ULTRATHIN NANOLAYER FILMS FOR HIGH ENERGY DENSITY, HIGH TEMPERATURE CAPACITORS

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Abstract

Fabrication of multilayer dielectric films to improve the dielectric properties was demonstrated by combining two or more polymers as a layered structure via coextrusion process. Recently, process innovations in film production scale-up of thin nanolayered films was demonstrated at PolymerPlus. Using conventionally used film metallization and capacitor winding capabilities nanolayer film capacitor prototypes were also created. Use of high temperature and high energy density films was demonstrated in capacitor applications. Recent results on effect of multilayer film thickness and number of layers on the dielectric performance is discussed in this paper.

Introduction

Polymer film capacitors are widely used in many applications ranging from consumer electronics to electric vehicles. [1,2,3,4] Polymer based dielectric materials are more advantageous than the ceramic and electrolytic capacitors in certain applications such as high-voltage/high current pulsed power, power conditioning applications for their graceful failure, and high voltage capabilities. Plastic film capacitors also find applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) use DC-link plastic film capacitors, which supplies periodic high currents enabling quick energy transfer to the insulated gate bipolar transistor (IGBT) circuit and typically runs at higher temperature (> 100 °C). Many of these applications use biaxially oriented polypropylene (BOPP) for its low losses (tan δ ~0.0002), and stable capacitance at room temperature. Biaxially oriented polypropylene (BOPP) film capacitors are the most suitable technology for high voltage, high temperature, and high ripple current power electronic systems in high performance electric vehicles (EVs) due to its low losses (tan δ ~0.0002), and stable capacitance at room temperature. These capacitors, however, occupy 1/4 to 1/3 of the power electronic unit and have a 50% voltage derating above 85 °C due to their drastically deteriorated breakdown strength and lifetime at high temperature. Development of a new dielectric material system for capacitors to increase temperature use and reduce size is critical in many EV related applications. In addition to EVs and HEVs, there are numerous applications such as oil and gas drilling, aviation, which require dielectric films for continuous high temperature use.

Another commonly used polymer, biaxially oriented poly (ethylene terephthalate) (PET) film, has a slightly higher energy density (6.0 J/cm³ at breakdown of 600 MV/m) and low dielectric loss (tan δ ~0.003). Low energy density and limited high temperature use are some of the key challenges in plastic film dielectrics industry.

To overcome these challenge, PolymerPlus LLC has developed the world’s first nanolayer film based high temperature, high energy density multilayer dielectric films, which contains two or more polymers with layered geometry. As demonstrated earlier, coextruded nanolayered films have been successfully developed for the use up to 150 °C. In this paper, recent development on ultrathin film fabrication, the effect of film and layer thickness on dielectric properties and overview of film metallization and capacitor prototype fabrication activities are discussed. It is also demonstrated that the higher energy density can also be used to produce compact capacitors. Increased breakdown strength and high dielectric constant in multilayer films allow increased energy density.

Conventionally, approaches combining high dielectric constant inorganic particles such as barium titanate, titanium dioxide with high breakdown strength polymers were attempted to achieve increased energy density. [5,6] Few approaches included development of copolymers and modification of BOPP. [7,8,9] Deteriorated breakdown properties, process scale-up challenges are some of the key challenges in most of these techniques. These key challenges – high temperature use and high energy density - in different types of dielectric materials including polymer films were overcome by developing nanolayered films as discussed in several publications and in this paper. [10,11,12,13,14]

PolymerPlus has demonstrated, using licensed coextrusion technology, multilayering a high dielectric constant polymer and a high electric breakdown polymer results in the achievement of high breakdown strength, high discharged energy density, and relatively low loss. For example, the PC/P(VDF-HFP) nanolayer films showed a much higher energy density (13.5 J/cc) than that of the state-of-the-art BOPP (5 J/cc), but a dramatically reduced hysteresis with linear D-E loops. It is known that PVDF and its copolymers are ferroelectric thereby causing significant hysteresis loss during dynamic poling
processes. However, the ferroelectric hysteresis is completely suppressed in PC/P(VDF-HFP) multilayered films.

