Open-circuit thermally stimulated current of PVDF/PMMA blends

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The influence of the structure of blends of semicrystalline poly(vinylidene fluoride) (PVDF) and amorphous poly(methyl methacrylate) (PMMA) on their electret properties was investigated in detail. Corona charged samples were studied by means of the open-circuit thermally stimulated current (t.s.c.) technique. In addition, direct current conductivity measurements were made. The t.s.c. thermograms of amorphous blends were found to exhibit a dipole orientation peak at the glass transition, the position of which was sensitive to the composition of the blend. A second t.s.c. peak was found to be related to the conductivity. A tentative interpretation of the t.s.c. diagrams of the semicrystalline blends is based on the occurrence of Maxwell–Wagner–Sillars charges at the interface between crystalline and amorphous regions.

(Keywords: poly(vinylidene fluoride); poly(methyl methacrylate); blends; electret properties; open-circuit thermally stimulated current; dipoles; glass transition; conductivity; interfacial charge trapping)

INTRODUCTION

The application of amorphous or partially crystalline polymers as electrets requires knowledge of the conductivity of the polymers, of their charge storage capability and of charge decay as a function of temperature and time. It has been known for some time that electret properties depend on details of the structural and dynamical properties of the polymer on both molecular and supermolecular level. Investigations concerned with the dependence of electrical properties on structure are, however, sparse. Appropriate model systems are required to obtain definite conclusions. Blends of two chemically different polymers that are partially compatible comprise such model systems. We chose blends consisting of amorphous poly(methyl methacrylate) (PMMA) and semicrystalline poly(vinylidene fluoride) (PVDF). The two polymers differ strongly in their glass transition temperatures, i.e. in their dynamical properties as well as in their structural properties.

PVDF/PMMA blends are compatible in the molten state at all compositions and form a homogeneous one phase melt[1-5]. This state can be frozen in by quenching the melt to room temperature, provided that the concentration of PVDF stays below about 60 wt%. The glass transition temperature is found to vary approximately linearly with composition between those of the pure components, i.e. ~ 105°C for PMMA and -40°C for PVDF. The blends that contain a higher amount of PVDF, or are slowly cooled from the melt or annealed below 170°C develop a crystalline PVDF phase, which preferentially displays the α- (or II-) modification. There is some controversy about the nature of the amorphous regions in the partially crystalline PVDF/PMMA blends. Dynamical (dynamical mechanical and dielectric) as well as structural (absolute small-angle X-ray) studies indicate that the amorphous state in blends with volume fractions of PVDF > 0.5 contains two phases[2,5-7]. The two phases contain amorphous PVDF and homogeneously mixed PVDF/PMMA, respectively.

The dynamical properties of the blend depend on those of its compounds. The dielectric relaxation processes that take place in PVDF are a high temperature α-relaxation, which is generally attributed to molecular motions in crystalline regions or at the crystalline–amorphous boundaries, the β-relaxation related to the glass transition, and the γ-relaxation arising from local motions of the frozen-in main chains in the amorphous regions[8-10]. PMMA exhibits an α-relaxation at the glass transition temperature, i.e. at about 105°C, and a β-relaxation, which is coupled with the mobility of the ester side group and is located at ~ -35°C for the t.s.c. frequency range[11].

In this paper results are presented of open-circuit t.s.c. measurements obtained for PVDF/PMMA blends. The results will be discussed with respect to the correlation between structural as well as dynamical properties and electrical properties of multiphase polymers. This particular t.s.c. technique allows detection of low frequency behaviour as well as the surface charge decay caused by thermally activated mobility of charge carriers.

EXPERIMENTAL

Materials

The polymers used were PVDF Solef X8N (Solvay, Solingen; $\bar{M}_n = 38\,000$; $\bar{M}_w = 100\,000$) and atactic PMMA 8N (Röhm, Darmstadt; $\bar{M}_n = 60\,000$; $\bar{M}_w = 120\,000$). After mechanically mixing and melt blending the components at 200°C, films of thicknesses between 40 and 60 μm were extruded. In addition, films with a thickness of 100 μm were moulded from the PMMA homopolymer. After annealing at 120°C for 1 h the crystallinity of the blends with 100, 90, 80, 60 and 40 wt% PVDF was 0.43, 0.34, 0.26, 0.15 and 0.05 wt fraction, respectively, as obtained from wide-angle X-ray scattering. A set of the blends with

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weight fractions of PVDF that exceeded 0.6 was uniaxially stretched by 400% at 85°C to induce an $\alpha \rightarrow \beta$ crystalline modification. The samples were stored at standard conditions (50% r.h., 23°C), and coated on one or both sides with 1000 Å of aluminium to act as an electrode, by vapour deposition.

