

Fabrication of high energy storage density all-organic dielectric films by melt extrusion-melt stretching

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Abstract. Organic polymer has great advantages and prospects in the field of electrostatic film capacitors and pulsed power systems. In this paper, composite films of Poly(vinylidene fluoride) (PVDF) and Poly(methyl methacrylate) (PMMA) were fabricated by twin-screw extrusion and melt stretching. PMMA with specific volume fractions was added as a composite phase into the PVDF matrix. As an all-organic dielectric film, the composite film (F/A) shows great performance in energy storage test. The composite film was highly compatible and combined the properties of both polymers. The dielectric constants of the F/A films with 2.5%, 5%, and 7.5% PMMA content were 12.52, 11.47, and 11.03, respectively, which is an improvement over the pristine PVDF film (10.56). The appropriate amount of PMMA doping effectively improved the charge-discharge efficiency of PVDF film while maintaining high energy storage density. At the electric field of 550 kV/mm, the energy storage density (U_e) of the F/A-2.5% film was able to reach 11.66 J/cm³, still maintaining an efficiency of 75.97%.

Keywords: PVDF; PMMA; Twin-screw extrusion; Melt stretching.

1. Introduction

With the development of the times and the progress of science and technology, organic polymer materials in the pulse energy storage system, electrostatic film capacitors and other fields have a very broad application prospect [1]. Currently, the most common commercially available polymer material, biaxially oriented polypropylene film (BOPP) has a very high market demand in application scenarios such as flexible DC power transmission system, medical defibrillators, automotive inverters, and electronic circuits [2]. However, the dielectric constant of BOPP is low (~2.2), which means it is not able to meet the application scenarios of higher energy storage density requirements [3]. While raising the operating voltage improves the storage density of films and capacitors, it introduces unnecessary risks and greatly reduces operational reliability.

In recent years, poly(vinylidene fluoride) has been widely researched due to its high dielectric constant (~9) and breakdown field strength [4]. According to the formula $U_e = \int_0^{E_{\max}} \epsilon_0 \epsilon_r E dE$, the U_e of PVDF is usually several times that of BOPP. However, PVDF has a low charge-discharge efficiency at high electric fields because of its high dielectric loss and conduction loss, which greatly limits the practical application of the material. Therefore, many research have been carried out to improve the energy storage properties of PVDF materials. Specifically, in terms of molecular structure, the mechanical or electrical properties of polymers can be directionally regulated through free radical polymerization, grafting of polar groups [5, 6]. Inorganic doping can significantly improve the dielectric response of the composites, which can effectively enhance the dielectric constant and energy density of the film [7, 8]. The all-organic composite approach can avoid the problems of low breakdown field strength and severe phase separation caused by doping of ceramic materials [9, 10]. In addition, surface modification (surface engineering) is gradually becoming one of the effective methods to enhance the electrical properties of dielectric film materials [11, 12].

Poly(methyl methacrylate) (PMMA) is a common industrial plastic with a wide range of application scenarios. As a nearly linear polar polymer, PMMA has excellent energy storage

property and good compatibility with PVDF. When PMMA is used for pulsed energy storage, it typically has low leakage conduction loss. In recent years, a number of research works on PMMA as a dopant phase to form composites with PVDF-based polymers have been reported [13, 14]. Typically, organic composite films are formed by solution casting, which is very easy to introduce impurity ions leading to a reduction in the insulating strength of the film. The mechanical strength of the film formed by solution casting is low, making it difficult to satisfy the process requirements for subsequent film metallization and capacitor packet winding. In this work, PVDF and PMMA polymer pellets were melted at high temperatures and then mixed into a composite melt of uniform density by a twin-screw extruder. The composite films fabricated by melt blending had well compatibility and electrical properties. The dielectric properties of the composite films were studied with a precision impedance analyzer. The crystalline phase changes of the films with specific PMMA doping concentrations were investigated using infrared spectroscopy. Energy storage parameters such as energy storage density, charge-discharge efficiency and current density of the composite dielectric films were investigated in detail using multiferroic ferroelectric test instrument.

