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Dielectric response of structured multilayered polymer films fabricated by forced assembly

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The effect of introducing a multilayer microstructure on the dielectric properties of polymer materials is evaluated in 32- and 256-layer films with alternating polycarbonate (PC) and polyvinylidene-hexafluoropropylene (coPVDF) layers. The permittivity, dielectric loss, dielectric strength, and energy density were measured as a function of the relative PC/coPVDF volume concentrations. The permittivity follows an effective medium model while the dielectric strength was typically higher than that predicted by a volume fraction based weighted average of the components. Energy densities as high as ~14 J/cm^3, about 60% greater than that of the component polymers, are measured for 50% PC/50% coPVDF films. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2897029]

There is a compelling motivation to develop high energy density dielectric materials that can reduce the size, weight, and cost of electronic devices and electrical power systems. Polymer films are widely used as the active dielectric medium in capacitors, for example, because they can exhibit high dielectric strength, low dielectric loss, high energy densities, fast speed, and high reliability.[1]

In energy storage capacitors, the maximum energy storage density (U_d) is related to the permittivity (ε_r) and the dielectric strength (E_B)

$$U_d = \tfrac{1}{2}\varepsilon_0 \varepsilon_r E_B^2, \quad (1)$$

where ε_0 is the vacuum permittivity (8.85×10^{-12} C^2 J^{-1} m^{-1}). E_B is the maximum applied electric field that a material can withstand prior to breakdown. In current capacitor materials, the U_d is limited by a low permittivity.[2,3] In higher permittivity polymers, U_d is usually constrained by a low E_B.

In the present paper we describe a *material structure* that can enhance the dielectric strength and, hence, the energy storage ability of high permittivity capacitor materials. The structure comprises thin alternating layers of two polymers, one with high ε_r and one with high E_B. The layered materials are readily fabricated by forced assembly techniques.[4,5]

The motivation for a multilayered structure is to take advantage of the barrier effect.[6–9] It is well known that introducing a component that presents a barrier to the propagation of the electrical breakdown channel can increase the dielectric strength of the material.[10] A multilayered polymer material provides many barriers to the propagation of a breakdown through the film.

The high ε_r material used herein is Solef 21508 (ε_r=10–15),[11] a copolymer of polyvinylidenefluoride and hexafluoropropylene [$-(CH_2-CF_2)_{85}-(CFCF_3CF_2)_{15}$], referred to as coPVDF. The barrier layers are polycarbonate (PC), a high dielectric strength ($E_B > 600$ kV/mm), low permittivity ($\varepsilon_r \sim 3$) polymer.

Samples with 32 and 256 alternating PC and coPVDF layers were prepared using multilayer coextrusion.[4,12–14] Films with component volume concentrations (relative layer thickness) of 10% PC/90% coPVDF, 30% PC/70% coPVDF, 50% PC/50% coPVDF, 70% PC/30% coPVDF, and 90% PC/10% coPVDF were prepared. The overall thickness of each film was ~0.5 mil (12.7 μm). Pure PC and coPVDF controls were also prepared.

The layer structure of the films is shown in Fig. 1. These images were obtained by focused ion beam (FIB) milling

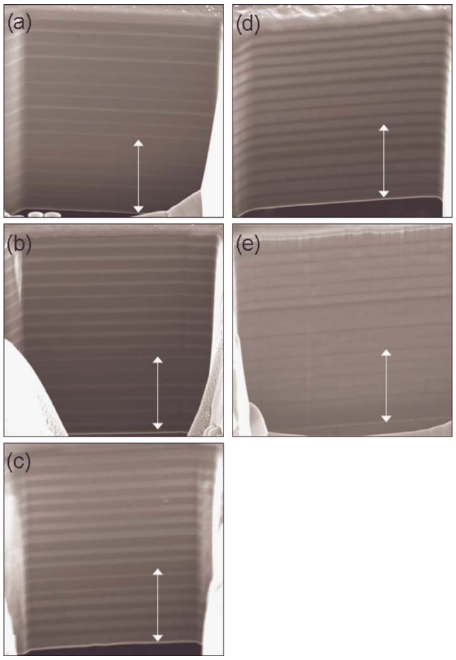

FIG. 1. (Color online) SEM images of layered films prepared by FIB: (a) 90% PC/10% coPVDF, (b) 30% PC/70% coPVDF, (c) 50% PC/50% coPVDF, (d) 70% PC/30% coPVDF, and (e) 10% PC/90% coPVDF. White arrows denote a distance of 5 μm.