Techniques

The poling that precedes the t.s.c. measurement was performed by a point-to-plane corona discharge with a wire mesh to control the surface potential, and by thermopoling, respectively. The poling time was 10 min. The surface potential was adjusted for each particular thickness of the sample to a value which provides a field strength of $100\,\mathrm{kV\,cm^{-1}}$. The magnitude of the surface potential was verified by a Monroe model 244 electrostatic voltmeter. For the t.s.c. and the conductivity measurements the samples were placed, in an electrostatically shielded chamber, on a plate of copper, the temperature of which was controlled. The t.s.c. heating rate was $3\,\mathrm{K\,min^{-1}}$. The release of the charges induced on a metal plate placed above the surface of the sample during the t.s.c. run was measured by a Cary model 401 vibrating reed electrometer.

For the direct current (d.c.) bulk conductivity measurements an electrical field of $5\,\mathrm{kV\,cm^{-1}}$ was applied and the current flowing through the sample was determined by a Keithley model 616 electrometer after 15 min. However, this was insufficient to give rise to a steady state current. Nevertheless, the frequency range thus tested corresponds to the time scale of the t.s.c. measurements. The samples had been provided with a guard ring of evaporated aluminium to prevent surface leakage currents. The t.s.c. and conductivity measurements were performed at least twice for each blend with virgin samples. The t.s.c. peak temperatures were reproducible within ±2 K. The variations of the conductivity of a blend appeared to be <10%.

OPEN-CIRCUIT T.S.C. MEASUREMENTS

Figure 1 shows the thermally stimulated current spectra of the blends with a wt fraction of PVDF ≤ 0.8. These blends are amorphous or are characterized by a negligible degree of crystallinity. The samples were corona charged at room temperature. The thermograms exhibit two individual peaks, the temperatures of which are sensitive to the blend composition. These temperatures are listed in *Table 1*. The nature of the two peaks will be described below.

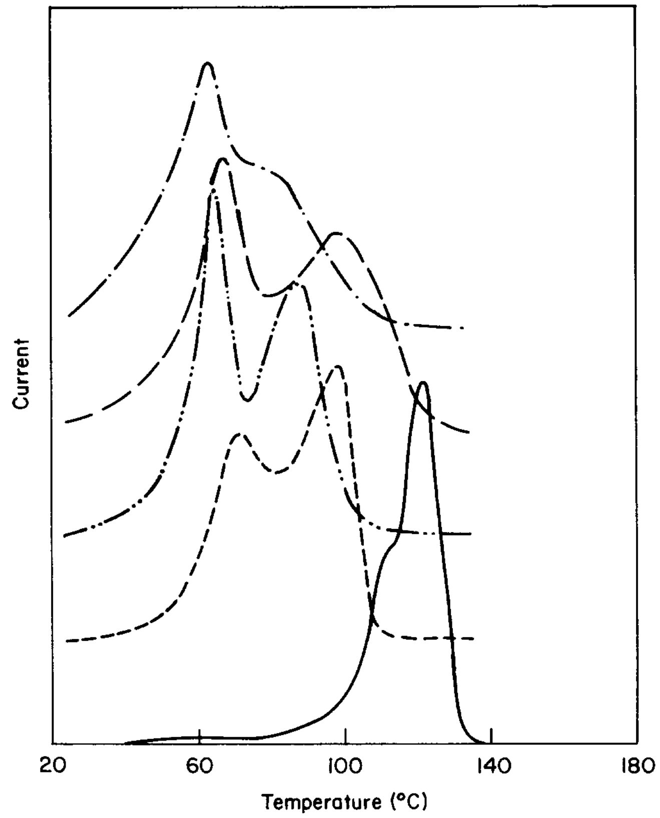

Figure 1 Open-circuit t.s.c. for PVDF–PMMA blends for various blend compositions. (———) 0; (— —) 20; (–··–··–) 40; (-----) 60; (–·–·–) 80 wt% PVDF. Poling temperature: 23°C; poling field: $100\,\mathrm{kV\,cm^{-1}}$; t.s.c. heating rate: $3^{\circ}\mathrm{C\,min^{-1}}$

