to the stronger adhesion between the nanotubes and rubber matrix or by the formation of the rigid Si-O-Si

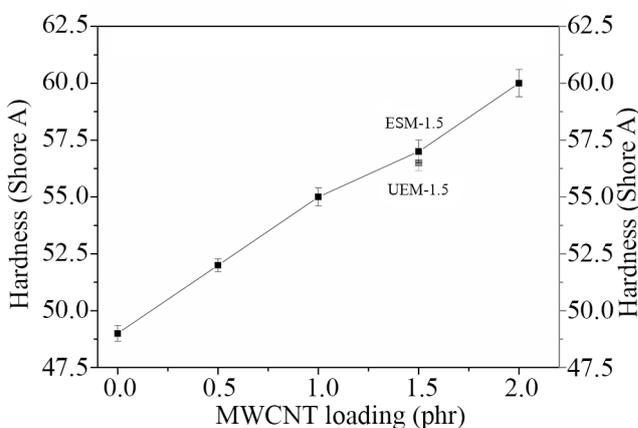


Figure 6. Hardness results for EPDM/MWCNT composites as a function of MWCNT concentration.

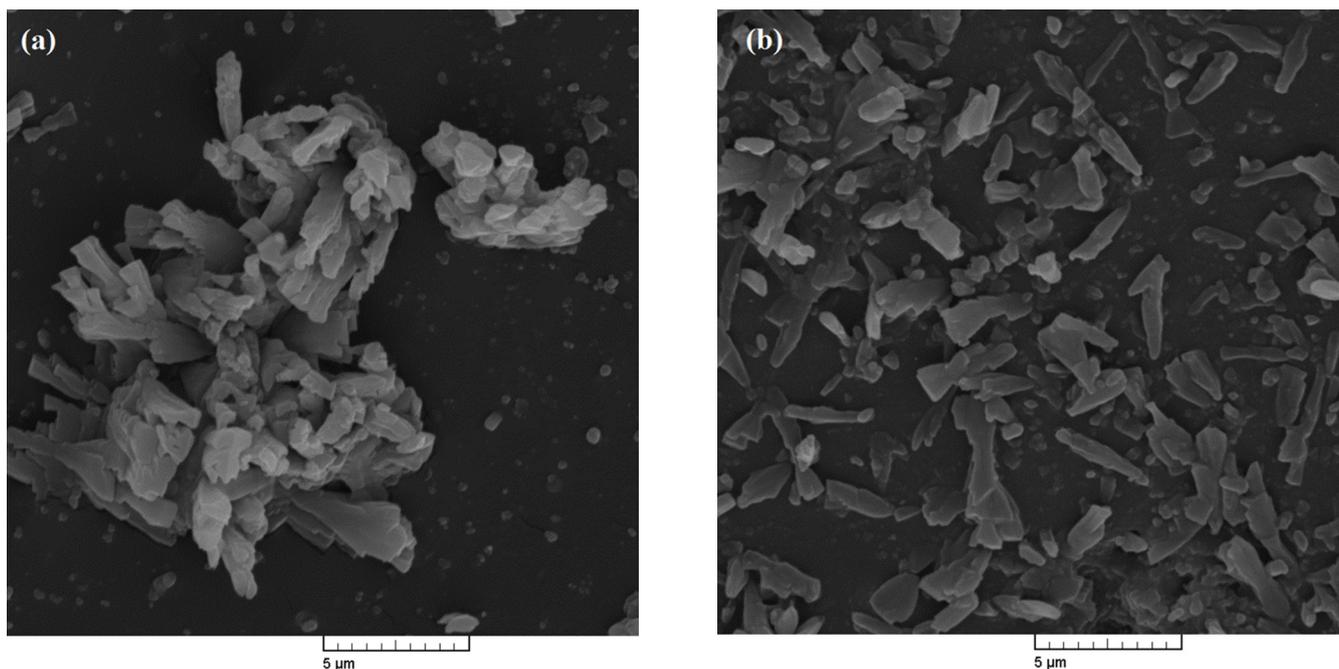


Figure 7. SEM images of the fracture surfaces of the EPDM/MWCNT composites: UEM-1.5, (b) ESM-1.5.

networks, resulting a decrease in elongation-at-break.

The hardness of the EPDM/MWCNT composites at different MWCNT concentrations is also shown in Figure 6. It can be seen that, the hardness of the composites increases linearly with increasing MWCNTs content. The improvement in hardness can be attributed to the high strength and Young's modulus of the MWCNT additive.

