Increased dielectric breakdown strengths of melt-extruded polypropylene films

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(Received 28 January 1992; revised 6 July 1992)

Melt-extruded polypropylene resin containing 1% or 2% ceresine wax yielded thin films that had significantly increased dielectric breakdown strengths but with virtually identical bulk dielectric properties. Ceresine wax acts as a trapping centre for electrons and by minimizing ionization of host polypropylene molecules, dielectric breakdown strength is increased.

(Keywords: polypropylene film; dielectric breakdown strength; melt extrusion)

Introduction

High quality, high reliability, spirally wound film capacitors for industrial energy storage applications require high quality dielectric films. At present, films are limited by poor insulation resistance and/or low dielectric breakdown strengths. The dielectric breakdown strength, V_b, of thin polymer films used as dielectrics plays a key role in increasing ultimate attainable energy densities of capacitors since energy densities increase with the *square* of the voltage applied across the capacitor. If V_b values of polymer films can be increased, these films can be made thinner, or, in other words, capacitors made from these films can be operated at higher voltages which could ultimately translate into higher electrostatic energy densities.

One way to increase V_b is to deliberately add small amounts of electron trapping centres (typically aromatic molecules or saturated paraffins) to bulk polymer films. When high energy electrons are injected from contacting metal electrodes under d.c. fields, they become localized around trapping molecules, their mean free path is reduced and their energies dissipated as heat without ionizing and/or causing damage to host molecules. V_b is therefore increased. All of this can be accomplished with substantially decreasing bulk dielectric constants or increasing bulk dielectric losses. Effects of adding small quantities of trapping centres on V_b of polyethylene has been the subject of several investigations. Addition of ceresine wax[1], acetophenone[2] and inorganic fillers[3] has been shown to increase V_b in polyethylene. Copolymerizing 0.4 wt% of polystyrene with polyethylene increased the impulse breakdown strength[4] by about 20%. Another electron acceptor, 2,4,7-trinitro-9-fluorenone, has been shown to enhance V_b in poly(ethylene terephthalate) (Mylar C) films without significant adverse effects on electrical or mechanical performance[5]. However, since in these papers experimental details for preparing these mixtures are not given, and since polypropylene (PP) films are more commonly used as solid dielectrics in high energy density capacitors, it was a logical extension to report effects on V_b of adding small quantities of ceresine wax to melt-extruded PP. The purpose of the work reported here was to examine dielectric properties of PP films derived from incorporating ceresine wax into PP and to compare these results with those of films melt extruded from pure PP.

Experimental

Polypropylene pellets (Himont 6823) were first ground to a powder using a 20 mesh delivery tube and an intermediate size Thomas–Wiley grinding mill. In order to uniformly disperse 1% ceresine wax in PP powder, the following procedure was used. Approximately 0.24 g of ceresine wax with a melting point of 65–72°C (Type 101, Frank B. Ross, Jersey City, NJ, USA) was dissolved in 100 cm^3 of *m*-xylene, added to approximately 24 g of ground PP resin and then gently heated to the boiling point of *m*-xylene. Upon cooling the solution, a rubbery gel formed. This gel contained *m*-xylene, which had to be removed. We chose not to remove *m*-xylene by simply boiling it off since the high temperatures caused PP to turn orange, probably due to oxidation. In order to remove *m*-xylene at lower temperatures, approximately 100 cm^3 of ethyl ether was added to the gel and mixed well. Ethyl ether was used as the extracting solvent since *m*-xylene is infinitely soluble in it, but ethyl ether does not dissolve either PP or ceresine wax. This mixture (PP, ceresine wax, *m*-xylene, ethyl ether) was then filtered through a fritted glass funnel in a sidearm distillation flask and the resulting white, fluffy material was vacuum dried at room temperature for at least 3 h. After drying, the odourless material was milled in the Thomas–Wiley mill using a 20 mesh delivery tube and sieved by vibrating it through a series of stainless steel sieves. Only those portions captured on 40 mesh sieves were used for extruding films for which the dielectric properties are reported here.

