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Phase Separation in Quenched Noncrystalline Poly(vinylidene fluoride)/ Poly(methyl methacrylate) Blends

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ABSTRACT: The dielectric characterization was carried out in poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blends quenched from the melts. In the quenching of 60/40 PVDF/PMMA, the phase separation between the PVDF phase and the mixed PVDF–PMMA amorphous phase was observed in apparently completely noncrystalline blends. The dielectric behaviors for this PVDF phase separated were the same as those of the PVDF crystal-amorphous interphase. The PVDF phase/mixed amorphous phase separation was explained by forming incipient crystallites of PVDF.

KEY WORDS Poly(vinylidene fluoride) / Poly(methyl methacryrate) / Blend / Crystal-Amorphous Interphase / Phase Separation / Quenching /

It is well known that poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) are completely miscible in the melt, and exhibits a lower critical solution temperature (LCST) behavior around 330°C.[1] Below the melting point (*ca.* 170°C) of PVDF, PVDF molecules crystallize in the blends with PVDF content larger than about 50%. It was shown previously[2–4] that these semicrystalline blends comprise three different phases: PVDF crystallites, PVDF crystal-amorphous interphase, and mixed PVDF–PMMA amorphous phases. Therefore, the phase separation below the melting point of PVDF occurs owing to the crystallization of PVDF, which is accompanied always by the PVDF crystal-amorphous interphase that completely excludes PMMA molecules[4] despite the favorable (enthalpic) interactions between the PMMA and PVDF segments. Moreover, a possible theoretical reason for the fact that the crystal-amorphous interphase always accompanies the PVDF crystallites was presented,[2] on the basis of severe (entropic) packing problems in dissipating order at the surface of lamellar semicrystalline polymers.[5]

In this paper, we present new experimental results that show the existence of a considerable amount of noncrystalline pure PVDF region in apparently completely noncrystalline PVDF/PMMA blends which are normally considered to be miscible. These blends that comprise two phases of the noncrystalline PVDF and the mixed PVDF–PMMA amorphous region, respectively, are prepared by rapid quenching from the melt into 2-methylbutane solid/liquid slurry at -160°C, and have been characterized by dielectric relaxation, DSC, IR, and small angle X-ray scattering measurements. The implications of this PVDF/mixed amorphous phase separation these apparently noncrystalline blends will be discussed.

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EXPERIMENTAL

A PVDF sample was obtained from Solvay Co., and its number- and weight-averaged molecular weights are $M_n = 38000$ and $M_w = 100000$, respectively. A PMMA sample was obtained from Röhur GmbH with its M_n and M_w of 60000 and 120000, respectively. Mixtures were melt-blended in an extruder at 220°C and thin films of 40—60 μm in thickness were extruded from the mixtures. Dielectric measurements were carried out with a Multi-Frequency LCR Meter (4275A model of Hewlett Packard Co.) with the frequency range between 10 kHz and 10 MHz at a heating rate of 1°C min^{-1}. The thermal properties were measured with a Du Pont 910 DSC connected with a Du Pont 1090 thermal analyzer.

The construction of the electrode cell is illustrated in Figure 1. Two or three sheets of film were sandwiched between two Kapton films, on which aluminum electrodes of 1 cm in diameter had been vacuum-deposited, and placed between two copper plates with Kapton film spacer of 75 μm in thickness. After melting at 210°C for 30 min, the sample assembly was plunged into the quenching medium of 2-methylbutane solid/liquid slurry maintained at −160°C. The sample was then transferred to the dielectric sample cell maintained at −60°C and then cooled to −110°C before starting the measurements. For comparison, slow-cooled samples were prepared by cooling the melt sample from 210°C to room temperature at 1°C min^{-1}.

