

The Effect of an External Electric Field on Phase Separation, Phase Dissolution, and Isothermal Crystallization Behavior of Poly(vinylidene fluoride)/Poly(1,4-butylene adipate) Blends

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Introduction

Since PVDF/poly(1,4-butylene adipate) blend shows much lower LCST curve compared with PVDF/PMMA blend, the PVDF/PBA blend can be a good candidate for investigating the effect of the electric field on the phase separation and dissolution behavior of an electro-active polymer and electro-inactive polymer blend.

The increase in the electric field strength shifted the LCST curve to the lower temperature. So, we discussed the effect of the external electric field on the phase separation. And the electric field-induced phase separation, the electric field removal-induced phase dissolution, and crystallization behavior under various conditions were also analyzed.

Experimental

Films of various compositions of PVDF(MW=480,000) and PBA(MW=12,000) were cast from the DMF solution of the PVDF/PBA mixture. After removing the residual DMF in the cast sample using the distilled water, the sample was dried at 85°C for 5 days in a vacuum oven.

A cloud point measurement was performed in the melt state by measuring the scattering intensity at a scattering angle of 10° during heating at a rate of 1°C/min in the presence of the electric field ranging from 0 to 0.09MV/cm. An abrupt change in the scattered intensity during phase separation was regarded as a cloud point.

A polarized light microscope equipped with a Mettler FP82HT hot stage, a photodetector, and a CCD-camera was used with crossed or parallel polarization to measure a transmitted light intensity and to identify the crystal morphology evolution during crystallization and phase morphology evolution during phase separation and dissolution.

Results and Discussion

In the absence of an electric field, the free energy of mixing per unit volume of the mixture, $\Delta G_m / V$, is expressed as the Flory-Huggins equation,

$$\Delta G_m / V = RT \left(\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \chi \phi_1 \phi_2 \right) \quad (1)$$

where ϕ_i is the volume fraction of the i_{th} polymer, V_i is the molar volume of the i_{th} polymer, and χ is the interaction parameter.

In the presence of an electric field, Eq.(1) can be modified by insertion of electrostatic energy term as seen in Eq.(2) or considering electric field-dependent χ parameter as seen in Eq.(3).

$$\Delta G_m / V = RT \left(\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \chi \phi_1 \phi_2 \right) - \frac{1}{2} \varepsilon_0 E^2 (\varepsilon - \phi_1 \varepsilon_1 - \phi_2 \varepsilon_2) \quad (2)$$

where ε_0 is the dielectric constant of vacuum, ε is the relative permittivity of the binary blend which is composition-dependent, and ε_i is the relative permittivity of the pure i_{th} polymer, and E is a field strength.

$$\Delta G_m / V = RT \left\{ \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 + \chi (1 - \mathbb{E}^2 / \langle \mathbb{F}^2 \rangle) \phi_1 \phi_2 \right\} \quad (3)$$

where \mathbb{E} is the internal electric field strength varied by the external electric field strength and electric property of blend, \mathbb{F} is the molecular spontaneously fluctuating electric field which is originated from the dipole-dipole van der Waals interactions between spontaneously mutually induced dipoles, and $\langle \rangle$ denotes time-average.

If ε is nonlinearly dependent on the composition in Eq.(2), Wirtz and Fuller [1] showed that the critical composition, $\phi_{2,c}(E)$, in the presence of an electric field is nearly same as in the absence of the field, the χ parameter at the critical condition, $\chi_c(E)$, in the presence of the field is always larger than in the absence of the field, and thus the critical temperature, $T_c(E)$, in the presence of the

field is lower than in the absence of the field for a UCST phase behavior. They also predicted that $T_c(E)$ is higher for a LCST phase behavior. Thus the electric field can be thought to suppress the phase separation for both UCST and LCST cases.

Since the χ parameter in the presence of the field, $\chi(E)$, can be expressed as $\chi(1 - E^2 / \langle F^2 \rangle)$ as seen in Eq.(3), the electric field is thought to reduce the χ parameter, which suppresses the phase separation [2].

