THE INVESTIGATION OF 6μM BIAXIALLY ORIENTED POLYETHYLENE 2, 6,-NAPHTHALATE AS A POSSIBLE DIELECTRIC FOR PULSE POWER CAPACITORS

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INTRODUCTION

The introduction of polyethylene -2, 6-Naphthalate (PEN) semicrystalline film with thicknesses of 0.9μm, 1.5μm, 4.0μm and 6pm by DuPont Co. brought great interest in the capacitor community. Its unique chemical and high temperature stability, as well as superior thermo-mechanical properties allow ultra thin (2pm) PEN film to be processed into miniature multilayer chip capacitors for surface mount technology (SMT) application that can be used with standard soldering techniques (260°C, 10 Sec. for wave soldering) .

The physical, thermal and electrical properties of ultra thin PEN film were published in 1992('), but no technical information was mentioned for the 6pm capacitor grade PEN film which can be used for high voltage pulsed power capacitors applications. Feyder[1] discussed the biaxially oriented semicrystalline commercial 2pm PEN film which has a structure that can be reorganized during subsequent exposure to a temperatures in excess of the crystallization temperature of the film during film processing. Based on this property, a thermal stabilization technique was developed which can further increase the thermal resistance of the film beyond its glass transition temperature (122°C) and approach its melting temperature (266°C). Nevertheless, the effects of the electrical properties and the morphological changes of thermally stabilized film were not studied.

For the first time in this paper, we report the thermal stabilization effect of 6μm PEN film on the electrical properties/ breakdown strength and related crystallinity change. Both x-ray diffraction (XRD) and differential scanning calorimetry (DSC) techniques were used to study the thermally treated 6pm PEN film at. different temperatures. The correlation of XRD and DSC results from the PEN film analysis yields an equation enabling calculation

of crystallinity from simple and inexpensive DSC heat of fusion data. This will allow PEN film users, as well as capacitor manufacture a method for monitoring quality and process control.

EXPERIMENTAL

Thermal Treatment of 6μm PEN Film

The 6μm PEN Film was provided by Dr. G. Feyder of DuPont de Nemours (Luxembourg) S.A. The film was wrapped on a glass cylinder and taped on all sides with high temperature Kapton adhesive tape before being placed in the oven for heat treatment. Three 6μm PEN films were heat treated as follows:

Sample 1: 2 hours at 245°C
Sample 2: 2 hours at 245°C +- 1 hour at 255°C
Sample 3: 2 hours at 245°C + 1 hour at 255°C + 1 hour at 258°C

ELECTRICAL PROPERTIES

Breakdown Strength

Breakdown voltage (BDV) measurements were performed according to the ASTM standards, p. 149 and 3755, which describe procedures of tests at commercial power frequency (60 Hz) and direct voltage-stress, respectively.

All breakdown tests were conducted in silicon oil using rounded (0.8 mm radius) brass electrodes 6.35mm (1/4") in diameter. The weight of the upper electrode was 60 ± 2g, as required by the standards. For DC breakdown Spellman RMP 50PN300 (50 kV, 6ma) power supply was used with voltage rate controlled by a voltage programmer. In all measurements, voltage was raised at a rate of 500 V/s until the breakdown occurred. The dc breakdown event itself was monitored on the Nicolet 4094 storage scope using Nicolet HV15HF high voltage probe. After each run, the sample was tested again for its ability to withstand voltage as an indicator of breakdown. Depending on the spread of the breakdown data, thirteen or more data points were obtained for each sample. Reported values are the averages and corresponding standard deviations.

Dielectric Constant and Dissipation Factor

Standard measurements of dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) at room temperature (23°C) were conducted using nonmetallized 6pm thick PEN film samples,mercury electrodes 1 .905 cm in diameter, HP4284A LCR bridge and HP16047C test fixture. The parameters used with LCR bridge were as follows: 1V ac signal, C_p-D function, frequency range 20Hz to 1 MHz averaging ten values at each frequency. The dielectric constant (ϵ_r) is calculated using a standard formula ($C = \epsilon_0\epsilon_r A/t$) with the thickness t checked before each measurement.

