Negative Permittivity Behavior in Flexible Carbon Nanofibers-Polydimethylsiloxane Films

Haikun Wu,¹,² Haowei Sun,¹ Fengjin Han,¹ Peitao Xie,¹,* Yiming Zhong,¹ Bin Quan,³ Yaman Zhao,⁴ Chunzhao Liu,¹,* Runhua Fan⁴ and Zhanhu Guo⁵

Abstract

Flexible electronic devices have recently become a research hotspot due to their potentials in different applications. However, there is a lack of studies about flexible metamaterials with negative parameters. In this work, the composite film with carbon nanofibers (CNFs) dispersed in polydimethylsiloxane (PDMS) matrix is designed to construct the flexible metamaterials with negative permittivity, showing excellent mechanical durability and flexibility. The microstructures, mechanical durability, alternating current conductivity (σac) and permittivity (ε' and ε'') were investigated and discussed in detail. A transition of conduction mechanism from jumping conduction to metal-like conduction was observed when the CNFs content was improved from 6 to 14 wt%. The CNFs-PDMS film with CNFs content of 14 wt% achieved negative permittivity over the whole frequency, which resulted from the construction of conductive CNFs network. The equivalent circuit models were used to analyze impedance (Z′ and Z″) behavior of the composites to determine the mechanism of negative permittivity. This study will provide theoretical and technical support for the design of flexible metamaterials and promote their practical applications in wearable electronic devices.

Keywords: Negative permittivity; Silicone rubber; Carbon nanofibers; Flexible film.

Received: 29 August 2021; Accepted: 20 November 2021.

Article type: Research article.

1. Introduction

In the past few years, silicone rubber (SR)-based composites have received much attention due to their unique characteristics, such as low toxicity, chemical stability, low-temperature toughness and low-surface energy.⁶⁻¹⁰ As for constructing SR-based composites, the nature, properties and dispersion of the filler, and interfacial interaction between filler and SR matrix are all significant for determining the final performance of composites.⁶⁻¹⁰ For example, metal nanoparticles, nanoscale carbon materials and silicates are incorporated into the SR matrix to fabricate SR-based composites, showing enhanced mechanical, electrical, thermal and other functional properties.¹¹⁻¹⁵ Due to these excellent performances, SR-based composites exhibit great potentials in applications of artificial skin, aerospace, electromagnetic interference shielding and absorbing, etc.¹⁶⁻¹⁸

Among carbon materials, carbon nanofibers (CNFs) exhibit excellent mechanical strength and electrical properties, which are attributed to CNFs’ graphite ordering and dimension.¹⁸ Besides, the properties of CNFs are related to their diameters and lengths, which are in the order of micrometers. As a result, CNFs are usually used to prepare SR-based composites with a lot of applications. Roy et al.²⁰ have reported that the tensile strength and modulus of carbon nanofibers-polydimethylsiloxane (CNFs-PDMS) composites are improved by 150% and 310% respectively, compared to pure PDMS. Enhanced electrical conductivity (in the order of 10⁻⁸ S·cm⁻¹) of CNFs-PDMS composites is reported, which is assigned to the better dispersion of CNFs.²¹

However, CNFs used as fillers in SR matrix to change dielectric properties and achieve negative permittivity are rarely investigated and reported. Due to intrinsic properties such as lower loss, outstanding electricity, excellent transparency and good mechanical property, PDMS is regarded as a promising candidate to construct flexible and wearable devices. In this paper, the CNFs-PDMS films with
excellent mechanical durability and flexibility were prepared to achieve negative permittivity and exhibit great potentials in the fields of electromagnetic functional materials and wearable electronics. The microstructures of CNFs and CNFs-PDMS films were characterized by field emission scanning electron microscopy (FESEM). Mechanical durability and flexibility were tested under various mechanical deformation. The dielectric properties including conduction mechanism and negative permittivity behavior were investigated. The equivalent circuit models from impedance ($Z'$ and $Z''$) were used to analyze the mechanism of the negative permittivity.

