Negative permittivity materials based on electro-active polyimide/carbon composites

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Introduction

Since 1968, the concept of left-hand material with negative permittivity and negative pemeability was proposed by Veselago[1, 2], great efforts have been made to develop this new kind of material, because of the distinctive behaviors such as negative refractive index, reversed Doppler Effect, and reversed Cherenkov radiation[3]. However, due to the special double negative properties, LFH materials do not exist in natural materials. Therefore, the research is focused on the fabricated metamaterial and most of the work is concentrate on physical structure including double-split-ring resonators, S-shaped resonators, multilevel dendritic structures, nano/small apertures, metallic nanoclusters[4-6]. While, the preparation of negative permittivity or negative permeability materials based on chemical structure or composition has aroused considerable interest in recent years[3, 5, 7].

In this paper, we introduced a polyimide/CNTs nanohybrid material with negative permittivity by using a fluorine containing polyimide (6FDA/DHTM) as electroactive polymer matrix and carboxyl surface treatment CNTs as fillers. The trifluoromethyl groups in the polyimide functioned as electron acceptor, and CNTs served as electron donor. Then an enhanced 3D network would be formed by CNTs connected with polyimide when the electric field reached the resonant frequency. And the hybrid material may exhibit a negative permittivity behavior at the same time.

Results and Discussion

Figure.1 shows the real permittivity as a function of the frequency for PI/CNTs hybrid films with different CNTs ultrasonic treatment time. From the dielectric characterization, the hybrid film shows a largest negative permittivity value of about -1.5×10^5 when the ultrasonic treatment time is 4h. It is widely accepted that the ultrasonic treatment can cut the CNTs into short fraction and will improve the distribution of CNTs in the polymer matrix[8]. So the reason of this phenomenon can be explained by the percolation models. The longer CNTs makes it easy to form 3D network in the polyimide matrix owing to the agglomerate of CNTs with large aspact ratio. While for the shorter CNTs, though the distribution of CNTs is improved, the continuity of 3D network was wrecked and a high positive permittivity was obtained, which has also been found by Sui in ultrasonic treat of CNFs[3, 5]. But for the 2h ultrasonic treatment time, the negative permittivity behavior only appears in the high frequency range. This probably due to the poor distribution caused by the short ultrasonic treatment time.

The dependence of the dielectric loss (tanδ) on the frequency was shown in Figure.2. The hybrid films with 12h ultrasonic treatment CNTs as fillers have a stable tanδ through the whole frequency. However, for the 4h and 6h ultrasonic treatment CNTs hybrid films, sharp peaks are observed in the frequency that negative permittivity behavior appears. This can also prove that the negative permittivity appears when the frequency reach the resonant frequency of CNTs agglomerates.

Figure.3 displays the dependence of real part of effectvie permittivity on the frequency with CNTs dopant as a parameter for 6FDA/DHTM polyimid. The ε' of pure 6FDA/DHTM polyimide and 6FDA/DHTM-CNTs hybrid material with CNTs concentration of 1 wt% shows a positive value through the whole frequency range. When the CNTs loading increased to 2 wt%, it is interesting to observe negative permittivity in the frequency from 5×10^2 Hz to 5×10^3 Hz and 10^6 Hz to 10^7 Hz as shown in the inset of figure.3. However, the negative permittivity behavior has not been found in the BPDA/DHTM-CNTs hybrid material (figure.4). This behavior is proberbly caused by the strong electron withdrawing effect of fluorine. An electron donor-acceptor interface can be formed by the trifluoromethyl in the matrix and the CNTs fillers. When the hybrid material is placed in an electric field, a lot of electrons are accumulated in the interface and lead to a shape change of permittivity.

Conclusions

In this work, negative permittivity behavior has been observed in the polyimide/CNTs hybrid films using electric active polyimide(6FDA/DHTM) as matrix and CNTs as fillers. Different from the previous research which focus on the material structure, the negative permittivity found in this paper is more dependent on the chemical composition of matrix and the aspect ratio of CNTs.

