Design and Properties of Fluoroelastomer Composites via Incorporation of MWCNTs with Varied Modification

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Abstract Multi-walled carbon nanotubes (MWCNTs) modified with silane coupling agent A-1120 (MWCNTs-A1120) were prepared. Compared with the raw MWCNTs, acidified MWCNTs (MWCNTs-COOH), and MWCNTs grafted with EDA (MWCNTs-NH₂), MWCNTs-A1120 have the best dispersion in fluoroelastomer at the same doping ratio. Therefore, fluoroelastomer/MWCNTs-A1120 composite has the best mechanical properties with tensile strength of 13.92 MPa and elongation at break of 111.78%. Then, the effects of doping amount of MWCNTs-A1120 on the electrical properties of the composites were investigated. The dielectric constant of the composite increases with the increase of MWCNTs-A1120, and the dielectric loss does not change much at the low doping amount such as 0.5 wt%. When the doping amount of MWCNTs-A1120 is 5 wt%, the dielectric constant and the dielectric loss value are greatly increased, and the volume resistivity is greatly decreased, which proves that the conductive network is formed in the composite, so the filling amount of 5 wt% is the percolation threshold. The tensile deformation of the sample also affects the electrical properties of the composites. As the tensile deformation increases, the dielectric constant and dielectric loss of the composite decrease. For the composite with 5 wt% MWCNTs-A1120, excessive tensile deformation will destroy the conductive network structure of the composite, so the composite will change from conductive material to dielectric material. Therefore, such composite is a good candidate for flexible conductive material or flexible dielectric material used in harsh environments such as high temperatures and various aggressive solvents.

Keywords Modified-MWCNTs; Fluoroelastomer nanocomposite; Interface compatibility; Dielectric properties; Volume resistivity

INTRODUCTION

Traditional single-component materials are hard to meet the developing requirements of today’s smart devices. In order to meet the complex and diverse requirements of materials, functional composites have attracted increasing attention.¹ In the rising of the development of artificial intelligence, the research and development of human portable devices become a research hotspot, which has attracted extensive attention in the research of flexible sensitive materials, such as flexible sensors (strain sensors, electronic skin, optical sensors, etc.), flexible conductors, dielectric elastomers, etc.²

A flexible functional material consists of a flexible polymeric matrix and an active material that provides functional properties. The flexible substrate acts as a load-bearing part to prevent physical damage of the device’s structure due to deformation.³ Active materials provide excellent mechanical, electrical, and optical properties for composite materials. Among them, nano-carbon materials are one of the ideal active materials for flexible electronic materials due to their excellent optical, electrical, and magnetic properties.⁴,⁵ Nanostructure provides unique and excellent properties for nano-carbon materials, but nano-materials are prone to agglomeration due to high surface energy, which is undesirable in flexible nanocomposites.⁶–⁸ Therefore, increasing the compatibility of active materials with flexible substrates has become a key research direction for the preparation of flexible functional materials.⁹,¹⁰

There are many researches and reports about flexible functional materials but still few applications of flexible functional materials in special environments such as high temperature, strong corrosive environment. It is due to traditional flexible substrates’ poor mechanical strength, poor high temperature resistance, and poor corrosion resistance. Among many elastomers, fluoroelastomer has become an excellent special elastomer due to its high mechanical strength, high temperature resistance, and excellent corrosion resistance.¹¹,¹² Fluoroelastomer has excellent electrical insulation and extremely low dielectric constant due to its unique chemical structure. So, to synthesize dielectric elastomer or conductive elastomer, dielectric filler or conductive filler needs to be doped into the matrix. Pawar et al.¹³ found that not only charge storage but also microwave absorption of the fluoroelastomer composites can be improved by doping the hybrid filler through anchoring sub-micron size Fe₃O₄...
particles with MWCNTs (MWCNT@Fe$_3$O$_4$). Shajari et al.\textsuperscript{[14]} synthesized a fluoroelastomer/MWCNTs nanocomposite that can be used in wearable devices. They found that there were two penetration thresholds, one at 0.45 parts per hundreds of rubber (phr) (single CNTs in contact), the other at 1.4 phr (dispersed and clustered CNTs in contact). This unique conductive network structure makes the nanocomposite material have high strain sensitivity.