RESULTS AND DISCUSSION

Figure 2 shows temperature dependence of dielectric loss $\varepsilon''/\varepsilon_0$ at 100 kHz for the slow-cooled PVDF/PMMA blends, designated by the PVDF weight% in the figure, where ε_0 is the permittivity of free space. For the PVDF homopolymer and the blends containing a large PVDF fraction, two relaxations with peaks at about 160 and 0°C were clearly observed, with no change in the relaxation temperature in the blends with different PVDF contents. However, the strengths of both relaxation peaks were affected strongly by the composition, decreasing with decreasing PVDF content and hence the crystallinity of PVDF. Finally both peaks disappeared in the noncrystalline blends. The relaxation at *ca.* 160°C is the well-established α_c relaxation occuring within the PVDF crystallites.[6] It therefore follows that the β relaxation at *ca.* 0°C is also related to PVDF crystallites, since its temperature and strengths change with the

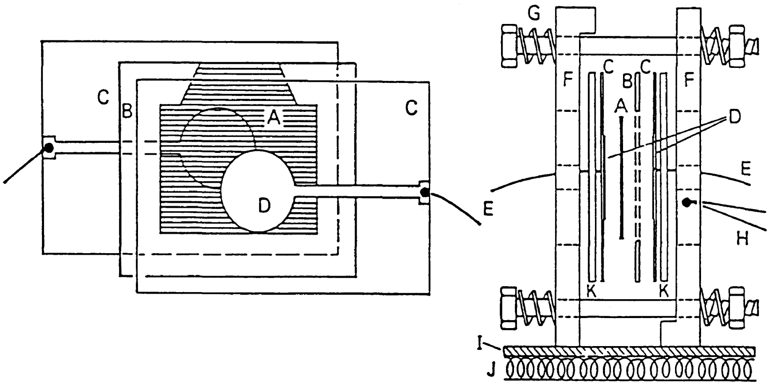

Figure 1. Construction of sample cell. A, sample film; B, Kapton spacer; C, Kapton film; D, aluminum electrode; E, electrode lead; F, brass plate; G, spring; H, thermo-couple; I, Kapton film; J, heater; K, copper plate.

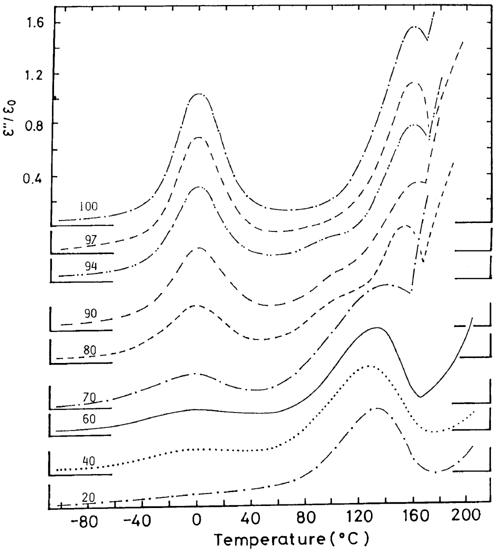

Figure 2. Temperature dependence of the dielectric loss $\varepsilon''/\varepsilon_0$ measured at 100 kHz for the slow-cooled PVDF and PVDF/PMMA blends, designated by the PVDF weight% in the figure.

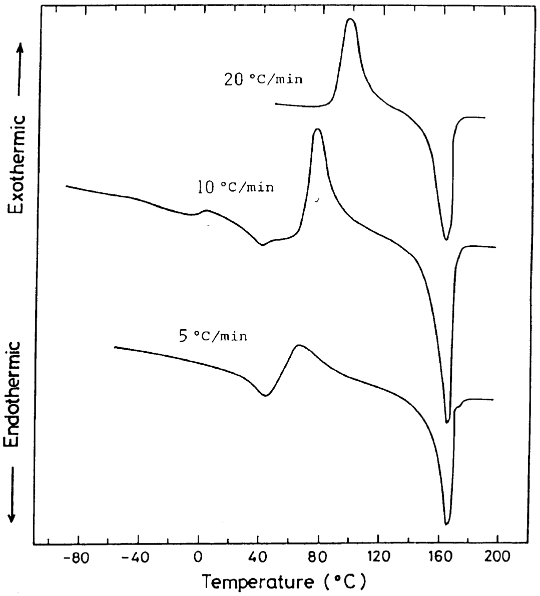

Figure 3. DSC thermograms of the quenched 60/40 PVDF/PMMA blend with heating rate of 20, 10, and $5^{\circ}\mathrm{C\,min}^{-1}$.