Table 1 Temperatures of open-circuit t.s.c. peaks

PVDF–PMMA (wt%)	T_{I} (°C)	T_{II} (°C)
0–100	107	120
20–80	71	95
40–60	65	85
60–40	66	95
80–20	61	70

Dipole relaxation peak of the amorphous blends

The low temperature relaxation observed in the t.s.c. measurement of the PVDF/PMMA blends (*Figure 1*) can be attributed to dipole orientation taking place at the common glass transition temperature of the homogeneously mixed phase. The dipoles become aligned in the electrical field of the surface charge, whereby they reduce the surface potential.

The glass transition temperature of a polymer blend can be predicted by the mixing rule of Couchman[12]:

$$\ln T_g = \frac{\sum_i \Delta c_{pi}\phi_i \ln T_{gi}}{\sum_i \Delta c_{pi}\phi_i}$$

T_{gi} is the glass transition temperature of the homopolymer, ϕ_i is its mass fraction and Δc_{pi} is its glass transition increment of isobaric heat capacity. This expression predicts that the glass transition temperature of the blends containing 60 and 80 wt% PVDF should be 44 and 13°C, respectively. The values used for Δc_p(PMMA) and Δc_p(PVDF) are $7.2\,\mathrm{cal\,g^{-1}}$ and $3.6\,\mathrm{cal\,g^{-1}}$, respectively[5]. These values, which should be characteristic for a single phase homogeneous blend, are located considerably below the temperatures T_{I} obtained by the open-circuit t.s.c. measurements. These are 66°C and 61°C, respectively. This discrepancy is attributed to a partial phase separation that has occurred in these blends in agreement with data in the literature[5,6]. The weight fractions of the incompatible non-crystalline PVDF in the blends with an overall PVDF concentration of 60 and 80 wt% are estimated to be ~0.2 and ~0.4, respectively. These calculations are based on the observed degree of crystallinity and the location of the glass transition temperatures as determined by open-circuit t.s.c.

The onset of mobility of the dipoles both of PVDF and of PMMA at the common glass transition temperature corresponds to a stepwise change of the dielectric constant of the material. This dielectric relaxation strength of the blend is related to the volume fractions and to the relaxation strengths of the components in the homogeneously mixed phase[13]. The relaxation strengths, at their glass transition temperatures, of semi-crystalline PVDF[10] and PMMA[14] are ~5 and 0.8, respectively. The relaxation strength of pure amorphous PVDF should be even larger. Thus the intensity of the dipole peak, relative to the total magnitude of the surface charge decay, is mainly influenced by the PVDF concentration in the homogeneously mixed phase, in agreement with the experimental data.

If the charging temperature is raised up to and above the temperature of the dipole relaxation this peak decreases and finally vanishes; this is shown in *Figure 2* for a blend of 40 wt% PVDF and 60 wt% PMMA. The interpretation is that the dipoles have already become oriented during the poling process at elevated temperatures so that they are no longer able to cause a decay of surface charge during the subsequent t.s.c. measurement. For elevated poling temperatures only the high temperature peak develops, which can be attributed to another mechanism of surface charge decay, which is discussed in the following section.

The high temperature peak of the amorphous blends can be attributed either to drift of surface charges into the sample or to neutralization by intrinsic charge carriers. In any case, it is the conductivity that controls the motion of charges as a function of temperature. The t.s.c. peak will occur at a temperature for which the relaxation time characteristic of the motion of charge will correspond to the characteristic time scale of the experiment. This is of the order of $10^{-3}\,s^{-1}$, so that the peak expectedly occurs at temperatures for which the conductivities of the various blends are approximately identical.

To test these assumptions conductivity measurements were made as a function of temperature and composition (*Figure 3*). It is observed that the conductivity is an increasing function of the temperature and of the volume fraction of PVDF in the blends. All the blends exhibit an conductivity of comparable magnitude at those temperatures at which the high temperature t.s.c. peak occurs. It is of the order of $2\times10^{-15}\,\Omega^{-1}\,cm^{-1}$. With this conductivity value and with the dielectric constant of the blends of about 7 (ref. 7). the calculated charge relaxation time $\tau=\varepsilon_0\varepsilon/\sigma$ is 5 min, which agrees with the time constant of the t.s.c. experiment.