In this work, fluoroelastomer was selected as the flexible matrix and multi-walled carbon nanotubes (MWCNTs) were used as the active component. To improve the interface interaction between MWCNTs and fluoroelastomer, and avoid the loss of electrical properties of MWCNTs due to excessive modification, various modified methods were used to prepare the modified MWCNTs (MWCNTs-COOH, MWCNTs-NH$_2$, and MWCNTs-A1120). The mechanical and dielectric properties of fluoroelastomer nanocomposites and the dispersion of MWCNTs in matrix were studied in detail, and the optimal modified MWCNTs were selected as the active fillers. Then, the effects of doping amount of the fillers and tensile deformation on the electrical properties of the composites were investigated.

**EXPERIMENTAL**

**Materials**

Fluoroelastomer (AFLAS 200P), an alternating copolymer of tetrafluoroethylene, propylene, and vinylidene fluoride, from AGC Chemicals Trading Co., Ltd, Shanghai, China, was the matrix in this study. The filler, multi-walled carbon nanotubes (MWCNTs, purity > 95%) with the outer diameter of 50 nm and length of 20 mm, were provided by Chengdu Organic Chemicals Co., Ltd, Chengdu, China. Bisphenol AF (BPAF, purity > 98%) was purchased from Aladdin Bio-Chem Technology Co., Ltd, Shanghai, China. Ethylenediamine (EDA), and Dimethylaminopyridine (DMAP) were added to dehydrated ethyl alcohol and ultrasonically stirred for 30 min to make them evenly mixed. Then, EDA was added and stirred for 24 h. Finally, the product was washed alternately with deionized water and dehydrated ethyl alcohol to remove excess reagent to obtain MWCNTs-NH$_2$. For MWCNTs-A1120, silane coupling agent A-1120 was added to mixed solution of deionized water and ethyl alcohol at a mass ratio of 1/4 with stirring for 1 h, then raw MWCNTs ethyl alcohol dispersion was added to the mixed solution followed by stirring for 3 h.\textsuperscript{[18]} The obtained product was labeled as MWCNTs-A1120.

**Preparation of Fluoroelastomer/Modified-MWCNTs Composites**

Firstly, the vulcanizing agent was made by using methanol, A-1120, BPAF, and TBAHS, and the specific formulation and configuration methods are detailed in Ref.\textsuperscript{[19]}. Secondly, 5.0 g of fluoroelastomer was dissolved in 20 mL of ethyl acetate and MWCNTs were dispersed in ethyl acetate (ethyl acetate is quantitative, MWCNTs are variables: 0.5 wt%, 1 wt%, 3 wt%, 5 wt%, or 7 wt%). Then, the above two dispersion systems

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were mixed together and 0.4 g of vulcanizing agent was added. The detailed ingredients’ ratio of the composite is shown in Table 1. After the system was uniformly mixed, the mixture was cast on a horizontal stainless steel plate. Finally, after the solvent was volatilized at room temperature for 12 h, the sample was placed in an oven for vulcanization treatment, and the vulcanization conditions are: heating from room temperature to 200 °C for 2 h and thermostating at 200 °C for 4 h.

| Component            | Dosage  |
|----------------------|---------|
| AFLAS 200P           | 5 g     |
| Vulcanizing agent    | 0.4 g   |
| Ethyl acetate        | 30 mL   |
| Modified MWCNT (variable) | 0.5 wt%, 1 wt%, 3 wt%, 5 wt%, 7 wt% |

### Characterization

The thermogravimetric analysis (TGA) of MWCNTs before and after modification was conducted on a TA instrument (TGA Q50 series analyzer system) under nitrogen atmosphere (sample purge flow 60 mL/min).

The modified MWCNTs were characterized by Fourier transform infrared spectroscopy (FTIR, NICOLET MX-1E Fourier transform infrared spectrometer, 400–4000 cm\(^{-1}\) range).