PVDF content in the same manner as those of the α_c peak. On the other hand, the relaxation observed between 80 and 140°C, denoted as β' relaxation, shown as shoulders in the high PVDF content samples or broad peaks in the blends of PVDF contents less than 60% depends on the blend composition; the relaxation strength increases and the relaxation temperature shifts toward higher temperature as the PVDF content decreases. So, these relaxations are related to the molecular motion of the homogeneously mixed PVDF–PMMA amorphous phase.[4] As discussed already,[2–4] the β relaxation has been shown to arise from the interfacial region of PVDF crystallites, or the crystal-amorhphous interphase, that totally excludes the PMMA segments.

Figure 3 shows the DSC traces during the first heating of the quenched 60/40 PVDF/PMMA blends at three different heating rates. The glass transition behavior of the mixed PVDF–PMMA amorphous phase is observed around 30°C. Above the glass transition, crystallization occurs between 60 and 100°C depending on the heating rate, and finally the melting of PVDF crystallites is seen around 170°C. The crystallization exotherm and the melting endotherm exhibit the enthalpy changes that are nearly the same within the experimental error. Furthermore, the infrared (IR) spectrum of the quenched 60/40 blend shows no crystalline absorptions as shown in Figure 4(a). In comparison, after annealing the quenched blend at 60°C for 30 min, the IR spectrum shows some crystalline absorptions of form II (795, 766, 612, 530, and 410 cm^{-1}) as indicated by arrows in Figure 4(b). Hence, the quenched 60/40 blend can be considered to be completely noncrystalline according to the normal standard. In such a quenched noncrystalline blend, the PVDF and PMMA molecules were considered to be completely miscible previously.[7]

Figure 5 indicates temperature dependence of the dielectric constants of the quenched blend at the frequency between 10 kHz and

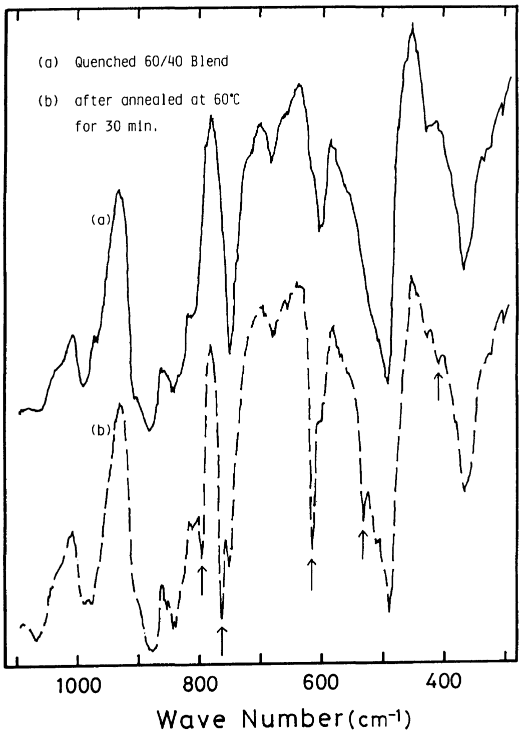

Figure 4. IR spectra of the quenched 60/40 PVDF/PMMA (a) and the sample after annealing at 60°C for 30 min (b).

4 MHz. It is clearly shown that the quenched sample exhibits a rather strong relaxation peak at 0°C at 100 kHz, which is well below the glass transition temperature (30°C) of the mixed amorphous phase. This is followed by the glass transition type relaxation and subsequent crystallization starting around 60°C as indicated by abrupt decrease in dielectric constant, $\varepsilon'/\varepsilon_0$, occuring at the same temperature at all frequencies. Upon completion of PVDF crystallization in the originally quenched sample around 100°C, the difference between the quenched and the slow-cooled samples becomes quite small. In Figure 5(b), high temperature relaxations observed between 100 and 150°C are due to the homogeneously mixed-amorphous phase.

Figure 6 shows plots of the frequencies of the maxima of $\varepsilon''/\varepsilon_0$ against the reciprocal of absolute temperature for the quenched and the slow-cooled 60/40 PVDF/PMMA blends, and the PVDF homopolymer. The relaxation time and its temperature dependence of the quenched blend agree with the β relaxation of the slow-cooled blend and the PVDF homopolymer samples within the experimental error. Hence, the relaxation observed in the quenched blend can be identified with the β relaxation of semicrystalline PVDF arising from the PVDF interphase.

