Energy storage properties of PVDF terpolymer/PMMA blends

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Abstract: Dielectrics can be used to store electric energy in capacitors and high-energy density of the materials is desirable to reduce the size or weight of capacitors. To improve the energy storage properties of poly(vinylidene fluoride–trifluoroethylene–chlorotrifluoroethylene) [PVDF–TrFE–CFE] terpolymer, P(VDF–TrFE–CFE)/poly(methyl methacrylate) (PMMA) blends were investigated in this study. By adding a small amount of PMMA into PVDF terpolymer (<5 wt%), the dielectric breakdown field of the blends can be improved as a result of the enhancement of elastic modulus of the blends. For the blends with <2.5 wt% PMMA, though their dielectric properties are reduced, under the same electric field, the energy density of the blends is almost the same as that of PVDF terpolymer. Consequently, the energy storage performance of the terpolymer can be improved by blending with a small amount of PMMA.

1 Introduction

High-energy-density dielectric materials are needed to reduce the size or weight of capacitors, which are critical components for some pulsed power systems and power electronics [1, 2]. The energy density of a dielectric material is related to the dielectric properties and dielectric breakdown field of the material. Polyvinylidene fluoride (PVDF)-based polymers are a type of ferroelectric polymers [3]. The polymers have a high dielectric polarisation response and dielectric breakdown field and the materials are promising for energy storage applications [4–6]. Especially in some defect-modified PVDF polymers such as P(VDF– trifluoroethylene (TrFE)–chlorotrifluoroethylene (CFE)) terpolymer, P [VDF–chlotrifluoroethylene (CTFE)] copolymer (CTFE), and P [VDF–hexafluoropropylene (HFP)] copolymer (HFP) the polarization hysteresis is reduced by the defect modification and high-energy density with improved discharging energy efficiency can be achieved [4–7].

Polymer blends, which exploit the merits of both the base polymer and the additive polymer, offer a great opportunity to improve and tailor the properties of the base polymer. Previous works have shown that polymer blends with properly selected compositions and processing conditions can remarkably alter or improve the mechanical, electromechanical, and electro-optical properties of the materials [8, 9]. PVDF-based polymers and poly(methyl methacrylate) (PMMA) blends have been studied for more than 30 years [9–14]. PVDF-based polymer/PMMA blends are thought to be miscible in all the compositions at a usual processing temperature range because the additional contribution to mixing enthalpy comes from the hydrogen bond formed between the PVDF-based polymer and PMMA. Miscibility and the electromechanical properties of the PVDF terpolymer and PMMA have been investigated, and improvement of the electromechanical properties of the PVDF terpolymer by blending with PMMA has been observed due to the increase of mechanical properties in the blends [9]. In this work, experimental results of the PVDF terpolymer/PMMA blends for dielectric energy storage application will be presented.

2 Experimental section

The PVDF terpolymer/PMMA blends were prepared by the solution casting method. The PVDF terpolymer [P(VDF–TrFE–CFE), 58.3/34.2/7.5 mol%] and PMMA were dissolved in N, N-dimethylformamide. The solution mixtures were poured on glass slides and dried at 70°C for 5 h. After the solution was dried, the blend films (with an approximate thickness between 12 and 20 μm) were peeled off the glass slides and further annealed at 120–140°C for 10 h in a vacuum oven to improve the crystallinity and remove the residual solvent. The compositions of the PVDF terpolymer/PMMA blends are 0, 1.5, 2.5, and 5 wt% PMMA.

For electrical testing, gold and silver electrodes were deposited on the surface of terpolymer film by the sputtering method. Temperature dependence of the weak field dielectric properties was measured by a characterisation system comprised of an LCR meter (HP4284), a furnace, and a computer for temperature control and data collection. The electric displacement–electric field (D–E loops) were measured by a modified Sawyer–Tower circuit. The dielectric energy density of the blends was calculated from the unipolar P–E loops. The breakdown electric field was measured by applying a linearly increasing voltage (ramp rate is 500 V/m) on the terpolymer and blend films. The electrode size of the samples for the breakdown test was 2.45 mm. Typically, 10–15 samples were tested. To analyse the breakdown field, the Weibull analysis is used [15]

\[
\ln \left( \ln \left( \frac{1}{1 - F(x)} \right) \right) = \beta \ln(x) - \beta \ln(\alpha)
\]

where \(F(x)\) is the cumulative failure of the tested samples; \(\alpha\) is the characteristic breakdown field; \(\beta\) is a parameter that indicates the distribution of breakdown field, and \(x\) is the measured breakdown field \(E_b\).