2. Experimental

2.1 Materials

Homopolymer PVDF particle with M_w of 670-700 kg/mol was provided by Solvay. PMMA particle was purchased from Arkema. N-Methyl pyrrolidone (NMP) solvent was purchased from Chengdu Kelong chemical reagent factory. All the chemicals used in the article were obtained from commercial and used as received.

2.2 Fabrication of composites films

(1) PMMA particles were added to the PVDF particles as dopant phase in the proportions of 2.5%, 5%, 7.5%, 10%, 15%, and 20% volume fraction, respectively.

(2) Melt blending, extrusion, cooling, pelletizing and drying processes were carried out sequentially. Polymer blend particles with different ratios of the two phases were obtained.

(3) The F/A composite melt was fabricated using a twin-screw extruder. The temperature distribution of the ten heating sections of the twin-screw extruder were 165, 200, 240, 250, 260, 260, 260, 260, and 270 °C from the feeding section to the die, respectively. (Screw speed 230 rpm.)

(4) The melt was extruded from the slit die and transferred to the sheet casting roller under roller traction. Low thickness and uniform transparency of the composite film can be obtained by controlling the temperature and speed of the casting roller. (Casting temperature 70 °C, traction rate 8 m/min)

(5) Pristine PMMA film was fabricated as reference sample using solution casting method.

2.3 Characterization and properties measurement

The thickness of the film was measured by magnetic induction thickness gauge (Fischer DUALSCOPE MPO). Fourier transform infrared (FTIR) was carried out on NICOLET iS20 from Thermo Scientific, with number scans of 32 at a resolution of 4 cm^{-1} . We deposited aluminum electrodes on both sides of the dielectric film (12 mm*12 mm of area, and 100 nm of thickness) using an ultra-high vacuum evaporation coater (GSL-1800X-ZF4, KEJING). The dielectric constant and dielectric loss were measured over the frequency range from 40 Hz to 5 MHz with a impedance analyzer (4294A, Agilent) at room temperature. The Polarization-Electric field loops (P-E loops) with 10 Hz and the DC leakage current density of dielectric films were acquired by multiferroic ferroelectric test instrument (Radiant Technologies, Inc.) at room temperature.

3. Results and Discussion

The effect of doping with different PMMA volume fractions on the structure of composite films was investigated. Fig. 1 shows the FTIR spectra of the composite dielectric films. Distinct α -phase characteristic peaks can be seen at 763, 975, 1149 and 1383 cm^{-1} , which indicated the conformation of melt-stretched films was mainly α -phase. Meanwhile, the crystalline shape of PVDF films did not influence significantly with the increase of PMMA content. The absorption peaks near 1725 cm^{-1} were specifically seen to have a very regular variation. The peak intensity gradually enhanced with PMMA volume fraction increasing, which implied that the F/A composite film had great compatibility. Unlike conventional solution casting, the composite films fabricated by melt extrusion-melt stretching have high mechanical strength and two-phase compatibility, due to the intertwining of molecular chains in the molten state under high-speed shear.

The dielectric properties of the composite films metallized were investigated in detail. Fig. 2(a) illustrates the dielectric constant of these films. As the frequency increases, the contribution of dipoles to the polarization decreases, resulting in a decrease in the dielectric constant. The dielectric constants of the composite films with 2.5%, 5%, and 7.5% PMMA content were 12.52, 11.47, and 11.03, respectively, which is an improvement over the pristine PVDF film (10.56). The enhancement of the dielectric constant may be caused by the additional contribution of interfacial polarization from the numerous microscopic interfaces formed by the blending of the two phases. At the frequency of 1 kHz, the dielectric loss of the composite films is elevated with a maximum value of 0.0369 (F/A-20%), as shown in Fig. 2(b).