2. Experimental
2.1 Procedures
The in-situ polymerization process was used to fabricate carbon nanofibers (CNFs)-polydimethylsiloxane (PDMS) films. The silicone (Sylgard 184 A, Dow Corning Company), n-heptane and curing agent (Sylgard 184B, Dow Corning Company) were mixed together with a 10:10:1 weight ratio in a beaker. Different contents of CNFs (6, 8, 10, 12 and 14 wt%) was incorporated into the mixed solution and ultrasonic treatment at room temperature was performed to allow CNFs to disperse uniformly in the solution. After that, the film applicator (Elcometer 3530) was used to coat the slurry on the glass substrate. The film with thickness of 100 μm was dried at 353 K for 2 hours in the oven. And then the CNFs-PDMS film was taken out and peeled off from the substrate.

2.2 Characterization
The microstructures of CNFs-PDMS films were observed by the FESEM (Hitachi, SU-70, Tokyo, Japan). The alternating current conductivity ($\sigma_{ac}$), complex permittivity ($\varepsilon'$, $\varepsilon''$), and the impedance ($Z'$, $Z''$) of the CNFs-PDMS films were measured by the impedance analyzer (Agilent E4991A). The real part of permittivity ($\varepsilon'$) and imaginary part of permittivity ($\varepsilon''$) were obtained from the formula $\varepsilon' = Cd/A\varepsilon_0$ and $\varepsilon'' = d/(2\pi f A\varepsilon_0)$, where $C$ is the output data, representing the capacitance, $d$ is the thickness of CNFs-PDMS film, $A$ is the area of electrode, $\varepsilon_0$ is the permittivity of vacuum ($8.85 \times 10^{-12}$ F/m), $f$ is the tested frequency. Alternating current conductivity was obtained by $\sigma_{ac} = d/R A$, where $R$ is output data, representing the resistance. The real part of impedance ($Z'$) and imaginary part of impedance ($Z''$) were measured directly.

3. Results and discussion
3.1 Microstructure of the CNFs-PDMS films
The microstructures of CNFs-PDMS films with different CNFs contents are shown in Fig. 1. From Fig. 1a, it was observed that CNFs exhibited cylindrical nanostructures with diameter in the order of nanometers and lengths in the order of micrometers, the CNFs stacked different arrangements in the form of herringbone or ribbon. When CNFs were incorporated into PDMS matrix to form CNFs-PDMS film with CNFs content of 6 wt% (Fig. 1b), CNFs were observed to be dispersed uniformly in the PDMS matrix and isolated by the insulating matrix. The CNFs with good electrical conductivity and insulating PDMS matrix could be equivalent to micro-capacitors, so there were many equivalent micro-capacitors in CNFs-PDMS films. When CNFs content was increased, more CNFs were distributed in the insulating matrix, indicating that more equivalent micro-capacitors were formed in CNFs-PDMS films. As shown in Fig. 1f, when CNFs content was improved to 14 wt%, CNFs connected to each other to form continuous pathways in the film. These results indicated that microstructures, equivalent micro-capacitors and conductive pathways in CNFs-PDMS films could be adjusted by changing CNFs content.

Photographs of the CNFs-PDMS film under various mechanical deformation such as cutting, winding, multi-twisting, folding and multi-folding are shown in Fig. 2. From Fig. 2a, it was observed that the CNFs-PDMS film was easy to be cut, just like paper, exhibiting good processibility, hence, the composite film can be processed into different shape when used as flexible electronic devices. As shown in Fig. 2b and Fig. 2c, the CNFs-PDMS film under winding and multi-twisting still exhibited good mechanical stability and durability. Even under folding and multi-folding (Fig. 2d and e), the CNFs-PDMS film was still not broken down, indicating excellent flexibility and robustness. The excellent mechanical durability and high flexibility allowed the CNFs-PDMS film to exhibit applications for wearable electronic devices.