Dielectric Constant and Dissipation Factor vs. Temperature

To measure the dependence of ϵ_r and $\tan\delta$ on temperature, a system designed by Polymer Laboratory was used. It includes the GenRad bridge (20Hz to 100kHz), temperature controller and high temperature (up to 300"c) dielectric fixture with unguarded 3.3 cm in diameter disk electrodes. The fixture is fully enclosed allowing the circulation of inert gas, in this case high purity argon. Metallized samples were used for this set-up. Once closed, the fixture with the sample inside was flushed with gas and continued flow of gas was maintained throughout the measurements. The temperature controller was set to start from 40"C and raising the temperature at the rate of 2°C/min. with 6 minutes dwelling (stabilization) time at each 10°C increment, at which the dielectric properties were measured. Three runs with three different limiting temperatures were performed on the same sample. In the first run, the limit was set to temperature just below PEN film T_g at 110"C. After cooling down, the second limit was set to temperature below crystallization at 160°C. After cooling the sample again, the limit of the third and final run was set to 220°C.

X-Ray Diffraction

The x-ray diffraction data was acquired using a conventional diffractometer stage. Since the diffraction intensity is a very sensitive function of sample position, the thin PEN films were positioned on a ribbon-like platinum foil which served as the sample support and provided a reference diffraction response for the calibration of the scattering angel. Different pieces of virgin material were individually heat treated. Only flat pieces were used in the analysis. The diffraction scans covered a two-theta range of 38 degrees starting at 5 degrees two-theta. Figure 1 shows the XRD spectra of commercial 6µm PEN film heat treated at different temperatures. The sum total of the x-ray counts from the amorphous and crystalline peaks was determined for each sample by subtracting the platinum spectrum from each sample spectrum. The usually intense crystalline peak was assumed to be symmetric and to be superimposed on a broad amorphous background. A plot of amorphous versus crystalline intensity is shown in Figure 2. The intercepts were calculated from a least-square, straight-li.ne fit to the data.

Differential Scanning Calorimetry

This method was used to determine the glass transition temperature (T_g) and melting point (T_m) of the films. The DSC experiments were done on a DuPont 910 at a heating range of 10°C/min. in lidded aluminum pans under an argon purge.

RESULTS AND DISCUSSION

XRD and DSC

The XRD method was used to determine the degree Of crystallinity of the PEN film. To determine the degree of crystallinity in a single phase polymer by x-ray diffraction, the Hermans-Weidinger method can be used(2). This method depends on the existence of proportionality between the crystalline diffraction intensity I_c and the crystalline portion of the material (XC), and between the amorphous diffraction intensity I_a and the amorphous portion (X,). This means that the crystalline fraction is proportional. to I_c by some proportionality constant. p, or

$$X_c = pI_c$$

and by the same reasoning

$$X_a = qI_a = 1 - X_c$$

therefore

$$X_c = \left[1 + \frac{(qI_a)}{(pI_c)}\right]^{-1}$$

If the values of I_c are plotted against I_a, the points should lie on a straight line that represent the regression line of the correlation between I_c and I_a. The points of intersection on the axis give the values for completely amorphous and completely crystalline samples, designated by I_{c100} I_{a100}. From this, the numerical values of the proportionality constants can be determined by:

$$p = \frac{1}{I_{c100}} \quad q = \frac{1}{I_{a100}}$$

To determine the integrated intensities (I_c) of the crystalline reflections, we used a Pearson VIII distribution

Table I lists the I_c and I_a values of four 6μm PEN films shown in Figure 1.

Figure 2 is the least square plot of I_a vs. I_c. The percent of crystallinity of the four films studied are listed in Table I.

The DSC spectra of four films studied are shown in Figure 3. No detectable glass transition temperature (T_g) was observed in any of the four samples. The melting point and heat of fusion values are listed in Table II. The virgin PEN 6μm film had lowest heat of fusion value, but with the highest melting point when compared with all heat treated films. The virgin film has the highest amorphous phase content which may have been entrapped in the crystalline phase and caused the increase of crystal thickness which gives the lower heat of fusion and higher melting point values. Figure 4

shows the relationship of percent of crystallinity (%X_c) and heat of fusion. The slope of the plot is 1.058 and the following equation can be established:

$$\%X_c = 1.058 \times \text{heat of fusion (J/gin)}$$

For a given PEN film, %X_c can be obtained when heat of fusion value is known. Table 3 listed the %X_c values determined by XRD, as well as calculated from DSC heat of the fusion results.

