Preparation of the high dielectric performance flexible materials achieved by polyacrylamide/poly(vinylidene fluoride) blends

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Abstract: A novel all-polymeric material with high dielectric constant (k) has been developed by blending poly(vinylidene fluoride) (PVDF) with polyacrylamide (PAM). The dependence of the dielectric constant on frequency and polymer volume fraction was investigated. When the weight fraction of PAM is 1wt%, the dielectric constant of the blend could be up to 24, and the dielectric loss $\tan\delta$ can be lowered to 0.06. The SEM investigations suggest that the enhanced dielectric behavior originates from significant interfacial interactions of polymer-polymer. XRD and FTIR demonstrate that blending PAM with PVDF affects the crystalline behavior of each component. Our finding suggests that the created high- k polymeric blends represent a novel type of material that are flexible and easy to process, and is of relatively high dielectric constant and high breakdown strength; moreover find applications as flexible electronics.

Introduction

Capacitors are manufactured as important electronic components for use in electrical engineering. Since the electrostatic capacitance can be controlled with high precision; they are key elements in microelectric systems [1]. In the past, capacitors were used in electrical and electronic products, but today they are used in fields ranging from industrial applications to space, medicine, hydro acoustic sensors, and other electronics. In the early reports, great advances have been achieved in capacitor technology [2,3]. Especially, the improvements were made possible by the introduction of new dielectric materials such as polymeric films [4]. In this field, polyvinylidene fluoride (PVDF) films have often been used as dielectric materials in engineering capacitors because of their combination of remarkable properties, such as mechanical properties, excellent chemical and thermal stability, and dielectric properties [5,6]. But as capacitors, the relative dielectric constant of the pure PVDF is too low ($k \approx 9$), so its applications cannot satisfy the new need. A number of studies concerning the dielectric properties in inorganic-polymer composites have been reported such as PZT/PVDF over the last two decades [7-10]. The complex material comprised of PVDF and other inorganic matters possess very distinct dielectric properties that can be applied in electronics. Regardless of the mechanical properties, machine-shaping process resulted from the inorganic component has slowed the progress in the application field [11-16]. Nowadays, all-polymer-based composites are gaining considerable research attention for applications, which

provide light weight, flexible, and volume efficient electrical components required for embedded passive technologies. On the other hand, the blending of different polymers is an important and efficient method to obtain the desired properties of polymer systems based on the structure and property of each component. In reviewing Ran.X.H et al [17-19], they have reported that functional polymer materials such as humidity sensor, exhibited fine sensitive behaviour after appropriate electro processing, especially when the PAM is comprised of other polymers. In addition, PAM (polyacrylamide) has a stable oleo phobic property due to its unique structure and adhesion properties so as to be used in the oil extraction, paper making, and water treatment, biomaterials processing and so on.

Here we put forward a simple and effective approach, leading to extremely stable high-k but rather low $\tan\delta$ of the all-polymer dielectrics. Furthermore the resultant high performance of such new all-polymer blends makes them particularly attractive for technological applications in flexible high-K components such as the micro-capacitors dielectric components, dielectric film in chip, and medical applications. More importantly, by using a direct synthesis method to obtain films with high-k values that are sufficient for future high-k applications, this work achieves a significant technology milestone over previous studies.

Results and discussion

Fig.1 shows the frequency dependence of the dielectric constant k and the dielectric loss $\tan\delta$ of PAM/PVDF blends before and after stretching. We can see from Fig.1a that, with the addition of PAM the dielectric constant k of PAM/PVDF blend is higher than pure PVDF, but the overall value is low.

Fig. 1. Frequency dependence of dielectric constant k and dielectric loss $\tan\delta$ for a,b) unstretched PAM/PVDF and c,d) stretched PAM/PVDF blends.

From Fig.1c, a sharp enhancement of dielectric constant k of PAM/PVDF blend can be observed with the addition of PAM, of which the amount is 1wt% weight fraction of the total of PAM and PVDF. Compared with pure PVDF, of which the k is 8.5, the dielectric constant of the PAM/PVDF blend with 1wt% PAM can be up to 24, which is more than two times higher than that of pure PVDF. It also can be seen, with the increment of PAM, the dielectric constant begins to decline over the frequency range of 102Hz to 105 MHz. We believe that the more quantity of PAM the easier cohesion, which effects the electric properties. Fig.1b and 1d show the frequency dependence of the dielectric loss $\tan\delta$ of the blends. It is clearly seen that the dielectric loss $\tan\delta$ of PAM/PVDF blends descends with the increment of PAM. It can be ascribed to that a small quantity of PAM can improve the compatibility between PAM and PVDF, inducing a uniformity structure formation between PAM and PVDF, therefore, the dielectric constants of PAM/PVDF blends with PAM increase remarkably. Besides, a good frequency stability of the blends can be also observed from the Fig.1.

