

Morphology, Barrier, Mechanical and Electrical Conductivity Properties of Oil-Extended EPDM/MWCNT Nanocomposites

Neha Jha, S. P. Mahapatra



ABSTRACT: Oil-extended ethylene propylene diene monomer (EPDM) elastomer nanocomposites have been made by using multiwalled carbon nanotube (MWCNT) nanofiller as a reinforcing agent. The effect of MWCNT concentration on morphology, bound rubber, swelling, and mechanical properties have been studied. EPDM/MWCNT interactions have been studied by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) techniques. From the studies, it is observed that at lower MWCNT concentration (up to 4%), nanofillers are well separated and dispersed, but at higher loadings (6%) formation of agglomerates takes place. Hence it is expected that percolation limit of MWCNT in oil-extended EPDM occurs at around 4% concentration. The extent of reinforcement of MWCNT in EPDM matrix has been calculated in form of bound rubber (BdR) content and degree of swelling when exposed to solvents. BdR values of EPDM nanocomposites increase with MWCNT concentration hence confirmed the reinforcing nature of filler. Physico-mechanical properties like tensile strength, modulus and toughness of EPDM nanocomposites increases up to 4% MWCNT concentration, beyond which the effects are very marginal or decreases as filler-filler interactions exceed polymer-filler interactions. This confirmed the percolation threshold of MWCNT at 4% concentration. In addition to above, electrical conductivity of EPDM/MWCNT nanocomposites have been obtained as a function of frequency to measure the capability of a material to conduct electric current and it shows both frequency independent (DC) and dependent (AC) characteristic which increases exponentially in the applied field. AC conductivity of EPDM/MWCNT nanocomposites increases with filler concentration due to conductive nature of nanotube and a decrease in the mean free path of nanoparticles.

Keywords: conductivity, barrier, ethylene propylene diene monomer, MWCNT and percolation.

I. INTRODUCTION

In recent time conducting polymer composites, have emerged as an advance class of materials. These polymer composites have received a lot of attention of academic and industrial researchers due to their vast variety of applications

in different fields. Polymer composites containing conducting and semiconducting particles in an insulated matrix have various applications in the electric and electronic system. They have many advantages as compared to non-conducting conventional polymer composites, which is mainly due to their electronic and optical properties. They become increasingly important for their technical applications like electrostatic charge in pressure sensor, transducer, shielding materials and as materials used for packaging in aircraft, electronics, and telecommunications. They are also used as energy storage systems like batteries, super capacitors, fuel cells and as antistatic materials in low-temperature heater. In recent decades, polymer nanocomposites whose at least one physical dimension is in the range of nanometre scale developed rapidly as a high-performance materials [1]. Generally, fillers introduced in the polymer matrix improve the properties like mechanical strength, conductivity, and other functional properties. In this paper conductive carbonaceous filler MWCNT is chosen which dramatically influence the properties of materials such as mechanical properties which include tensile and flexural strength and electrical properties as well as maintaining its light weight and corrosion resistance properties. Among carbon-based fillers CNTs have a much significant effect due to their exceptional high electrical, thermal, mechanical, chemical, electrochemical and thermo-electrical properties [2]. Some kinds of literature are found on the applicability of MWCNT as nanofiller in rubber, such as styrene-butadiene rubber [3], fluoro elastomer [4], epoxy [5], and natural rubber [6]. The designs of such composites are mainly based on the loading of filler which could be more effective by augmenting the interaction of polymer matrix and filler [7]. The dielectric response of several polymers has been investigated in the last two decades [8-13]. In elastomer nanocomposites relaxation spectroscopy is time, temperature, frequency and strain dependent. Main objective of the present work is to provide the information about the consequences of MWCNT loadings on morphology, barrier, mechanical and conductivity properties of oil-extended EPDM elastomer nanocomposites. EPDM is an inorganic macromolecule with saturated backbone and unsaturated in the diene side of the chain.

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It is a very non-polar polymer compared to other polymers. Although the behaviour of polymers are insulating in nature, by adding conductive fillers in the polymer matrix as a second phase, electrical conductivity of resulting composites is increased. This paper deals with morphology, bound rubber content, swelling, electrical conductivity of oil-extended EPDM elastomer nanocomposites as a function of frequency and MWCNT concentrations. Effects of MWCNT loadings and time on bound rubber content and swelling are also studied. Dielectric properties like dielectric permittivity and electrical conductivity have also been reported.

