Study on novel carbon-nanotube / sulfonated poly(aryl ether ketone) composites with high dielectric constant at low percolation threshold

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Abstract Nanocomposites of Sulfonated Poly(Aryl ether ketone)(SPAEK) and functional multiwall carbon nanotubes (a-MWNTs) were fabricated by a solution method. Carbon-nanotubes had a great dispersing in the polymer. The composites exhibited a higher dielectric constant that was near 600 when the volume fraction of carbon-nanotubes was 0.07 (7 vol%) at 10^3 Hz. The percolation threshold of the a-MWNTs/SPAEK composites was only 3 vol% of a-MWNTs, and the dielectric constant could reach 210. The dielectric constant of composites changed little with frequency increase when the content of carbon nanotubes was more than 3 vol%, and the composites could keep high dielectric constant at the high-frequency(>200, at 10^6 Hz).

Key words: Dielectric properties; Sulfonated Poly(Aryl ether ketone); Carbon-nanotube.

1. Introduction

Conductive fillers, such as metal particles, carbon fibers, graphite, carbon black, and carbon nanotubes (CNTs), have attracted extensive attention for their superior electric conductivity.(1-3) A few years earlier, CNTs/polymer nanocomposites have been extensively studied since CNTs shows nanometer-scale dimensions, along with their large shape anisotropy, high mechanical strength, and very high thermal and electrical conductivity, in which even a very small amount of CNTs could induce significant changes in the material's properties.(4-6) Recently, due to the potential application of the CNTs/polymer nanocomposites with high dielectric constant and good electromechanical properties, they have been paid more attention, for instance super capacitors, on-chip capacitors, and electromechanical devices and microelectromechanical systems.

In these fields, several groups have found an extraordinary increase in the dielectric constant of CNTs/polymer composites. The past works has devoted effort to studying how to increase the dielectric constant and keep flexibility of composites in order to provide good electromechanical actuation. To achieve flexibility and high dielectric constants, it is important for the polymer composites to exhibit a low percolation threshold. Though more and more works have been performed to improving the dielectric constant and electromechanical actuation, numerous works are still focus on the preparation process of the nanocomposites with good dispersion of CNTs and the mechanism of high dielectric constant.(7-8) To obtain nanocomposites that have high dielectric constant, high mechanical strength and low percolation threshold, we present a simple, wet-chemistry procedure for preparing multiwalled-CNTs/Sulfonated Poly(Aryl ether ketone) (SPAEK) nanocomposites in this paper. Due to the side-chain with polarity sulfate group, which make it has a higher dielectric constant (about 6.5, at 10^3 Hz and room temperature). Therefore, all the composites of MWNTs/SPAEK could show a great dielectric performance. They still possessed a higher dielectric constant when the content of MWCNTs is more than 3 vol % at a higher frequency (10^6 Hz).

2. Experimental

2.1. Preparation of functional carbon nanotubes(a-MWNTs)

MWNTs grown by using chemical-vapor deposition were from Chengdu Organic Chemicals Co., LTD., Chinese Academy of Sciences. The diameter and length of MWNTs were about 10-20 nm and 30 μm, respectively. MWNTs was treated in mixing acid (H_2SO_4: HNO_3 = 3: 1) under sonication for 4 h in order to remove the impurities and the amorphous carbon, and to generate carbonyls on the surface of the MWNTs. This mixture was diluted and washed by deionized water, the a-MCNTs were obtained after dried in vacuum oven at 50 °C.(9)

2.2. Synthesis of SPAEK(10)

As shown in Scheme 1, poly(ether ether ketone)s were obtained by 4,4'-difluorobenzophenone (0.07 mol), sodium 5,5'-carbonyl-bis-(2-fluoroben-zenesulfonate) (0.03 mol), and Bisphenol A(0.10 mol) via nucleophilic aromatic substitution using toluene to remove the water formed during the polycondensation. The polymer was transformed to acid-form (SPAEK) by ion exchange in 2M H_2SO_4.