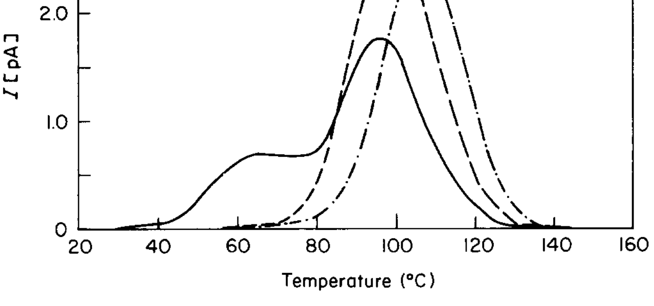

Figure 2 Open-circuit t.s.c. for 60 wt% PMMA and 40 wt% PVDF for various poling temperatures. (———) 40°C; (- - -) 80°C; (-·-·-) 100°C. Absolute value of the current signal of the curve for $T_p=100°C$ was thickness-corrected

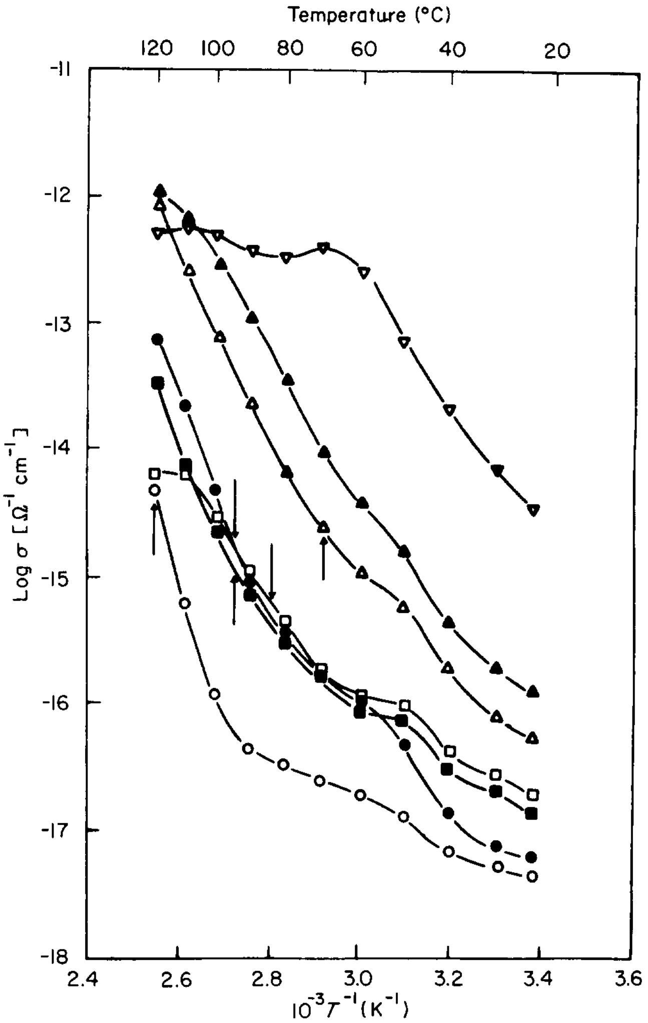

Figure 3 Temperature variation of direct current bulk conductivity of PVDF–PMMA blends for various blend compositions. (○) 0; (●) 20; (□) 40; (■) 60; (△) 80; (▲) 90; (▽) 100 wt% PVDF. Arrows indicate the temperatures at which the open-circuit t.s.c. peaks are located

Superimposed on the surface charge decay, owing to conductivity, is the disorientation process of the dipoles that were oriented during low temperature decay of surface charge.

Surface charge decay of the semicrystalline blends

The open-circuit t.s.c. thermograms of the blends with a PVDF fraction of ⩾0.8, are expected to reflect the electrical properties of the PVDF crystals as well as of the crystalline–amorphous boundaries in addition to those of the amorphous regions. Thermograms of the 90/10 wt% PVDF/PMMA blend, which was uniaxially stretched, will be used to discuss the main features in *Figures 4–7*.