Morphological examination is a key method for the investigation on the dispersion characteristics of CNTs in the matrix [8]. The fracture surface of EPDM and EPDM-g-VTMS composites containing 1.5 wt% of f-MWCNT are shown in Figure 7 (a, b). For the EPDM/MWCNT sample which does not contain grafted VTMS (Figure 7a), a large amount of partially agglomeration is observed on the fracture surface. Figure 7b presents a highly uniform distribution of MWCNTs with a small amount of aggregate in the EPDM matrix. In the VTMS-grafted EPDM, the dispersion of MWCNTs in the matrix is improved in compare to the un-modified matrix (UME-1.5). It is concluded that, size of aggregates is reduced and a homogenous dispersion is obtained through the grafting of VTMS into the matrix. This observation is attributed to the stronger chemical interactions between carboxyl groups of MWCNT and VTMS-grafting EPDM chains that lead to formation of well wetted nanotube particles with homogeneous dispersion in the matrix. Therefore, the MWCNT dispersion in the VTMS-grafted EPDM is

finer than that in pure EPDM.

The TEM image of the 1.5 wt% MWCNT/EPDM-g-VTMS sample is shown in Figure 8. It shows a fine and homogeneous distribution of MWCNTs throughout the EPDM matrix. Individual CNTs are randomly dispersed (without preferred alignment or orientation after melt compounding) within the matrix and no CNTs aggregation is observed. The TEM image also confirmed the interaction of CNT particles with the surface of the EPDM-g-VTMS matrix as the mechanical properties were also improved.

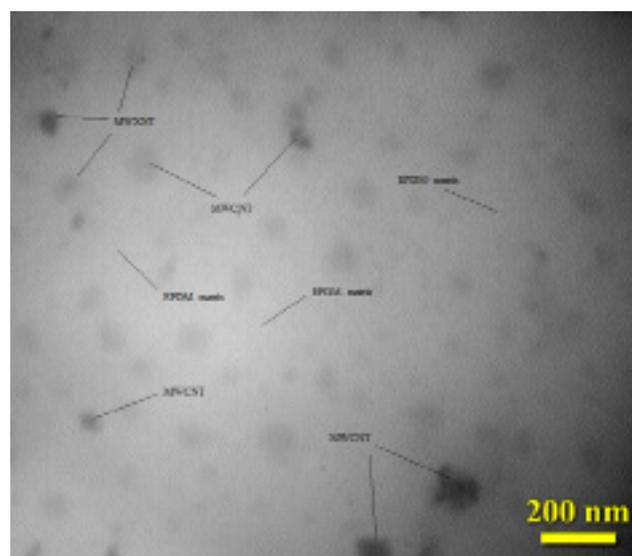


Figure 8. TEM image of the EPDM-g-VTMS/MWCNT composite (ESM-1.5).