Fig. 2. Variations of the tensile strength and the tensile elongation of PAM/PVDF blend versus weight fraction of PAM.

The effect of the PAM weight fraction on the tensile strength and the tensile elongation of blends are shown in Fig. 2. It can be seen that the tensile strength changed continually and irregularly with increasing PAM content. With increasing PAM content, the tensile strength of PAM/PVDF blends increased slowly, but subsequently decreased sharply, and the largest tensile strength reached 42.33 MPa when the PAM content was 1wt%. Furthermore, the tensile elongation of the PAM/PVDF blends is from 40% to 95%. These phenomena suggest that the PVDF is good compatible with 1wt% content PAM and the PAM/PVDF blends are surpassed by few other compounds as flexible materials with high k .

As we know, the miscibility played a crucial role in deciding the morphology and properties of the PAM/PVDF blend composites. Fig. 3 is the scanning electron micrograph (SEM) of the PAM/PVDF blend. As shown in Fig.3a, the boundaries between PAM and PVDF were obscure. When the photo was magnified tenfold, a well-connected interface can be obviously observed in Fig.3b, which show that the PAM phase in the PAM/PVDF blend composite was dispersed in the PVDF matrix as particles 0.5 μ m-2 μ m in diameter. This can be ascribed to the adding PAM made it disperse more evenly and the dimension of dispersed phase smaller. That is to say

that the PMA in blends can improve dielectric properties by interface intermolecular reaction.

Fig. 3. The SEM of PAM/PVDF blends.

The XRD patterns of PVDF and PAM/PVDF blend are shown in Fig. 4a. We note that the diffraction peak of pure PVDF weakened distinctly as the content of PAM added was 1wt%. We believe that the NH and C=O in PAM and polar CF_2 groups in PVDF would interact with each other. It illuminates that the crystallization transmutation of PVDF from α to β is controlled by the content of PAM and other conditions (such as stretch); that is, for the melt-quenched PAM/PVDF blends, the PAM content has the dominant position in the blends properties, which can be attributed to the fact that the crystal structure of PAM is good at polarization so as to produce electricity.

Fig. 4. a) The XRD spectra of PVDF and PAM/PVDF blend; b) The FTIR spectrum of PAM/PVDF blends.

To study the effect of PAM on the dielectric properties of the PAM/PVDF, we investigated the function of the PAM using Transform Infrared Spectroscopy (FTIR). Fig. 4b is the IR spectrum analyses of PAM/PVDF film (the thickness of the sample is 1.5 mm). We found that the characteristic peak of PAM turns out in 3250cm^{-1} and 1625cm^{-1} , and the peak in 1414 cm^{-1} indicates the formation of the cyclic amide group [20, 21]. In addition, the characteristic peak in 840cm^{-1} and 511cm^{-1} suggested

that PVDF appear as β crystallization. These phenomena explained that a new composite was produced by the reaction between PAM and PVDF. Therefore, adding a proper amount of PAM is one of the important measures to improve the electric properties.

Through the measurements of dielectric constant k and dielectric loss $\tan\delta$ at room temperature, it is confirmed that by the addition of PAM the PAM/PVDF blends are of higher dielectric constant k and lower dielectric loss $\tan\delta$ than before, and also exhibited good frequency stability. Compared with the samples of pure PVDF, a very large enhancement was obtained in dielectric response for the PAM/PVDF.

The dielectric performance testing in this work was unexpectedly far better than before; a feasible explanation being that the influence of the polarization between two phases on the dielectric properties is possible. On looking into the interface intermolecular microstructures, the well-connected interface appears on the interface intermolecular configuration. As such, the PAM/PVDF blends are of excellent flexible property with respect to mechanical properties and the dielectric properties of the composites with different quality PAM were determined respectively according to the applications such as capacitor, sensor and so on.

Experimental part

The PVDF($M_w=37\times10^5$, $d=1.75\text{g/cm}^3$) and PAM($M_w=3\times10^5$, $d=1.03\text{g/cm}^3$) powders were supplied by the Shanghai Organism Institute and the Chinese Academy of Science, respectively. The PAM/PVDF blends of a thickness of 3 mm were produced by co-melt-pressing at 170°C and were subsequently quenched in ice water. After being dried in drying equipment for 2 h at 50°C , finally the co-melt-pressed-quenched films were uniaxially oriented by drawing to a ratio of 2:1 at room temperature, and clamping immovably for 30 min. The samples were circular with a diameter of 12 mm.

The dielectric properties of the samples were measured using a HIOKI3532-50 LCR meter. Fourier transforms IR (FTIR) spectra of PAM/PVDF blends were measured by a Nicolet FTIR spectrometer. In order to analyze the compatibility and flexibility of the blends, the surface topographies of PAM/PVDF blends were observed on a JSM-5610LV scanning electron microscope (SEM), and the mechanical performances of samples were tested on a RGT-30A tensile-testing machine.

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