II. EXPERIMENTAL

A. Materials

An oil-extended EPDM rubber, Ethylene-Norbornene (7.5 wt %), oil 20 phr, Mooney viscosity 53, manufactured by DSM Elastomers, Singapore was used in this study. Multiwalled carbon nanotube (purity $\geq 99\%$) was used as conductive filler and purchased from Nanoshel LLC, USA. Dicumyl peroxide was used as curative (with purity 98%), produced by Aldrich Chemical Company, USA. Zinc Oxide and Stearic acid was used as an accelerator and accelerator-activator respectively were purchased from standard suppliers.

B. Sample Preparation

The elastomer oil-extended EPDM was mixed with high purity components according to the proportions listed in Table 1. Mixing of polymer with other components was done in a two roll mixing mill at friction ratio 1:1.25 according to ASTM D 3182 standards and maintaining the temperature (around 65-70 °C), mixing time, nip gap, and uniform cutting operation during mixing. Then the prepared compositions were electrically heated and moulded by using Moore hydraulic press and moulding environment was determined by Monsanto Rheometer (R-100; St Louis, Missouri, USA) as per ASTM D2084 and ASTM D5289 procedures.

I. Mixing proportions of EPDM elastomer nanocomposites

| Ingredients | Phr |
|--------------|---|
| EPDM Rubber | 120 |
| Stearic Acid | 1.5 |
| Zinc Oxide | 5 |
| DCP | 1 |
| MWCNT | 0(EPDM1), 2(EPDM2), 4(EPDM3), 6(EPDM4) |

C. Testing

a. Scanning Electron Microscopy (SEM)

Scanning electron microscope (an INCA PENTA FETX3-8113) has been used to study the surface morphology of compounds. For this experiment, samples were placed on sample stud with the help of double-sided adhesive tapes and then the samples were sputter coated with gold.

b. High Resolution Transmission Electron Microscopy (HR-TEM)

Dispersion of filler in EPDM nanocomposites is qualitatively analysed by high resolution transmission electron microscopy. It gives the proper information about the internal structure of nanocomposites and their spatial distribution by direct visualization. This technique also provides information about agglomeration formed in the EPDM matrix.

Bound Rubber Studies

The extent of bound rubber was obtained by separating the unbound materials by dipping the small amount of uncured rubber in two different solvents for seven days. Samples were dried at room temperature for two days and then their weights were taken by using sensitive weighing balance. BdR contents were calculated by the equation given below,

$$BdR = 100 \times \frac{W_{fg} - W_1 \left[\frac{m_1}{m_1 + m_r} \right]}{W_1 \left[\frac{m_r}{m_1 + m_r} \right]} \quad (1)$$

Where BdR give amount of bound rubber, W_{fg} denotes combined weight of nanofiller with gel, W_1 is the weight of the cured rubber sample, m_1 is the fraction of MWCNT filler in the prepared sample and m_r is the fraction of EPDM rubber in the prepared sample

.Swelling Studies

Swelling response of EPDM/MWCNT elastomer nanocomposites using two solvents, benzene and n-hexane, have been studied. In this method, samples were cut in the square shape from the rubber sheets and then by using sensitive weighing balance weight of every sample were reported. Weighed samples were then dipped in solvents for 5, 10, 15, 30, 60 mins time interval. After every time intervals, the samples were removed from the solvent, wiped and reweighed. The degree of swelling was then obtained by given equation:

$$\frac{m - m_0}{m_0} \quad (2)$$

Where, weight of unswelled samples denoted by m and weight of swelled sample denoted by m_0 .

c. Mechanical Properties

Shore-A durometer was used to measure the hardness of EPDM elastomer nanocomposites according to D676-59T. Physico-mechanical properties (modulus, tensile strength, elongation at break and modulus) were obtained by using Universal Testing Machine (Hounsfield H10KS). All properties were tested with at least five specimens per sample and mean values were calculated.

d. Electrical Studies

Electrical conductivity of conducting oil-extended EPDM/MWCNT nanocomposites were obtained by phase sensitive LCR meter (model PSM 1735) using aluminium foil as a blocking electrode in the frequency range 1-10⁶ Hz. Dielectric data was obtained from electrical conductivity (σ_{ac}) using the relation:

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (3)$$

Where, $\omega = 2\pi f$ and f is the frequency, ϵ_0 is electric field vacuum permittivity in free space, and ϵ' is dielectric constant of material which can be calculated by the following equation:

$$\epsilon' = \frac{C_p}{C_0} \quad (4)$$

Where, C_p denotes obtained capacitance and C_0 is the cell vacuum capacitance and the equation used to calculate is given below:

$$C_0 = \epsilon_0 A/d \quad (5)$$

Where, A and d denotes the area and thickness of the sample, respectively and $\tan \delta$ (eq.1) is the loss angle or dissipation factor.