3.2 Alternating current conductivity of the CNFs-PDMS films
Fig. 3 exhibits the frequency dependence of alternating current conductivity ($\sigma_{ac}$) for CNFs-PDMS films with different CNFs contents. It was observed that $\sigma_{ac}$ went up as the CNFs content increased from 6 to 14 wt% within the tested frequency range, which was attributed to the addition of CNFs with good electrical conductivity. For CNFs-PDMS films with CNFs content from 6 to 12 wt%, the $\sigma_{ac}$ increased with frequency, following the Jonscher power law: $\sigma(\omega) \propto A\omega^n$ where $A$ is the pre-exponential factor, $\omega (\omega = 2\pi f)$ represents the angular frequency, and $n$ is the fractional exponent. The fitted results using the formula were shown as solid red lines in Fig. 3, and the R-square of fitted results for CNFs-PDMS films with CNFs contents from 6 to 12 wt% was 0.99, 0.98, 0.98 and 0.96 respectively, indicating that the experimental data were strongly relevant to Jonscher power law and thus hopping conduction behavior played a significant role in these composite films. These results were consistent with the

---

$^{4}$ College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai.
$^{5}$ Integrated Composites Laboratory (ICL), Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States.

*E-mail: xiepeitao1991@qdu.edu.cn (P. Xie); czliu@qdu.edu.cn (C. Liu)
Fig. 1 FESEM images of the carbon nanofibers (CNFs) powders (a) and carbon nanofibers-polydimethylsiloxane (CNFs-PDMS) films with different CNFs contents of 6 wt% (b), 8 wt% (c), 10 wt% (d), 12 wt% (e), and 14 wt% (f).

results of microstructures, because CNFs were isolated by insulating matrix and electrons could just jump between isolated CNFs for films with CNFs content from 6 to 12 wt%. However, when CNFs content was increased to 14 wt%, the $\sigma_{ac}$ exhibited a direct-current (dc) conductivity plateau and decreased with frequency in the high-frequency range. This indicated another conduction mechanism: metal-like conduction behavior, attributed to the formation of conductive CNFs network in the composite films.[28]

Fig. 2 The photographs of high flexible CNFs-PDMS films with different operation. (a) Cutting, (b) Winding, (c) Multi-twisting, (d) Folding, and (e) Multi-folding.
3.3 Dielectric properties of the CNFs-PDMS films

The frequency dispersions of real permittivity ($\varepsilon'$) for the CNFs-PDMS films with different CNFs contents are shown in Fig. 4a. For films with CNFs content from 6 to 12 wt%, it was found that the value of $\varepsilon'$ was positive over the whole frequency, and the $\varepsilon'$ increased with increasing CNFs content at low frequencies. When CNFs content was low, the CNFs isolated by insulating PDMS matrix could be equivalent to micro-capacitor electrodes, which was observed and discussed from microstructure results. Moreover, interfacial polarization appeared between CNFs and PDMS due to the accumulation of charge carriers in the interface under the external electrical field.\[29,30\] The micro-capacitors effect and interfacial polarization effect were enhanced with the increase of CNFs content, leading to the improvement of positive permittivity. In the dielectric materials, the macroscopic electric field ($E_M$) is composed of two parts, that is, tested electrical field ($E_T$) and electrical field ($E_D$) caused by surface bound charges, $E_M = E_T + E_D$. The direction of $E_D$ is opposite to that of $E_T$ in the materials with positive permittivity, so $E_M < E_T$ and $E_D$ is also called depolarization field.\[31\] From Fig. 4a, it was also found that the $\varepsilon'$ decreased with the frequency, which was attributed to the dielectric relaxation behavior at higher frequency.\[32,33\]