The %X_c values obtained from XRD method has an error of ±10% which is less accurate than the value obtained form DSC method due to the difficulty of separating I_a and I_c from x-ray spectrum.

Electrical Properties

The electrical breakdown strength of virgin 6μm PEN films heat treated at different temperatures, and %X_c obtained from DSC method are listed in Table 4. The sample 2 (2 hrs. 245°C + 1 hr. 255°C) has best of the BDS value of 3.84 ±0.29 kV, which is -17% higher and the %X_c also has 12% higher value of crystalline than the virgin film. The dielectric constant (ϵ_r) and dissipation factor ($\tan\delta$) of virgin 6μm PEN film measured at room temperature and 1 KHz with mercury electrode yield values of ϵ_r=3.04, $\tan\delta$=0.0043, which are identical with the data reported by Feyder[1]. Figure 5 shows dielectric constant, dissipation factor of commercial 6μm PEN film as a function temperatures and frequencies. The low ϵ_r due to the removed volatile species such as water, which are removed during metallization of aluminum on both sides of the film to make electrodes. The increase of ϵ above 120°C is due to the volume increase above the T_g of the film. At temperatures near T_g (~120°C), a $\tan\delta$ minimum at frequencies lower than 100 Hz is observed, but at temperatures near 180°C, a second minimum at frequencies lower than 100 Hz may be caused by the polymer chain structure reorganized during subsequent exposure to temperatures in excess of the crystallization temperature of the film during film processing.

CONCLUSION

1. DSC and XRD results shown heat treated 6μm PEN films had higher crystallinity.
2. An equation to calculate %X_c from heat of fusion (from DSC) was developed, which will provide capacitor manufacturers and PEN film users a method for monitoring film quality and process control.
3. Electrical breakdown strength (EBS) of PEN film increases when crystallinity of the film increases. For 6pm PEN film heat treated at 2 hrs. 245°C plus 1 hr. 255°C gave the best EBS value. This is ~17% higher than that of virgin film with similar standard deviation of the EBS value.

4. **The** above results suggest when 6μm PEN film is used as capacitor dielectric film for pulsed power application. The **energy density of the capacitor can be increased by heat treatment of capacitor winding section at 2 hrs.** 245°C -t- 1 hr. 255°C to increase the EBS of the film before packaging.

ACKNOWLEDGEMENTS

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REFERENCES

(1) Gusty Feyder, "Ultra-Thin PEN Film for Metallized Film Capacitors" , CART-Europe, Oct. 5-8, 1992, Brugge, Belgium.

(2) P. H. Hermans and A. Weidinger, Makromockulare Chem., 24, 44-46, 1.961.

FIGURE 1: X-RAY DIFFRACTION SPECTRA OF COMMERCIAL 6μM PEN FILM HEAT TREATED AT DIFFERENT TEMPERATURES

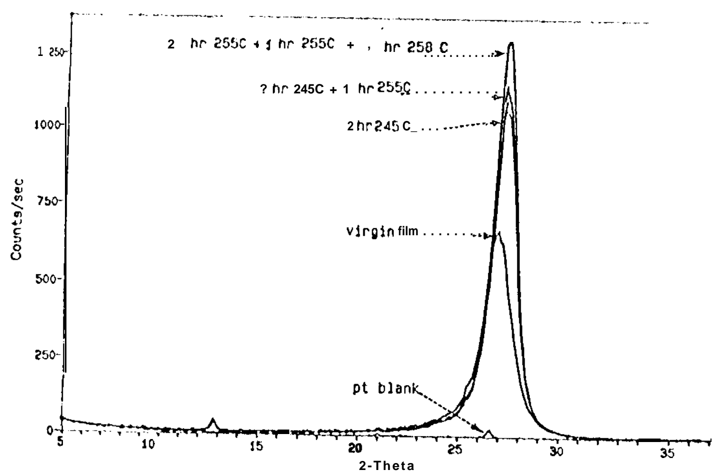
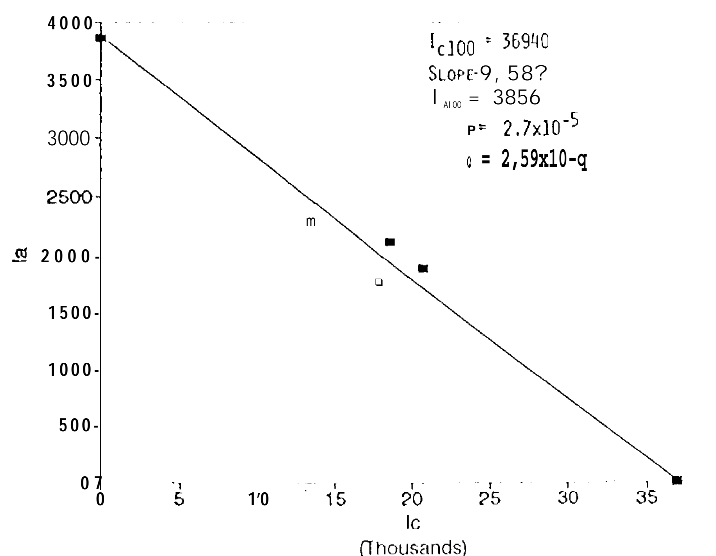


