Piezoresistive polymer composites based on EPDM and MWNTs for strain sensing applications

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Abstract: Elastomeric composites based on Ethylene-Propylene-Diene-Monomer (EPDM) filled with multi-wall carbon nanotubes (MWNTs) have been prepared, showing improved mechanical properties as compared to the pure EPDM matrix. The results have been discussed using the Guth model. The main focus of the study was on the electrical behavior of these conductive polymer composites (CPCs), in view of possible sensor applications. A linear relation has been found between conductivity and deformations up to 10% strain, which means that such materials could be used for applications such as strain or pressure sensors. Cyclic experiments were conducted to establish whether the linear relation was reversible, which is an important requirement for sensor materials.

Keywords: Nanocomposites; carbon nanotubes; conductive; elastomers; strain sensing

Introduction

This work is focused on piezoresistive behavior where a mechanical stimulus induces a change in resistivity and which is the basis of many commercial pressure sensors and strain gauges. A piezoresistive effect is predicted for heterogeneous solids composed of conducting particles dispersed in an insulating polymer matrix, e.g. conducting polymer composites, CPCs [1]. Such materials are characterized by an insulator-to-conductor transition when a certain concentration of conducting particles is reached. This transition has been interpreted within the framework of percolation theory [2]. The percolation effect is related to the material microstructure. In particular, the separation between the conducting particles plays a crucial role on the electrical behavior of the bulk material. For CPCs with a certain filler loading, any parameter that can alter the interparticle distance will affect the conductivity. Several groups have investigated the change of conductivity of CPCs as a function of temperature [3, 4], solvent vapors [5-9], pressure [10] or mechanical stretching [11-21]. Such materials have the potential to become a new generation of sensors if the dependence is reversible. In this paper, the effect of incorporating small amounts of MWNTs into an Ethylene-Propylene-Diene-Monomer (EPDM) elastomeric matrix will be explored. The mechanical and electrical behavior will be studied, with an emphasis on the effect of strain on the conductivity.
Results and discussion

Dispersion quality

Dispersion quality was analyzed using an optical microscope [22]. Figure 1 shows optical micrographs of the composite solution at different stages of preparation.

![Optical micrographs of composite solutions showing the evolution of dispersion of MWNTs in EPDM matrix. The sonicat](image)

**Fig. 1.** Optical micrographs of composite solutions showing the evolution of dispersion of MWNTs in EPDM matrix. The sonication of MWNTs in xylene is not effective in producing a high degree of dispersion and results in large agglomerates (1\textsuperscript{st} micrograph). The addition of EPDM solution improved the quality of dispersion and by mechanical stirring a homogenous composite solution is obtained (2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th} micrographs).

The mixture of MWNTs in xylene showed a poor degree of dispersion even after sonication (left hand side). The solvent can only swell the nanotube bundles and loosen up the agglomerates, which are still visible and in large number. However, the dispersion quality improved with the addition of EPDM solutions. In fact, as soon as the EPDM solution is added, the agglomerates are reduced in size. Because the solvent is allowed to evaporate during stirring, the viscosity of the mixture gradually increases. This leads to more efficient mixing, because of the higher shear forces as compared to the initial mixture. In addition, the high viscosity of the final mixture has a second purpose, i.e. it prevents possible phase separation and re-aggregation [23, 24] of CNTs upon drying. In order to obtain a better analysis of the level of dispersion of the MWNTs within the matrix, SEM micrographs were collected in charge contrast imaging mode [25]. This imaging mode is very efficient in the visualization of the nanotube organization within the matrix. Figure 2 shows a general view of a composite containing 5 wt.% MWNTs, where the nanotubes can be clearly identified. As it can be seen, there are areas (areas 1 and 3) where large aggregates of nanotubes are present and areas (area 4) where very few nanotubes are visible. However, there are also areas (area 2) where a better dispersion of nanotubes had been achieved. It seems that the simple stirring is too mild to completely break up the interaction between nanotubes.
Mechanical properties

In contrast to a previous study by Kim et al. [26] who created EPDM/CNT composites with high levels of nanotube loading (5-30 wt.%), this study focused on adding small quantities of nanotubes to improve mechanical and electrical properties. Figure 3a shows representative stress-strain curves for pure EPDM and EPDM/MWNT composites. It is clear that the Young’s modulus is significantly enhanced as the concentration of MWNTs increases, as shown from Figure 3b.

