

# Preparation and Characterization of Pure Organic Dielectric Composites for Capacitors

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**Abstract.** This work reports the excellent dielectric composites were prepared from polyimide (PI) and poly(vinylidene fluoride) (PVDF) via solution blending and thermal imidization or chemical imidization. The dielectric and thermal properties of the composites were studied. Results indicated that the dielectric properties of the composites synthesized by these two methods were enhanced through the introduction of PVDF, and the composites exhibited excellent thermal stability. Compared to the thermal imidization, the composites prepared by chemical imidization exhibited superior dielectric properties. This study demonstrated that the PI/PVDF composites were potential dielectric materials in the field of electronics.

## 1 Introduction

Polymer-based composites with high dielectric constant, low dielectric loss and easy processibility have attracted much attention in the fields of high-charge storage capacitors, energy, electrical engineering [1-8]. Polyimides (PIs) have extraordinary characteristics such as excellent mechanical and chemical properties, and outstanding thermal stability, so that they are being widely applied as matrix materials for the advanced applications [9-11]. However, pure PIs only have a low dielectric constant which could limit their applications in electronics [12, 13]. A series of related studies has been proposed to solve this problem [14-17]. A general method is to use high  $k$  materials as fillers to significantly improve the dielectric properties of polymers [18-23]. It is well known that polyvinylidene fluoride (PVDF) has a relatively high dielectric constant (10–14) [24, 25] which can be used as a high dielectric filler to improve the dielectric constant of PI.

In this study, polyimide-based dielectric composites were synthesized by two imidization methods. We studied the properties of such composites.

## 2 Experimental section

### 2.1 Materials

4, 4'-Diaminodiphenyl ether (ODA) and pyromellitic dianhydride (PMDA) were all analytical grade and purchased from Aladdin (Shanghai, China). PVDF (JHR-150) was supplied by Zhejiang Juhua Chemical

Reagent Co. (Zhejiang, China). N, N-dimethylacetamide (DMAC) was obtained from Chengdu Kelong Chemical Reagent Co. (Chengdu, China). Acetic anhydride (Ac<sub>2</sub>O) and triethylamine (TEA) were purchased from Chengdu Jinshan Chemical Reagent Co. (Chengdu, China).

### 2.2 Preparation of PI/PVDF composites

The polyamic acid (PAA) precursor was polymerized from ODA and PMDA in freshly distilled DMAC under stirring at room temperature for 24 h. Then, different amounts of PVDF powders (10, 20, 30, 40, and 50 wt.%) were ultrasonically dispersed in DMAC for 1 h. In order to prepare homogeneous and different concentrations of PVDF/PAA solution, various weight fractions of PVDF/DMAC dispersion were added into the PAA solution with further vigorous stirring for 24 h. Then, the PAA was imidized using a standard thermal imidization method. Subsequently, the mixture was cast onto a piece of clean glass plate, and thermally imidized at 50, 100, 150, 200, and 250 °C for 1 h and 300 °C for 0.5 h to form PI/PVDF composite films. Consequently, composite films with 0, 10, 20, 30, 40, and 50 wt.% PVDF were obtained. Composites were also prepared by chemical imidization of PAA. Ac<sub>2</sub>O and TEA, acted as the dehydrating and catalyst agent respectively, were added simultaneously to the PVDF/PAA solution which was stirred for an additional 24 h to produce PI/PVDF composite. The whole synthesis process was carried out at ambient temperature under nitrogen protection. Afterwards, the PI/PVDF solution was precipitated in distilled water. Subsequently, filtering and washing with distilled water and methanol, and drying in a vacuum oven at 80 °C for

24 h to obtain PI/PVDF composite powders. After this, the composite powders were molded by hot pressing at about 150 °C under uniaxial pressure of 30 MPa for 1 h. For convenience, the sample codes were defined according to the amounts of PVDF, e.g. the thermally imidized PI/PVDF (70/30) blend was defined as T-30%, the chemical imidized PI/PVDF (70/30) blend was defined as C-30%.