The X-ray photoelectron spectroscopy (XPS) of MWCNTs-A1120 was performed on Escalab 250Xi (XPS). The spectra of Si 2s were fitted by “XPS Peak 4.1” software.

The morphology of modified MWCNTs (MWCNTs-A1120) was analyzed by a ZEISS Libra 200 FE transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV.

The composites were pulled off on a tensile testing machine. The fracture surfaces were evenly attached with gold powder and were observed under an accelerating voltage of 20 kV with a JEOL JSM-5900LV for scanning electron microscopy (SEM) experiment.

Both dielectric properties and conductive properties of fluoroelastomer/MWCNTs-A1120 composites were measured by a TH 2826 LCR meter. Before test, both sides of the samples were coated with a thin layer of conductive silver paste to form a plate capacitor.

### RESULTS AND DISCUSSION

#### Characterization of Modified-MWCNTs

FTIR spectra of raw MWCNTs, MWCNTs-COOH, MWCNTs-NH\(_2\), and MWCNTs-A1120 are shown in Fig. 2(a). The bands at 3442 and 1631 cm\(^{-1}\) are stretching vibrational band and bending vibration band of –OH groups, which proves that raw MWCNTs contain –OH groups.\(^{[18,20,21]}\) The band appearing at 1669 cm\(^{-1}\) for MWCNTs-COOH and MWCNTs-NH\(_2\) corresponds to the stretching vibration of C=O of –COOH groups on MWCNTs-COOH and C=O of –CONH\(_2\) groups on MWCNTs-NH\(_2\).\(^{[17,22]}\)

As shown in XPS spectra (Fig. 2b), the peaks at 284 and 531 eV correspond to C 1s and O 1s, respectively. Compared with MWCNTs-COOH, the XPS peak of N 1s at 400 eV can be observed from MWCNTs-NH\(_2\), indicating that EDA was successfully grafted on MWCNTs-COOH. The XPS peak of N 1s at 400 eV can also be observed from MWCNTs-A1120. Besides, the Si 2p peak at 103 eV can be observed from MWCNTs-A1120. The peak fitting of XPS spectra of MWCNTs-A1120 is shown in Fig. 2(c). For Si 2p spectrum, it can be deconvoluted into two peaks at 102.4 eV (–Si–O–C–) and 103.2 eV (–O–Si–O–).\(^{[23]}\) These results indicate that the MWCNTs were coated by the silane coupling agent A1120.

In order to further verify that silane coupling agent A-1120 was successfully coated onto MWCNTs, the thermogravimetric curve of the MWCNTs-A1120 and its TEM characterization are shown in Fig. 3. It can be seen from Fig. 3(a) that the surface boundary of MWCNTs-A1120 is blurred and coated with a layer of material. At the same time, it can be seen from the

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thermal weight loss curve of Fig. 3(b) that MWCNTs-A1120 is decomposed prior to the raw MWCNTs, which is caused by poor thermal stability of the silane coupling agent A-1120,[24] implying the successful grafting of silane coupling agent A-1120 onto the surface of MWCNTs.

**Characterization of Fluoroelastomer Composites with Various Modified-MWCNTs**

To study the effect of different modified-MWCNTs on the comprehensive properties of fluoroelastomer nanocomposites, and to select the optimal modification method, we prepared neat fluoroelastomer film and four kinds of fluoroelastomer/MWCNTs composites with the same doping ratio. According to the relevant references,[25] the unmodified MWCNTs started to agglomerate at about 0.5 wt%, so the doping ratio was controlled to be 0.5 wt%. For brevity, the fluoroelastomer, fluoroelastomer/raw MWCNTs composite, fluoroelastomer/MWCNTs-COOH composite, and fluoroelastomer/MWCNTs-NH₂ composite, and fluoroelastomer/MWCNTs-A1120 composite are labelled as #0, #1, #2, #3, and #4, respectively.