The commercial BOPP capacitor films are typically fabricated between 3 to 4 µm thickness range. For multilayer dielectric film to be competitive, film thickness reduction is a key parameter. In recent development PolymerPlus has successfully demonstrated fabrication of film thickness down to 4 µm, comparable with commercial BOPP film. As the film thickness is reduced, the individual layer thicknesses also changed significantly impacting the dielectric properties. This paper summarizes the film thickness effect on the dielectric properties such as breakdown strength, hysteresis, and dielectric constant. These properties are critical in capacitor design activities.

**Experimental**

Multilayer film fabrication was conducted using coextrusion process creating nanolayered dielectric film structures of two or more polymers as shown in Figure 1. Films with thicknesses ranging from 4 to 12 µm range were fabricated using forced assembly layer multiplying melt coextrusion process as described previously.[10] Multilayer films were tested for various dielectric properties including breakdown strength (BDS), energy density, and dielectric hysteresis. The number of layers in the films were also changed to investigate the layer thickness effect on dielectric properties.

The breakdown strength (BDS) was measured with a Quadtech Guardian 20 kV HiPot tester using plane-plane electrodes and a voltage ramp of 500 V/s. The voltage was increased until breakdown occurred. Test samples were sandwiched between flexible electrodes consisting of metalized polypropylene films. The sample area was 2 cm² and controlled using a thick sample mask. Each measurement was repeated at least ten times.

The energy density of multilayered films was measured with a charge/discharge circuit. 1 cm² gold electrodes were coated on both sides of the film samples using a sputter coater. A pulsed voltage with duration of 500 ms was applied using a Quadtech Guardian 20 kV HiPot tester in increments of 0.5 kV. The electrodes and sample were immersed in mineral oil to minimize surface and corona discharge. The resulting charging and discharging currents were measured by placing two resistors (150 MΩ and 100 kΩ) in parallel with the sample and recording the voltage across the precision 100 kΩ resistor with a data acquisition card (NI AT-MIO-16E-1). The energy density was determined by integrating the discharge current with respect to time.

Electric displacement–electric field (D–E) hysteresis measurements were carried out using a Premiere II ferroelectric tester from Radiant Technologies, Inc. The applied voltage was a bipolar triangular waveform at 1 Hz. Gold coated film samples with a 1 cm diameter were used for testing. For each sample, various electric fields were applied in 50 MV/m increments. Dielectric spectroscopy was also conducted to measure the dielectric constant as a function of frequency.

A select films were further selected for metallization and capacitor fabrication activities.

**Results**

**Nanolayer Film Processing:** Using previously described multilayer coextrusion process, film rolls with varying number of layers and film thicknesses were fabricated as summarized in Table 1. A two component multilayer film system with two resins, identified as Resin A and Resin B in a film structure. Example of layer multiplying die and layering process is also shown (b) PolymerPlus coextrusion line (c) a schematic representation of dielectric film structure consisting of alternating layers of two polymers.

**Figure 1:** (a) Coextrusion process schematic showing a two polymer system, with alternating layers of Resin A and Resin B in a film structure. Example of layer multiplying die and layering process is also shown (b) PolymerPlus coextrusion line (c) a schematic representation of dielectric film structure consisting of alternating layers of two polymers.
As the ratio of the two materials was kept constant, increasing the number of layers changed the thickness significantly. The number of layers were changed approximately by a factor of 4 in these three systems i.e. for a given film thickness, the individual layer thickness of Resin A and Resin B varied by a factor 4 in these systems. It is interesting to note that film thicknesses down to 4 µm are comparable with current commercial BOPP film thickness of 3-4 µm. The individual layer thicknesses can vary from few tens of nanometers to few hundreds of nanometers in these films.