### 3 Characterizations

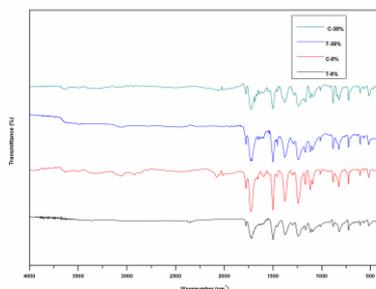
Fourier Transform Infrared (FTIR) spectra were obtained using a Fourier transform infrared spectrometer (FTIR8400S) at wave numbers of 400–4000cm<sup>-1</sup>, and samples were ground and mixed with potassium bromide and compressed into pellets for testing. The surface morphologies of the composites were investigated using a field-emission scanning electron microscope (FEI Co., USA) with an accelerating voltage of 20 kV. All the samples were coated with a homogeneous gold layer prior to analyses to avoid charge accumulation. The thermal behavior of the PI/PVDF composites was examined using a thermogravimetric analyzer (TA Q50, TA Instruments, USA) under nitrogen flow at a heating rate of 20 °C/min from room temperature to 800 °C. Dielectric behavior was measured using an Agilent 4294A precision impedance analyzer (Agilent Technologies, USA) within the frequency range of 100 Hz to 1 MHz. Before measurement, all the samples were sputter coated with aluminum on the two sides as electrodes. The relative permittivity of the samples is measured in a sandwich structure (aluminum /polymer/ aluminum) and calculated using the following equation (1):

$$\epsilon_r = \frac{C \times d}{\epsilon_0 \times A} \quad (1)$$

where  $\epsilon_r$  is the relative permittivity of the hybrid films,  $C$  is the capacitance,  $d$  represents the thickness of the hybrid films,  $\epsilon_0$  is the dielectric constant in vacuum ( $\epsilon_0 = 8.85 \times 10^{-12}$  F/m), and  $A$  is the area of the electrodes. Reported data were the average value of at least three individual measurements.

## 4 Results and discussions

### 4.1 FTIR analysis

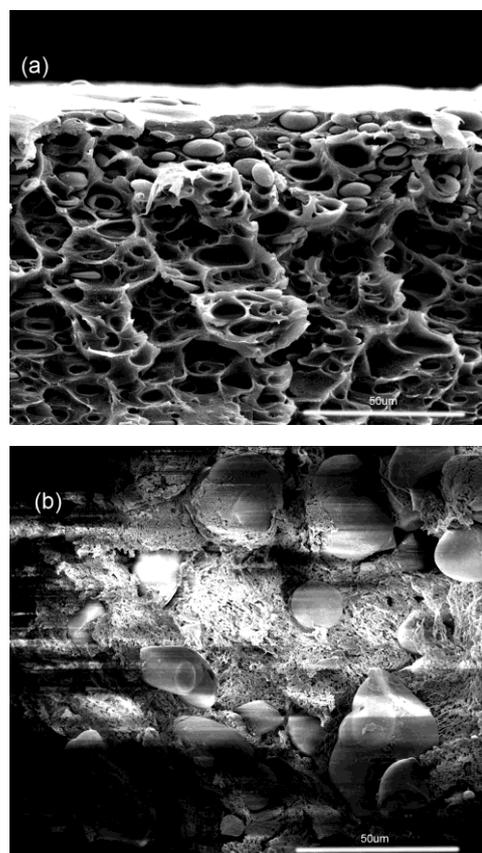


**Figure 1.** FT-IR spectra of composites.

The FTIR spectra of pure PI and the composites are shown in Fig. 1. Either after thermal imidization or after chemical imidization, the FTIR spectra show the typical absorption peaks of the imide groups of PI. The presence of absorption peaks at approximately 1780 cm<sup>-1</sup> corresponds to the C=O asymmetric stretching vibration, 1720 cm<sup>-1</sup> corresponds to the C=O symmetric stretching vibration, 1370 cm<sup>-1</sup> corresponds to the C-N-C stretching vibration, and 720 cm<sup>-1</sup> corresponds to the C=O bending vibration [26-28]. Furthermore, the absence of the characteristic absorption bands of PAA at approximately 1660 cm<sup>-1</sup> corresponds to the amic acid C=O symmetric stretching vibration and 1535 cm<sup>-1</sup> corresponds to the amide C-N asymmetric stretching vibration indicates complete imidization in the resulting composites [29, 30].