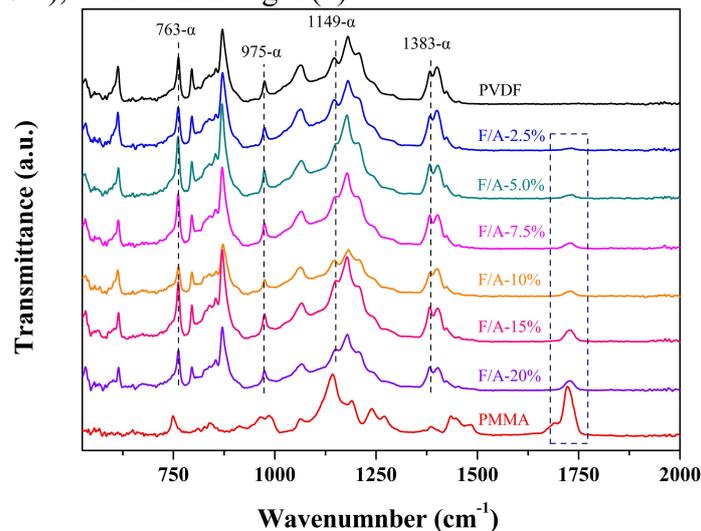


Fig. 1 FTIR spectra of the composite films with specific PMMA volume fraction.

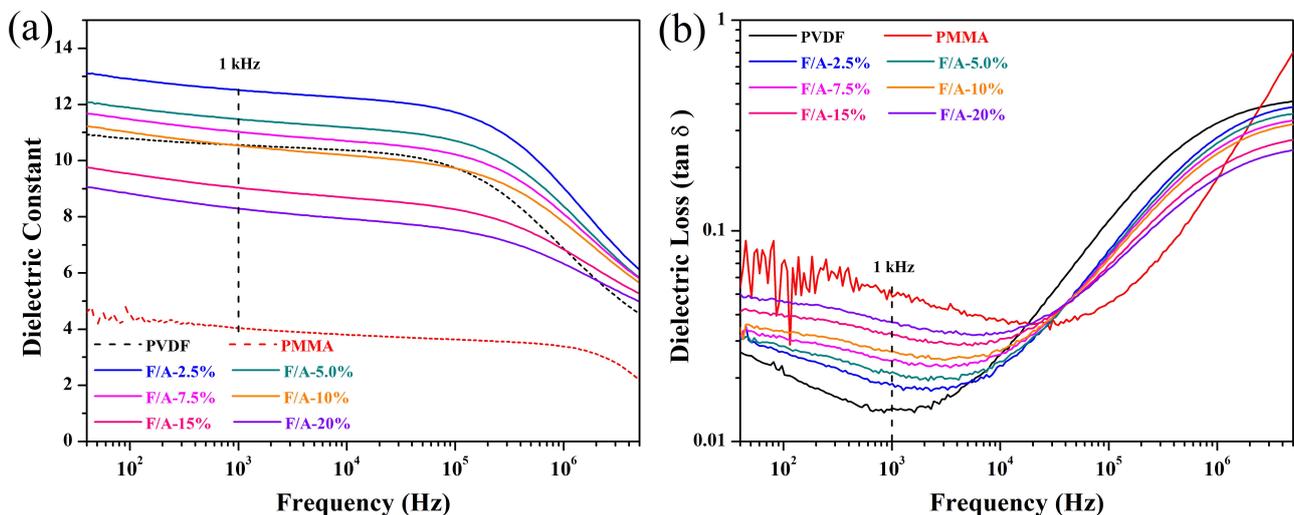


Fig. 2 Dielectric performance of the composite films with specific PMMA volume fraction.

We tested the unipolar P-E loops of the composite films with 10 Hz at room temperature and summarized the variation patterns of polarization intensity. Fig. 3(a) and 3(b) show the variation patterns of the maximum polarization (P_{max}) and remanent polarization (P_r) of P-E loops at different electric field strengths, respectively. As a strongly polar polymer, PVDF has a stronger dipole moment than PMMA and also has a much higher P_r than PMMA. The F/A composite films maintain a high maximum polarization strength while effectively reducing the effect of high remanent polarization of the matrix material, which positively contributes to the reduction of energy loss. Fig. 3(c) shows the U_e and efficiency of the composite films. As the electric field strength increases, the composite films are still able to maintain a high efficiency, while the energy density magnitude is very close to pristine PVDF film. For example, the energy storage density of F/A-2.5% film was able to achieve 11.66 J/cm³ at field of 550 kV/mm, while still maintaining an efficiency of 75.97%. To investigate the source, we tested the current density-electric field strength (I-V) variation curves of the composite films (Fig. 3(d)). The current density of the F/A films are much lower than pristine PVDF film at high electric fields, which means the composite films have low conduction loss, effectively hindering charge injection at high fields and inhibiting the development of breakdown dendrites. In conclusion, the energy storage characteristics of the F/A films are comprehensively superior to pristine PVDF and PMMA films.

