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Electrical polarization phenomena, dielectric relaxations and structural transitions in a relaxor-ferroelectric terpolymer investigated with electrical probing techniques

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Abstract

Dielectric Relaxation Spectroscopy (DRS) and Thermally Stimulated Depolarization Current (TSDC) measurements were employed to study dielectric-relaxation processes, structural transitions and electric-polarization phenomena in poly(vinylidenefluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) terpolymer films. Results from DRS confirm the existence of two separate dispersion regions related to a para-to-ferroelectric phase transition and to the glass transition. The dipolar TSDC peak correlates with the loss peak of the α relaxation that represents the glass transition. The electric polarization calculated from the dipolar TSDC peak (glass transition) shows a non-linear electric-field dependence and saturates at high electric poling fields. As the observed behaviour is essentially the same as that of the electric polarization obtained from direct polarization-versus-electric-field hysteresis measurements, TSDC experiments are also suitable for studying the polarization in relaxor-ferroelectric polymers. A saturation polarization of 44 mC m$^{-2}$ was found for an electric field of 190 MV m$^{-1}$.

1. Introduction

Polyvinylidene fluoride (PVDF) relaxor-ferroelectric (R-F) terpolymers based on copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) plus a partially chlorinated and fluorinated third monomer, such as chlorotrifluoroethylene (CTFE), chlorodifluoro-ethylene (CFE) or chlorotrifluoro-ethylene (CTFE), attracted significant scientific interest in recent years because of their particular relaxor-ferroelectric behaviour and also due to the possibilities to adjust their nanostructure and their relevant properties via control of the monomer ratio and of the processing conditions. The relaxor-ferroelectric (R-F) terpolymers exhibit a very low (Curie) temperature $T_C$ for their ferroelectric-to-paraelectric (F-P) transition—similar to that of ceramic R-F materials such as lead magnesium niobate (PMN) and lead lanthanum zirconate titanate (PLZT) [1]. At room temperature, the R-F terpolymers also show larger piezoelectricity and higher dielectric permittivity in comparison to non-R-F polymers, which makes them very attractive for actuator applications [2].

The development of VDF-based R-F terpolymers was partially driven by the desire to overcome shortcomings of other ferroelectric polymers such as their relatively low direct and inverse electromechanical responses. It was found that ferroelectric materials showed improved electro-mechanical properties when operated near their F-P transition region [3]. Thus, by reducing $T_C$, the applications potential of such materials can be strongly improved. Remarkable progress was achieved in 1985 by Odajima et al who showed that electron-beam irradiation of a P(VDF-TrFE) copolymer led to a significant reduction of its $T_C$ [4] and probably to the very first VDF-based relaxor ferroelectric polymer. In 1998, Zhang et al showed that high-energy electron-irradiated P(VDF-TrFE) (known as HEEIP) exhibits an electrostrictive strain of up to 4%, i.e. the highest
electromechanical response of all ferroelectric polymers known so far—comparable to that of conventional inorganic R-F materials [5]. Later, a similar effect was found by Chung et al who modified the P(VDF-TrFE) copolymer chains by including a third co-monomer with at least one chlorine atom [6].

Even though VDF-based R-F terpolymers are structurally relatively similar to the ferro-, pyro- and piezoelectric PVDF homopolymer and to the VDF-based copolymers P(VDF-TrFE), P(VDF-TFE) and P(VDF-HFP) (copolymer with hexafluoropropylene), they exhibit marked differences in their properties. In contrast to the VDF-based ferroelectric polymers which show a predominant polar ferroelectric phase with all-trans conformation at room temperature, VDF-based R-F terpolymers consist mainly of a non-polar paraelectric phase (mixture of Tγ⁺Tγ⁻ and Tγ⁺Tδ⁺Tγ⁻ conformations) due to sterical effects of the bulky chlorine atoms in the third monomer [7] that also interrupt the ferroelectric domains and reduces their linear dimensions to a few nanometers [8]. This also results in the decrease of Tc to ambient temperatures and gives rise to the very high polarization and electrostrictive strain found in these materials.