Figure 4 shows the open-circuit t.s.c. diagrams of these blends, charged at different temperatures. The surface charge decay peak that is related to conductivity shifts to higher temperatures. Apart from this, the surface charge decays in two steps for the blends which were charged at elevated temperatures. The nature of the high temperature peak will be discussed later.

Figure 5 displays the temperatures at which the t.s.c. peaks occur as a function of the poling temperature. The additional charge decay at higher temperatures occurs just above the poling temperature.

The peak area of the high temperature charge decay, relative to the total sum of the peak areas of the t.s.c.

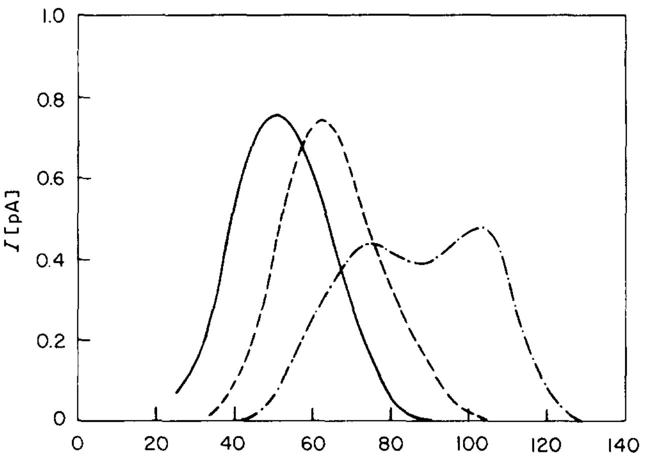

Figure 4 Open-circuit t.s.c. for 10 wt% PMMA and 90 wt% PVDF (stretched samples) for various poling temperatures. (———) 24°C; (– – –), 80°C; (–·–·–) 100°C. Poling field: 100 kV cm^{-1}

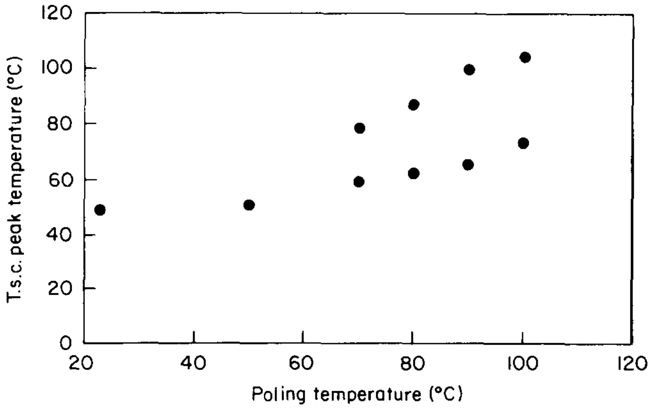

Figure 5 Open-circuit t.s.c. results for the blends of 10 wt% PMMA and 90 wt% PVDF (stretched samples). Variation of temperatures of the t.s.c. peaks with the poling temperature

thermogram, is plotted as a function of the poling temperature in *Figure 6* where the parameters are the blend composition and the sample treatment. For the 90/10 wt% PVDF/PMMA blend, which was uniaxially stretched and poled at a temperature of 100°C, the relative magnitude of the high temperature peak amounts to 0.5 as is clear from *Figure 6* and also from *Figure 4*.

For the discussion of the nature of the high temperature peak it is assumed that the predominant charge transport in the blends is of an ionic nature, at least at the elevated charging temperatures. This assumption is supported by the conductivity measurements, which reveal a strong increase in conductivity for PVDF/PMMA blends in the vicinity of their glass transition temperatures. It is concluded that the amorphous matrix has a higher conductivity than the dispersed crystalline regions, for which the probability of ion jumping occurring is small. The current flow through the sample will be accompanied by an accumulation of Maxwell–Wagner–Sillars interface charges[15–17] at the crystalline–amorphous boundaries. These charges form a macroscopic polarization with similar sign to that of the poling charges and their release will be apparent in the open-circuit t.s.c. thermogram. The level of these interface charges is expected to increase with the size of crystalline–amorphous interface, with the difference in the conductivity of the crystalline and the amorphous regions, and with the magnitude of the current flowing through the sample.