III. RESULTS AND DISCUSSION

A. Morphology

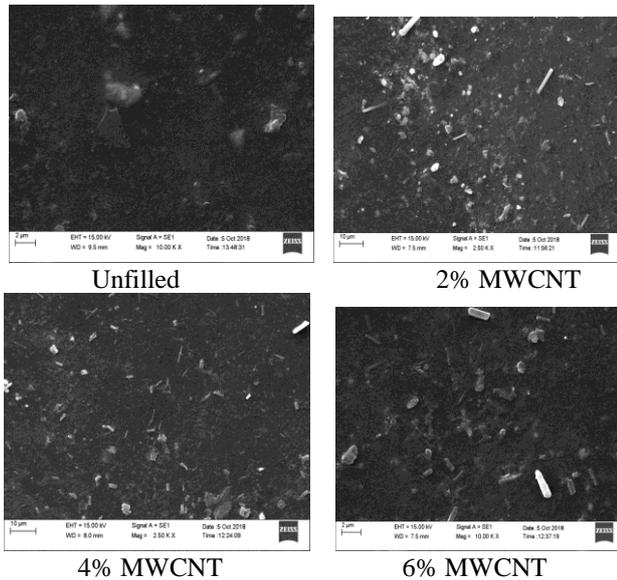


Figure 1. SEM images of EPDM/MWCNT nanocomposites

Surface morphology of EPDM nanocomposites observed through scanning electron microscopy. Figure 1 shows the SEM images of EPDM elastomer nanocomposites with different loadings of MWCNT (unfilled, 2%, 4% and 6%). MWCNT being conductive filler, can be seen clearly from photomicrographs and separated from each other at lower concentration but at higher concentration agglomeration are observed due to increase in volume fraction of reinforcing agent inside the matrix.

The bulk properties of EPDM nanocomposites have been studied by transmission electron microscopy. For TEM studies, the samples were prepared by ultramicrotomy and their images are presented in figure 2. TEM images of MWCNT appear dark and hence sufficient density contrast would appear between MWCNT and polymer matrix. The figure shows that MWCNT are individually and evenly dispersed in polymer matrix, however at high concentration cluster formation takes place. This observation is in good agreement for different mechanical properties. It is observed from the figure that at higher concentration agglomerate formation takes place and these agglomerates initiated the fracture in nanocomposites under pressure and hence elongation at break also decreases with increased filler loadings. However, high amount of filler in polymeric materials significantly improve the hardness of material and decreases the impact strength of the composites.

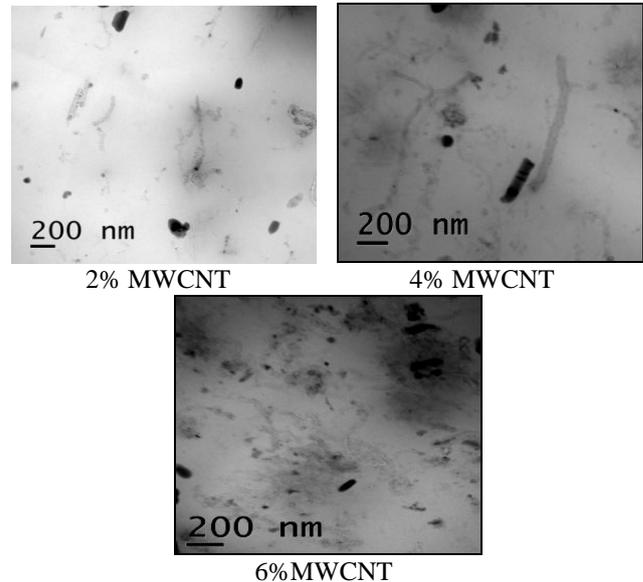


Figure 2. HR-TEM images of MWCNT/EPDM elastomer nanocomposites

B. Bound Rubber Studies

II. BdR content of EPDM elastomer nanocomposites with n-hexane and benzene for 7 days.

| MWCNT concentration | BdR content with n-hexane | BdR content with benzene |
|---------------------|---------------------------|--------------------------|
| 2% | 46.69 | 38.31 |
| 4% | 56.81 | 43.88 |
| 6% | 62.18 | 48.00 |