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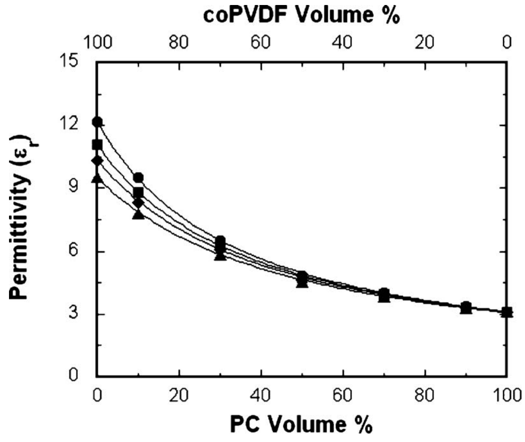

FIG. 2. Permittivity of 32-layer films as a function of volume concentration, measured at 100 Hz (circles), 1 kHz (squares), 10 kHz (diamonds), and 100 kHz (triangles). Solid lines represent permittivity calculated with Eq. (2).

followed by scanning electron microscopy (SEM). The contrast in the SEM images is due to the lower electron density of PC compared to PVDF.[15,16] The brighter layers are PVDF and the darker ones are PC. There are some variations in the individual layer thicknesses; however, the concentration over the entire sample was within about ±1% of that reported.

The capacitance, dielectric loss, and stored energy density were measured on films featuring Au electrodes. The circular electrodes (50–100 nm thick, 6.2 mm in diameter) were sputtered onto both sides of the films through a shadow mask, under Ar plasma using a Bal-Tec SCD005 sputter coater. The capacitance and dielectric loss were measured at 100 Hz, 1 kHz, 10 kHz, and 100 kHz using a Protek Z9216 *LCR*. The low field permittivity ε_r was determined from $\varepsilon_r = c_p^* d/(\varepsilon_0^* A)$, where c_p is the measured capacitance, d is the thickness of the film, ε_0 is the vacuum dielectric permittivity, and A is the area of the device.

The permittivity of 32-layer films as a function of polymer volume composition is shown in Fig. 2. The observed permittivity of the PC and coPVDF control films at 100 Hz are in good agreement with reported values.[11] The permittivity of the layered films increases with the volume concentration of PVDF. The relationship between the permittivity and the relative layer thickness (volume fraction) fit a layered effective medium or capacitors in series[17] model given by

$$\frac{1}{\varepsilon_r} = \frac{\varphi_1}{\varepsilon_{r1}} + \frac{\varphi_2}{\varepsilon_{r2}}, \tag{2}$$

where φ_1 and ε_{r1} are the volume fraction and permittivity of component one and φ_2 and ε_r are the volume fraction and permittivity of component two, respectively. The observed permittivity for both the 32- and 256-layer films was within 3% of that predicted by Eq. (2) at all frequencies measured.

The dielectric loss, expressed as the imaginary part of the dielectric constant, was also consistent with the effective medium model. For both the 32- and 256-layer films, the measured tan δ is within 10% of the values predicted from Eq. (2) for all frequencies.

The dielectric strength (E_B) was determined under quasi-homogeneous field conditions using a sphere-plane geometry. Polymer films (1×1 in.^{2}) were placed on an aluminum ground plane (diameter=3/4 in.) and a spherical copper electrode (diameter=2 in.) was used to make contact to the top surface of the film. The films were submersed in Fluorinert FC-40 to prevent arcing and surface discharge. The voltage source was a Quadtech Guardian 12 kV Hi Pot tester with a ramp rate of 500 V/s. 35–50 samples were tested at each volume concentration. The measured E_B of the layered polymers is shown in Fig. 3. The observed breakdown field for multilayered films is as much as 20% greater than the weighted average of the component concentrations. The highest breakdown field for the 32-layer samples (nearly 800 kV/mm) is observed for 90% PC/10% coPVDF films.

