

Increased Breakdown Strengths of Polypropylene Films Melt-Extruded from Plasma-Treated Resin

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SYNOPSIS

Thin (11–36 μm) films formed by melt extruding polypropylene resin after the resin had been briefly exposed to low pressure, low temperature, 96% CF_4 /4% O_2 gas plasma, exhibited approximately a 20% increase in dielectric breakdown strength. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

High reliability, spirally wound, film capacitors for industrial applications such as high powered lasers or microwave sources require high quality dielectric films. Film limitations are presently due to poor insulation resistance and/or low dielectric breakdown strengths. Dielectric breakdown strengths V_b (V/ μm) of thin polymer films play a key role in determining ultimate attainable electrostatic energy densities when these films are used as dielectrics in capacitor applications. This is because energy densities stored in film capacitors increase as the square of the voltage across the capacitor. Therefore, if V_b of polymer films can be increased, capacitors constructed using those polymer films as dielectrics can be operated at higher voltages, which automatically translate into higher potential electrostatic energy densities.

In the capacitor industry, constantly increasing demands are being made to lower cost, and improve reliability and performance of materials. One rapid and inexpensive way to increase V_b of polymer films is to briefly expose them to low-pressure, low-temperature gas plasmas.^{1–4} These plasmas are formed when low-pressure gas at room temperature is sub-

jected to an electric discharge, e.g., a radio frequency or microwave field. As a whole, the plasma is neutral. It consists mainly of neutral species as well as small fractions of free electrons, ions, radicals, photons, and excited molecules. These activated species can interact with exposed surfaces to initiate chemical reactions such as degradation, crosslinking, and/or chemical modification. Effects of gas plasmas on exposed surfaces depend on the gas used, treatment time, and equipment parameters such as gas flow, energy input, and geometry. Effects of gas plasma treatment on a number of materials has been reviewed.⁵

Considerably less information, however, is available on effects of gas plasma on finely divided *powders* where morphological changes, as well as modification of specific surface areas, surface functionalities, and charge densities, may occur. Such changes in surface properties for powders, with extremely high surface to volume ratios, could subsequently affect their wetting, adhesion, and stability. Changes in surface properties of treated polymer resins may also manifest themselves as changes in bulk dielectric properties when these resins are subsequently melt extruded (or perhaps even solvent cast) into thin polymer films. In the present study, we measured V_b , of melt extruded polypropylene (PP) films where the powdered PP resin had been briefly exposed (prior to melt extrusion) to CF_4/O_2 gas plasma.

EXPERIMENTAL

High purity, capacitor grade, PP resin (Himont PD-064K) was milled in a Thomas-Wiley mill and exposed to 96% CF₄/4% O₂ gas plasma by evenly distributing a thin layer of ground-up resin on aluminum foil in a Branson/IPC (Gasonics Inc., Fort Washington PA, (215) 628-4430) Model 4150 barrel plasma etcher at power levels of approximately 0.006 W/cm³ for 4 min. Treated and untreated PP resins were sieved, and portions of powdered resin captured by a 30-mesh screen were extruded. Based on the sieves used, particle sizes were in the range of 600–850 μm. Melt extrusion was carried out on a screw type, Randcastle Microextruder under the following conditions: screw rpm 50; die temperature 232°C; barrel zone temperatures were 177°C for zone 1, 204°C for zone 2, and 232°C for zone 3. Translucent PP films, of various thicknesses (ranging from 11 to 36 μm) and about 40 mm wide were made from both untreated PP resin and PP resin that had been exposed to 96% CF₄/4% O₂ plasma.

In order to accurately measure V_b without arcing effects or external flashover, our melt-extruded films were immersed in silicone oil and sandwiched between $\frac{1}{4}$ in., highly polished, brass electrodes. Twelve V_b measurements were taken for each film thickness. Standard deviations in calculated averages of V_b ranged from 6 to 13%.

RESULTS AND DISCUSSION

Resulting thicknesses of films formed by extruding plasma-treated and untreated PP resins under the

same extrusion conditions were not identical. Plasma-treated PP resins, when melt-extruded, produced films that were about 20–30% thinner than films formed by extruding (under identical conditions) untreated PP resin. The reason for this may be related to different flow characteristics of melted PP resins after plasma treatment. Assuming that plasma-treated PP resins have improved flow characteristics, treated resins should yield thinner films. Dielectric constants and losses for thick films extruded from both plasma-treated and untreated PP resin were comparable. Both films had dielectric constants of approximately 2.2 and dielectric losses in the range of $7-8 \times 10^{-4}$.

