Polyarylene ether nitriles based nanocomposites with enhanced mechanical and dielectric properties by unidirectional orientation

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Abstract. In this work, the 3-aminophe-noxyphthalonitrile (3-APN) was successfully grafted onto the multi-walled carbon nanotubes (MWCNTs) (MWCNTs-CN) via solvent-thermal method. Then, the MWCNTs-CN was used as fillers for different mass fraction Nano composites films with polyarylene ether nitrile (PEN) matrix through solution casting method. Subsequently, the prepared Nano composite films were hot-stretched with different stretch ratios at 280 °C to improve their orientations. Results showed that the highly oriented Nano composite films exhibit outstanding mechanical and dielectric properties. Therefore, the highly orientation is an effectively way to enhance the mechanical and dielectric properties Nano composite films.

1. Introduction
Recently, as the electronics industry moves towards a higher functionality, the high dielectric permittivity (high-k) materials have widely used in electronics, various microelectronic systems and energy storage fields.[1, 2] However, traditional high dielectric ceramic materials are hard to meet the requirements of miniaturization and lightweight devices due to their high production cost, brittle quality and difficult processing.[3, 4] Therefore, high performance polymer based Nano composites is becoming a research hotspot owing to its flexibility, light weight, easy processing and other advantages.[5, 6] The polymer-based Nano composites are usually composed of two or more components, which are polymer matrix and reinforcing phase, respectively. As for polymer matrix, Polyarylene ether nitriles (PEN), a special thermoplastic engineering plastics, has been used in extreme environments like aerospace and military contribute to its outstanding thermal stability, mechanical properties and process ability. [7, 9] Besides, as the reinforced phase of high dielectric Nano composites, there are many types of the fillers. Carbon nanotube (CNT), as the conductive additives, leads to the percolation threshold of Nano composites is reached with a low mass fraction. It is also indicated that the permittivity enhanced when filling with low content. [10, 11] However, the well interfacial compatibility between the polymer matrix and the CNTs is still a big challenge. Fortunately, the surface modification and chemical grafting techniques provide a possible way to improve the compatibility between CNTs and PEN.

As is known to all, the introduction of a large number of fillers in Nano composites will inevitably lead to a decrease in mechanical properties. Herein, unidirectional orientation through hot-stretching
progress is another effectively method to enhanced the mechanical performances of PEN based Nano composites. [7]

In this study, the surface of MWCNTs was grafted with 3-APN successfully. Then, the PEN/MWCNTs-CN Nano composite films were prepared by solution casting method, and the Nano composites were unidirectional hot-stretched with different ratios at 280 °C for further improve their properties. The mechanical, thermal and dielectric properties of the Nano composite films are extensively investigated.

2. Experimental section

2.1. Surface functionalization of MWCNTs nanoparticles
The MWCNTs nanoparticles were surface-grafted with 3-APN (MWCNTs-CN) by solvent-thermal route according to the literature reported before. [11]

2.2. Preparation of PEN/MWCNTs-CN composite films
PEN/MWCNTs-CN composite films were prepared by solution casting method according to the report before.[6] The PEN/MWCNTs-CN composite films with the mass fraction of MWCNTs-CN are 0 wt.%, 2.0 wt.%, 3.0 wt.%, 4.0 wt.% and 5.0 wt.%, respectively.

2.3. Hot-stretching of PEN/MWCNTs-CN composite films
The process of hot-stretching was carried out with self-made stretching apparatus in an oven according to the previously method reported [9]. When the Nano composite films were hot stretched to the expected stretch ratios (50% and 100%) at 280 °C within the specified time, the samples were removed from the oven quickly and quenched with cooling water immediately. Furthermore, the unstretched Nano composite films were dealt with the same condition for comparison.

2.4. Characterization
X-ray photoelectron spectroscopic (XPS) measurements were carried out on ESCA 2000 (VG Micromesh, UK). Differential scanning calorimetric (DSC) analysis was performed on the TA Instruments DSC Q100 (New Castle, DE, USA). Thermo gravimetric analysis (TGA) was tested under nitrogen atmosphere on a TA instrument Q50 (New Castle, DE, USA). Mechanical properties of the samples were tested with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China). The microstructures of the nanoparticles were characterized by a scanning electron microscopy (SEM) (JSM, 6490LV). Dielectric properties of the samples were tested with a TH 2819A precision LCR meter (Tong Hua Electronic Co., Ltd.).

3. Results and Discussion
TGA analysis was often used to research the thermal stability of components of surface functionalized MWCNTs nanoparticles. On the basis of the literature reported before, [11] MWCNTs showed excellent thermal stability and there is no obvious weight loss until the temperature reached 800 °C on the TGA curve. Besides, the TGA curves of the MWCNTs-COOH and MWCNTs-CN nanoparticles were shown in Fig. 1a. It can be clearly seen that when the temperature reached 800 °C, there were still 94.85% residual in MWCNTs-COOH and 87.04% residual in MWCNTs-CN. What’s more, a significant weight loss of MWCNTs-CN was observed at the temperature range from 300 to 600 °C, which is mainly caused by the decomposition of 3-APN. Therefore, According to the analysis of TGA data, the content of covalent bonds between 3-APN and MWCNTs-COOH was calculated, and the total mass fraction was about 7.81 wt.%. Besides, the XPS spectrum was further used to approve the surface functionalization of MWCNTs-CN particles. As shown in Fig. 1b, the full scanned XPS spectrum of MWCNTs-COOH and MWCNTs-CN were showed the existence of carbon (C) and oxygen (O) elements, respectively. Furthermore, the nitrogen (N) element was observed in the MWCNTs-CN nanoparticles. What’s more, the surface morphology of MWCNTs-COOH and
MWCNTs-CN were characterized by SEM. (Fig. 1c and 1d) it showed that the MWCNTs-COOH exhibited smooth surface morphology, and the surface of MWCNTs-CN presented much rougher obviously. All the results confirmed that 3-APN was successfully grafted onto the MWCNTs-COOH.

