Measurement of the internal electric field in a poly(vinylidene fluoride)/poly(methyl methacrylate) blend

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A melt-quenched blend of 80 wt% poly(vinylidene fluoride) (PVDF) and 20 wt% poly(methyl methacrylate) (PMMA) has the β-crystal form of PVDF, which grows larger on annealing at higher temperature. The internal electric field E_i induced by poling in the PVDF/PMMA (80/20) blend was measured using the technique of electrochromic peak shift of dye dissolved in the blend. It was found that E_i was of the order of 10^6 V cm^{-1} (larger than the poling field), and that E_i was anomalously stable when the sample was annealed at higher temperature, whereas the pyroelectricity decreased above the glass transition temperature. We speculated that the space charge may be related to the anomalous stability of E_i.

(Keywords: electric field; poly(vinylidene fluoride); poly(methyl methacrylate))

Introduction

Poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) blends are compatible in all proportions in the molten state[1]. Fourier transform infra-red spectroscopy of PVDF/PMMA has shown that the 70/30 blend by weight leads directly to the β-crystal form of PVDF, providing the blend is quenched from the melt and then annealed at higher temperature[2]. A separate study of PVDF/PMMA blend revealed that a melt-quenched blend of 80 wt% PVDF and 20 wt% PMMA also preferentially forms the β-crystal form (type I) and this crystallite grows larger when the sample is annealed at higher temperature[3]. Such a film has clear and transparent optical quality even after being annealed at higher temperature[3].

Recently, we measured the internal electric field (E_i) induced by poling in vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer[4], using the technique of electrochromic peak shift of dye dissolved in the copolymer. We found that E_i was of the order of 10^6 V cm^{-1} which is larger than the poling field, and that it had a good correlation with the remnent polarization and was stable up to the Curie temperature.

We report here the E_i created between the PVDF β-crystallite dipole in PVDF/PMMA (80/20) blend and discuss the thermal stability of the pyroelectric coefficient (C_{pyro}) and E_i in this blend and the possibility of using this blend as a non-linear optical material. The E_i was determined from the electrochromic shift of a peak in the optical spectrum of a dye, as was done previously for the VDF–TrFE copolymer[4].

Experimental

PVDF (Kureha, KF-polymer, $M_w = 141\,000$, $M_n = 64\,000$) and PMMA (Mitsubishi Rayon, Acrypett-VHK, $M_w = 168\,000$, $M_n = 96\,400$) were used. 4-Dimethylamino-4′-nitrostilbene (DANS) from Eastman Kodak Co. was recrystallized from amyl alcohol. The polymers were mechanically melt blended at 200°C and films were melt-pressed between 50 μm thick films of Upilex (Ube Industry, Japan) on a heated press to a thickness of 40–70 μm. The molten films were quenched into liquid nitrogen.

The solute probe DANS was introduced by soaking the polymer films in n-propyl alcohol solutions saturated with DANS at the boiling point of the alcohol (97°C) for 4 h followed by drying overnight at room temperature *in vacuo*. The concentration of DANS in the blend was 5.0–6.5 mmol l^{-1}. The blend films were poled by applying a constant field of 0.8 MV cm^{-1} for 1 h at 80°C in a nitrogen atmosphere to aluminium electrodes which had been evaporated onto opposing surfaces of the films. The value of C_{pyro} was determined by measuring the current generated upon heating and cooling the poled film at a measured rate, usually ~0.6°C min^{-1} in the vicinity of 30°C. Wide angle X-ray scattering (WAXS) of the films was measured with a Toshiba model ADG-301 X-ray diffractometer with nickel-filtered CuKα radiation. The glass transition temperature (T_g) of the film was determined from a first penetration temperature on a temperature profile by thermomechanical analysis, using Seiko Instruments model TMA100 thermomechanical analyser controlled by a model SSC5200 disc station. U.v.–visible spectra of the films were measured on a Shimadzu model UV-2101PC spectrophotometer and measured spectra data were stored by computer for analysis.

The absorption spectrum in the presence of a field $A(\nu, E)$ can be expressed by a Taylor series expansion of the unperturbed spectrum $A(\nu, 0)$ with the wavenumber shift $\Delta\nu$ as the perturbation. Following Havinga and van Pelt[5]:

$$\frac{A(\nu,E)}{\nu} - \frac{A(\nu,0)}{\nu} = \delta\frac{A(\nu,0)}{\nu} + \langle\Delta\nu\rangle\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu} + \frac{1}{2}\langle(\Delta\nu)^2\rangle\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu} \qquad (1)$$

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The term involving δ accounts for a change in absorbance due to reorientation of the dye in the presence of the field. Terms involving $\langle \Delta\nu \rangle$ and $\langle (\Delta\nu)^2 \rangle$ describe field-induced shifts in the band and field-induced broadening of the band[5].