### 4.2 Microstructure of PI/PVDF composites

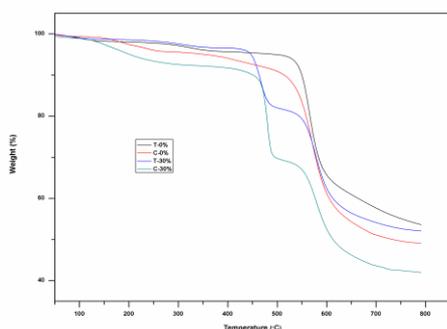
As shown in Fig. 2, in both two methods, the PVDF elliptic particles are uniformly distributed in the PI matrix without apparent aggregation. The surface morphology of composites synthesized by chemical imidization method was obviously better than that of composites synthesized by thermal imidization method at the same mass fraction. The uniform distribution of the composites may be propitious to enhance the dielectric constant. In addition, the phase separation could be attributed to the incompatibility between PI and PVDF [27].



**Figure 2.** Surface morphology of composites (a): 30wt%PVDF synthesized by thermal imidization (b): 30wt%PVDF synthesized by chemical imidization.

### 4.3 Thermal analysis of composites

Thermal stability is one of the most important properties that should be investigated for potential high-performance engineering materials. As shown in Fig. 3, two stages of weight losses were observed from the pure PI. The first weight loss within 100 °C can be mainly attributed to the evaporation of residual solvent and the second stages were attributed to the degradation of PI. In both imidization methods, pure PI did not appear to suffer from a large weight loss when subjected to up to 500 °C. However, the decompositions of T-30% and C-30% both include three stages: the first weight loss stage starting below 100 °C was attributed to the removal of residual solvent; the second and the third weight loss at approximately 432 °C and 500 °C, which could be attributed to the difference in thermal stabilities between PVDF and PI [31]. Moreover, their characteristic yields after pyrolysis at 800 °C were over 40%. This indicates that the composites exhibited outstanding thermal stabilities.

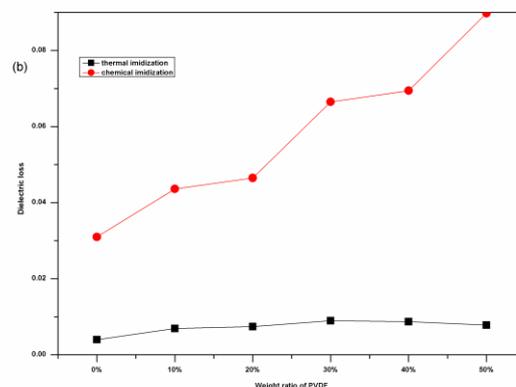
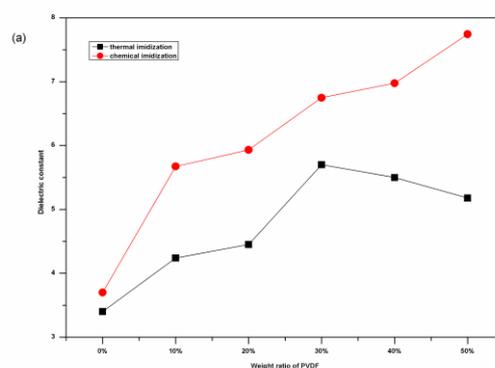