Fig.1 shows the variation of cloud point as a function of an electric field. As seen in Fig.1, cloud point trace shows the typical LCST behavior. Cloud point with an electric field was shifted to 10~20°C lower temperature. This result is completely opposite to the above prediction. The shift of cloud point to lower temperature for LCST in the presence of the field suggests that the electric field favors phase separation in the PVDF/PBA blend system.

The cloud points in the absence of the field can be fitted with the binodal points, which are a pair of co-tangential points calculated on the basis of Eq.(4) considering the interaction parameter χ dependent on temperature and composition as follows;

$$\chi = a + b/T + c\phi_2/T \quad (4)$$

where a , b , and c are entropy, enthalpy, and composition-dependent enthalpy coefficients, respectively, which were determined from the best fitting result.

In the presence of an electric field, the cloud points must be fitted to obtain binodal curve using Eq.(2) or (3). Since, however, the composition-dependent relative permittivity of the binary blend, ϵ , cannot be easily expressed as a function of composition and temperature from the data obtained experimentally and it is impossible to obtain the general equation about $E^2 / \langle F^2 \rangle$ as a function of temperature and composition, one cannot obtain the binodal and spinodal curves, critical temperature, critical composition, and the χ parameter at the critical condition. Thus, even in the presence of the field, cloud points were fitted using Eq.(1) to know how the field strength affects the values of a , b , and c parameters, critical temperature, critical composition, and the χ parameter at the critical condition. In Fig.1, fitted binodal curve is also seen with the experimentally obtained cloud points. All parameters, critical temperature, critical composition, and the χ parameter at the critical condition are listed in Table 1.

As the electric field strength is increased, the entropy coefficient, a , is increased, the enthalpy coefficient, b , is nearly unchanged, c is decreased, the critical temperature is decreased, the critical composition is a little shifted to the left, and the critical parameter, χ_c , is increased

When an electric field of 0.07MV/cm was applied to the blend sample in a single phase state (235°C, $\phi_2 = 0.4240$), a field-induced phase separation was observed due to the downward shift of LCST. After removing the field, phase dissolution took place reversibly due to the LCST's returning to the initial position. Isothermal crystallization behavior after quenching from a single phase state or a two-phase state to lower temperature than the melting temperature of PVDF with or without an external electric field is also discussed.

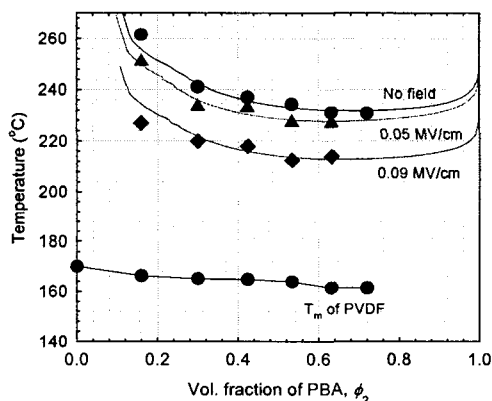


Fig.1. Phase diagram of the PVDF/PBA blends in the presence of an external electric field.

Table 1. Thermodynamic parameters obtained from curve-fitting

	0 MV/cm	0.05MV/cm	0.09MV/cm
a	7.50×10^{-4}	7.60×10^{-4}	7.77×10^{-4}
b	-0.332	-0.331	-0.331
c	-0.0118	-0.0150	-0.0130
T_c (°C)	231.76	227.61	212.84
$\phi_{2,c}$	0.69201	0.64083	0.66456
χ_c	7.63×10^{-5}	7.98×10^{-5}	7.81×10^{-5}

References

1. D. Wirtz and G.G. Fuller, *Phys. Rev. Lett.*, **71**, 2236 (1993).
2. E. Gurovich, *Macromolecules*, **28**, 6078 (1995).

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