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The Effects of Humidity on the Dielectric Response in Ferroelectric Polymers Made by Langmuir-Blodgett Deposition

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The effects of humidity on Langmuir-Blodgett poly(vinylidine fluoride-trifluoroethylene) 70/30 were investigated by measuring dielectric properties. At a constant temperature, the capacitance of the films increases linearly with the humidity. The experimental drying rate of the films ranges from 2 to 3 hours in the temperature range of 10°C to 30°C.

Keywords: PVDF; crystalline polymers; water absorption

AIP Classification Scheme 77.84.Jd, 77.22.Ch

INTRODUCTION

This study looked at the effects of humidity as it is introduced into poly(vinylidine fluoride-trifluoroethylene) Langmuir-Blodgett films. Earlier studies showed a dielectric anomaly in the thinnest films, which was originally attributed to a first order ferroelectric transition [1]. When a film is heated in ambient laboratory air, a peak occurs in the capacitance vs. temperature graph between 0 and 30 degrees Celsius. When this experiment is

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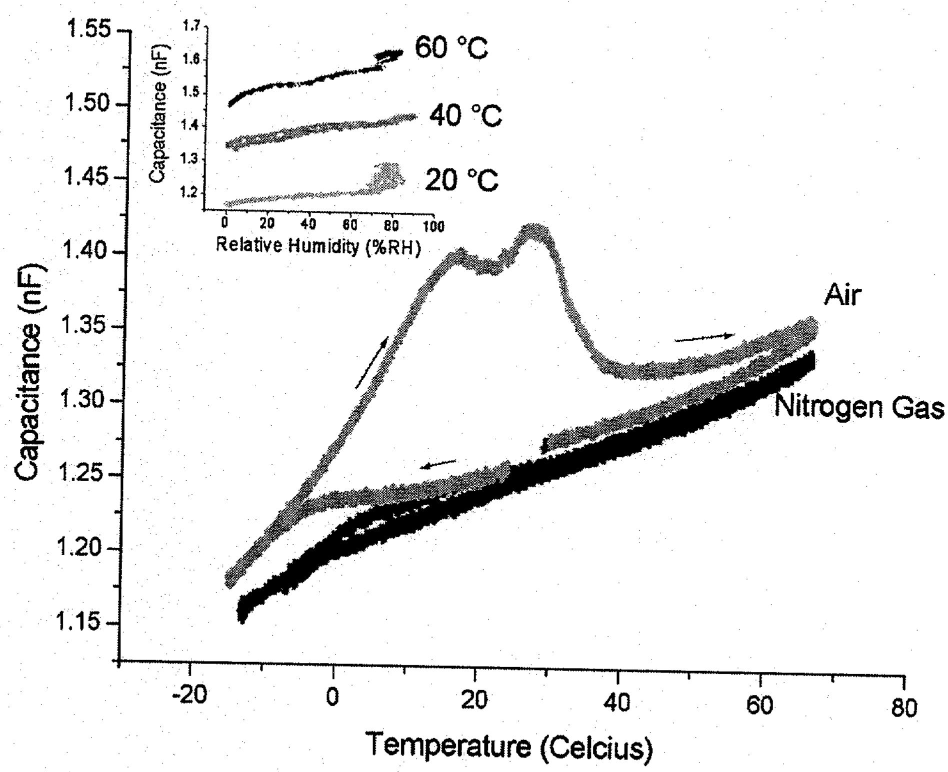

Figure 1. When the sample is heated under ambient conditions, a peak in the capacitance occurs between 10 and 30°C. Under dry conditions, no bump is observed. Inset: When the humidity is increased at a constant temperature, the increase in capacitance is linear.

repeated in dry nitrogen gas environment, the peak is no longer present. See Fig. 1. Also, the peak does not appear when the sample is heated in a vacuum. This led us to suspect that water vapor was responsible for the change in capacitance. For this experiment, we investigated how the dielectric constant changed as we increased and decreased the humidity at a constant temperature. Also investigated was the effect on the capacitance as the humidity leaves the film and how the capacitance changes in non-equilibrium conditions.

SAMPLE PREPARATION

The samples for this experiment are made of P(VDF-TrFE) 70/30 deposited on a glass substrate by Langmuir-Blodgett deposition as described elsewhere [2]. Dielectric properties were measured by making parallel plate capacitors with aluminum electrodes. The samples were annealed at 130°C for one hour. For the constant temperature study and the non-equilibrium study, two samples were used, a five-layer and a twenty-layer sample. For the desorption study, five layers of the film were deposited and the leads were soldered to the aluminum electrodes with indium.

EXPERIMENTAL SETUP

The sample is placed in a small chamber made of copper where the relative humidity level and temperature can be controlled independently. In the constant temperature and desorption experiments, the humidity is regulated by mixing a dry nitrogen flow with humid air. The saturated air is monitored by a polymer humidity sensor (HYCAL Sensing Products, Model HIH-3206-C) and controlled by proportional feedback. This system can control the humidity to $\pm 2\%$. The temperature of the sample was measured with a J-type thermocouple in all experiments.

For the non-equilibrium study, a temperature-controlled stage with nitrogen purge was used. The sample was cooled from room temperature to $-15°C$ in ambient air. It was then heated to 60°C and cooled back to 20°C. For this study, the HP 4192A Impedance Analyzer was used to measure the capacitance.