Figure 7 indicates the Cole–Cole plot at 0°C by the method of least squares for the quenched and the slow-cooled blends and the PVDF homopolymer, and the dielectric parameters are listed in Table I. The relaxation strength of the quenched blend is about 55% of the PVDF and double that of the slow-cooled blend sample. In the view point of the dielectric characteristics, these results show convincingly that the quenched apparently noncrystalline 60/40 PVDF/PMMA blend is not homogeneous, but rather phase separated into the mixed PVDF–PMMA amorphous region and the pure PVDF phase, the dielectric properties of which are quite similar to those of the PVDF crystal-amorphous interphase.

Since the PVDF and the PMMA segments exhibit favorable interactions, the reason for this phase separation is obviously the tendency of PVDF to crystallize out of the miscible blends. Indeed, in the blends with PVDF content of 80% or larger, it was impossible to obtain a completely noncrystalline blend even under our rapid quenching condition. Moreover the degree of the crystallinity of such a sample is not much different from that of the slow-cooled sample. In addition, the blends in which the PVDF does not crystallize easily, such as 40/60, 20/80 PVDF/PMMA, the dielectric properties of the quenched samples were exactly the same as the slow-cooled ones, since these samples consisted of only homogeneously mixed PVDF–PMMA amorphous region. The noticeable facts are then

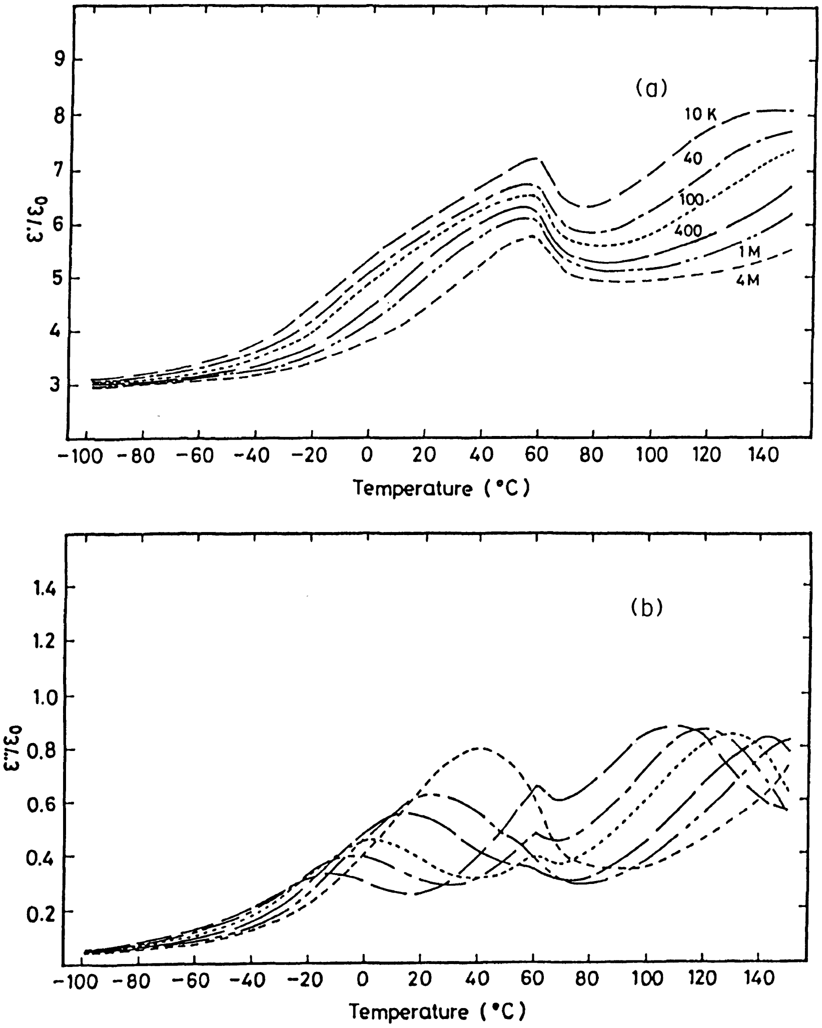

Figure 5. Temperature dependence of the dielectric constant $\varepsilon/\varepsilon_0=\varepsilon'/\varepsilon_0-i\varepsilon''/\varepsilon_0$ for the quenched 60/40 PVDF/PMMA blend measured at the frequencies indicated.

the apparent absence of any detectable crystallinity and the quite large amount of the PVDF phase in the quenched 60/40 PVDF/PMMA blend.

