4.3. Layer-by-Layer Fabrication of Thin Polypropylene-based Dielectrics

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ABSTRACT

This work reviews recent advancements in the development of nanocomposite film capacitors fabricated via a layer-by-layer approach using printable polypropylene (PP)-based inks. By incorporating nanoparticles such as barium titanate (BT) and silicon dioxide (SD), and applying surface treatments with polymer coatings or surfactants, issues related to agglomeration, voids, and dielectric breakdown were mitigated. The layered structure enabled tailored material configurations within the dielectric, offering control over electrical properties. Replacing central PP layers with nanocomposites more than doubled the dielectric constant compared to polypropylene, while preserving a stable frequency response. Moreover, the integration of both BT and SD led to a 22% improvement in dielectric strength compared to neat PP. These combined enhancements resulted in a twofold increase in energy density, reaching 4.1 J cm^{-3}. The study also revealed that the dielectric performance was highly sensitive to the arrangement of nanocomposite layers, with specific stacking sequences significantly influencing breakdown strength. Overall, the results highlight the potential of structural and compositional optimization in nanocomposite dielectrics to enhance the performance of film capacitors, making them promising candidates for advanced energy storage applications.

INTRODUCTION

Polymer film capacitors are widely used in electronics for filtering and smoothing in power supply circuits, for example in automotive or renewable energy systems [1]. They are built from two electrodes separated by an insulating dielectric material [2], and polypropylene (PP) is currently dominating the dielectric film market due to its high dielectric strength, low dielectric loss and well-established large-scale production [3]. However, the dielectric constant of PP is just 2.2, which leads to energy density within 1-4 J/cm^3 [4-6]. In contrast, the energy density of aluminum electrolytic capacitors is around 5 J/cm^3 [7]. Consequently, any application requiring high capacitance values will lead to an increase in volume and weight of the capacitors, effectively decreasing the weight efficiency and increasing volume of power electronic systems. A common approach toward increasing the dielectric constant is doping the dielectric with nanoparticles, but they must be well dispersed to observe an improvement in dielectric properties [8]. On the other hand, the layer-by-layer (LbL) fabrication technique has emerged as a promising method for creating thin polypropylene-based dielectrics, offering precise control over dielectric properties and enabling the development of advanced capacitors. This method involves the successive deposition of ultra-thin layers of polypropylene or other polymers, allowing for the fine-tuning of dielectric thickness and morphology, which is crucial for optimising the performance of film capacitors [9, 10].

This work reviews our previous papers [11, 12] on LbL of nanocomposite film capacitors and its potential in increasing the energy density through doping PP with barium titanate and silicone dioxide. It was observed that chemical functionalization and specific arrangement of nanoparticles were crucial to increasing the dielectric constants and breakdown strengths, and effectively the energy density. Therefore, this method provides a versatile and scalable approach to producing high-performance dielectrics with tailored properties, paving the way for the development of next-generation film capacitors.

METHODOLOGY

The first step in the fabrication process of film capacitors (see Figure 1) was the preparation of a suspension of amorphous PP in a mixture of two solvents. The suspension was heated to 140°C in a vial and subsequently cooled down in a test tube, creating a semi-transparent liquid. It was then diluted and homogenised to the desired weight fraction of PP in solvents (typically 4-4.5 wt.%), making it ready for the fabrication of PP dielectrics. The dielectric layers were manufactured through a multi-layer spin coating process on a glass substrate. Thin layers of titanium (10 nm) and silver (200 nm) were used as the bottom electrode on the glass substrate. Subsequently, approx. 60 µl of the suspension was deposited on the electrode, and the spin-coating equipment rotated the substrate with a speed of 1200 rpm to remove the excess material. The sample was then placed on a hot plate to evaporate the solvent and achieve a homogenous layer. The process was repeated for the desired number of layers. After spin-coating and drying, a top electrode, made of aluminium (200 nm), was deposited on top of the dielectric layers using a thin film deposition system. A shadow mask was used to deposit four independent electrodes, and each had an area of 5.4 mm². The thickness of the dielectric layers was determined by scanning the samples with a surface profilometer (Veeco Dektak 150).