For the constant temperature study, the humidity was increased and decreased at the rate of 1% per minute while the temperature was held steady. The capacitance for this study was measured with a HP 4192A Impedance Analyzer.

For the desorption experiment, the sample was first heated in a dry atmosphere to 80°C and then cooled to the desired temperature. Humidity was introduced into the chamber at the rate of 0.4% relative humidity per every minute. The humidity was increased until it reached 80%, and this level was maintained for 20 minutes. At the end of this time, the humidity was turned off and Nitrogen gas was used to flush the chamber. The capacitance of the sample was measured by a QuadTech 1689M Digibridge.

RESULTS

When the sample is heated in non-equilibrium conditions, a bump is produced on the initial heating. See Fig. 1. As the sample cools in an ambient atmosphere, water starts to condense on the sample surface at about 10°C causing the capacitance to become level. As the temperature crosses 0°C, the water freezes and the capacitance decreases more quickly. Upon heating the sample, a bump is seen on the graph when the water starts to melt on the surface and distribute itself through the sample. When the water is evaporated from the sample, the peak decreases until the capacitance is same as the value expected from the dielectric change from heating the sample. When the sample is heated in dry gas or a vacuum, this peak is not observed because there is no condensation present. As the humidity is increased and decreased there is no noticeable hysteresis.

When the temperature is held constant and the humidity is increased, the capacitance increases linearly. See inset to Fig. 1. This was calculated for temperatures from 10°C to 60°C. The added humidity causes the capacitance to increase by 1 pF per 1% relative humidity at 40°C. The volume percentage of water in the film can be estimated for 80% relative humidity at 40°C. If the dielectric contribution from water is about 73 at this temperature, the calculated percent volume is 0.046% for a 20 layer film. This calculation is made with the assumption that the film does not swell during absorption of water. Also, the DC conductance of the sample follows the same trend as

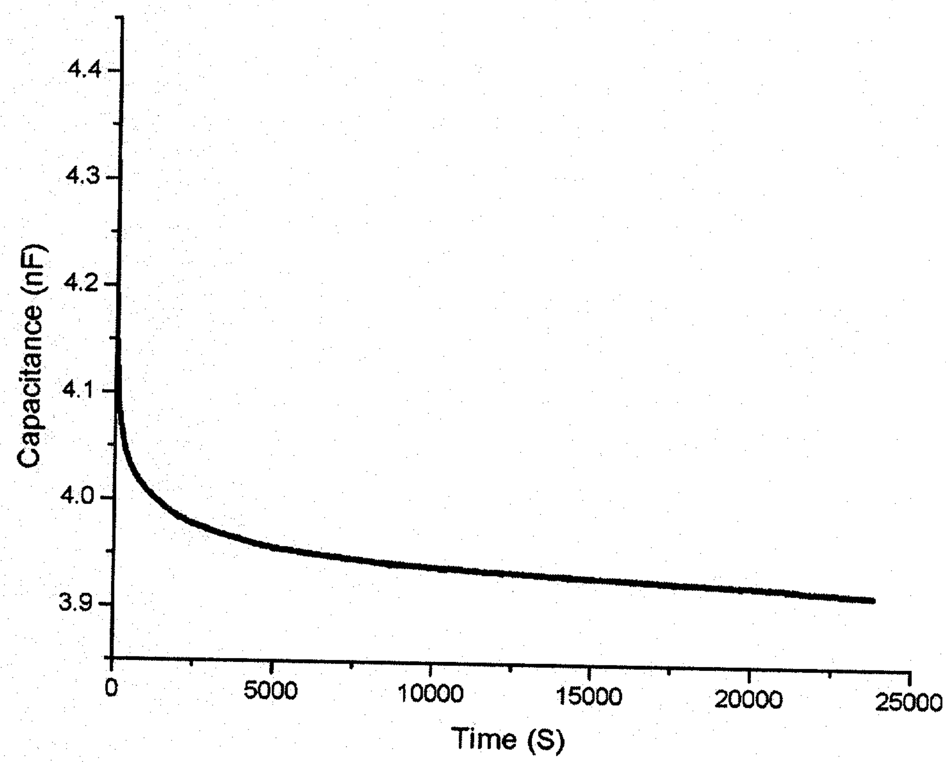

Figure 2. For a sample held at a constant temperature (40°C), the capacitance decreases exponentially as the humidity leaves the sample.

the capacitance, indicating that the water vapor is in the bulk of the film, not just in the electrode or on the surface of the film. The change in capacitance for the non-equilibrium and equilibrium conditions can be attributed to a change in dielectric constant.

As the humidity leaves the sample, the capacitance decreases exponentially. See Fig. 2. Preliminary studies show the time constant ranges from 2 to 3 hours in the temperature range of 10°C to at 30°C.

CONCLUSION

As water vapor enters the sample the capacitance of the sample increases corresponding to the change in dielectric constant. It also appears that the water can easily enter and leave the films. The amount of water in the film is about 0.046% by volume. The water leaves the sample with a time constant of 2 to 3 hours in the temperature range of 10°C to 30°C.

Further work in the future includes determining the temperature dependence of the desorption and the role the electrodes play. Also, further investigation into the reason for the large increase in capacitance for the increase of water.

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