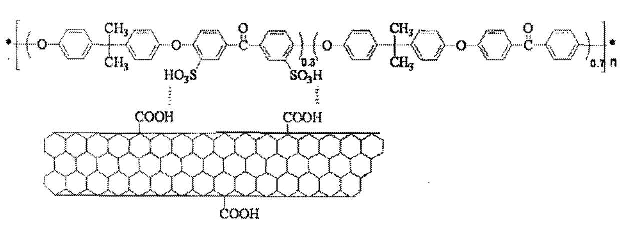
2.3. Preparation of functionalized a-MWNTs/SPAEK composite membranes

The a-MWNTs were ultrasonically dispersed in N-Methyl pyrrolidone(NMP) for up to 2 - 4 h in order to form a stable suspension. At the same time, SPAEK was also dissolved in NMP. Then, the suspension of a-MWNTs in NMP was added to the SPAEK solution, and the solution was subjected to ultrasonic treatment for 2 - 4 h. Afterwards, the solution was heated to 80 °C for 24 h to remove the solvent and then thermally treated it at 80°C for 48 h in vacuum oven to obtain the a-MWNTs/SPAEK composite membranes.

2.4 Instrumentations. The microstructures of the a-MWNTs/SPAEK composites were characterized by using scanning electron microscopy (JEOLJSM-6700). For electrical measurements, electrodes were painted on the sample surface by using silver paste. The dielectric response of the composites was measured by using an Alph-A High Performance Frequency Analyzer in the frequency range of 200 Hz–10^6 Hz.

3. Results and discussion

The microstructures of the fractured surfaces of the a-MWNTs/SPAEK composites with a-MWNTs of 1-3 vol% were showed in Figure 1a. The a-MWNTs/SPAEK composites showed good interphase interaction, because of the hydrogen-bonding interactions between sulfonic groups of SPAEK and carboxylic groups of a-MWNTs, as shown in Scheme 1.



Scheme 1. Synthesis of Sulfonated Poly(Aryl ether ketone) copolymers and a-MWNTs/SPAEK composite membranes.

Figure 1b showed schematic pictures of a-MWNTs distribution in polymer composites at different concentrations of a-MWNTs. When the volume fraction of the carbon nanotube was lower, a-MWNTs clusters was wrapped by polymer matrix, and then a great number of tiny capacitor was formed and the dielectric constant of the composites was improved. With the increase of a-MWNTs of concentration, a-MWNTs clusters couldn't be wrapped completely, so conductive pathways in the composites would be formed. Therefore when the conductivity increases quickly, the dielectric constant will increase, too.

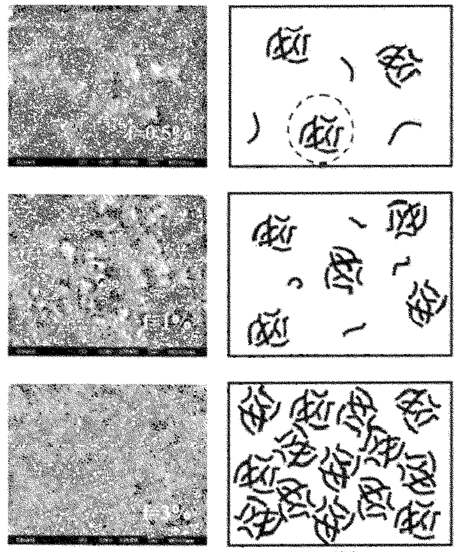


Figure 1. (a) Scanning electron microscopy image illustrating the morphology of a section of the a-MWNTs/SPAEK nanocomposite with the a-MWNTs volume fraction of 0.005, 0.01 and 0.03. (b) Schematic pictures of a-MWNTs distribution in polymer composites at different concentrations of a-MWNTs.

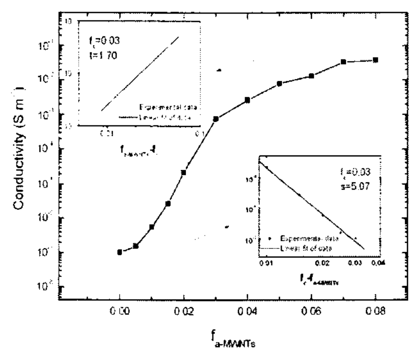


Figure 2. Dependence of the conductivity of a-MWNTs/SPAEK nanocomposites on the a-MWNTs volume fraction,measured at room temperature and 103 Hz. The insets show the best fits of the conductivity to Equation 1.

