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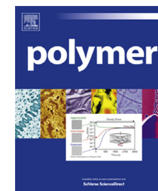

Crystalline microstructure and dielectric properties of oriented poly(ethylene-co-tetrafluoroethylene)

Yun Huang [a, b], Daniel F. Miranda [a], Ciprian Iacob [a], Shihai Zhang [c], James Runt [a, *]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA, 16802, United States
[b] State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University, Chengdu 610065, China
[c] PolyK Technologies, LLC, 2124 Old Gatesburg Road, State College, PA 16803, United States

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In the present investigation, we explore the influence of uniaxial orientation and subsequent thermal annealing on semi-crystalline poly(ethylene-tetrafluoroethylene) (ETFE) microstructure and dynamics, and the connection to dielectric breakdown strength. Understanding the influence of crystalline microstructure on dynamics and breakdown, and in turn how processing influences microstructure, is critical for establishing rational design of polymer dielectrics. When drawn below the glass transition temperature (T_g), the Weibull breakdown strength decreases compared to that of the undrawn precursor film, but increases on thermal annealing near or above T_g. This behavior is associated with the formation and elimination of drawing-induced microvoids, respectively. When drawn above T_g, the breakdown strength increases to ~870 MV/cm, dominated by orientation of amorphous segments, and decreases on thermal annealing above T_g to near that of the undrawn film.

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1. Introduction

Advanced polymer film capacitors are desired for continued miniaturization and increased functionality of modern electronic devices, including for use in pulsed power and power conditioning applications. Biaxially-oriented, semi-crystalline polypropylene (BOPP) is the predominate polymer film capacitor in use today: BOPP exhibits very low dielectric loss (~0.02% tan δ) and high dielectric breakdown strength, critical features for commercially relevant film capacitor materials [1]. However, non-polar BOPP has a rather low dielectric constant (2.2 at 1 KHz [2], originating almost entirely from electronic polarization), limiting the maximum achievable energy density. As a consequence, considerable research has been devoted to the rather difficult challenge of enhancing polymer film dielectric constant, while maintaining low loss and high breakdown strength. e.g. Refs. [2–5] In addition, BOPP's modest melting point (T_m, ~160 °C) precludes it for use in higher temperature applications (in the absence of active capacitor cooling).

Of particular importance in capacitor films is the dielectric loss, which contributes to capacitor inefficiency as well as Joule heating, the latter important since practical dielectric breakdown is likely thermo-mechanical in nature [6]. Contributions to dielectric loss arise from dissipative energy from molecular motions and, at temperatures above the glass transition (T_g), to conduction contributions from impurity ionic species (controlled by polymerization processes, purification and subsequent manufacturing). For a given material/resin grade, reduction in dielectric losses can be achieved by suppressing amorphous phase molecular motions, through maximizing the degree of crystallinity and otherwise constraining the amorphous segments. Mobility of non-crystalline segments is restricted by attachment to crystals or can be constrained by mechanical drawing.

Much research has been conducted on strain-induced crystallization of crystalline polymers and their oriented microstructure on drawing, and separately on dielectric properties of crystalline polymers including dielectric breakdown. However, there has been little work devoted to connecting the two, rather surprising considering most polymers considered for film capacitors are semi-crystalline. There have been a modest number of reports on the role of chemical structure, crystallinity, molecular motion, defects and other factors on the breakdown strength of dielectric polymers [7–9]. For example, the dielectric breakdown strength of polyethylene has been reported to increase with crystallinity [8], and biaxial orientation of polypropylene also greatly increases the

* Corresponding author.
E-mail address: runt@matse.psu.edu (J. Runt).

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breakdown strength of the polymer film [1].

Semi-crystalline fluoropolymers are a higher T_m alternative to BOPP, in particular poly(ethylene-co-tetrafluoroethylene) [ETFE] and poly(tetrafluoroethylene) -co-(perfluoroalkylvinylether) [PFA]. Although their dielectric constants are in the same range as BOPP, they can be melt extruded into thin films, have high dielectric stability at elevated temperatures, and exhibit very low dielectric loss [10]. Building on our previous work [11,12], we focus in this paper on the role of uniaxial orientation and subsequent thermal annealing on the semi-crystalline microstructure and low electric field dynamics of ETFE, as well as high field dielectric breakdown measurements on selected drawn and annealed ETFE films. Experimental Weibull dielectric breakdown strengths are found to increase with uniaxial orientation (draw ratio = 3) to values as high as 870 MV/cm, over 10% larger than commercial BOPP films measured under similar conditions [13,14]. Understanding how crystalline microstructure affects polymer dynamics and breakdown strength, and in turn understanding how processing conditions affect microstructure, is critical for establishing rational design of polymer dielectrics utilizing ETFE and similar polymers.