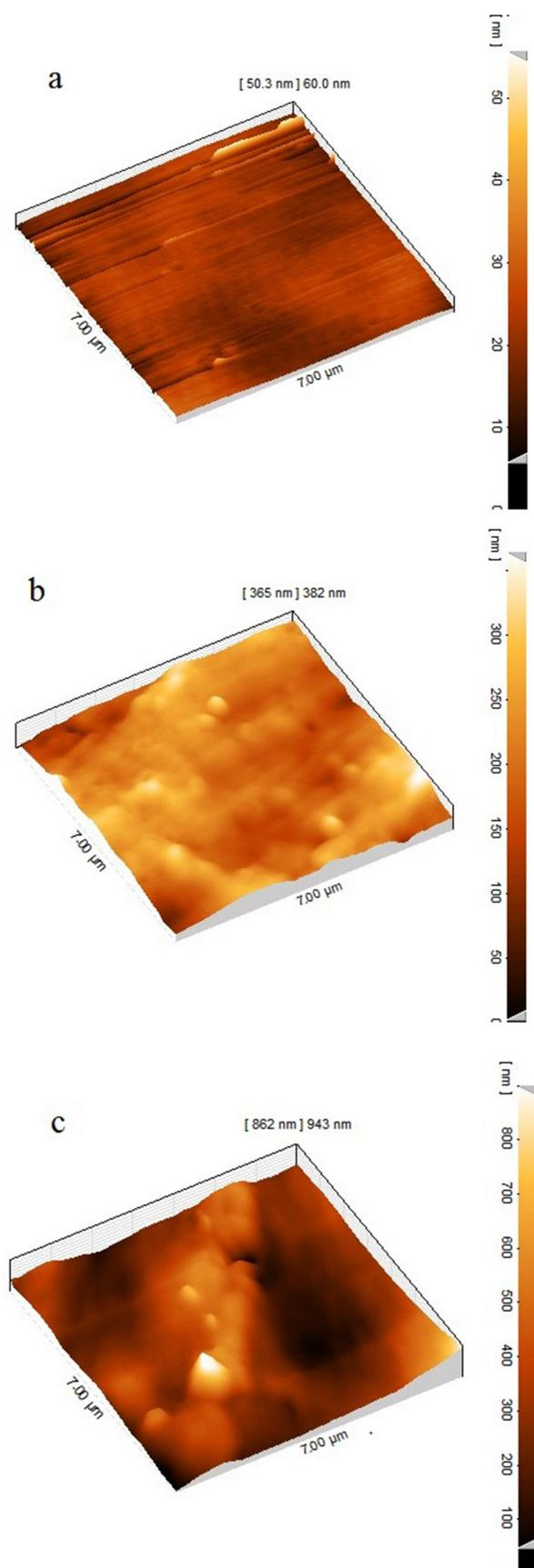


Figure 9. AFM topography images of the fracture surfaces of the EPDM/MWCNT composites: (a) ESM-0, (b) ESM-1, (c) ESM-1.5.

Additional information on how the nanotubes are actually changing the stiffness of the polymer matrix can be obtained from atomic force microscopy. AFM topography of un-filled EPDM (ESM-0) and EPDM containing various amounts of MWCNTs are presented in Figure 9. The bright parts, representing nanotube particles, are located at the elevated position relative to the EPDM matrix. The height of these bright parts varies from place to place depending on the connectivity between the MWCNT particles forming the structure and MWCNTs location. Comparison of these images clearly demonstrates the marginal enhancement of micro roughness of the modified surfaces (b, c) with un-filled EPDM (a).

In general, rheological analysis provides a better understanding of structural features such as dispersion degree of a filler in a matrix, wet ability of a filler, matrix/fiber interaction and process ability of composites. First, the linear viscoelastic range (where the properties are independent of strain) was determined by a strain sweep test. The frequency sweep test (Figure 10) was then conducted to obtain the corresponding curves for storage modulus (G') and complex viscosity (η^*) of the MWCNT/EPDM composites containing VTMS-g-EPDM. As it is observed, at the low frequencies, the effect of composition is pronounced so that the modulus and viscosity increase significantly but the difference reduces as the frequency is increased. The interaction between MWCNTs and matrix can be attributed to a good dispersion of MWNTs into the matrix. The viscosity of the VTMS-g-EPDM without MWCNTs (ESM-0) exhibited a Newtonian behavior at low frequencies, while the viscosity of all the other composites showed a shear thinning behavior over the entire range of shear rates studied here. As it is

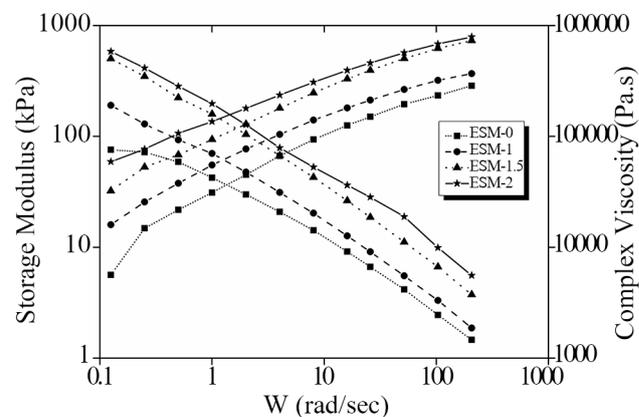


Figure 10. Rheological properties of the EPDM/MWCNT composite as a function of MWCNT concentration.

predicted the rheological behavior of both compounds ESM-1.5 and ESM-2 are quite similar.

As it is observed, by increasing the MWCNT loading, the storage modulus and complex viscosity are increased. This can be related to the homogeneous dispersion of the MWCNTs in the matrix and the strong interactions between VTMS-g-EPDM matrix and functional groups of MWCNTs. On the other hand, the improved interfacial interactions due to the VTMS-g-EPDM as matrix decreased the mobility around the MWCNTs, and therefore the increase in the storage modulus and complex viscosity was also observed.

CONCLUSION

EPDM was modified with vinyltrimethoxysilane (VTMS) through melt mixing process by a novel approach. The occurrence of the grafting reaction between VTMS and EPDM chains was confirmed by the FTIR peaks at 803, 1070 and 1250 cm^{-1} corresponded to the Si-OH, Si-O and Si-C stretching vibration. The effect of the MWCNTs concentration on the mechanical and rheological properties of the modified EPDM was also studied. The mechanical properties such as tensile strength were improved, whereas elongation-at-break was decreased. The morphological investigations carried out by TEM and SEM revealed a homogeneous dispersion of MWCNTs within the EPDM matrix. The increase in the storage modulus (G') and complex viscosity (η^*) of the composites could be attributed to the good interaction between MWCNT and EPDM.

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