![SEM pictures of EPDM containing 5 wt.% MWNTs.](image)

The most widely used models for the change in modulus of a filled elastomer are the Guth hydrodynamic models [27]. The model for rod-like particle reinforced elastomers is based solely on the aspect ratio and volume fraction of the filler, and does not take any other properties of the filler into account, except to assume that the fillers are much stiffer than the matrix:
where $E_c$ and $E_m$ are the moduli of the composite and the pure matrix respectively, and $l/d$ and $V_f$ are the aspect ratio and volume concentration of the filler.

\[
E_c = E_m \left(1 + 0.67 \left(\frac{l}{d}\right) V_f + 1.62 \left(\frac{l}{d}\right)^2 V_f^2\right) \tag{1}
\]

Note that, to use Equation 3, the measured weight fractions were converted to volume fractions, $V_f$, using densities of 2100 kg.m$^{-3}$ and 867.4 kg.m$^{-3}$ for MWNTs and matrix, respectively. Using nanotube aspect-ratio $l/d$ as an adjustable parameter for the fitting, the model shows a good agreement with the experimental data. Using $l/d \sim 100$, a good correlation is achieved except for the composite containing 5 wt.% (~2.2 vol.%) MWNTs, as shown in Figure 3b. At such a high loading, it is extremely difficult to obtain a good level of dispersion, and as a consequence, the aspect ratio and therefore the mechanical properties are lower than expected. These $l/d$ values are at the lower end of the range calculated from the typical dimensions provided by the supplier ($d = 10$ nm, $l = 0.1-10$ μm, $l/d = 10 - 1000$). Only if the dispersion of MWNTs is improved and individual nanotubes are obtained in the matrix, then the aspect ratio can be increased and a higher reinforcement could be reached.

**Electrical properties**

-Initial electrical properties

The percolation threshold is a basic characteristic of a conductive composite, as mentioned in the introduction. In this case, the percolation threshold defines the ideal composition for studying the effect of stretching on conductivity, i.e. above percolation threshold. Figure 4 shows the DC conductivity of EPDM/MWNT composites as a
function of weight fraction of MWNTs. A log-log plot of conductivity as a function of the reduced mass is shown in Figure 5a. A linear relationship can be clearly seen.

![Log-log plot of conductivity as a function of MWNT wt [%].](image)

**Fig. 4.** Electrical conductivity as a function of MWNT wt.%. The squares are experimental data and the solid line is a fit of the data using Equation 5.

According to Equation 3, the best fitted values are for \( p_c = 2 \text{ wt.\%} \) and \( t = 2.09 \). The percolation threshold value falls within the range of percolation thresholds calculated by Munson–McGee [28] for cylindrical conductors in an insulating matrix. In its study, statistical analysis was used to show that a percolation threshold in the region of 1-5% is expected for a system of conductive fillers of aspect ratio between 40 and 130, which is consistent with the nanotube aspect ratio calculated from the suppliers data as well as those obtained through fitting the mechanical properties with the micromechanical model. The conductivity exponent \( t \) generally reflects the dimensionality of the system with values typically around 1.3 and 2.0 for two and three-dimensions, respectively. Here the conductivity critical exponent’s value of 2.09 is very close to the universal value for three-dimensional percolating systems. Furthermore, \( \sigma_0 \) can be extrapolated when \( p = 100\% \), i.e. for a nanotube film. \( \sigma_0 = 7 \times 10^{-4} \text{ S.m}^{-1} \) is lower than the expected conductivity for nanotube mats [29]. This might be due to the morphology of the nanocomposite, where large conductive nanotubes agglomerates are separated by regions of insulating matrix, as shown by SEM pictures. Hence, conduction is limited by tunneling between potential barriers between conductive regions. This phenomenon was previously reported by Kilbride et al. [30]. They extrapolated conductivity for nanotube film of \( 10^{-3} \text{ S.m}^{-1} \) and ascribed this result to the formation of a thick crystalline polymer layer, which prevented direct contact between nanotubes. They modeled this behavior with the fluctuation induced tunneling model, which takes into account tunneling through potential barriers of different heights due to local temperature fluctuations. If temperature is constant, they obtain a simple relation between conductivity and inter-nanotube gap width, \( w \),