2. Experimental

2.1. Materials

ETFE resin (Tefzel® 200), a nearly alternating copolymer of ethylene and tetrafluoroethylene, was obtained from DuPont. Films were extruded using a 1 inch single screw extruder with a 6 inch flex lip film die, at a temperature of 300 °C. It was determined that extrusion imparted some preferred orientation to the film, which could complicate the findings of later experiments. Therefore, prior to any further experiments, the as-extruded film was pre-treated at 140 °C for 3 h. This treatment was shown to effectively erase the history imparted by extrusion [11]. Samples for drawing were then cut from the unoriented film and marked with horizontal and vertical gage lines using a square grid template, each line separated by 0.5 cm.

Thinner ETFE film (~12 μm) was used for dielectric breakdown measurements and provided by PolyK Technologies, produced with a single screw extruder at 310 °C. As above, these films were initially pre-treated at 140 °C for 3 h, and drawn and annealed following the same procedure described below for the thicker film. Wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) results on the thinner films confirmed that both microstructure and relaxations of the thinner films underwent very similar changes during the drawing and annealing processes compared to the somewhat thicker films.

Unoriented films were uniaxially drawn at 50 °C and 140 °C (i.e., below and above the reported T_g ~ 100 °C [15,16]), using an Instron Model 5866 equipped with an air oven and pneumatic grips. For films drawn at 140 °C, after drawing to a predetermined extension ratio (λ), they were maintained at the particular λ and cooled for 6 min (during that time the temperature decreased to 60–70 °C, i.e., below T_g). The tension was subsequently released and the film was removed from the temperature chamber. This step was used to avoid sample shrinkage after removal from the clamps. Films drawn at 50 °C were taken out of the temperature chamber immediately after the conclusion of drawing. Finally, the drawn films were annealed at 110 °C and 140 °C (in the vicinity of, and above T_g) for different times. Samples in this study were coded based on preparation conditions. For example, 50C-4λ-140C-2min represents that the film was drawn at 50 °C to a draw ratio of 4λ and annealed at 140 °C for 2 min. Other samples were likewise coded.

2.2. Characterization

DSC was conducted using a TA Instruments model Q2000 and used to determine the degree of crystallinity under different preparation conditions. Circular samples were obtained for each sample using a hole puncher, with each sample weighing between 3 and 5 mg. The samples were packed into standard aluminum DSC pans, and heated from 40 °C to 300 °C at a rate of 5 °C/min. Measurements on all samples were conducted 3 times. Crystallinities were determined by comparison of measured heats of fusion to that of the 100% crystalline polymer (113 J/g [17]).

Small-angle X-ray scattering (SAXS) and WAXD were used to characterize the morphology of the films. SAXS data were collected using a Molecular Metrology instrument with a Cu Kα radiation source (λ = 0.154 nm) at 45 kV and 66 mA, using a two-dimensional multiwire detector with a sample-to-detector distance of 1.5 m. The wavevector range (q) was calibrated by a standard sample of silver behenate and the scattered intensity converted to an absolute differential cross-section (cm^{-1} units) by a high density polyethylene secondary standard [18]. WAXD data were collected on a Rigaku DMAX/rapid micro diffractometer in transmission mode, using a copper point-focused source (λ = 0.154 nm) at 50 kV and 40 mA.

DMA measurements were carried out on a TA Instruments model DMA Q800, equipped with a NPC cooler using liquid nitrogen. Samples were prepared as rectangular strips and mounted in standard tension clamps provided by TA Instruments. The film draw direction is oriented parallel to the DMA stress direction. A temperature sweep was carried out from −150 °C to 200 °C, with a heating rate of 3 °C/min, at a constant strain of 0.25% and frequency of 1 Hz. Data were collected on heating.

Low electric field dielectric relaxation spectroscopy measurements were performed using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Frequency sweeps were performed isothermally from 0.1 Hz to 10 MHz in the temperature range from −150 °C to 200 °C, with data collected on heating. The analyzer was supported by a Quatro temperature controller providing temperature stability better than 0.1 °C. Two brass electrodes were used to create a parallel plate capacitor geometry. The applied voltage for each experiment was 1.5 V.

Dielectric breakdown measurements were carried out on metalized film specimens with 50 nm thick gold electrodes on both sides. The diameter of the metalized area was 3 mm. Specimens were immersed in a silicone dielectric fluid and a DC voltage was applied at a ramp rate of 500 V/s. The film thickness for dielectric breakdown measurements was typically between 7 and 13 μm. A minimum of 30 measurements were made on each sample type, and all results were obtained at similar ambient temperature and humidity conditions. The dielectric breakdown strength was determined using conventional Weibull statistical analysis, where the Weibull cumulative distribution function is defined as:

$$P = 1 - \exp\left[-(E/E_b)^{\beta}\right]$$

E is the measured electrical breakdown strengths of individual test areas and β is the shape parameter of the probability distribution, inversely correlated with the width of the distribution. E_b is the Weibull dielectric breakdown strength, that is, 63% of the specimens statistically fail at an electric field below E_b [19–21].

3. Results and discussion

3.1. Melting behavior

Prominent melting endotherms were observed for all samples, as shown in Fig. 1 for drawn films annealed at 140 °C. DSC traces for

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