Figure 1. Methodology flowchart.

Nanoparticles were added to the PP gel to fabricate nanocomposite dielectric layers. Barium titanate (BT) nanoparticles had a diameter of approximately 50 nm, while silicone dioxide (SD) around 8 nm, and both were purchased in a non-modified form from US Research Nanomaterials, USA. Adding nanoparticles directly into PP leads to a problems with agglomeration due to poor compatibility between the materials [13]. Therefore, BT nanoparticles were added to the PP suspension together with either an ionic sodium dodecyl sulfate (SDS) or a nonionic Triton X-100 surfactants. They work by modifying the surface properties of the nanoparticles to make them more compatible with the polypropylene matrix, thereby reducing their tendency to form large agglomerates [11]. An alternative approach to tuning interfacial interactions in PP gels for capacitor fabrication is covering the nanoparticles with a thin layer of PP. That is done through anti-solvent displacement condensation, which involves combining a dispersion of BT or SD nanoparticles in toluene with amorphous polypropylene. The mixture was heated to 140°C and stirred until homogenous, then rapidly transferred to a flask containing dimethyl sulfoxide (DMSO) and crash-cooled to room temperature. The coated nanoparticles were then isolated by centrifugation and washed with ethanol and o-xylene to remove the excess polymer. It was shown that this method leads to approx. 1 nm-thick shell around nanoparticles, easily distinguishable from the crystal lattices of the nanoparticle [9].

The LbL approach allows for precise control over composition and thickness of the dielectric film, such as introducing nanoparticles into specific areas, which is not achievable with conventional methods like melt extrusion. This work compares two systems, where: 1) BT were mixed with PP gel together with SDS and Triton X-100 surfactants; 2) BT and SD were chemically modified to create a PP shell around the nanoparticles. The advantage of using surfactants is their easy introduction to the PP gel as a solid or gel, but they will remain in the dielectric layer and at the interface area between the polymer and nanoparticles. On the other hand, the PP shell is formed from the exact same material as the dielectric, thus improving the interfacial compatibility, but the synthesis process involves multiple stages, which might be costly and difficult to scale up. All compared films in this work were built from five layers, and the bottom and top layers were made of PP. The internal three layers were fabricated using nanocomposite gels with 0.8 volume percent of nanoparticles. In the first configuration, the dielectric had layers with embedded BT treated with the two surfactants. Another series included BT, SD or a mixture of both treated by PP coating. As the materials can be changed during the LbL process, the nanocomposite layers were alternated, forming either BT-SD-BT or SD-BT-SD arrangements.

Electrical testing was performed to derive the dielectric constant and energy density of the film capacitors. The capacitance measurements were taken using a Keysight impedance analyzer E4990A using a frequency sweep to investigate the capacitance stability between 20-10^6 Hz. The dielectric constant (ε_r) was calculated based on Equation 1 using the measured capacitance (C), the determined dielectric thickness (d), and the vacuum permittivity (ε_0).

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A} \qquad \text{Equation 1}$$

Breakdown tests involved applying a DC voltage ramp up to 1000 V to the capacitor devices using the Vitrek 951i Electrical Safety Compliance Analyzer. Weibull analysis was performed to determine the breakdown strength (E_b). Energy density (U) of the film capacitors was calculated through Equation 2.