**Mechanical properties**

The mechanical properties of fluoroelastomer/MWCNTs composites are shown in Fig. 4. The tensile strength of #0 is 11.94 MPa, and the elongation at break is 118.23%. Compared with #0, the tensile strength of composite elastomer doped with MWCNTs has been improved to varying degrees. The composites doping modified MWCNTs are greater than #1, and the tensile strength of #3 and #4 are greater than that of #2. The tensile strength of #3 is 13.64 MPa, which is 14.24% higher than that of #0, and the tensile strength of #4 is 13.92 MPa, which is 16.58% higher than that of #0. While the elongation at break of the composite elastomers has been decreased compared with #0, the elongation at break of #3 and #4 maintains at around 111%. This phenomenon is closely related to the interfacial interaction between the filler and elastomer matrix.[26] For the composite elastomer with the same MWCNTs doping amount, the stronger the interfacial interaction between MWCNTs and fluoroelastomer matrix is, the higher the tensile strength of the composite will be, and the better the performance of elongation at break can be maintained.[27,28] So, the MWCNTs containing amino-group (MWCNTs-NH₂, MWCNTs-A1120) are proved to have good interfacial compatibility with the elastomer matrix.

**Dielectric properties**

The dielectric properties of fluoroelastomer/MWCNTs composites are shown in Fig. 5. Compared to #0, the incorporation of MWCNTs will enhance the dielectric properties of composite elastomer. It can be seen from Fig. 5(a) that #1 has the highest dielectric constant, with the dielectric constant being 7.35 at 10 kHz. The dielectric constant of #4 is 7.11 at 10 kHz, which is similar to that of fluoroelastomer/raw MWCNTs composite. Besides, the dielectric constant of #2 is 6.76 and the dielectric constant of #3 is 6.70. Fig. 5(b) shows the dielectric loss of raw fluoroelastomer and composites. At high frequencies, the incorporation of MWCNTs has little effect on the dielectric loss of the elastomer, but the dielectric loss and dielectric constant...
before 10 kHz experience a sudden decrease, which is caused by dielectric relaxation.\textsuperscript{29,30} Meanwhile, the dielectric properties of composites are mainly affected by interfacial polarization between the fillers and the matrix. The good dispersion of MWCNTs in the matrix will contribute a large number of interfaces in the composite, which means that there will be more microcapacitors in the composite.\textsuperscript{[17]} Therefore, enhancing the dispersion of the filler in the composite is an effective way to improving the dielectric properties of the composite material. In summary, MWCNTs-A1120 has excellent electrical properties which are comparable with those of raw MWCNTs.

**Dispersion of fillers**

Fig. 6 corresponds to the fracture morphology of the elastomer composites and the cross-linking schematic between MWCNTs and fluoroelastomer matrix. It can be seen from Figs. 6(a) and 6(c) that raw MWCNTs are easily agglomerated due to their high surface energy, and the interface compatibility between MWCNTs and elastomer matrix is poor, so there are obvious traces of MWCNTs extraction on the cross section. On the other hand, it can be seen from Figs. 6(b) and 6(d) that MWCNTs-A1120 are uniformly dispersed in the elastomer matrix, and there is no obvious extraction trace. This phenomenon is mainly due to the fact that the carbon-carbon double bond (\(-C\equiv C\)) formed by the elastomer during the crosslinking process can be chemically bonded to the amino group on the MWCNTs-A1120, so MWCNTs-A1120 and fluoroelastomer have a strong interface with each other.\textsuperscript{[17]} This is also the reason why the composites containing amino MWCNTs (MWCNTs-NH\textsubscript{2}, MWCNTs-A1120) have excellent mechanical properties.

The modification of MWCNTs can improve the interfacial compatibility between the filler and the matrix, and enhance the mechanical properties of the composite to some extent. However, the surface modification will also cause different degrees of damage to the MWCNTs’ structure, which will affect their electrical properties.\textsuperscript{[31]} MWCNTs-A1120 has a good interface compatibility with fluoroelastomer, and comparable electrical properties with those of raw MWCNTs. Therefore, among these modification methods, the method of using silane coupling agent A1120 for modification is the optimal modification method.