DIELECTRIC BREAKDOWN STRENGTHS

Table I lists V_b of melt-extruded films formed from both untreated PP resin and from PP resin that had been exposed to CF₄/O₂ plasma. There are a number of things to notice in Table I. First, melt extruded film samples showed a general trend towards decreased V_b as film thicknesses increased above 14 μm. This well-known phenomena represents increased defects present in thicker polymer films. Films thinner than 14 μm were of poorer quality than thicker films and their V_b 's were therefore lower. Finally, exposure of PP resin (prior to melt extrusion) to CF₄/O₂ plasma, when melt-extruded, yielded films whose V_b were about 20% higher than baseline PP films made from unexposed PP resin. This increased V_b for films made from PP resin that had been exposed to CF₄/O₂ plasma translates into a $(1.2)^2 = 40\%$ increase in maximum stored elec-

Table I Dielectric Breakdown Strengths for Various Thickness of Film Melt-Extruded from Baseline, Unexposed PP Resin and from PP Resin Exposed to CF₄/O₂ Gas Plasma Prior to Melt Extrusion

PP Resin Type	Film Thickness (μm)	Dielectric Breakdown Strengths	
		(kV/mil)	V/μm
Unexposed	14	15.2 ± 2.0	598
	20	14.9 ± 3.2	587
	36	13.3 ± 1.3	524
Treated with CF ₄ /O ₂ plasma	11	16.7 ± 1.1	657
	14	19.2 ± 1.9	756
	26	16.3 ± 1.3	642
	32	16.8 ± 1.1	661

VOLTAGE BREAKDOWN FOR POLYPROPYLENE (baseline and plasma treated resins)

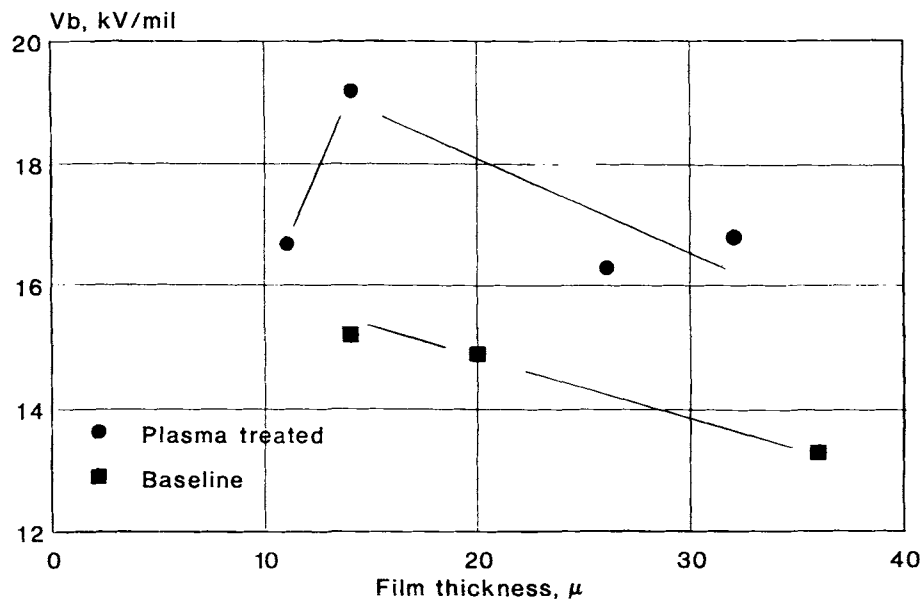


Figure 1 Plot of dielectric breakdown strength for various thickness of film that had been melt-extruded from either unexposed PP resin or PP resin after it had been briefly exposed to CF_4/O_2 gas plasma.

trostatic energy density for capacitor applications. The data of Table I plotted in Figure 1 clearly shows the trend towards decreased V_b as film thicknesses increased above $14 \mu\text{m}$ and the overall increase in V_b for films melt-extruded from plasma-treated PP resin.

One likely reason for this observed increase in V_b may be simply due to removal of surface contaminants, inhibitors or antioxidants which would normally be adsorbed on finely powdered resin surfaces. These species could become trapped within PP film during melt extrusion, thereby lowering V_b . Removal of these species from PP resin surfaces (by reaction with CF_4/O_2 gas plasma) yields purer resin, which, when melt-extruded, produces films having higher V_b . Another possible explanation is that thin, cross-linked or chemically modified (perhaps fluorinated) surface layers formed upon powdered PP resin surfaces by either direct exposure to CF_4/O_2 plasma or by surface activation by gas plasma and subsequent exposure to ambient atmosphere (i.e., oxygen). This hypothesis is not unreasonable. Spectroscopic studies on isotactic PP films after exposure to carbon dioxide⁶ or nitrogen⁷ gas plasmas have indicated

that surface chemical groups are indeed altered. If we assume that such chemical changes are actually occurring in the case of exposure of PP to CF_4/O_2 plasma as well, one anticipated change in surface chemistry could be fluorination or oxidation of surface groups. When chemically modified PP resin (with high surface to volume ratios) is subsequently melt-extruded, chemically modified species, formerly localized on the surface, now blend into the bulk to form films having higher V_b than films formed from pure PP resin. This hypothesis, however, does not adequately explain why films formed from plasma-treated PP resin do not show greater differences in bulk dielectric properties when compared to extruded films formed from untreated PP resin.

CONCLUSIONS

Dielectric breakdown strengths of thin, melt-extruded PP films have been increased by about 20% by briefly exposing PP resin (prior to melt extrusion) to low-pressure, low-temperature CF_4/O_2 gas plasma.

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