We assumed that ceresine wax concentrations were uniformly distributed throughout the milled and extracted material and that ceresine wax concentrations remaining in the 40 mesh sieve were identical to the original prepared concentrations. Control samples (prepared by mixing milled PP resin with *m*-xylene and then extracting with ethyl ether) were prepared in exactly the same manner as PP samples containing added ceresine wax.

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0032-3861/93/051093-02

Table 1 Comparison of dielectric constants, dielectric losses and breakdown voltages for films formed by melt extruding PP resin containing 1% and 2% ceresine wax

	PP[b]	PP*[c]	PP* + 1% wax	PP* + 2% wax
Thickness (μm)	25	26	19	24
Dielectric constant				
at 1000 Hz	2.19	2.13	2.12	2.10
at 10000 Hz	2.19	2.13	2.12	2.09
Dielectric loss ($\times 10^4$)				
at 1000 Hz	6.6	6.1	4.1	5.1
at 10000 Hz	5.5	5.7	4.4	4.9
Breakdown voltage[a]				
V μm^{-1}	205±28	213±39	303±39	315±35

[a] Breakdown voltages are averages of five measurements with uncertainties estimated by the standard deviation
[b] Resin that has been milled and melt extruded
[c] Resin that has been milled, mixed with *m*-xylene and extracted with ethyl ether

Translucent films, approximately 25 μm thick and 40 mm wide, were melt extruded from PP resin with and without 1% or 2% added ceresine wax. Resin was extruded through a 12.7 mm screw type laboratory scale (Randcastle Microextruder, Little Falls, NJ, USA) under the following conditions: length to diameter ratio, 24:1; screw speed, 50 rev min^{-1}; die temperature, 232°C; temperature of barrel zone 1, 177°C, barrel zone 2, 204°C and barrel zone 3, 232°C.

PP resins containing 1% and 2% ceresine wax, when melt extruded under identical conditions, were expected to yield films having distinctly different thicknesses due to different flow characteristics of resin containing added ceresine wax. Since resin containing ceresine wax should flow more readily through the extruder, more resin should be extruded per second and the resulting films would be thicker. This was indeed observed. For example, under identical extrusion conditions, films extruded from baseline PP resin were 11 μm thick, films extruded from resin containing 1% ceresine wax were 19 μm thick, while films extruded from resins containing 2% ceresine wax were 24 μm thick. In order to obtain dielectric measurements on comparable film thicknesses, screw speeds for extruding baseline resin had to be increased (from 50 to 100 rev min^{-1}) so that film thicknesses would be increased. V_b values of these films were measured by placing them between two pools of mercury at room temperature and ramping the applied voltage at 500 V s^{-1} until breakdown occurred and the film could not hold off additional voltage.

Results and discussion

Dielectric properties and V_b values for films of approximately similar thicknesses containing 1% and 2% added ceresine wax are listed in *Table 1*. Although dielectric properties are essentially unchanged for different PP samples, their V_b values were clearly quite different. The first important point to notice is that there is no appreciable difference in V_b between baseline PP resin and PP resin that has undergone solvent extraction using ethyl ether. This result indicates that our baseline PP resin was relatively pure and that no significant amount of extractable impurities was present. Had this PP resin contained a significant amount of extractable impurities, films prepared from this resin after extraction with ethyl ether (which removes impurities) would have yielded significantly higher V_b values.

Addition of only 1% or 2% ceresine wax to PP resin yielded films having a 40% increase in V_b; a possible explanation for this increase is as follows. Since PP is semicrystalline and since crystalline portions tend to have higher V_b values than amorphous regions, film breakdown is essentially limited by breakdown in amorphous regions. During crystallization of PP containing ceresine wax, the wax tends to gather in amorphous regions. Since ceresine wax contains aromatic compounds, the delocalized π electron structure of these compounds added to PP tends to capture electrons and thereby reduce mean free paths of injected electrons. This factor possibly contributes to increased overall V_b in PP.

Conclusions

Dielectric breakdown strengths of melt-extruded PP films can be increased by up to 40% by addition of 1% or 2% ceresine wax.

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