We relied heavily on wavelength shifts in the absorbance maxima and band broadening to deduce E_i in the same manner we applied to the VDF–TrFE copolymer[4], because the decrease of absorption intensity by poling is not only due to reorientation (alignment) of DANS to E_i, but also the loss of some DANS when the sample is poled at 80°C and annealed at a higher temperature (up to 120°C). This necessitated the introduction of the factor f in equation (2).

$$\frac{1}{(1-f)}\frac{A(\nu,E)}{\nu}-\frac{A(\nu,0)}{\nu} = \delta\frac{A(\nu,0)}{\nu}+\langle\Delta\nu\rangle\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu}+\frac{1}{2}\langle(\Delta\nu)^2\rangle\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu} \tag{2}$$

where

$$\delta = -G(u) \tag{3}$$

$$\langle\Delta\nu\rangle = \frac{G(u)}{1-G(u)}3C \tag{4}$$

$$\langle(\Delta\nu)^2\rangle = \frac{G(u)}{1-G(u)}3C^2 \tag{5}$$

$$G(u) = 1-\frac{3\coth(u)}{u}+\frac{3}{u^2} \tag{6}$$

$$u = \frac{E_i\mu_g}{kT} \tag{7}$$

$$C = \frac{kT\Delta\mu}{hc\mu_g} \tag{8}$$

where μ_g is the dipole moment of DANS in the ground state, k is Boltzmann's constant, T is the absolute temperature, $\Delta\mu$ is the difference between the dipole moments in the excited state and in the ground state, h is Planck's constant and c is the speed of light.

Then E_i was calculated using the final equation of

$$\frac{1}{(1-f)[1-G(u)]}\frac{A(\nu,E)}{\nu}-\frac{A(\nu,0)}{\nu} = \frac{G(u)}{[1-G(u)]^2}\left[-3C\frac{\partial}{\partial\nu}\frac{A(\nu,0)}{\nu}+\frac{3}{2}C^2\frac{\partial^2}{\partial\nu^2}\frac{A(\nu,0)}{\nu}\right] \tag{9}$$

The first and second derivatives of $A(\nu,0)/\nu$ were evaluated as a function of ν to determine the value ν_N, for which the right-hand side of equation (9) was zero. When $\partial[A(\nu,0)/\nu]/\partial\nu = (C/2)\partial^2[A(\nu,0)/\nu]/\partial\nu^2$, a value of $(1-f)[1-G(u)]$ was chosen to make the spectra of the poled and unpoled samples intersect at ν_N, i.e. $A(\nu_N,E)/\{(1-f)[1-G(u)]\nu_N\} = A(\nu_N,0)/\nu_N$. Having normalized the curves at ν_N, the difference in absorbance between the two spectra at several other values of ν were then determined, the derivatives were evaluated at the corresponding values of ν as required for equation (9) and the quantity $\{G(u)/[1-G(u)]^2\}$ was evaluated from a linear least squares fit. From $G(u)$ and equation (6), a value of u was obtained from which E_i was evaluated.

Results and discussion

Figure 1 shows the WAXS patterns of blend samples with various thermal histories and of a melt-quenched PVDF homopolymer. The WAXS pattern[6] of the melt-quenched PVDF homopolymer shows typical peaks of the α-crystal form at 17.6, 18.4, 20.0, 26.6 and 38.7°. Peaks at 20.8, 36.8 and 41.2° due to the β-crystal form[6] which appear in the melt-quenched sample of the blend become larger when the sample is annealed at temperatures up to 150°C. The sample annealed at 160°C exhibits a WAXS pattern of a mixture of α- and β-crystal forms; the α-crystal phase forms in the vicinity of 160°C.

The blend film has good optical quality with little light scattering in the u.v. and visible regions, even when the film is annealed at higher temperature to grow the β-crystallite of PVDF. The poling causes a small shift in the maximum peak in the spectrum to longer wavelength, which shows that the electronic state of DANS dissolved in the amorphous region is subject to a strong E_i. As described above, the decrease in absorption intensity by poling is due to the reorientation (alignment) of DANS in E_i and the loss of some DANS when poling at 80°C. After normalizing the poled DANS spectrum using the procedure described above, E_i was calculated.