$$U = \frac{1}{2} \varepsilon_r \varepsilon_0 E_b^2 \qquad \text{Equation 2}$$

RESULTS

One of the fundamental parameters of a film capacitor is the dielectric constant, which defines the ability of the dielectric film to store electrical energy. As shown in Equation 1, it considers the capacitance and the geometry of the device, thus allowing for direct comparison of different materials. The dielectric constant of a commercial PP is around 2.2 [14], but a higher dielectric constant could allow for making more compact capacitors. A common drawback of using materials with a higher dielectric constant is the reduced frequency stability due to increased losses arising from ferroelectric polarisation hysteresis. On the other hand, PP is known for its excellent frequency stability, which is relevant for such applications as high-frequency filtering, pulse circuits, and precision timing. Figure 2 shows the stability of the dielectric constants of the fabricated devices up to 10^7 Hz. The PP device had a dielectric constant at 2.2 at 1 kHz, which remained stable until 10^6 Hz. Above this frequency, the capacitor shifts its behaviour from the capacitive to inductive. The small amount of nanoparticles added to PP did not affect the frequency stability, and all devices performed similarly to neat PP. However, the nanoparticles had a greater impact on the dielectric constant values. Replacing the internal PP layer with the nanocomposite with BT reduced the dielectric constant to 2. However, when the BT were treated with either SDS or Triton, the dielectric constant increased to 3.2 and 2.85, respectively. A decrease in dielectric constant with the addition of untreated BT NPs was likely driven by clustering and the tendency for macroscopically mixed systems to result in increased electric field density being localised to the material with a lower dielectric constant [15]. On the other hand, when the middle layer was replaced with a nanocomposite with SD, the dielectric constant increased to 4.7, which was the highest value among the compared capacitors. Given the smaller size of the nanoparticles and resulting larger interfacial area, it indicates that the surface treatment of the nanoparticles plays a significant role in determining the dielectric constant of the overall nanocomposite [16, 17].

Another important aspect of film capacitors is the Equivalent Series Resistance (ESR), which determines the resistive losses of the devices, causing energy dissipation as heat, reducing the overall efficiency. The ESR of the PP devices was 800 mΩ, while it is typically lower for commercial PP capacitors. The higher than usual ESR was most likely caused by the leads used for measurements, and therefore, the uncertainty from that should remain constant for all devices. As shown in Figure 2b, introducing any of the surfactants led to a spike in ESR, which was 20 times higher than PP in the case of Triton and 11 times higher when the nanoparticles were treated with SDS. The polymer coating procedure led to a significantly lower increase in ESR, and in the case of the layup with three BT layers, it was less than 6 times higher than neat PP. The lowest increase in ESR was achieved by incorporating two SD layers and 1 BT layer, leading to an ESR value 14% higher than neat PP.

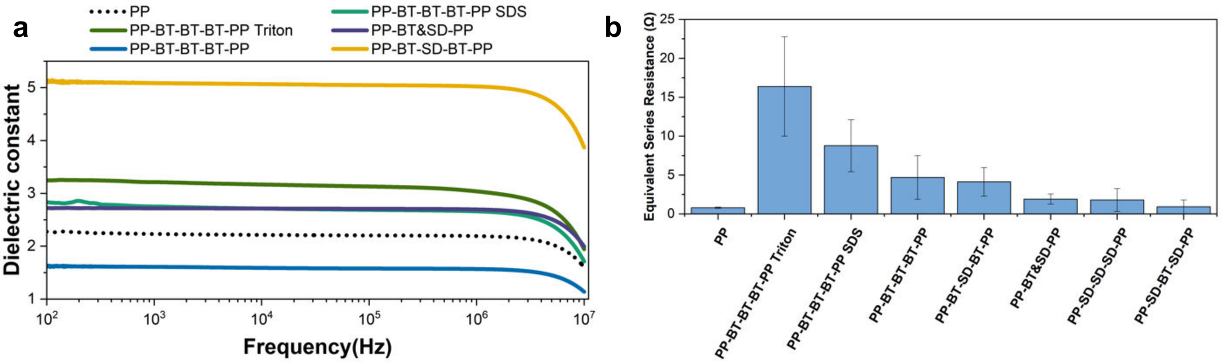

Figure 2. The effect of different chemical treatments and nanoparticles on the capacitance frequency response (a) and the Equivalent Series Resistance (b).