However, when CNFs content was increased to 14 wt%, it was observed that the $\varepsilon'$ was negative within the tested frequency, resulting from the formation of conductive CNFs network in the film. In the materials with negative permittivity, the direction of $E_D$ is the same as that of $E_T$, so $E_M > E_T$ and this phenomenon is also called Local electric field enhancement effect.\[31\] The type of negative permittivity was not consistent well with the Drude model which was usually used to describe the negative permittivity behavior in metal conductive network.\[34,35\] It was observed that the negative permittivity showed small negative value ($0 < \varepsilon' < -30$), moreover, the negative permittivity value was less dependent on frequency compared with the typical Drude-type ones, which exhibited great potentials in double negative metamaterials, electromagnetic shielding and none-winding inductor due to good impedance matching behavior. The negative permittivity could be explained by the combination of Lorentz-type dielectric behavior and Drude-type behavior. The dielectric constant was given:\[36,37\]

$$\varepsilon'_r = 1 - \omega_p^2 / (\omega^2 + \Gamma_D^2) + K \omega_L^2 (\omega_L^2 - \omega^2) / (\omega_L^2 - \omega^2)^2 + \Gamma_L^2 \omega^2$$ \hspace{1cm} (1)$$

where, $\Gamma_D$ is the damping constant, $\omega_p = 2\pi f_p$ is the plasmon angular frequency, $\Gamma_L$ is the damping constant of Lorentz resonance, $\omega_L = 2\pi f_L$ is the Lorentz resonance angular frequency, and $K$ is the dc electric susceptibility. Different dispersion of CNFs resulted in different dielectric responses, conductive CNFs networks made contributions to Drude-type dielectric response while isolated CNFs made more contributions to Lorentz-type dielectric response.\[37\] Therefore, these results showed that the appearance of negative permittivity was affected directly by microstructures.

---

Fig. 3 Frequency dependences of alternating current conductivity ($\sigma_{ac}$) from the CNFs-PDMS films with different CNFs contents of 6, 8, 10, 12 and 14 wt%.
The frequency dispersions of imaginary permittivity ($\varepsilon''$) for the CNFs-PDMS films with different CNFs contents are shown in Fig. 4b. The $\varepsilon''$ increased with increasing CNFs contents from 6 to 14 wt%, which was ascribed to the enhancement of dielectric loss in films. The dielectric loss mainly resulted from interfacial polarization loss and conduction loss.[38-44] For films with CNFs content from 6 to 12 wt%, interfacial polarization effect was obvious and enhanced with increasing CNFs content, so the $\varepsilon''$ increased and interfacial polarization loss was the main dielectric loss mechanism in these films. However, for the film with CNFs content of 14 wt%, the continuous conductive network was formed and the conduction current was generated, resulting in the conduction loss which mainly contributed to dielectric loss mechanism. The flexible CNFs-PDMS film with negative permittivity and relatively low dielectric loss could be a promising candidate to make wearable sensors, new antenna, perfect lens and electromagnetic interference shielding materials.[45-50]

3.4 Impedance and equivalent circuit analysis of the CNFs-PDMS films

The equivalent circuit analysis based on impedance spectra of CNFs-PDMS films was performed to study the influence of microstructures on negative permittivity behavior and mechanisms (Fig. 5). From Fig. 5a to Fig. 5d, it was found that the imaginary part of impedance, which represents the reactance, was negative over the whole frequency for films with CNFs content from 6 to 12 wt%, exhibiting a capacitive behavior. The fitted results, which were based on their equivalent circuit models consisting of a series resistor ($R_1$), a capacitor (C) and a parallel resistor ($R_2$), are shown as solid lines. The Chi-squared value was used to describe the correlation between simulated equivalent circuit models and experimental data, the smaller value of Chi-squared, the stronger correlation between simulated equivalent circuit models and experimental data. The Chi-squared statistic for films with CNFs content of 6, 8, 10 and 12 wt% was $1.07 \times 10^{-2}$, $2.33 \times 10^{-3}$, $5.66 \times 10^{-4}$ and $1.22 \times 10^{-3}$, respectively. The capacitor C in the model originated from equivalent micro-capacitors in microstructures and distributed capacitance in the CNFs microregions. When CNFs content increased from 6 to 12 wt%, it was found that the simulated C value improved from $3.51 \times 10^{-12}$ F to $1.15 \times 10^{-11}$ F, indicating that more equivalent micro-capacitors were formed. These results were consistent with the analysis of microstructures and dielectric constant.