When studying the electrical properties of conducting-polymer-based composites, the critical volume fraction at the percolation threshold (*fc*) was a key parameter. Near the percolation threshold, the electrical conductivity and dielectric permittivity of the composites would increase by several orders of magnitude. Figure 2 showed the conductivity of the a-MWNTs/SPAEK composites as the volume fraction of a-MWNTs. The conductivity clearly demonstrated the transition from insulator to conductor at fa-MWNTs = 0.02 - 0.04. Percolation theory allowed one to describe using power laws of the conductivity of the composite near the insulator-conductor transition as follows: [3, 11]

$$\sigma(f_{a\text{-}MWNTs}) \propto (f_c - f_{a\text{-}MWNTs})^{-s} \quad \text{for } f_{a\text{-}MWNTs} < f_c \qquad (1a)$$

$$\sigma(f_{a\text{-}MWNTs}) \propto (f_c - f_{a\text{-}MWNTs})^{t} \quad \text{for } f_c > f_{a\text{-}MWNTs} \qquad (1b)$$

where $\sigma(f_{a\text{-}MWNTs})$ is the conductivity of the composites, $f_{a\text{-}MWNTs}$ is the filling factor, *fc* is the percolation threshold, *s* is the critical exponent in the insulating region and *t* is the critical exponent in conducting region. According to Eq.(1a) and Eq.(1b) in the a-MWNTs/SPAEK composites, the best fits of the conductivity data to the log–log plots of the power laws give $f_c = 0.03$, $s = 5.07$ and $t = 1.70$, as shown the insets in Figure 2. The percolation threshold of a-MWNTs/SPAEK composites, $f_c = 0.03$, was lower than common two-phase random composites($f_c \sim 0.16$) and the critical exponent s was larger than the universal values (sun $\approx 0.8 \sim 1$ for 3D fillers).[11] These result were attributed to the high aspect ratios and special characteristics of the a-MWNTs.

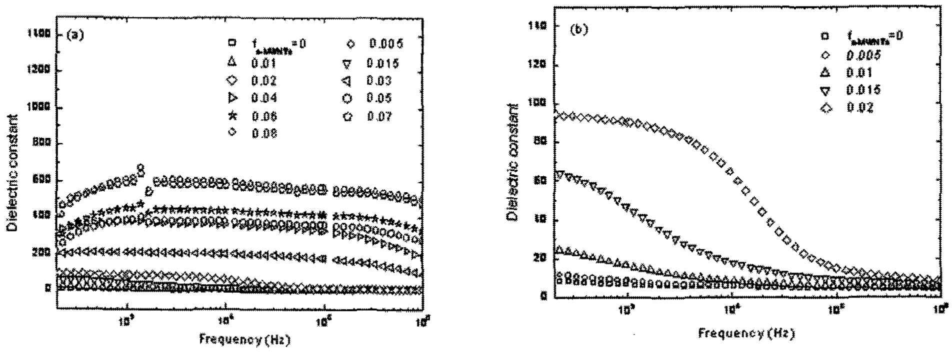


Figure 3. Dependence of dielectric constant of the a-MWNTs/SPAEK nanocomposites on frequency at room temperature when the fa-MWNTs = 0 - 0.08(a), and (b) is magnified imageof (a) when fa-MWNTs = 0 - 0.02.

Figure 3 showed the dielectric permittivity of the SPAEK/a-MWNTs nanocomposites as function of frequency for different a-MWNTs content at room temperature. The composites exhibited a higher dielectric constant, which was near 600 when the volume fraction was 7 vol% at 10^3 Hz and room temperature, the value was about 90 times larger than SPAEK. In addition, The dielectric constant of composites changed little with frequency when the content of carbon nanotubes was more than 3 vol%, and the composites can keep high dielectric constant in the high-frequency(>200, at 10^6 Hz).

In summary, the novel a-MWNTs/SPAEK polymer nanocomposites, with high dielectric constant, high mechanical strength and low percolation threshold, were prepared by using a solution blending technique. The composites exhibited a higher dielectric constant, and which was near 600 when the volume fraction of carbon nanotubes was 7 vol% at 10^3 Hz. The percolation threshold of the a-MWNTs/SPAEK composites was only 3 vol% of a-MWNTs. The dielectric constant of composites changes little with frequency when the content of carbon nanotubes was more than 3 vol%, and the composites could keep high dielectric constant in the high-frequency(>200，at 10^6 Hz).

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