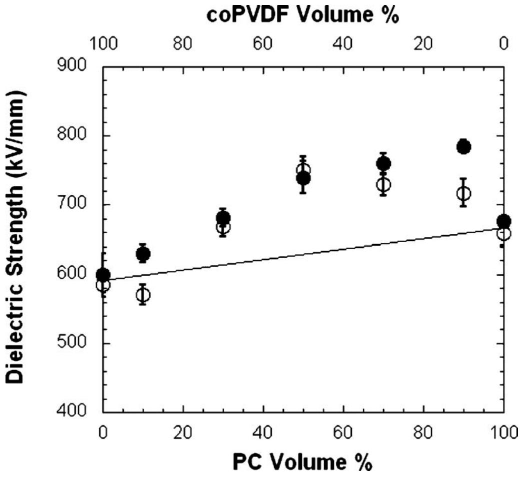

FIG. 3. Average dielectric strength (E_B) of 32-layer (solid circles) and 256-layer (open circles) PC/coPVDF films as a function of volume concentration. The solid line represents the expected E_B based on a weighted average.

The increase in E_B in the layered films implies an enhanced energy storage density according to Eq. (1). The projected energy density calculated using the measured ε_r ($v = 100$ H$_2$) and E_B is shown in Fig. 4 for 256-layer films. The highest projected energy density is $U_d \sim 17$ J/cm^3 for 10% PC/90% coPVDF films.

The experimental U_d of sample capacitor films featuring Au electrodes was measured with a charge/discharge circuit.[18] The films were placed on a brass ground plane and charged for approximately 0.5 s with an IDI spring contact probe connected to a Trek 610D power supply. The discharged current was measured with an Agilent 54622A oscilloscope. Eight samples (submersed in Fluorinert FC-40) were measured for each volume concentration. The average

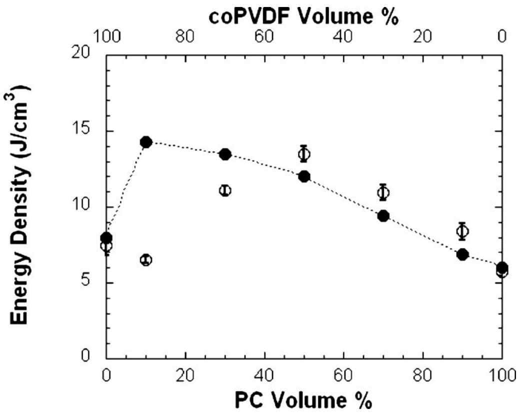

FIG. 4. Maximum projected (filled circles) and measured (open circles) energy density of 256-layer PC/coPVDF films as a function of volume concentration. The projected value for the coPVDF control film was determined from data reported in Ref. 13.

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measured U_d for 256-layer films is compared to the projected U_d in Fig. 4. There is a good agreement for films ranging in volume concentration from pure PC to 50% PC/50% coPVDF. The highest measured energy density, $U_d \sim 14\ \mathrm{J/cm^3}$, for the 50/50 layered material is ~60% greater than that measured for pure coPVDF and nearly double that of pure PC. The 32-layered films showed comparable results for high PC concentrations but much lower U_d at high PVDF concentrations.

The measured U_d of films containing >50 vol % coPVDF were lower than that projected primarily because the breakdown field in films with electrodes was lower than that measured in the sphere-plane geometry. In these samples, a delamination of the gold electrodes was observed. Electromechanical deformations in coPVDF (Ref. 11) may degrade the electrode/polymer interface and lead to premature breakdown. Also, a polarization hysteresis reported in coPVDF (Ref. 19) may reduce the extractable U_d.

In summary, we have demonstrated that multilayering a high permittivity polymer (coPVDF) with a high dielectric strength polymer (PC) is an effective strategy to increase the extractable energy density relative to the component polymers. The dielectric strength increases in the layered materials while the permittivity, which fits an effective medium model, remains relatively large. Energy densities as high as $U_d \sim 14\ \mathrm{J/cm^3}$ or ~60% higher than that of either component were measured. Even higher energy densities, as much as double that of the component polymers, are implied by the measured permittivity and breakdown field.

It is reasonable that the improvement in dielectric strength results from the barrier effect of the layers. The forced assembly fabrication technique provides an ability to control the number and thickness of the barriers. It is likely that the layer structure can be optimized to further enhance the breakdown field and stored energy density.

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