When CNFs content increased to 14 wt% (Fig. 5e), the imaginary part of impedance became positive within the tested frequency, corresponding to inductive characteristics. Its equivalent circuit model consisted of a capacitor C, inductors ($L_1$ and $L_2$) and resistors ($R_1$ and $R_2$), the Chi-squared value was $9.07 \times 10^{-4}$. It was found that the simulated C value decreased from $1.15 \times 10^{-11}$ F to $9.26 \times 10^{-12}$ F when CNFs content was increased from 12 to 14 wt%, which was attributed to the formation of continuous conductive CNFs network. In the process, CNFs microregions were mainly used to form conductive pathways instead of the micro-capacitor network, so equivalent micro-capacitors effect was degenerated gradually. Inductors in the equivalent circuit model originated from conductive CNFs network and represented the conductive loop in films. The results showed that microstructures had a significant effect on dielectric properties and the negative permittivity behavior was closely related to conductive CNFs network.

Fig. 4 (a) Frequency dependences of the real permittivity ($\varepsilon'$) for the CNFs-PDMS films with different CNFs contents from 6 to 14 wt%. (b) Frequency dependences of the imaginary permittivity ($\varepsilon''$) from the CNFs-PDMS films with different CNFs contents from 6 to 14 wt%.
Fig. 5 Equivalent circuit analysis of the CNFs-PDMS films. CNFs-PDMS films with CNFs content from 6 to 12 wt% were equivalent to the circuit model consisting of a capacitor and resistors (a, b, c and d). The CNFs-PDMS film with CNFs content of 14 wt% was equivalent to the circuit model consisting of a capacitor, resistors, and inductors (e). Re (Z) was the real part of impedance. Im (Z) was the imaginary part of impedance.

4. Conclusions
In summary, the flexible CNFs-PDMS films with tunable negative permittivity and excellent mechanical durability were prepared. Continuous conductive CNFs network was observed when CNFs content was 14 wt% in the composite film, and micro-capacitor effect was obvious when CNFs was below 14 wt%. When the content of CNFs increased from 6% to 14 wt%, a transition in the conduction mechanism from jump conduction to metal-like conduction was observed. Negative permittivity behavior was found in the CNFs-PDMS film with CNFs content of 14 wt% due to the formation of conductive network, which was explained by the combination of Lorentz model and Drude model. The equivalent circuit model showed that inductors represented the appearance of negative permittivity. The flexible CNFs-PDMS films with adjustable negative permittivity will have great significance in designing novel electromagnetic devices and intelligent materials, where the excellent mechanical durability is essential for designing wearable electronic devices.

Acknowledgements
This work received the financial support from Natural Science Foundation of Shandong Province [ZR202003031], the China Postdoctoral Science Foundation [2020M671992], Key Research and Development Project of Shandong Province [grant No. 2019GSF109079], National Natural Science Foundation of China [grant No. 52101176], and support from State Key Laboratory of Bio-fibers and Eco-textiles, Institute of Biochemical Engineering.

Conflict of interest
There are no conflicts to declare.

Supporting information
Not applicable.

References
Chunzhao Liu, professor of materials science and engineering in Qingdao University. His main research field is biochemistry, studying the biochemical separation/catalytic applications by using functional magnetic beads modified with multi-functional groups, and realizing industrial applications in cell/protein magnetic separation and magnetic nano-enzyme catalysis.

Publisher’s Note: Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.