One may understand these results by postulating that incipient PVDF crystallites formed at a large supercooling. Namely, during the quenching from the completely mixed melt of the PVDF and PMMA segments, crystallizable PVDF molecules start incipient crystallites (nucleation). At a slow cooling rate, such PVDF nuclei can grow and form the crystalline phase and the accompanying crystal-amorphous interphase, while the liquidlike amorphous PVDF mixes homogeneously with the PMMA molecules, when the weight fraction of PVDF is more than 50%. At a large supercooling, however, the crystallizable PVDF molecules can not completely crystallize, since the crystallization rate of the PVDF decreases with increasing PMMA content in the blend.[7] In addition, the glass transition

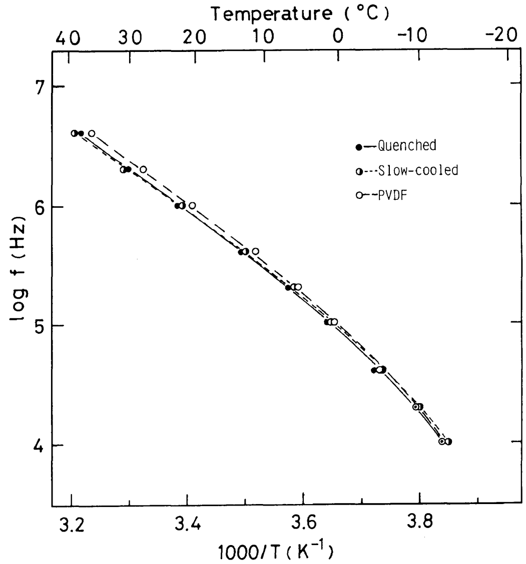

Figure 6. Logarithm of loss-maximum frequency *vs.* reciprocal of absolute temperature for the PVDF homopolymer, the quenched, and the slow-cooled 60/40 PVDF/PMMA blends.

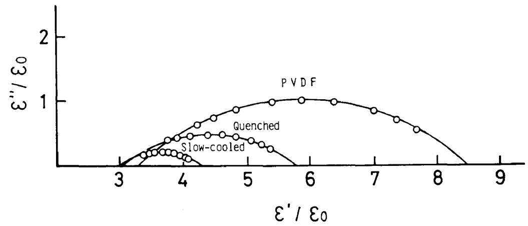

Figure 7. Cole–Cole plots of the PVDF homopolymer, the quenched, and the slow-cooled 60/40 PVDF/PMMA blends at 0°C.

Table I. Dielectric parameters of the quenched and the slow-cooled 60/40 PVDF/PMMA blends and PVDF homopolymer at 0°C

Sample	ε_l	ε_h	$\Delta\varepsilon$	τ (10^{-7})	β
Quenched	5.80	3.02	2.78	5.1	0.43
Slow-cooled	4.35	2.98	1.37	4.8	0.41
PVDF	8.45	3.30	5.15	5.6	0.48

ε_l, ε_h, limiting values of the dielectric constant at low and high frequency; τ, mean relaxation time; β, Cole–Cole distribution parameter.

temperature of the mixed amorphous phase which surrounds the PVDF nuclei is rather high, *ca.* 30°C (60/40 PVDF/PMMA). Therefore, the incipient PVDF crystallites formed are expected to be very small surrounded by much larger PVDF interfacial region or interphase. It seems then that the decrease in the crystallization rate of the PVDF molecules from the homogeneously mixed melt and the rapid quenching resulted in freezing these incipient crystallites of the PVDF. This region may have some molecular order but not so perfect like crystallites and such PVDF segments demixed with PMMA segments are mobile even below the glass transition of the mixed PVDF–PMMA amorphous phase. Above the T_g of the mixed phase, the crystallizable PVDF can start crystallizing, free from the restriction from the surrounding mixed amorphous region and therefore forms the well-developed crystallites and the crystal-amorphous interphase. So, the relaxation strength at the β relaxation becomes much smaller for the slow-cooled sample than that for the quenched one.