Table 1: Multilayer Film System Details

<table>
<thead>
<tr>
<th>Film System</th>
<th>No. of Layers</th>
<th>Film Thicknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Resin A/Resin B</td>
<td>X</td>
<td>11, 8, 6</td>
</tr>
<tr>
<td>2-Resin A/Resin B</td>
<td>Y</td>
<td>12, 8, 6, 4</td>
</tr>
<tr>
<td>3-Resin A/Resin B</td>
<td>Z</td>
<td>12, 8, 6, 4</td>
</tr>
</tbody>
</table>

Dielectric Properties:

The films were characterized for various dielectric properties such as - breakdown strength, D-E hysteresis, and broadband dielectric spectroscopy for dielectric constant. The comparison of the breakdown properties multilayer film systems with various formulations is shown in Figure 2. It is interesting to note that the breakdown strength properties followed a similar trend irrespective of the number of layers in the current investigation. The overall breakdown strength increased with decreasing layer thickness without any significant change in number of layers.

![Figure 2: Breakdown strength of multilayer film with varying number of layers and film thicknesses](image)

Dielectric constant as high as 4 was measured in some formulations, measured at 1 kHz. The measured dielectric constant is 1.8X times higher than the BOPP dielectric constant of 2.2.

![Figure 3: Comparison of D-E hysteresis loops as a function of film thickness for X-number of layers.](image)

Furthermore, the high temperature stability of this multilayer films was also demonstrated. An example of breakdown strength as a function of temperature in Resin A/Resin B film system with X number of layers is shown in Figure 4. It was observed that the breakdown strength at 140 °C was as high as 1000 MV/m in 6 µm films, which is important in proposed use in DC-link capacitors.

![Figure 4: Breakdown strength of multilayer dielectric film with different thickness and same number of layers as a function of temperature](image)

Multilayer Film Production Scale-up and Metallization: Based on the detailed analysis of various film formulations, one film system was downselected for production scale-up and capacitor fabrication trial. Two rolls of 3000 ft. films, with 8 µm thickness, were fabricated and metallized. As PolymerPlus uses commercially available resins, the film production scale-up is viable to produce commercially relevant quantities. It is interesting to note that the metallization was carried out on conventional BOPP metallizers without any equipment modifications. Multilayer film product can be directly used as a drop-in product in existing capacitor
fabrication processes without significant process modifications.

Figure 5: (left) example of 3000 ft. film roll supplied for metallization, (right) 500 m reels of metallized film for capacitor fabrication trials.

Film Stretching to Reduce Film Thickness: Achieving film thickness down to 4 µm is critical in many EV related applications. As demonstrated earlier film thickness reduction to 4 µm was successfully achieved at PolymerPlus using coextrusion process. An alternative approach to reduce the overall film thickness was also investigated. The approach consisted of producing thicker multilayer film, followed by uniaxial or biaxial stretching of the films to reduce the overall thickness. The stretching trial involved using oil-heated temperature-controlled roll for film pre-heating followed by slow and fast drawing of the film and annealing process. For the film samples, draw rates of 2.1X and 2.0X was achieved. The 25 µm film thickness was stretched down to 12-13 µm and 12.5 µm film thickness was stretched down to 6-7 µm.

Conclusions

PolymerPlus successfully coextruded high temperature nanolayered polymer films. This commercially scalable technology has been successfully used to fabricate films and capacitors with high energy density and high temperature properties. These results provide opportunity to meet demands of high energy density and higher operating temperature capacitors in many applications.

A film thickness reduction from 12 to 4 µm was demonstrated with comparable properties for films with varying number of layers. Higher breakdown strength was observed in thinner films. Overall multilayer film thicknesses are now comparable with current state-of-the-art, commercially produced BOPP films. Effect of number of layers and film thicknesses on dielectric properties was successfully investigated. Furthermore, an alternative approach of post-processing film stretching was also demonstrated to achieve reduced film thicknesses. The dielectric performance of the film over RT to 140 °C was successfully demonstrated for high temperature applications such as power electronics.

Acknowledgements

We thank the Department of Energy (Contract No. DE-EE0007211) for supporting this work.

References

5. J. Wang, F. Guan, Q. Wang, J. Huang, W. Li, L. Zhu, PMSE Preprints, 100, 437 (2009)