FIGURE 2: REGRESSION CURVE OF COMMERCIAL 6μM PEN FILM, HEAT TREATED AT DIFFERENT TEMPERATURES



Sample No.	Condition of heat treatment	Ic (crystalline count)	Ia (amorphous count)	%Xc *
0	virgin	13458	2278	36.3
1	2 hrs 245° C	18007	1765	48.6
2	2 hrs 245° C + 1 hr 255° C	18621	2106	50.3
3	2 hrs 245° C + 1 hr 255° C + 1 hr 258° C	20716	1884	55.9

* $\%X_C$ calculate from $\%X_C \cdot PI_a$ (P=2.7 x 10^{-5})

Table 1. x-ray diffraction results of commercial 6 μm virgin and heat treated PEN films.

Sample No.	Condition of heat treatment	Melting Point (Tm) °C	Heat of Fusion (J/gm)
0	virgin	266.13	42.57
1	2 hrs 245° C	258.86	52.83
2	2 hrs 245° C+ 1 hr 255° C	262.12	53.85
3	2 hrs 245° C+ 1 hr 255° C+ 1 hr 258° C	264.4	54.59

Table 2. DSC results of commercial 6 μm virgin and heat treated PEN films.

FIGURE 4: HEAT OF FUSION VS $\%X_C$ OF COMMERCIAL 6μM PEN FILM "TREATED AT DIFFERENT TEMPERATURES

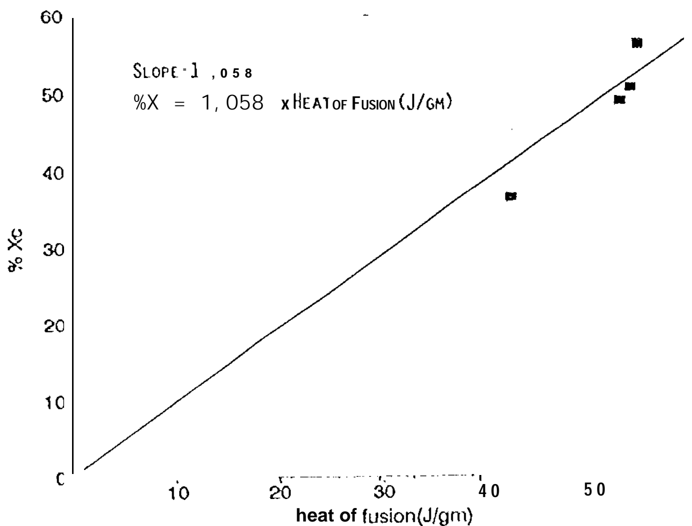
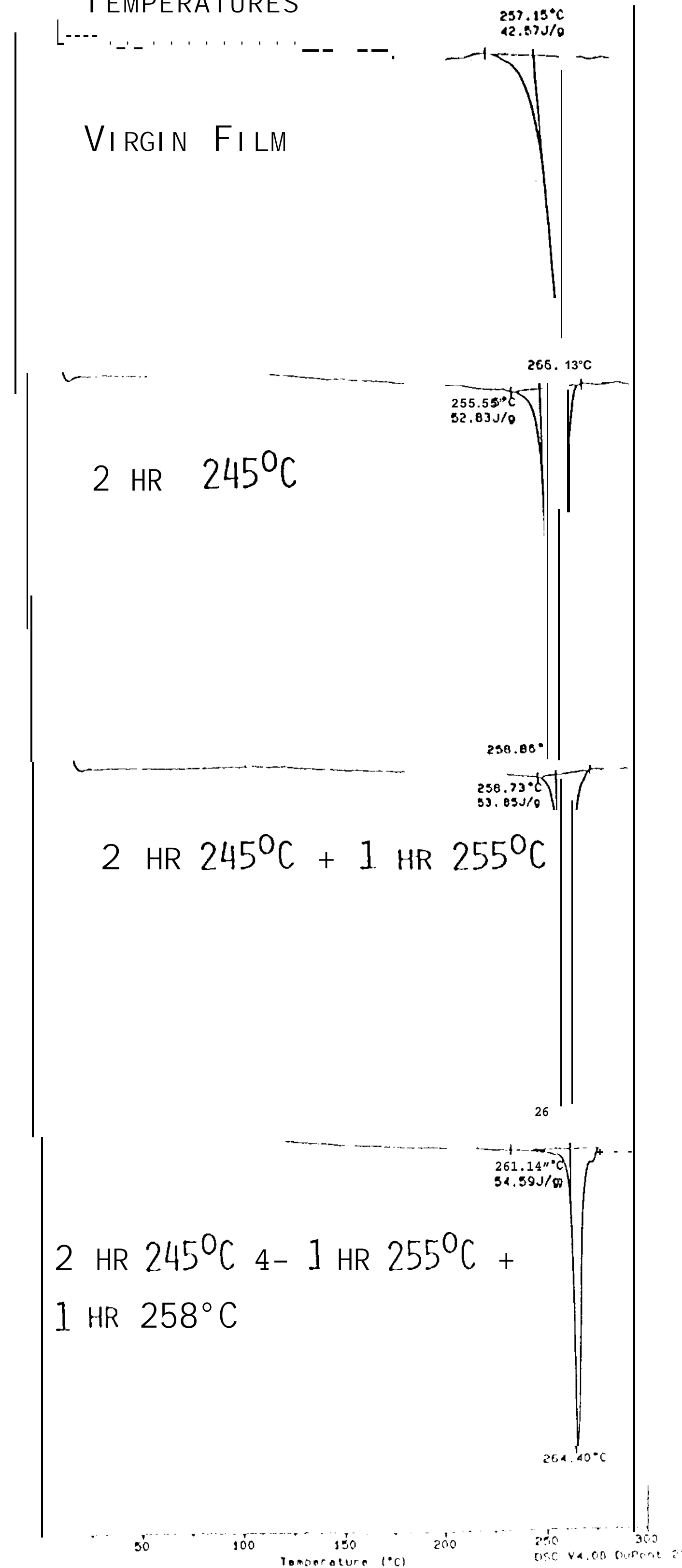