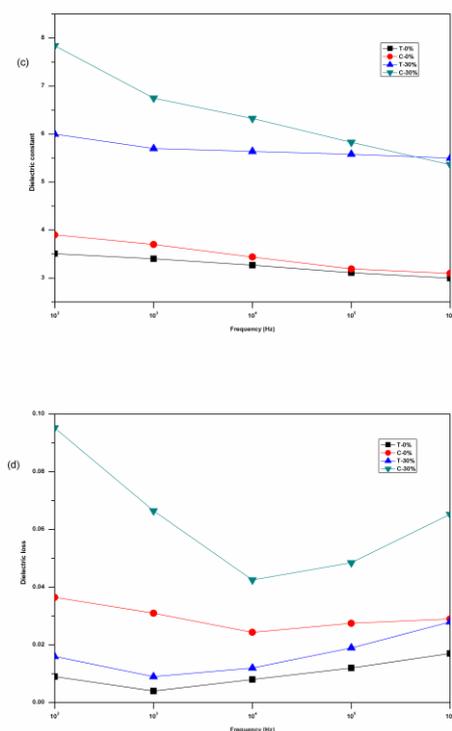
**Figure 3.** TGA curves of composites.

### 4.4 Dielectric properties of composites

Figs. 4(a) and 4(b) show the dependence of the dielectric constant and dielectric loss of the composites on the mass fraction of PVDF measured at room temperature and at 1 kHz. The dielectric constant of the composites synthesized by these two methods remarkably increased when PVDF was introduced into PI. This excellent enhancement in dielectric constant should be mainly attributed to the interfacial space charge polarization between PI and PVDF as well as the homogeneous dispersion of PVDF [32]. The dielectric constant of composites synthesized by chemical imidization method was much higher than that of composites synthesized by thermal imidization method at the same mass fraction. For instance, in chemical imidization, the dielectric constant was 7.745 when PVDF content was as high as 50 wt.%, which was about 1.5 times higher than that of composites synthesized by thermal imidization. The more uniform distribution of the composites synthesized by chemical imidization may be propitious to enhance the dielectric constant [33]. In addition, in thermal imidization method, the dielectric constant drastically increased to 5.7 when 30 wt.% PVDF was added,

whereas when PVDF exceeded 30%, the dielectric constant decreased to 5.18. PVDF accumulation could hinder interfacial polarization and was responsible for decreasing relative permittivity. The dielectric loss of the composites synthesized by thermal imidization method was smaller than the dielectric loss of the composites synthesized by chemical imidization method. However, in both two methods, the dielectric loss of the composites was small, i.e., less than 0.1, which made it acceptable for practical applications. Furthermore, the frequency dependence of the dielectric constant and dielectric loss of the composites is presented in Figs. 4(c) and 4(d), respectively. The dielectric constant of the composites exhibited weak correlation with frequency and slightly decreased with the increase in frequency from 100 Hz to 1 MHz. The dielectric constant decreased at a higher frequency because the interfacial polarization and orientation polarization of dipoles could not rapidly follow the change in the external electric field [34, 35]. However, dielectric loss decreased at a low frequency range and then increased. The reason was that the space charge polarization contributed to the main part of the loss tangent while the conduction contributed less as the frequency increasing [33]. In addition, the maximum value of the dielectric loss was lower than 0.1 within the testing frequency range. This finding indicates that the PI/PVDF composites are promising dielectric materials for practical applications.





**Figure 4.** (a) Dielectric constant and (b) dielectric loss as a function of mass fraction of PVDF at 1 kHz; (c) dielectric constant and (d) dielectric loss as a function of frequency for PI/PVDF composites at room temperature.

## 5 Conclusions

All-organic PI/PVDF high dielectric composite materials were synthesized via thermal imidization or chemical imidization. The composites exhibited excellent thermal stability and dielectric properties. The characteristic yields after pyrolysis at 800 °C were over 40%. The dielectric constant of composites synthesized by thermal imidization rapidly increased to 5.7 at 1 kHz when PVDF content reached 30 wt.%, which was 1.7 times higher than that of pure PI, whereas dielectric loss was only 0.009. When PVDF content was as high as 50 wt.%, the dielectric constant of composites synthesized by chemical imidization was 7.745, which was about 2.1 times higher than that of pure PI. Furthermore, the dielectric constant of the composites was stable, and dielectric loss was lower than 0.1 within the testing frequency range (100 Hz–1 MHz). Thus, the PI/PVDF composites were demonstrated to be promising dielectric materials in the field of electronics. We will further improve the thermal and dielectric properties of composites in future research. In addition, we will also study issues such as material compatibility and thermal conductivity.

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