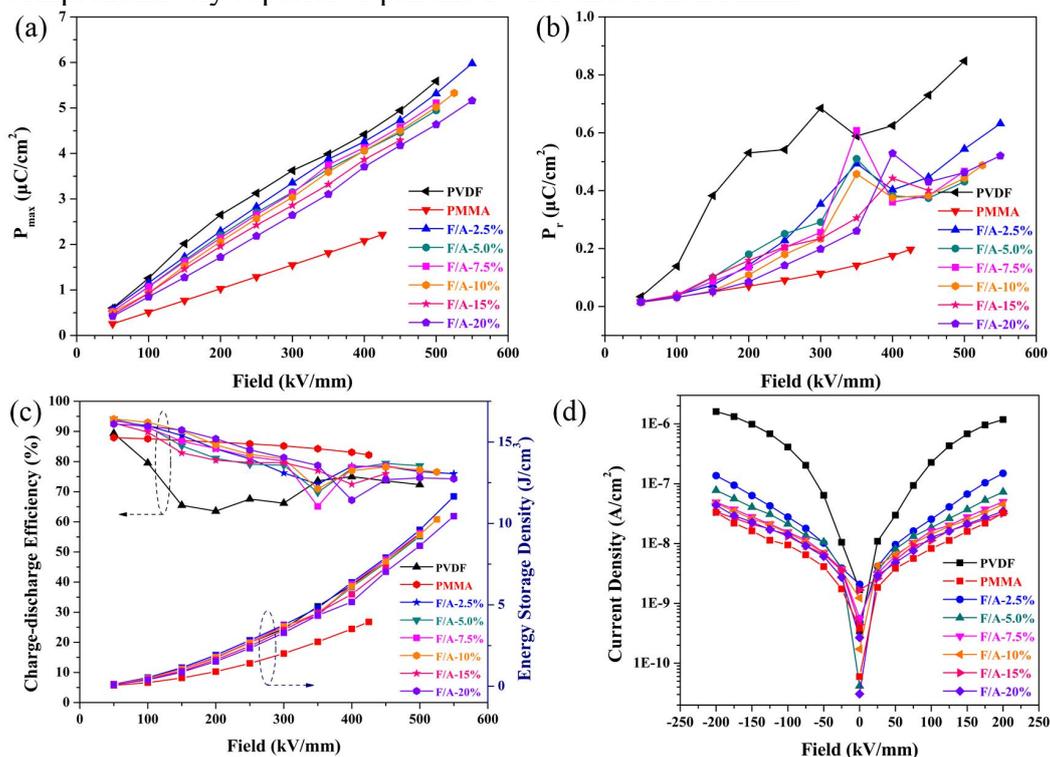


Fig. 3 (a) P_{max} , (b) P_r , (c) Charge-discharge and Efficiency Energy Storage Density, (d) DC Current Density of dielectric films under evaluate electric filed.

4. Summary

In this paper, the composite films of PVDF and PMMA were fabricated by melt extrusion-melt stretching, which has great potential with high reliability, rapidity and large-scale to fabricate all-organic composite film. The composite films have excellent compatibility without the use of additives or adhesives. The F/A film has a maximum dielectric constant of 12.52 and an energy storage density of 11.66 J/cm³. Our work provides a fast and effective research means for development of high energy storage density dielectric film.

5. Acknowledgements

We are grateful for the funding from the National Natural Science Foundation of China (NSFC) (Grant No. 62201231) and the China Postdoctoral Science Foundation (Grant No. 2022MD713827).

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