FIGURE 3. DSC RESULTS OF COMMERCIAL PEN 6μM, HEAT TREATED AT DIFFERENT TEMPERATURES



Sample No.	Condition of heat treatment	%Xc from XRD method	%Xc from DSC method
0	virgin	36.3	45
1	2 hrs 245° C	48.6	S5.89
2	2 hrs 245° C + 1 hr 255°	50.3	56.97
3	2 hrs 245° C + 1 hr 255° C + 1 hr 258° C	55.9	57.76

Table 3. Comparison of $\%X_C$ values of 6 µm virgin and heat trated PEN films obtained from XRD and DSC methods .

Sample No.	Condition of heat treatment	EBS (KV)	%Xc from DSC
0	virgin	3.27 ± 0.2	45.04
1	2 hrs 245° C	3.75 ± 0.46	55.89
2	2 hrs 245° C + 1 hr 255° C	3.84 ± 0.29	56.97
3	2 hrs 245° C + 1 hr 255° C + 1 hr 258° C	3.84 ± 0.36	57.76

Table 4. Comparison of D.C. Electric breakdown Strength (EBS) with $\%X_C$ obtained from DSC method of 6 pm virgin and heat trated PEN films.

FIGURE 5 : DIELECTRIC CONSTANT AND DISSIPATION FACTOR OF COMMERCIAL 6µM PEN FILM AS A FUNCTION OF TEMPERATURES AND FREQUENCIES

(A) DIELECTRIC CONSTANT VS (T^0C)

(B) DISSIPATION FACTOR VS (T^0C)