In the explanation above, it is important whether the incipient crystallites really exist in the apparently noncrystalline blend. In order to clarify the idea of the incipient crystallites of PVDF, we measured temperature dependence of small angle X-ray scattering (SAXS) for the quenched 60/40 blend between room temperature and 170°C. Though the results of the SAXS will be presented in detail, separately,[8] the scattering curves for the quenched 60/40 blend and the sample after annealing above the crystallization temperature are shown in Figure 8. A small but distinct long period of *ca.* 50 Å can be observed below T_g of the sample. At the temperature between 60 and 70°C, which is crystallization range, it became larger to *ca.* 190 Å and the scattering intensity increased due to the increase of the density contrast between the crystalline and the noncrystalline regions. Finally it disappeared at 169°C upon melting of PVDF crystallites. These results clearly confirm that

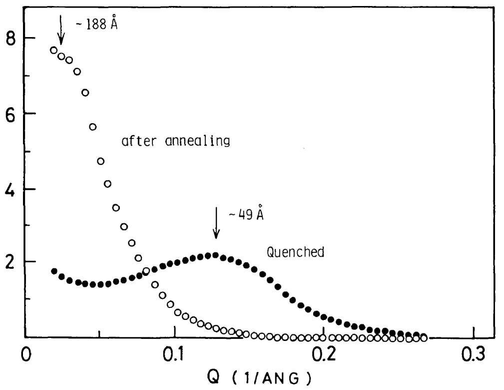

Figure 8. SAXS scattering curves for the quenched 60/40 PVDF/PMMA and the sample after annealing at *ca.* 80°C.

there is a phase separation with the characteristic length of *ca.* 50 Å in the quenched 60/40 blend, which is caused by the incipient crystallites that can not be detect by IR shown in Figure 4(a). Moreover, the large disparity in the relative amount of the crystalline *versus* interfacial region then implies that these incipient crystallites are not lamellar, but most likely to be more spherical. Indeed, this is consistent with the recent observation of Hsu and Geil,[9] who reported non-lamellar microcrystalline (or micellar) PVDF crystallites in thin PVDF films which were prepared by warming the previously ultraquenched glassy sample.

Recently, Saito *et al.*, reported the existence of a upper critical solution temperature (UCST) in PVDF/PMMA blends, based on the observation of microscopic and dynamic mechanical measurements.[10] We also carried out the dielectric measurements of similar samples as described in their publication. Following their method, after 70/30 PVDF/PMMA blend was melted at 210°C for 30 min, the blend was cooled to 150°C with cooling rate of 1°C min^{-1}, which is above the UCST, and then annealed for 9 hours at this temperature. After annealing, the sample was quenched in liquid N_2 and then the dielectric measurement was carried out from -110 to 150°C. However, we could not confirm the existence of the UCST, since we only observed the β relaxation of the PVDF crystal-amorphous interphase and the β' relaxation of the mixed PVDF–PMMA, very close to those of the slow-cooled blend.

CONCLUSION

The discussions above clarifies convincingly that the phase separation between the PVDF phase and the mixed PVDF–PMMA amorphous region occurs upon quenching the homogeneously mixed melt in the blends with relatively high PVDF content. The phase separation becomes apparent by the measurement of the dielectric relaxations and small angle X-ray scattering, and it seems to be caused by mainly two reasons; one is the slow crystallization rate of the PVDF in the blends and the other is rather high glass transition temperature of the homogeneously mixed region. Furthermore, one may also conclude that crystallization of polymers at large supercoolings is more likely to result in non-lamellar (micellar) crystallites that contain substantial amounts of interfacial region, of considerably large volume fraction than those of slow-crystallized, lamellar semicrystalline samples. This conjecture seems to be supported by available experimental results on isotactic polypropylene, for example.[11,12]

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