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Pyroelectricity in Stretched Film of Poly(Vinylidene Fluoride)/Poly(Vinyl Fluoride) Blends

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Poly(vinylidene fluoride) (PVDF) has been known to exhibit high pyroelectricity when poled under a high d.c. electric field.[1~3] Poled poly(vinyl fluoride) (PVF) also shows pyroelectricity of approximately one third of that observed in poled PVDF.[3] The pyroelectricity in PVDF is due to the orientation of the polar micro-domains under the poling field.[3] Crystallographic studies have shown that PVDF consists of three crystalline phases, namely the α-, β-, and the γ-phases, and the amorphous phase.[4~6] The α- and the amorphous phases are nonpolar while the β- and the γ-phases are polar and responsible for the pyroelectricity in this polymer. Attempts have been made to enhance the crystallinity of the polar phases and eventually to enhance the pyroelectricity in this polymer by stretching the film,[3] by making blends with other polymers,[3] or by making copolymers, etc. It has been known that the unstretched film of blend of 88.5% of PVDF and 11.5% of PVF shows a larger pyroelectric coefficient than that observed in the unstretched films of either pure PVDF or pure PVF.[3] Appearance of the maximum in the plot of pyroelectric coefficient versus the compositions for the unstretched blend film was attributed to induced crystallization of the polar phase of PVDF by making blend with PVF.[3] Question has been raised if a maximum will also appear in the pyroelectric coefficient of the stretched films of the blends. However, the poor mechanical properties of the blend made it difficult to enhance the pyroelectric coefficient by stretching the film.[3] Recently, we succeeded in stretching the blend films and the pyroelectricity is reported here.

Experimental

PVDF of molecular weight 140,000 was obtained from Polyscience, Inc. and PVF of molecular weight 126,000 from Scientific Polymer Products. Films of PVDF/PVF with weight ratio of 100/0, 88.5/11.5, 60/40, 20/80, and 0/100 were cast from the solutions in N,N-dimethyl formamide (DMF). The films were drawn by pressure-extrusion of the sandwiched film between two polyethylene billets using a capillary rheometer (Instron, Model 3211). The drawing temperatures were 50 and 110 ℃. The draw ratio was calculated from the cross sectional areas of the exit and the entrance of the die. The schematic diagrams of the billet and the die is shown in Figure 1. More detail about the extrusion procedure has been described elsewhere.[7,8]
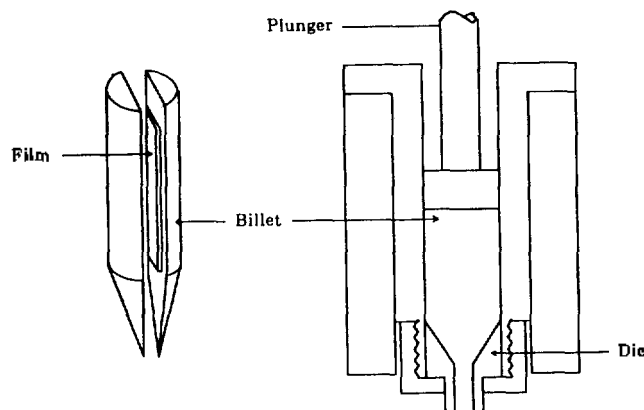
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Figure 1. Schematic diagram of the extrusion die and the sample configuration.
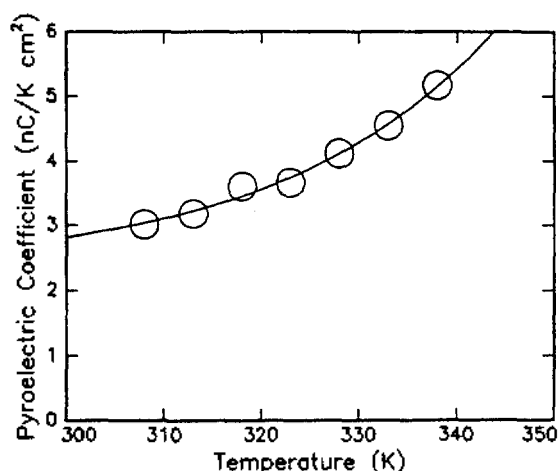

Figure 2. Temperature dependence of the pyroelectric coefficient in the stretched film of 40/60-blend. Draw ratio=400%.