Figure 2 shows plots of E_i and C_{pyro} after the poled sample film was stored at room temperature for the

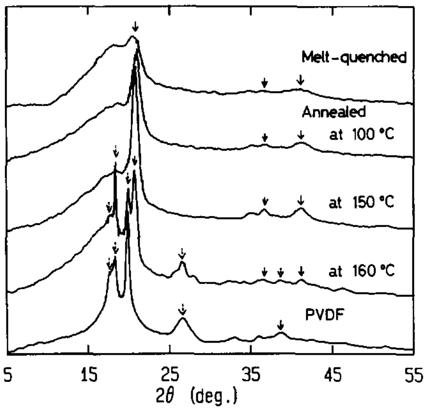

Figure 1 WAXS patterns of the PVDF/PMMA blend with various thermal histories and a melt-quenched PVDF homopolymer. The solid and broken arrows indicate the characteristic peaks of the β and α phases, respectively

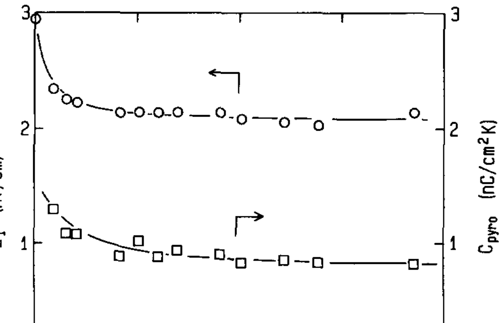

Figure 2 Dependence of E_i (○) and C_{pyro} (□) on ageing time at room temperature. The sample is poled by applying a constant field of 0.8 MV cm^{-1} at 80°C for 1 h in a nitrogen atmosphere

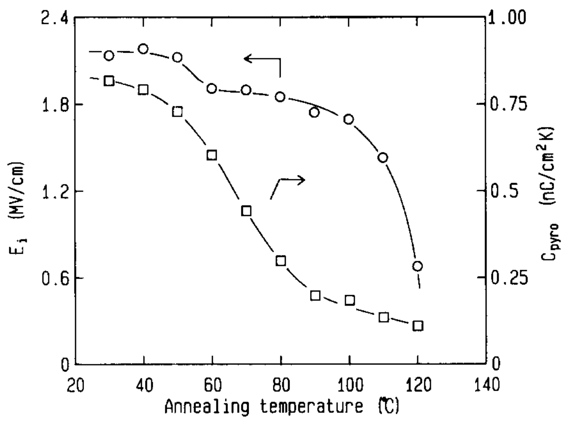

Figure 3 Dependence of E_i (○) and C_{pryo} (□) on annealing temperature. The poling conditions are the same as in *Figure 2*

indicated ageing time. The poling was carried out to apply a constant field of 0.8 MV cm^{-1} at 80°C for 1 h in a nitrogen atmosphere. E_i decayed in the several hours after poling and almost levelled off in a few days. An E_i of 2.9 MV cm^{-1} immediately after poling levelled off to $\sim$2.1 MV cm^{-1}. The first pyroelectric measurement (4 h after poling) gives a C_{pyro} of 1.3 nC cm^{-2} K^{-1} which is about half the value for well poled PVDF. The decay of C_{pyro} seen in *Figure 2* is definitely more extended in time than the decay of E_i, and the total decrease is greater. The failure to observe a proportionality between E_i and C_{pyro} in *Figure 2* suggests that the main contribution to E_i is from the dipole polarization but the space charge may relate to the stability of E_i discussed below.

Figure 3 shows E_i and C_{pyro} after the poled film is annealed for 2 h each at successively higher temperatures. The poling was done under the same conditions as in *Figure 2*. C_{pyro} starts to largely decrease around the T_g of 60°C, which shows that the thermal treatment has depolarized the sample. However, E_i shows an anomalous stability extending well above T_g up to at least 100°C, except for the small drop around the T_g of 60°C. The small decrease of E_i around T_g may be an indication that the part of E_i that is proportional to the dipole polarization starts to decrease when C_{pyro} starts to decrease. Measurement of the polarization distribution by the thermal pulse method[7,8] was carried out for samples annealed at 25, 72 and 122°C for 2 h. The profiles of the polarization distribution exhibit strong evidence of the space charge in addition to the dipole polarization. Mean polarization decreases with increasing annealing temperature, which is consistent with the result for C_{pyro}. However the profile of the polarization distribution is unchanged even after the sample is annealed at higher temperature. The main contribution to E_i is from the dipole polarization. At the present stage, we cannot provide an appropriate and exact mechanism for the stabilization of E_i by space charge, but speculate that the space charge may be related to the stabilization of E_i.

This blend has good optical quality with little light scattering in the visible region. These properties will allow this blend to be a candidate as a second harmonic generation (SHG) material. Indeed the preliminary SHG experiment of this blend showed that the poled film has a non-linear coefficient d_{33} of the order of 9×10^{-9} esu.

Conclusions

It was found that the space charge strongly stabilizes the E_i in the PVDF/PMMA blend. Further, incorporation of a large amount of non-linear optical dye in this blend and the orientation of the dye by E_i will give high non-linear optical properties.

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