Reference

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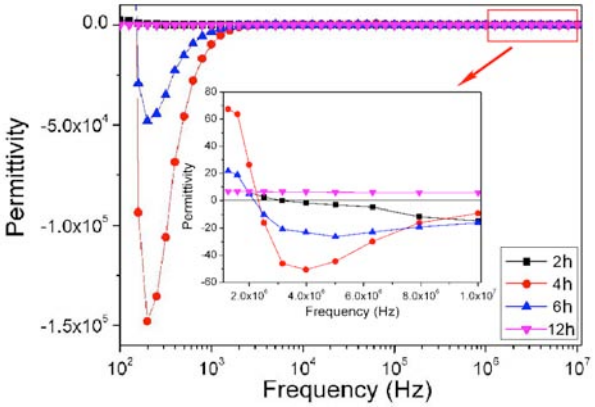

Figure 1. Dielectric properties of 6FDA/DHTM-CNTs hybrid film with different ultrasonic treatment time of CNTs. The inset is the enlarge photo for the high frequency of 10^6 to 10^7Hz.

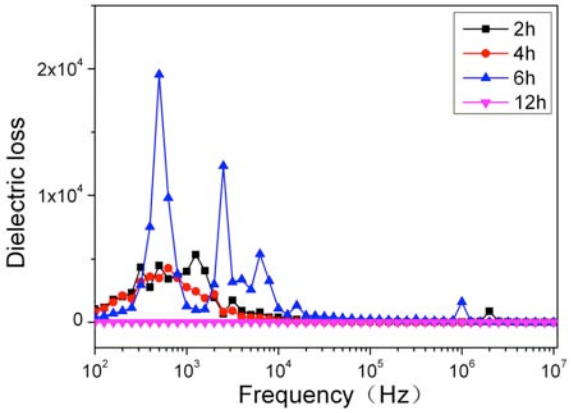

Figure 2. Dielectric loss of 6FDA/ DHTM-CNTs hybrid film with different ultrasonic treatment time of CNTs.

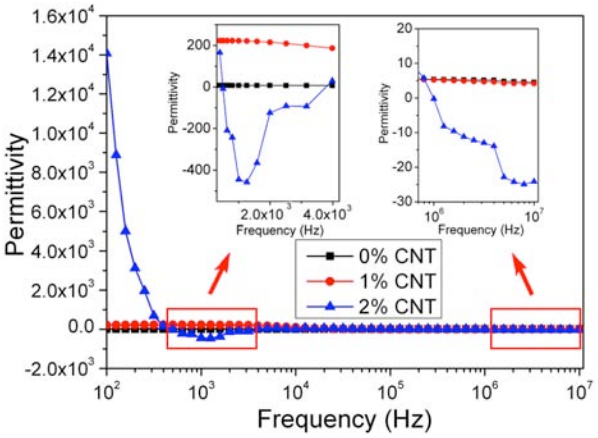

Figure 3. Dielectric properties of 6FDA/DHTM-CNTs hybrid film with different CNTs content. The inset is the enlarge photo for the frequency of 10^3 to 10^4Hz and 10^6 to 10^7Hz.

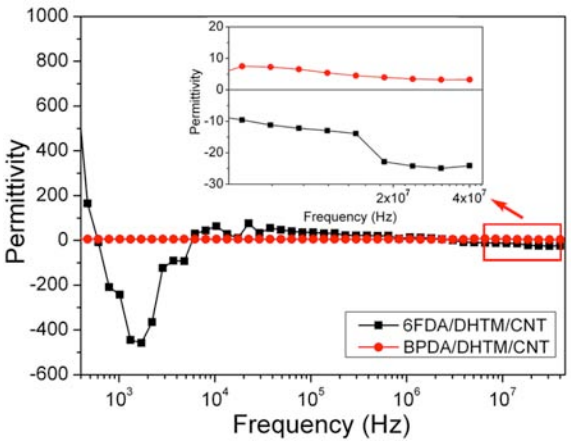

Figure 4. Dielectric properties of 6FDA/DHTM -CNTs hybrid film and BPDA/DHTM-CNTs hybrid film.