\[
\ln \sigma_{DC} \propto w
\]  

(2)
Due to spatial consideration, the inter-nanotube gap width is proportional to $p^{-1/3}$, which combined with the previous equation leads to:

$$\ln \sigma_{dc} \propto p^{-1/3} \quad (3)$$

Figure 5b shows a semi-logarithmic plot of the conductivity as a function of $p^{-1/3}$, where a linear relationship can be clearly seen.

**Electrical properties under uniaxial strain**

Once the percolation threshold has been identified, an appropriate range to study the relationship between resistivity and mechanical deformation can be chosen. In the present case, nanocomposites containing 5 wt.% and more MWNTs have been chosen because they are above the percolation threshold and even upon stretching the level of current is within the measurable range. The conductivity of nanocomposites containing 5 and 6 wt.% MWNTs as a function of strain for different amounts of MWNTs is displayed in Figure 6.

The decrease of conductivity with increasing strain is similar to the trend shown by carbon black filled elastomers [11-19]. In that case, the change in conductivity upon straining is generally explained in terms of two simultaneous processes that operate on a continuous conductive network of secondary aggregates in an insulating matrix. Rotation and translation of asymmetric particles preserves the number of contacts and hence the number of conducting pathways in the direction of stretching. In opposition to this effect, elongation also causes breakage of the existing continuous conducting network by increasing the gap between particles, which results in a reduction of the total number of possible conduction paths [12]. In a similar way, it could be thought that stretching of EPDM/MWNT nanocomposites results in network breakage by loss of contacts. Decreasing the number of possible conduction paths
present above the percolation threshold results in a decrease of conductivity. However, as shown previously the morphology of the nanocomposite consists of large conductive agglomerates separated by regions of insulating matrix. This suggests that the conduction mechanism here is tunneling through potential barriers, rather than a classical percolation network that involves direct contact between the nanotubes. So it is more likely that the mechanical stretching causes a further separation of the agglomerates resulting in lower conductivity. It is interesting to note that a linear relation exists between conductivity and strain up to 10% strain. This could be used for application such as sensor materials. However, the change in conductivity needs to be repeatable as well, so repeated cycling experiments need to be performed.

![Conductivity vs Strain](image.png)

**Fig. 6.** Conductivity of nanocomposites containing 5 and 6 wt.% MWNTs as a function of strain.

**Cyclic loading experiments**

Repeated cyclic loading of a 5 wt.% MWNTs nanocomposite up to 5% and 10% strain produced the normalized conductivity curves shown in Figure 7a-b. The normalized conductivity decreases steeply during the first loading. The conductivity differs significantly from the subsequent cycles due to a transient set strain. Then, it gradually increases, as shown by the succeeding loading and unloading cycles (2<sup>nd</sup> - 5<sup>th</sup> cycles and 10<sup>th</sup> cycle), and continues to increase up to the 40<sup>th</sup> cycle when the experiment was terminated. Presumably this was due to formation of additional conducting paths by breakdown of matrix material between CNTs. To a large extent, the strain induced contacts were lost when stress was removed, however, as cycling proceeded, permanent changes occurred and there was a gradual increase in conductivity.

For application as sensor materials, it is interesting to look in more detail into the profile of the cycles. Figure 8 shows the profile of strain and normalized conductivity as a function of time for the cycles 1 to 5 for the experiment in which the nanocomposite was stretched up to 5% strain. The normalized conductivity does not return to the original value after the first cycle, indicating the occurrence of
irreversible damage during the first loading. For every cycle there are two portions of normalized conductivity – one portion is irreversible while the other portion is reversible.

