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Interfacial polarization and layer thickness effect on electrical insulation in multilayered polysulfone/poly(vinylidene fluoride) films

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ABSTRACT

In this study, we report layer thickness effect on the electrical insulation property of polysulfone (PSF)/poly(vinylidene fluoride) (PVDF) multilayer films having a fixed composition of PSF/PVDF = 30/70 (vol./vol.). Breakdown strength, dielectric lifetime, and electrical conductivity were studied for 32- and 256-layer films having various total film thicknesses. Among these films, those having thinner PVDF and PSF layers exhibited lower breakdown strength, shorter lifetime, and higher electrical conductivity than those having thicker layers. These experimental results were explained by Maxwell–Wagner–Sillars interfacial polarization due to contrasts in dielectric constant and electronic conductivity for PVDF and PSF, respectively. When both PVDF and PSF layers were thick (ca. > 100–200 nm), more space charges were available in PVDF and no electronic conduction was allowed for PSF. These accumulated interfacial charges could serve as effective traps for injected electrons from metal electrodes under high electric fields. As a result, reduced electrical conductivity and enhanced breakdown strength/dielectric lifetime properties were obtained. When both layers were thin (ca. < 100 nm), fewer space charges were available in PVDF and significant electronic conduction through PSF resulted in low interfacial polarization. Consequently, higher electrical conductivity, lower breakdown strength, and shorter lifetime were observed. These results provide us insights into potential physics to enhance electrical insulation property of polymer films using a multilayered structure having large dielectric constant contrast.

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1. Introduction

In contrast with supercapacitors [1] and electrolytic capacitors [2], polymer film capacitors [3,4] show high breakdown strength and extremely low dissipation factor. They are especially suited for electrical insulation applications requiring high voltage, high ripple current, or high operating frequency (>10 kHz). Examples include DC-link capacitors [5] for hybrid electric vehicles and multi-megawatt stationary power electronics, inverters [6] for grid-tied renewable (solar, wind, and fuel cell) power generation, and pulsed power [7] for high energy physics and military applications. In addition, the "graceful failure" (or self-clearing) capability [3,4] makes polymer film capacitors more attractive than ceramic capacitors for high performance and long life operation. Nonetheless, current state-of-the-art polymer film capacitors, which rely on an old technology of biaxially oriented polypropylene (BOPP) films, suffer from a low energy density and a low upper operation temperature of 85 °C due to increased electronic conduction at elevated temperatures [8]. With the emerging broadband semiconductor (SiC and GaN) switch technology for next generation power electronic systems [9], polymer film capacitors are awaiting breakthroughs in high temperature capability (>120 °C) and high energy density (for smaller sizes and thus lower costs) while maintaining extremely low losses.

Currently, several strategies have been undertaken to achieve the above goals. First, dipole-modified dielectrics or polar/ferroelectric polymers are pursued in order to utilize dipolar orientational polarization for high energy storage [10]. Present challenge lies in the reduction of nonlinear dielectric or ferroelectric losses related to hysteresis in dipole switching [11]. Second, polymer/ceramic nanocomposites (i.e., nanodielectrics) are being actively

pursued because ceramic (especially ferroelectric) nanoparticles possess high dielectric constants [12]. Current research efforts focus on uniform dispersion of ceramic nanoparticles in polymer matrices while preventing a decrease in breakdown strength.

Recently, we proposed a unique strategy, i.e., multilayer films comprised of a high dielectric constant (or ferroelectric) polymer such as poly(vinylidene fluoride) (PVDF, including its copolymers) and a highly insulating (or linear dielectric) polymer such as polycarbonate (PC) (Scheme 1) [13−20]. Generally speaking, all types of polarization are present in these multilayer dielectric films. First, electronic and atomic polarizations, which are ubiquitous for all dielectric polymers, are responsible for the linear dielectric responses [21]. Second, dipolar orientational polarization in PVDF needs to be avoided in order to minimize the ferroelectric hysteresis. This can be achieved by lowering the PVDF content and non-uniform electric field distribution due to the dielectric constant contrast between PVDF and PC [15]. Third, impurity ion migrational loss in PVDF layers (inherited from the suspension polymerization) can be minimized by reducing the PVDF layer thickness via a nanoconfinement effect [15,16]. Fourth, due to contrasts in dielectric constant (ε_r) and/or bulk conductivity (σ) between PC ($\varepsilon_{r,PC} = 3$ and $\sigma_{PC} \approx 10^{-15}$ S/m) and PVDF ($\varepsilon_{r,PVDF} = 10^{-12}$ and $\sigma_{PVDF} \approx 10^{-11}$ S/m) [22], Maxwell−Wagner−Sillars (MWS) interfacial polarization [23] can build up at the PC/PVDF interfaces in response to the application of an electric field (see Fig. 5A and the explanation later). These interfacial charges serve as effective charge traps to decrease conductivity, eventually enhancing the ultimate dielectric properties including breakdown strength [14]. Similar phenomenon of interfacial polarization is also reported for ceramic multilayer films [24,25]. Finally, electronic conduction shall be minimized, especially at elevated temperatures.