**Properties of Fluoroelastomer/MWCNTs-A1120 Composites**

From the above experiments, it is concluded that the modified MWCNTs (MWCNTs-A1120) have excellent comprehensive properties, which is mainly due to the fact that MWCNTs-A1120 can be bonded together with the fluoroelastomer matrix in cross-linking process, and the specific cross-linking reaction diagram is shown in Fig. 7. Under the action of TBAHS, the molecular chain of fluoroelastomer will form \(-\text{CF}=\text{CH}#\) by eliminating HF. Then, during the second stage of vulcanization, BPAF will react with the molecular chain to form \(\text{C}#\text{O}\text{H}=\text{R}\) to crosslink the fluoropolymers together.\textsuperscript{[32,33]} At the same time, the amino group on the surface of MWCNTs-A1120 can react with \(-\text{CF}=\text{CH}#\) on the molecular chain of the fluoroelastomer to form \(-\text{C}=\text{N}#\). Therefore, MWCNTs-A1120 and the crosslinker system can construct dual crosslinking networks in the fluoroelastomer matrix.

**Morphology of fluoroelastomer/MWCNT-A1120 composites**

Fluoroelastomer/MWCNTs-A1120 composites with different
MWCNTs-A1120 doping ratios (1 wt%, 3 wt%, 5 wt%, and 7 wt%) were prepared by a simple solution blending method. [34] Fig. 8 shows the fracture morphology of the composite materials with different doping ratios of MWCNTs-A1120. At 1 wt% and 3 wt% doping ratios, MWCNTs are uniformly dispersed in the fluoroelastomer matrix. As the filler content increases, MWCNTs begin to contact each other to form a conductive network. And a significant agglomeration began to occur at a content of 7 wt% MWCNTs-A1120, which can be seen in the dashed wireframes in Fig. 8(d) clearly.

**Dielectric properties**

For dielectric materials, high dielectric constant corresponds to high capacitance value, meaning that the material has a strong charge capacity. Dielectric loss is also called the dielectric loss tangent, and the high dielectric loss means that the material consumes a large amount of electricity. Therefore, a good dielectric material should have high dielectric constant and low dielectric loss.

Fig. 9 shows the relationship between the dielectric properties and the filler content of fluoroelastomer nanocomposites. The dielectric constant and dielectric loss of the composite increase with the increase of filler content. As shown in Fig. 9(a), especially for the sample with 5 wt% MWCNT-A1120, the dielectric constant and dielectric loss increase in an order of magnitude, meaning the formation of a conductive network. For example, the dielectric constant of neat fluoroelastomer at 10 kHz is 5.836, the composite with 1 wt% MWCNT-A1120 has a dielectric constant of 6.805, and the composite with 3 wt% MWCNT-A1120 has a dielectric constant of 11.209, which is 92.07% higher than that of the neat fluoroelastomer. Meanwhile, the dielectric loss is substantially unchanged and remains below 0.06. When the amount of filler is 5 wt%, the dielectric constant increases to 6588.901 and the dielectric loss is 26.064. When the amount of filler is 7 wt%, the dielectric constant increases greatly to 33666.48, and the dielectric loss is as high as 72.512.

**Volume resistivity**

The volume resistivity of the fluoroelastomer nanocomposite is shown in Fig. 10. When the doping amount of the composite is 1 wt% and 3 wt%, a significant frequency dependence can be observed, and the volume resistivity decreases with an increase...
in frequency, especially in the frequency range of 100 Hz to 10 kHz (Fig. 10a). Such a relaxation phenomenon was caused by the interfacial polarization between the fluoroelastomer molecules and the conductive MWCNTs-A1120.\textsuperscript{36,37} When the filler amount reaches 5 wt\% and more, the volume resistivity is significantly reduced, and the phenomenon of frequency dependence is also weakened, so 5 wt\% is the percolation threshold.\textsuperscript{38} Moreover, it can be seen from Fig. 10(b) that the volume resistivity of the composite at 5 MHz decreases with the increase of MWCNTs-A1120, and it can be seen that when the amount of filler increases from 1 wt\% to 7 wt\%, the volume resistivity decreases from 718 Ω·m to 63 Ω·m.