![Diagram](image1)

**Fig. 7.** (a) Cycling up to 5% strain and (b) up to 10% strain, showing that the normalized conductivity decreases steeply during the first loading. Then, it gradually increases, as shown by the succeeding loading and unloading cycles.

![Diagram](image2)

**Fig. 8.** Cycles 1-5 at 5% strain, showing the profile of strain and normalized conductivity as a function of time.

A similar trend was observed in short carbon fiber filled epoxy by Wang and Chung [31]. They showed that the irreversible portion increased with strain amplitude and attributed the irreversible portion to damage, probably related to the nanotube-matrix contact resistivity increase (interface weakening), rather than fiber breakage, no changes in the stress-strain relationship during the experiment were observed. They attributed the reversible portion to piezoresistivity. In a similar way, it could be thought that also here the irreversible portion of the conductivity is related to interface
weakening, while the reversible portion is due to piezoresistivity. Furthermore, it can be noted that for every single cycle of strain, a double peak is registered for the normalized conductivity. This phenomenon has been already observed for carbon black filled elastomers by Kost et al. [32], although it was not fully understood. They attributed this phenomenon to orientation effects of the filler particles. According to them, at low strain, orientation effects are insignificant and only destruction and re-formation of the conductive network are important. Hence, the conductivity peak follows the strain peak. However, at higher strain, orientation effects become important, which may cause the appearance of a double conductivity peak in correspondence of a single strain peak.

Figure 10 shows the profile of strain and normalized conductivity for cycles 30-35, when the material has stabilized and the change in normalized conductivity is more reproducible. The irreversible portion of normalized conductivity is reduced as compared to the first cycles. The double peak can still be observed.

Fig. 9. Cycles 30-35 at 5% strain, showing the profile of strain and normalized conductivity as a function of time.

Conclusions

EPDM/MWNTs nanocomposites have been investigated. The nanocomposites with 0.5 – 5 wt.% MWNTs exhibited improved mechanical properties as compared to the pure EPDM matrix, and results have been discussed using the Guth model. The results suggested that improvement in the dispersion state could lead to even bigger improvements in mechanical properties. The main focus of the study was on the electrical behavior of the nanocomposites, in view of possible sensor applications. The percolation threshold has been determined and was consistent with the predictions of Munson-McGee for a system of conductive fillers with an aspect ratio between 40 and 130, which is consistent with the aggregation state of nanotubes used in the study. This result was used to establish the range of concentrations to study the effect of mechanical stretching on the conductivity. A linear relation has been found between conductivity and strain up to 10% strain, which means that such materials could be used for applications such as pressure sensors. Cyclic experiments showed that the change in conductivity presents a reversible portion and an irreversible one, which was attributed to damage (the irreversible portion) and to piezoresistivity (the reversible portion). Although this behavior is detrimental for the use as sensor, the experiments also showed that the material stabilizes during cyclic loading and the change in normalized conductivity becomes more repeatable.
Although further optimization is needed these initial results showed that CNTs have great potential for the creation of conductive elastomeric sensors that can be used in future smart material applications.

**Experimental**

**Materials**

Ethylene-Propylene-Diene-Monomer (EPDM) rubbers belong to the family of the ethylene-propylene (EPM) rubbers. Copolymerization of ethylene with propylene gives an EPM rubber, which needs to be cross-linked. For that a third monomer, a diene, is added in small amounts (3-8% of the total monomer weight). The diene used in EPDM rubber is mostly dicyclopentadiene (DCPD). Since the polymer main chain of EPDM is completely saturated, the resistance to degradation from oxygen and chemicals is excellent. For this reason, products made of EPDM are very durable. EPDM (VISTALON 3666) was kindly supplied by Exxon Mobile Chemicals and used as received. Dicumyl peroxide (DCP) was supplied by Aldrich. MWNTs were kindly supplied by Nanocyl (Belgium) (Batch No MWA P 041206). They were produced by CVD and their purity was 95%. Xylene, supplied by Romil, was used as solvent.