In a recent work, we observed that adding a thin poly(methyl methacrylate) (PMMA) tie layer between PC and P(VDF-co-hexafluoropropylene) [P(VDF-HFP)] layers could further enhance breakdown strength and energy density for multilayer films [20]. This was qualitatively attributed to better interfacial adhesion, because PMMA is miscible with P(VDF-HFP) and compatible with PC. Nonetheless, the fundamental insight of the interphase (i.e., the tie layer) between PC and P(VDF-HFP) layers was not well-understood. In this communication, we report a layer thickness effect on electrical insulation properties of polysulfone (PSF)/PVDF multilayer films. This effect is explained by the MWS interfacial polarization in the PVDF layers and subsequent electronic conduction in the PSF layers. When the more conductive PVDF layer is thick, more space charges are available to be polarized. When the insulating PSF layer is thick, no internal electronic conduction is allowed. As a result, the MWS interfacial polarization will be high

and the accumulated charges at multilayer interfaces serve as effective traps to prevent electronic conduction. On the contrary, when the PVDF and PSF layers are thin (ca. < 100 nm), the interfacial polarization will be low due to fewer available space charges in PVDF layers and electronic conduction through thin PSF layers. Consequently, the overall conductivity will be relatively high, resulting in reduced breakdown strength and shorter lifetime.
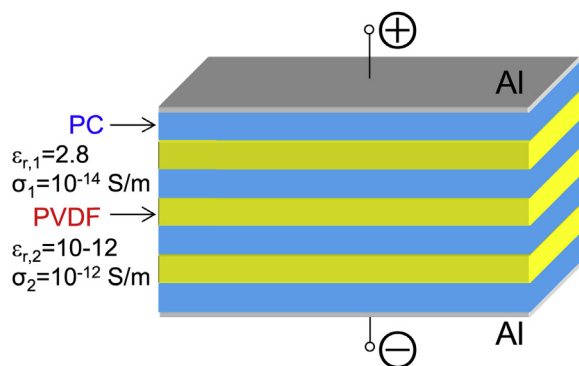
2. Experimental

2.1. Materials

PSF (Udel® P-3703) and PVDF (Solef® 6010) resins were obtained from Solvay Specialty Polymers (Alpharetta, GA). Linear low density polyethylene (LLDPE) for the skin layers was purchased from Dow Chemical Company.

2.2. Multilayer film coextrusion

Melt viscosity for the PSF and PVDF resins was determined using a Kayeness Galaxy 1 melt flow indexer under a low shear (10 s^{-1}) condition. The melt viscosities as a function of temperature for both PSF and PVDF are presented in Fig. S1 in the Supplementary material, and a coextrusion temperature of 285 °C was chosen based on the rheological compatibility between PSF and PVDF.

Films with alternating PSF/PVDF layers were fabricated using the two-component forced assembly multilayer coextrusion process. Prior to multilayer film coextrusion, all resins were dried at 80 °C under vacuum for 24 h. Two sacrificial LLDPE skin layers were laminated on the outside of the multilayer or control films to improve the surface quality, protect from damage, and reduce surface defects of the film [26]. These sacrificial LLDPE layers were removed prior to additional film processing and testing. The polymer composition, which was controlled by the ratio of feed speeds in PSF and PVDF extruders, was fixed at 30/70 (vol./vol.) during multilayer coextrusion. This composition was chosen because of high interfacial polarization in PVDF layers and relatively easy internal electronic conduction in PSF layers for this study. Both 32- and 256-layer (32L and 256L) films were collected and the ultimate film thickness was controlled by tuning the uptake speed during the film uptake process. For the 32L PSF/PVDF films, three total film thicknesses were obtained; 4.6 ± 0.2, 9.5 ± 0.5, and 11.6 ± 0.9 μm. The thickness of the 256L PSF/PVDF film was 12.0 ± 0.9 μm. Film thicknesses were measured to ± 0.2 μm accuracy using an LE 1000-2 MT12 precision film gauge (Measureitall.com, Cornelius, NC). The characteristics of these films are summarized in Table 1. Due to the presence of the polar sulfone groups, PSF layers adhered reasonably well to PVDF layers and no easy delamination was observed under normal film handling processes.

Table 1
Sample information of the PSF/PVDF 30/70 (vol./vol.) multilayered films.

No. of layers	Total film thickness (μm)	PSF layer thickness (nm) [nominal/ measured]	PVDF layer thickness (nm) [nominal/ measured]	PSF/PVDF (vol./vol.)[a]
32	11.6 ± 0.9	$218/244 \pm 25$	$508/519 \pm 42$	29/71
32	9.5 ± 0.5	$178/206 \pm 24$	$415/433 \pm 27$	27/73
32	4.6 ± 0.2	$86/83 \pm 6$	$201/241 \pm 18$	33/67
256	12.0 ± 0.9	$28/NA^b$	$66/NA^b$	27/73

[a] The PSF or PVDF volume fractions are determined by density measurements. The measured densities of PSF and PVDF are 1.23 and 1.72 g/cm^3, respectively.

[b] No accurate data are obtained. Because of possible interfacial charging, the bright PSF layers appear nearly the same thickness as the dark PVDF layers in the inset of Fig. 1D.

Scheme 1. Schematic of the PC/PVDF multilayer film with contrasts in both dielectric constant and/or bulk conductivity.