3 Results and discussion

Fig. 1a shows the dependence of the dielectric constant on temperature at 1 kHz of the blends with various compositions. A continuous decrease of the dielectric constant of the blends with an increasing amount of PMMA can be observed in this figure. At room temperature, the dielectric constant of the blends decreases significantly with PMMA content. For the blend with 5 wt% PMMA, the dielectric constant is about two thirds that of the pure terpolymer.
PMMA is an amorphous polymer with a lower dielectric constant (about 3.2 at 1 kHz at room temperature), much higher glass transition (about 105°C) and a higher Young’s modulus (>1800 MPa) than the terpolymer [16, 17]. PMMA and the PVDF-based polymer are miscible in the amorphous phase and PMMA is not included in the crystalline phase [9]. One significant effect of adding PMMA into PVDF-based polymers is the reduction of crystallinity. For the terpolymer and PMMA blends, the heat of melting changes from about 21 J/g for the pure terpolymer to 20 and 18.5 J/g for blends with 2.5 and 5 wt% PMMA, respectively. Since the dielectric constant of PMMA is much lower than that of the terpolymer and PMMA only exists in the amorphous phase, the contribution of PMMA to the dielectric constant is very small. The dielectric response of the terpolymer and the blends comes mainly from the crystalline phase of the terpolymer. However, as shown in Fig. 1b, the decrease of the dielectric constant at room temperature is much faster than the decrease of crystallinity, which indicates that the reduction of crystallinity is only one factor that results in the reduction of the dielectric constant.

From Fig. 1a, the shift of the dielectric maxima to a higher temperature with PMMA can be noted. A similar phenomenon was also observed in electron irradiated P(VDF-TrFE)/PMMA blends [14]. It was thought that though PMMA was in the amorphous phase, it might influence the interface between the crystalline and amorphous phases. PMMA, which has a much higher glass transition temperature than does the terpolymer, may retard the chain movement of the terpolymer and dipole orientation, leading to a lower dielectric constant.

Fig. 2 shows the unipolar P–E loops of the terpolymer and blends with different compositions. Corresponding to the decrease of the weak field dielectric constant, the induced polarisation was reduced by adding PMMA into the terpolymer. The decrease of polarisation is still faster than crystallinity change, but a little slower than the weak field dielectric constant, which suggests the retarding effect maybe mitigated by the high electric field or due to the frequency dependence effect (the frequency for the P–E measurement is 10 Hz).

Another effect of PMMA addition is the improvement of the mechanical property of the terpolymer. The elastic modulus of the blends with 0, 1.5, and 5 wt% PMMA is shown in Fig. 3. As shown in this figure, at room temperature the elastic modulus of the blends was significantly increased by blending PMMA into PVDF terpolymer. The increase of the glass transition temperature is the reason for the improvement of storage modulus in the blends [9].

Several mechanisms have been proposed to explain the dielectric breakdown of dielectrics. For electromechanical breakdown mechanism, the breakdown field \( E_b \) is correlated with the elastic modulus \( Y \) of dielectrics \( (E_b \propto Y^{1/3}) \) [18]. Our results suggest that the increase of elastic modulus in the blends can improve the dielectric breakdown field of the materials. The Weibull analysis of the breakdown test results of the terpolymer and the 2.5 wt% PMMA blend is shown in Fig. 4. The breakdown field of the 2.5 wt% blend is 314 MV/m, which is about 30 MV/m higher than that of the pure terpolymer (280 MV/m).

The discharged energy density of the terpolymer and the blends is calculated based on the unipolar P–E loops and the results are shown in Fig. 5. For blends with a small amount of PMMA (1.5 and 2.5 wt%...
that of the terpolymer (also 83.6%). The efficiency under an electric field, but because the breakdown field of the 2.5 wt% blend is higher than that of terpolymer, the maximum energy density of the blend is also higher. The addition of a small amount of PMMA does not affect the charge-discharge efficiency of the terpolymer significantly. For example, based on the P–E loops under an electric field of 250 MV/m (Fig. 2), the efficiency is ~83.6% for the blend with 2.5 wt% PMMA, which is the same as that of the terpolymer (also 83.6%). The efficiency was reduced to ~76.8% when 5 wt% PMMA was added to the terpolymer.

4 Conclusion

In summary, the energy storage properties of PVDF terpolymer/PMMA blends are investigated. The P(VDF–TrFE–CFE) terpolymer and PMMA polymer are completely miscible in the amorphous phase. Owing to the much higher elastic modulus of PMMA, the elastic modulus of P(VDF–TrFE–CFE)/PMMA blends was improved and the breakdown field of the blends was also increased. Owing to the lower dielectric response of PMMA and the reduction of crystallinity of the terpolymer, the dielectric constant of the blends was reduced by adding PMMA. For a small amount of PMMA addition (<2.5 wt%), the energy density of the blend is almost the same as that of the pure terpolymer under the same electric field, but a higher breakdown field can be obtained in these blends.

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Fig. 4 Weibull analysis of the breakdown field of
a P(VDF–TrFE–CFE) terpolymer (α = 280 MV/m, β = 2.46)
b P(VDF–TrFE–CFE) terpolymer/PMMA (2.5 wt% PMMA) blends (α = 314 MV/m, β = 3.47)

Fig. 5 Energy density of P(VDF–TrFE–CFE) terpolymer/PMMA blends

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