Mixing of an elastomer with reinforcing filler results in strong interactions and hence by adding good solvent to the polymer composites free rubber can be extracted. Due to this process, rubber component adsorbed on to the surface of nanofiller. This portion of uncured rubber is called as bound rubber. It provides several informations regarding the activity that occurs on to the filler surface and degree of reinforcement into the polymer matrix. BdR formation involves physical adsorption, chemisorptions and mechanical interaction. Many studies have been done on the phenomena of bound rubber and filler gel formation and its effect on rubber-filler network and their vulcanizates [14-20]. When nanofiller are mixed with rubber various types of bonds developed in between rubber molecule and filler particle. These may be weak Van der Waals forces or strong covalent linkages. These interactions may be developed during mixing or curing process. After adding solvent, every particle of nanofiller was surrounded by a layer of rubber and those parts of rubbery segments which are directly attached to the particle surface will experience the most restriction in chain mobility and relaxation behaviour. After certain distance from the particle surface the chain mobility and relaxation behaviour are solely depends on the pure rubber which is not influenced by the rubber. Several research works have been done on the techniques and factors that affect bound rubber content in polymer nanocomposites [21-24].

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Bound rubber formation results from the strong interactions between elastomer and filler particles and it depends on the structure and surface chemistry of rubber and filler. Variation of bound rubber with MWCNT has been given in Table 3. Two different solvents (n-hexane and benzene) have been used to study bound rubber content. Figure 3 exhibit the consequences of MWCNT concentrations with different solvents on the extent of bound rubber. Due to increased amount of filler in polymer matrix, bound rubber content of polymer nanocomposites also increases. Effect of different solvent on the extent of bound rubber as a function of filler loadings in EPDM/MWCNT nanocomposites is shown in swelling studies.

C. Swelling Studies

Physical and chemical cross-links formed within the macromolecules in polymer due to reinforcing filler can be quantified from cross-link density. Kinetics of swelling etiquette gives the approximate estimation about the extent of cross-linking in between polymer macromolecules. Irrespective of solvent, swelling degree increases progressively with time however decreases with filler percentage. Figure 3 shows variation of degree of swelling with increasing MWCNT concentration with solvents n-hexane and benzene, respectively.

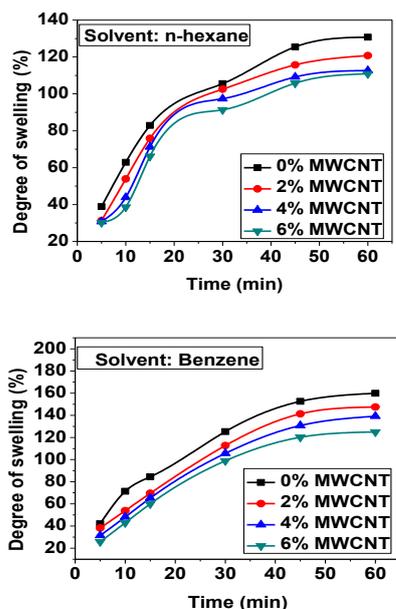


Figure 3. Swelling studies of EPDM/MWCNT nanocomposites with n-hexane and Benzene.

From the figures it is observed that degree of swelling decreases with MWCNT concentration and increases exponentially with time followed by a plateau. This shows the reinforcing effect of MWCNT in both n-hexane and benzene solvents.

D. Mechanical Properties

Mechanical properties of EPDM/MWCNT elastomer nanocomposites have been given in Table 3. Mechanical properties of EPDM nanocomposites have been improved due to the addition of MWCNT in matrix. Tensile strength, hardness and modulus increases with MWCNT concentration however strain and elongation at break decreases with filler concentration. Improvement in tensile strength due to incorporation of filler, EPDM rubber becomes tougher and resistant to deformation.

Shore-A durometer was used to measure the hardness of nanocomposites and it shows the expected increase in hardness with increasing surface area of MWCNT. Hardness is a measure of materials resistance of deformation and progressively increases with increase in degree of crosslink density. High surface area nanotube gives high value of hardness. Elongation at break decreases as filler concentration increases. At low filler loading crosslink density is low due to which elongation at break increases, however at high concentration elongation at break decreases due to increase in density and viscosity. The most important factor for a filler to be reinforcing is force of adherence in the matrix. If the tendency of filler to cling on the polymer matrix is low then the increase in modulus of polymer composites is not much significant. However, if the adherence is large, then the magnitude of polymer filler interaction gives the modulus of mixture. Increase in modulus is mainly due to sturdy interaction of MWCNT and rubber which are further confirmed by bound rubber study.