**Composite preparation**

EPDM was dissolved in xylene (1:10 weight) at 90 °C and subsequently cooled to room temperature. MWNTs were dispersed in xylene by ultrasonication using a high power tip. The MWNT concentration needed in xylene was calculated in order to obtain a range of loadings between 0.5 and 5 wt.% in the final composite. EPDM solution was slowly poured into the dispersion of MWNTs/xylene. 2 wt.% DCP was added to the mixture, which was mechanically stirred for 4 hours. During this time, the mixture became highly viscous, since the solvent was allowed to evaporate during stirring. The homogeneous mixture was cast into an aluminum tray. After all the xylene evaporated, the dried material was cured for 30 minutes at 170 °C.

**Composite characterization**

*Scanning Electron Microscope (SEM)*

The SEM (XL30 ESEM-FEG, Fei Co., The Netherlands) was equipped with a field emission electron source. High vacuum conditions were applied and a secondary electron detector was used for image acquisition. The SEM was operated either in conventional high-voltage or low-voltage mode. No additional sample treatment such as surface etching or coating with a conductive layer had been applied. Standard acquisition conditions for charge contrast imaging were as follows: working distance of ~5 mm for low-voltage mode and ~10 mm for high-voltage charge contrast imaging, spot 3, slow scan imaging with approximately 2 min/frame.

*Tensile tests*

The uniaxial mechanical tests were carried out at room temperature using an Instron 5576 equipped with a 1 kN load cell. The strain was monitored using an Instron non-contact video extensometer. The samples were cut from the compression molded sheet in dumbbell shape with approximate length of 60 mm. The thickness was 1 mm and the width of the centre was 3 mm.
Bulk electrical measurements

Bulk electrical measurements were conducted on a square specimen with dimensions of 15 mm × 15 mm × 1 mm. The sample surfaces were gold coated in order to create parallel electrodes. An Agilent DC power supply E3612A was used as voltage source and a Keithley 6517A Electrometer was used for voltage and current measurement. Each resistance measurement was made from the slope of the voltage-current plot within the linear range. From the electrical resistance, \( R \), the electrical conductivity was calculated using the following equation:

\[
\sigma = \frac{l}{R \cdot A}
\]  

(4)

where \( l \) and \( A \) are the thickness and surface area of the sample, respectively. The percolation model is used to describe the behavior of the conductive polymer composites. Its conductivity, \( \sigma \) at and above the percolation threshold, \( p_c \), is generally described by a power law relationship:

\[
\sigma = \sigma_0 (p - p_c)^t
\]  

(5)

for \( p > p_c \)

where \( \sigma_0 \) is a constant, \( p \) the weight fraction of the conductive filler and \( t \) the critical exponent. \( p - p_c \) is known as the reduced mass.

Electrical measurements during uniaxial stretching

To measure changes in conductivity during uniaxial stretching, rectangular strips with initial dimensions 40 mm × 10 mm × 1 mm were cut from the compression molded sheets. Pneumatic grips were used to clamp the sample.

Fig. 10. Experimental set-up for measurement of electrical resistance of the nanocomposite as a function of tensile strain.
A DC power supply was used as voltage source and a Keithley Electrometer was used for current measurement (Figure 10). Electrically insulated fixtures were required for the conductivity measurements to ensure that the test piece was isolated and that there was no conduction path through the mechanical test machine. These fixtures consisted of an isolating layer coupled with a metallic part to be in contact with the sample. The conductivity was obtained from the measurement of the resistance and the geometrical changes in the specimen. Equation 1 can be used to calculate the resistivity, where $A$ is the instantaneous cross-sectional area, equal to $A_0/\lambda$, where $A_0$ is the initial cross-sectional area and $\lambda$ is the draw ratio of the test piece; $l$ is the initial length.

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