The energy density of film capacitors is strongly influenced by their breakdown strength, as demonstrated in Equation 2. The spin-coated polypropylene (PP) devices exhibited a breakdown strength of 457 MV m^{-1}, which is lower than the typical value for biaxially oriented polypropylene (approx. 700 MV/m^{-1} [18]). However, the authors have made advances with this technique to produce films with breakdown strengths exceeding 1000 MV m^{-1}, which will be detailed in an upcoming publication. A well-known drawback of incorporating nanoparticles into PP is the reduction in breakdown strength, often due to agglomeration, voids, interfacial incompatibilities, and space charge accumulation at defect sites [19]. As shown in Figure 3, the breakdown strength dropped to 134 MV m^{-1} when the dielectric was constructed from alternating layers of SD and BT nanocomposites. Interestingly, reversing the layer sequence (i.e., PP–BT–SD–BT–PP) led to a doubling of the breakdown strength to 366 MV m^{-1}. A comparable value (325 MV m^{-1}) was observed when all three central layers of the dielectric were composed of the BT composite. These results suggest that the inclusion of the SD nanocomposite tends to reduce breakdown strength, a trend propelled by the increased film thickness. For example, the PP–SD–SD–SD–PP configuration reached a total thickness of 3 microns, whereas replacing the SD layers with BT reduced the thickness to just 0.4 microns. Notably, the same BT-based structure (PP–BT–BT–BT), when treated with either a polymer coating or Triton, yielded similar breakdown strengths of 325 MV·m^{-1} and 305 MV·m^{-1}, respectively. In contrast, employing a nanocomposite that combined both SD and BT significantly improved breakdown strength to 557 MV·m^{-1}. The three devices with the highest breakdown voltages achieved values in the range of 760–860 V. The total film thickness remained below 1 micron, which enabled a higher energy density of 4.7 J cm^{-3}—more than double that of neat PP, which reached just 2 J cm^{-3}. Thus, the hybrid device simultaneously allowed for an increase in the dielectric constant (37% higher than PP), dielectric strength, and at the same time, it avoided high ESR values.

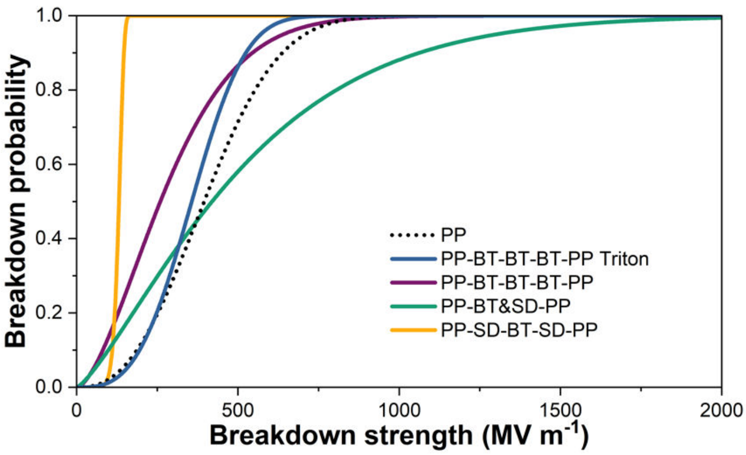

Figure 3. The probability of breakdown strength of PP and nanocomposite film capacitors.

CONCLUSIONS

This paper reviewed our previous work on nanocomposite film capacitors fabricated using a layer-by-layer approach. The devices were constructed from inks composed of polypropylene (PP) and various nanoparticles, which were treated with polymer coatings or surfactants to prevent agglomeration and minimise issues such as void formation and localized electric field concentrations. This layered fabrication strategy enabled tailoring the material composition of the dielectric stack, incorporating barium titanate, silicon dioxide, or a combination of both nanomaterials. As a result, the dielectric constant increased from 2.2 (for neat PP) to as high as 4.7 when three central PP layers were replaced with nanocomposite materials—while maintaining a frequency response comparable to that of unmodified PP. In addition to the enhanced permittivity, the inclusion of both nanomaterials improved the dielectric strength by 22% relative to neat PP. Together, these enhancements led to a twofold increase in energy density, reaching up to 4.1 J cm^{-3}. These findings underscore the potential of structural and compositional tuning in dielectric films to significantly boost capacitor performance. However, the work also highlighted key challenges associated with nanocomposite dielectrics, including increased equivalent series resistance and the strong dependence of breakdown strength on the specific layer arrangement.

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