III. Mechanical properties of MWCNT/EPDM elastomer nanocomposites.

| Sample | Tensile Strength (MPa) | Modulus (MPa) | Elongation at Break (%) | Toughness (MPa) |
|------------|------------------------|---------------|-------------------------|-----------------|
| 0 phr | 1.033 | 1.694 | 988.125 | 7.704 |
| 2phr MWCNT | 1.332 | 1.835 | 759.375 | 7.052 |
| 4phr MWCNT | 1.642 | 1.708 | 697.255 | 7.781 |
| 6phr MWCNT | 1.971 | 1.752 | 656.875 | 8.481 |

E. Electrical Studies

a. Dielectric Permittivity

Dielectric permittivity is the property that characterizes the effect of an external electric field on the extent of electrical polarization. It also measures the capacitance and alignment of dipoles. Variation of dielectric permittivity of EPDM elastomer nanocomposites with frequency as a function of MWCNT concentration are shown in Figure 4.

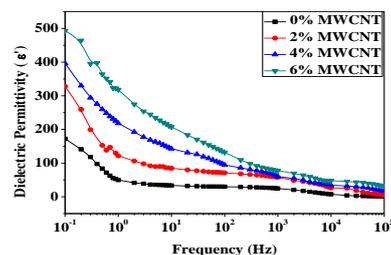


Figure 4. Dielectric permittivity of EPDM/MWCNT elastomer nanocomposites.

According to the figure dielectric permittivity for all filler loading continuously decreases and it becomes constant after 10^4 Hz. The figure also shows that with increasing filler loading dielectric permittivity increases. Due to a large number of electrons supplied by MWCNT space charge polarization occur which results with increased dielectric permittivity.

At high frequency dipole will easily orient themselves in the direction of alternating electric field as compared to the direction of applied field. Extent of interfacial polarization is very high in low frequency region as compared to high frequency region and this may be due to the heterogeneity formed in polymer composites. Periodic repetition of applied electric field takes place at high frequency which results in sudden decrease in the diffusion of dipoles in the field direction and hence amount of polarization as well as permittivity decreases. Also addition of nanofiller in polymer matrix suddenly restricts the free motion of polymer chain and their mobility mainly depends on the percolating filler networks which also explain the increased value of permittivity of elastomer nanocomposites with MWCNT concentration.

b. Electrical Conductivity

Electrical conductivity is an intrinsic property that measures the amount of electrical current a material can carry. Figure 5 shows the change in electrical conductivity of EPDM elastomer nanocomposites with frequency and MWCNT loadings at room temperature.

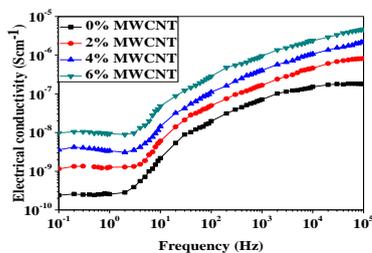


Figure 5. Electrical conductivity of EPDM/MWCNT elastomer nanocomposites.

The figure clearly shows that irrespective of filler loadings, the conductivity of EPDM/MWCNT elastomer nanocomposites increases with increasing frequency and at higher filler fraction insulator-conductor transitions are clearly observed. An electrical property of reinforced polymers greatly depends on the distribution of fillers throughout the polymer matrix (also called as mesostructure) [25]. At lower filler concentration, the electrical conductivity between the grains can occur through the process called hopping and tunnelling. During this process, the electron transfer may be coupled strongly with the molecular and ionic processes in the polymer matrix. Generally hopping transport is restricted to a particular place and also it affects the frequency dependence of electrical conductivity in polymer nanocomposites. The distribution of filler is localized, disordered and heterogeneous and hence hopping rates are widely distributed which results in a strong distribution of the ac conductivity. Taking into account the model RC parallel circuit, as the concentration of nanofiller increases they are more connected and strongly pressed against each other due to which total reduction in the internal contact resistance occur and hence, the total resistance of material decreases with increased filler loading level. This results in increased electrical conductivity.

IV. CONCLUSIONS

The amount of MWCNT in EPDM matrix significantly affects the overall behaviour of polymer nanocomposites as compared to conventional polymeric systems. Morphological properties confirmed the homogeneous distribution of MWCNTs in EPDM matrix up to 4% concentration beyond which agglomerates formed. Barrier properties show the increase in bound rubber content and decrease in degree of swelling with MWCNT concentration. The ultimate strength of EPDM/MWCNT nanocomposites observed from mechanical properties. Tensile strength, hardness and modulus increases with MWCNT concentration while strain and elongation at break decreases due to increase in volume fraction of the reinforcing nanofiller. Dielectric characteristics of EPDM/MWCNT elastomer nanocomposites have been obtained as a function of frequency and MWCNT concentration. Irrespective of MWCNT concentration, dielectric permittivity of EPDM nanocomposites decreases slowly with varying frequency while electrical conductivity increases exponentially with frequency. Electrical conductivity measurements also give the percolation threshold of MWCNT at 4% concentration in EPDM matrix.

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