Aluminum electrodes of overlapping area of 0.05 to 0.15 cm² were deposited on both sides of the film. Poling and measurements were performed in a microscope-hot stage (Mettler, FP80) which has functions of controlled heating and cooling. Samples were poled under a D.C. electric field of 1 MV/cm at 80 ℃ for 30 minutes and cooled to room temperature before the removal of the poling voltage. The pyroelectric current was measured by stepwise heating technique as described in reference.[3,8,9]

Results and Discussion

The pyroelectric coefficient, (dP/dT), was calculated from the value of the pyroelectric current (I_p), heating rate (dT/dt), and the electrode area (A) by means of the following equation.

$$I_p = A\left(\frac{dP}{dT}\right)\frac{dT}{dt} \tag{1}$$

The pyroelectric coefficient of the stretched film of 40/60-blend is shown in Figure 2 as a function of the measuring temperature. The temperature dependence of the pyroelectric coefficient showed similar feature to that observed in

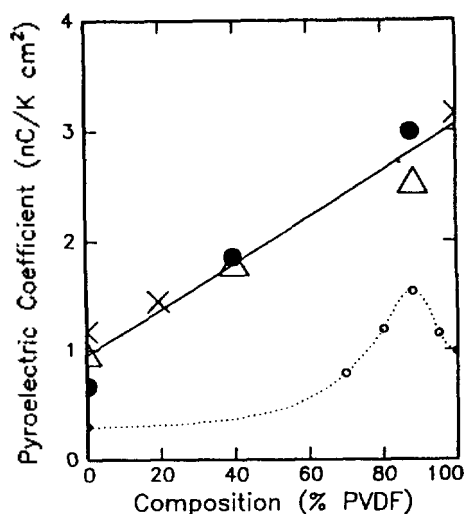1134 *Bull. Korean Chem. Soc.* **1995**, Vol. 16, No. 11

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Figure 3. Pyroelectric coefficients of the PVDF/PVF-blend measured at 30 30°C as a function of the composition; ×, drawn 600% at 50 °C; ●, drawn 500% at 50 °C; △, drawn 400% at 50 °C; —, fit to all the data points of the drawn samples; ···○···, data for the undrawn samples, cited from reference 3.

pure PVDF film except that the pyroelectric coefficient is higher in the blend. The pyroelectric coefficients of the blend films of various compositions stretched at 50 °C are shown in Figure 3 together with those of the unstretched films from reference 3. The data points for the films stretched at 110 °C, which are not shown in Figure 3, lie somewhat lower than those for the samples stretched at 50 °C. But the overall tendency of variation with the composition of the film was more or less the same as in the samples stretched at 50 °C. It should be noted that the pyroelectric coefficients of the stretched films vary linearly with the composition of the blends while the pyroelectric coefficients in the unstretched films of blends showed a maximum at 88.5%

of PVDF. Thus, in the stretched samples, the pyroelectricity of the blends is always lower than that of the pure PVDF. This is so even in the 88.5%/11.5% (PVDF/PVF) blends in which the highest pyroelectric coefficient has been observed in the unstretched specimens. Therefore, in the highly stretched samples (with the draw ratio greater than approximately 400%), blending PVDF with PVF does not seem to enhance the crystallinity of the polar phases of PVDF. This indicates that, in the stretched specimens, blending does not enhance the crystallinity of the polar phases any further, *i.e.* most of the PVDF chains have already been converted to the polar forms by stretching and, unlike in the unstretched film, no further increase of crystallinity of the polar phases can be induced by making blend with PVF.

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