**Figure 1.** The characterization of nanoparticles: (a) TGA curves; (b) XPS spectra; (c) SEM image of MWCNTs-COOH; (d) SEM image of MWCNTs-CN.

The Thermal behaviors of PEN/MWCNTs-CN Nano composite films after hot-stretching at 280 °C with different ratios were investigated by DSC from room temperature to 380 °C under a nitrogen atmosphere. As shown in Fig. 2a, the obvious melt points (Toms) are observed for the pure PEN films with different stretch ratios. Besides, the melt points and melting enthalpy (Ohms) are all increased with the increment of the stretch ratios. The Toms of the PEN/MWCNTs-CN Nano composite films increased from 330.6 °C to 332.2 °C and 334.4 °C and the corresponding Ohms are enhanced from 2.1 J/g to 14.6 J/g and 18.9 J/g with the stretching ratios increased from 0% to 50% and 100%, respectively. It is indicated that the crystallinity of the PEN films increased with the increment of stretching ratios. What’s more, it also can be seen that the glass transition temperatures (Tag) increases from 214.5 °C to 216.1 °C and 217.3 °C when the stretching ratio are 0%, 50% and 100%, respectively. The increment of Tag, Toms and Ohms of the Nano composites increased with the increasing of the stretching ratios are caused by several reasons as follows: first of all, the macromolecular chains of PEN are oriented along the hot-stretching direction during hot-stretching progress, which is beneficial to the formation and growth of crystals. Secondly, during hot-stretching progress, the some amorphous regions of the polymers are rearranged to form crystalline regions. Lastly, many irregular crystals gradually become to the regular crystals during the hot-stretching progress. Furthermore, the similar results are also observed from the PEN/MWCNTs-CN Nano composites (5.0 wt. %), which is shown in Fig. 2b.
The mechanical properties of the PEN/MWCNTs-CN Nano composite films with different stretch ratios were shown in Fig. 3. The tensile strength of the all Nano composite films are over 90 MP, and it reached the maximum value (126.6 MP) when the filler content was 2.0 wt.%. (Fig. 3a) However, once the filler content increased, the tensile strength decreased gradually, which was due to the massive fillers trended to agglomerate in the PEN matrix. Besides, the tensile modulus of Nano composite films presented the similar trend. (Fig. 3b) What’s more, as shown in Fig. 3a and 3b, it can be clearly seen that the tensile strength and modulus of the PEN/MWCNTs-CN Nano composite films had a distinct enhancement after hot-stretching. When the filler content was 2.0 wt. %, the tensile strength of Nano composites with an increment rate of 101% from 126.7 MP to 254.9 MP at stretch ratios of 100%. Besides, the tensile modulus of the Nano composite films showed the similar trend. The improvement of the mechanical properties is mainly owing to the highly orientation and alignment of crystals in polymer. [7]

The dielectric properties of Nano composites were tested with a frequency range from 100 Hz to 200 kHz. Fig. 4a showed that the dielectric constant enhanced from 3.91 to 20.17 at 1 kHz with the fillers content increased from 0% to 5.0 wt. %, which can be explained by the micro-capacitor networks model. [6] Besides, as shown in Fig. 4b, the dielectric properties-temperature dependence of the Nano composite films (5.0 wt. %, pure PEN was shown in a small view in Fig. 4b) were tested from 25 °C to 250 °C at 1 kHz. It is can be clearly seen that when the temperature is below Tag, the dielectric constant was relatively stable. And the dielectric constant was increased rapidly after Tag of Nano composites, which is due to the macromolecular motion and polarization were improved when the temperature is over Tag of the Nano composites. In addition, Fig. 4c and 4d showed the dielectric constant of the Nano composites (0 wt. % and 5.0 wt. %) with different stretching ratios. It showed
that the dielectric constant was increased with the increment of stretching ratios, which were contributed to the well dispersed and crystallinity of MWCNTs-CN in PEN after hot-stretching progress.

![Figure 4](image-url)

**Figure 4.** (a) The dielectric constant of the Nano composite films; (b) The dielectric constant of the Nano composite films with different temperatures at 1 kHz; The dielectric constant of nan composite films with (c) 0 wt.% and (d) 5.0 wt.% under different stretching ratios.

### 4. Conclusion

In summary, the MWCNTs-CN was successfully prepared through the reaction between 3-APN and MWCNTs via solvent-thermal method. Besides, the PEN/MWCNTs-CN nan composite films were obtained by solution casting method, and the Nano composites were unidirectional hot-stretched with different ratios at 280°C. Results clearly showed that the mechanical and dielectric properties of Nano composites were improved obviously, which indicated that the hot-stretching progress was an effectively way to enhance the properties of PEN/MWCNTs-CN nan composite materials.

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