

Miscibility and Piezoelectricity of the Blends of  
Poly(vinylidene fluoride-tetrafluoroethylene) and  
Poly(vinylidene fluoride-hexafluoroacetone)

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### 1. Introduction

Poly(vinylidene fluoride) (PVDF) and its copolymers with other fluorocarbon have attracted much interest recently because of their large piezoelectricity. The piezoelectric properties are attributable to the nature of polar phase of PVDF whose unit cell consists of two all-trans chains. In this study, the piezoelectricity of the blends of two crystalline vinylidene fluoride copolymers was investigated in order to better understand the relation between the piezoelectricity and the superstructure of polymers. On the other hand, there existed very rare examples of cocrystallization in the polymer blends consisting of two crystalline polymers. The cocrystallization of two polymers was also emphasized in this study.

### 2. Experimental

The two polymer samples were poly(vinylidene fluoride-tetrafluoroethylene) (P(VDF-TFE)) and poly(vinylidene fluoride-hexafluoroacetone) (P(VDF-HFA)) and were supplied from Daikin Kogyo Co. Ltd. and Central Glass Co. Ltd., respectively. Homogenous mixtures of P(VDF-TFE) and P(VDF-HFA) were obtained by dissolving the polymers at various weight percent in the solvent of tetrahydrofuran at room temperature. From the homogenous mixtures, films were cast and dried at room temperature for 12 hours and then dried in a vacuum oven for 24 hours at 100 °C. Quenched samples were prepared by melt-pressing the cast films at 200 °C and by subsequent quenching them into the ice/water mixture. The piezoelectric properties were measured after annealing at 110 °C for 6 hours and poling at various conditions. The electrodes were aluminum evaporated on both sides of the samples under a high vacuum.

### 3. Results and Discussion

Samples prepared by quenching the polymer mixture into ice/water from the melt showed two glass transition temperatures  $T_g$ 's corresponded to each of pure components in the dynamic mechanical measurements. However, the samples annealed at 110 °C and immediately quenched into the liquid nitrogen showed the single  $T_g$  between  $T_g$ 's of two components over all the compositions of the blends. It indicates that the blends show the upper critical solution temperature behavior as shown in Fig.1. On the other hand, samples annealed at 110 °C showed a sharp single melting temperature on DSC and their single melting shapes were not affected by the heating rate. However, the results of annealing below 100 °C which is in the immiscible state of amorphous phase showed the double melting temperatures. The temperature dependence of miscibility of amorphous phase, i.e.

UCST behavior is likely to be attributed to the cocrystallization. Therefore, the melting behaviors of blends suggested the possibility of cocrystallization of two crystallizable polymers in the miscible state.

The piezoelectric properties of the blends were measured to investigate the origin of piezoelectricity and the mechanism of dipole reorientation. The piezoelectricity of the sample may be originated from the residual polarization of the polar crystals and the internal strain induced to the polar crystals. The piezoelectric stress constant of the samples showed the equilibrium value in the poling above the electric field of 250 KV/cm as shown in Fig.2. For the saturatedly polarized samples, the 180° rotation of dipoles was supported by the fact that the measured value of the maximum polarization agrees with the calculated value using the frozen dipole model. The polarization can be represented as following equation;

$$P = \frac{\epsilon_{\infty} + 2}{3} \frac{\mu}{V} \times \chi \phi f$$

where P is the polarization,  $\epsilon_{\infty}$  is the high-frequency dielectric constant (=3), V is the molar volume,  $\mu$  is the dipole moment of VDF monomeric unit, x is the fraction of VDF in the sample,  $\phi$  is the  $\beta$  phase crystallinity, f is the fraction of head to tail polarization, and  $\chi$  is the average contribution of the dipole moment to the polarization.

The x-ray diffraction and the DSC measurements showed the ferroelectric-to-paraelectric transition of the blends but no ferroelectric evidence was obtained in pure P(VDF-HFA).

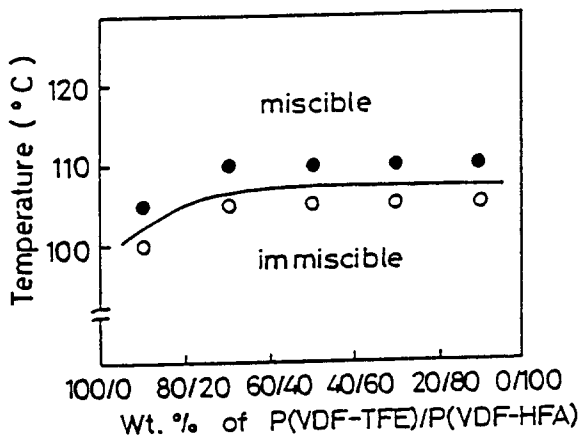


Fig.1 Phase diagram of blends of P(VDF-TFE) and P(VDF-HFA).

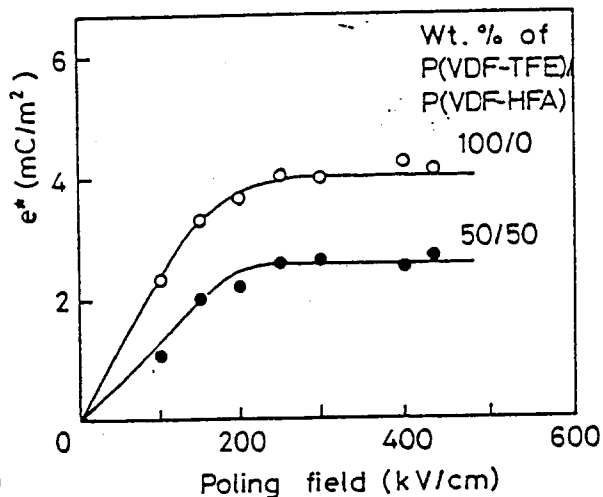


Fig.2 Effect of poling field on piezoelectric stress constant of blends.