**Fig. 9** Dielectric constants (a) and dielectric loss (b) of fluoroelastomer/MWCNTs-A1120 composite with the increase of MWCNTs-A1120 contents. To express the dielectric properties of each content clearly, the dielectric data with content of 0 wt\%, 1 wt\%, and 3 wt\% are supplemented in the upper right corner.

**Fig. 10** The volume resistivity of fluoroelastomer/MWCNTs-A1120 composites (a); The volume resistivity of composites with the increase of MWCNTs-A1120 contents at 5 MHz (b).

**Electrical properties under mechanical stretching**

In the case of a small amount of fillers, a conductive network has not yet formed between the MWCNTs in the composite, so the conductivity of the composite mainly depends on the tunneling effect and the electron migration during thermal vibration between the MWCNTs.\textsuperscript{39} Therefore, at low doping ratios, the frequency dependence of the composite material is large, and the higher the frequency, the lower the resistivity of the composite. When the amount of fillers reaches the percolation threshold, MWCNTs contact with each other to form a conductive network, so the volume resistivity of the composite material is stable and has a low frequency dependence. Fig. 11 shows the volume resistivity of fluoroelastomer nanocomposite with the increase of tensile deformation.

It can be seen from the figure that as the deformation increases, the volume resistivity increases, which is caused by the increase in the spacing between MWCNTs-A1120 due to stretching. When the filling amount is 5 wt\%, there is a huge increase at 30% deformation in volume resistivity, which means the break of the MWCNTs’ conductive network. However, when the amount of fillers reaches 7 wt\%, the volume resistivity of the composite does not change much with the increase of tensile deformation, which proves that the conductive network structure of the composite will not be destroyed under 30% deformation. It can be seen from the above experiments that 5 wt\% is the penetration threshold of the composite. At this time, MWCNTs in the composite form a conductive network, and the composite material becomes a conductor; nevertheless, the stability of the MWCNTs’ network is low, so it will be significantly damaged under 30% deformation. Fig. 12 shows the changes in dielectric properties of composites with 5 wt\% MWCNTs-

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A1120 under tensile deformation. It can be seen that both dielectric constant and dielectric loss of the composites decrease as the tensile deformation increases, which is consistent with the change of volume resistivity in Fig. 11(c). Under the low strain of 10%, the dielectric constant decreases only due to the increase of distance between the fillers. As the strain increases, the dielectric constant drops significantly, demonstrating that the conductive network of the sample is damaged by deformation, so the tensile deformation will cause the composite to transform from a conductive material to a dielectric material.

CONCLUSIONS

A variety of modified MWCNTs have been successfully prepared. Compared with other modified MWCNTs, MWCNTs-A1120 has a
better interfacial interaction with fluoroelastomer matrix, so it has the best dispersion in the matrix and the composite shows the best mechanical properties (the tensile strength is increased by 16.58% compared to that of the neat elastomer; the elongation at break is maintained above 111% with 0.5 wt% fillers). What is more, MWCNTs-A1120 has comparable electrical properties to those of original MWCNTs (The dielectric constant of fluoroelastomer/MWCNTs-A1120 at 10 kHz is 7.11 while the dielectric constant of fluoroelastomer/raw MWCNTs is 7.35), so grafting MWCNTs with silane coupling agent A-1120 is a good modification method. The effects of filler content and tensile deformation on the electrical properties of composites were investigated with MWCNTs-A1120 as filler. The experimental results show that as the amount of MWCNTs-A1120 increases, the dielectric constant and dielectric loss of the composite increase, and the volume resistivity decreases. When the doping amount of the filler is 5 wt%, the dielectric constant and dielectric loss of the composite increase dramatically, and the volume resistivity decreases sharply. It can be proved that a conductive network is formed by MWCNTs-A1120, so the doping amount 5 wt% of MWCNTs-A1120 is the percolation threshold of the composite. At the same time, as the tensile deformation increases, the dielectric constant and dielectric loss of the composite decrease, and the volume resistivity increases. It is proved that the tensile deformation can increase the spacing of the conductive filler or even destroy the conductive network structure, thus affecting the electrical properties of the materials. Therefore, fluoroelastomer/MWCNTs-A1120 composites have potential applications in flexible dielectric materials and flexible conductive materials.

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