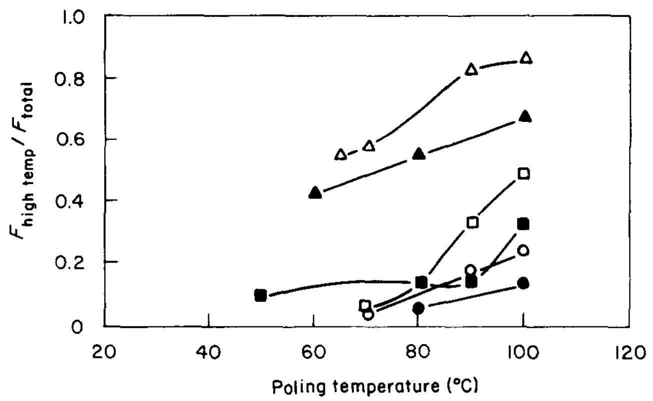

Figure 6 Relative magnitude of the high temperature t.s.c. peak as a function of the poling temperature for various blend compositions and sample treatments. (▲) 100; (■) 90; (●) 80 wt% PVDF; (△, □, ○) corresponding stretched samples

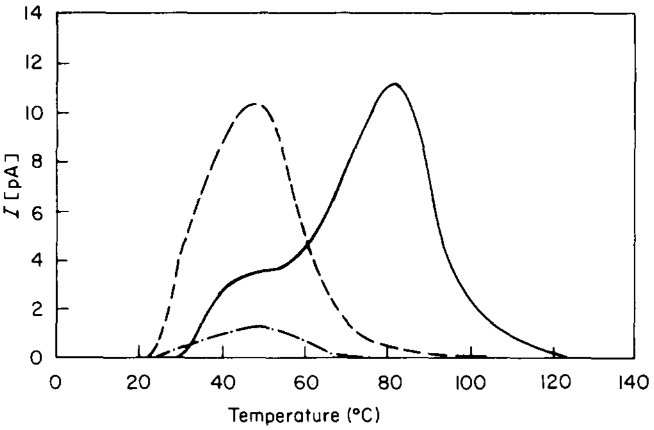

Figure 7 Open-circuit t.s.c. for blends of 10 wt% PMMA and 90 wt% PVDF (stretched samples) for various poling field strengths. (–·–·–) 0.1 MV cm^{-1}; (– – –) 1 MV cm^{-1}; (———) 1.5 MV cm^{-1}. Poling temperature: 23°C

The thermograms of *Figures 4–6* show that the variations of the structure and of the poling conditions influence the magnitude of the high temperature peak as expected for the appearance of interface charges. The magnitude of the high temperature peak increases with increasing charging temperature and with PVDF concentration in the blends; the latter is related to the volume fractions of crystalline and amorphous PVDF, i.e. to the magnitude of the crystalline–amorphous interface area and to the ion mobility in the amorphous component.

In addition to the formation of interface charge, owing to different conductivities and dielectric constants of the structural components, the polarity of the crystalline regions may cause trapping of charge carriers at the interface. Thermopoling or poling with high electrical fields, which typically amount to 1 MV cm^{-1}, are well known techniques for inducing a permanent dipole orientation in PVDF crystals of the β-form[18,19]. The strong dipole polarization of the crystalline regions enhances the charge carrier trapping at the crystalline–amorphous interfaces as suggested by a number of authors[19,20] in discussions of the piezo- and pyroelectric properties of PVDF.

An increase of the high temperature relaxation is observed for the thermopoled samples with polar β-crystals relative to those containing crystals in the α-modification as is obvious from *Figure 6*. Similar results were obtained for samples that were corona charged with various field strengths. In the thermograms of *Figure 7* the uniaxially stretched 90/10 wt% PVDF/PMMA blend exhibits a strong increase of the high temperature peak as soon as the poling field surpasses a value of 1 MV cm^{-1}. This peak is believed to indicate a larger number of interface charges, which accumulate as soon as the orientations of dipoles occur in the crystals and which become released during the t.s.c. run.

CONCLUSIONS

The conductivity and the charge storage behaviour of PVDF/PMMA blends are strongly affected by variations of the structure, especially of the composition of the amorphous components, of the magnitude of the crystalline–amorphous interface and of the crystalline modification. The open-circuit t.s.c. measurements revealed, in particular, the invariance of the temperature of the dipole relaxation, i.e. the glass transition temperature of the homogeneously mixed phase in the blends, with volume fractions of PVDF between 0.4–0.8. This indicates the presence of an amorphous phase separated PVDF component.

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