Previous studies have shown that both, the amount of the third monomer and the crystallization conditions strongly influence the various crystalline phases and the resulting crystalline morphology in P(VDF-TrFE-CFE) terpolymers which so far exhibit the highest electromechanical effects of polymeric R-F materials [8–12]. Therefore, it makes sense to study dielectric relaxation processes and structural transitions through the combined use of dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDCs). The results of such experiments provide new insight into the origins of the relaxor-ferroelectric behaviour of P(VDF-TrFE-CFE) terpolymer films and allow to better understand the underlying phenomena.

2. Experimental details

The terpolymer samples (obtained from Piezotech SA, France) had a VDF/TrFE/CFE composition of 55.5/37.2/7.3 mol%. The terpolymer powder had been produced by suspension polymerization with an oxygen-activated initiator at 40 °C under a constant pressure of 10 MPa [8]. Terpolymer films were prepared from the powder by drop casting an acetone solution onto glass slides. The solvent was allowed to evaporate at room temperature overnight. Subsequently, the films were annealed at 120 °C in vacuum for about 12 h before slow cooling to room temperature. Finally, the films were peeled from the glass substrate. Their resulting thicknesses were found to be between 20 and 40 μm. In addition, for TSDC measurements after poling at high electric field, terpolymer samples with a thickness of 4 ± 2 μm were prepared on aluminum-coated glass substrates by means of spin coating. As a reference, 20 μm thick P(VDF-TrFE) copolymer films with 75/25 mol% VDF/TrFE were prepared by means of drop-casting a solution of P(VDF-TrFE) powder from Piezotech S.A. (France) in acetonitrile. The spin-coated terpolymer and the drop-cast copolymer samples were also annealed at 120 °C.

For the DRS and TSDC measurements, the free-standing film samples were evaporated on both sides with aluminum electrodes (thickness about 60 nm). The electrical measurements were carried out under dry nitrogen in a Novocontrol Quatro cryosystem by means of a Novocontrol Alpha dielectric analyzer or a Keithley 6578 electrometer. Permittivity and dielectric loss were determined at temperatures from −60 to +50 °C in 2.5 °C steps over the frequency interval from 10⁻² to 10⁴ Hz on both co- and ter-polymer samples. For the TSDC measurements, the samples were poled at Tp = 40 °C for tp = 10 min with a DC field of Ep = 30 MV m⁻¹ and then rapidly cooled down to −60 °C under the electric field and finally short-circuited via the electrometer. The TSD current was recorded from −60 to +100 °C at a heating rate of 4 K min⁻¹. For dielectric-hysteresis measurements, a Sawyer-Tower circuit was used in which an alternating sine-wave voltage was applied to the sample at a frequency of 2.5 mHz.

3. Results and discussion

3.1. Dielectric relaxation spectroscopy

Figure 1 (a) illustrates the temperature- and frequency-dependent dielectric-relaxation spectra (real part) taken on a P(VDF-TrFE-CFE) terpolymer film. At room temperature, the permittivity shows a local maximum of ε' = 60 at 0.1 Hz, shifting to higher temperatures with increasing frequency. The appearance of a permittivity maximum with a value that is significantly higher than the static permittivity of PVDF (εstat ≈ 12) and its shift to higher temperatures with increasing frequency are typical features of a relaxor-ferroelectric material [1,8,10]. The associated dielectric-loss curves (figure 1(b)) indicate that the local permittivity maximum consists of two processes labelled as processes A and B. At 10 Hz, for instance, there is (1) a peak at about −5 °C (process B) and (2) a local maximum at +20 °C (process A). Process B shifts to higher temperatures with increasing frequency while it becomes more pronounced, which is typical for a relaxation process that is related to the glass transition. Process A, however, exhibits frequency-independent loss peaks that are characteristic of a structural transition [13]. The evolution of processes A and B with both temperature and frequency is shown as a 3D plot in figure 2.
Figure 1. (a) Dielectric-permittivity (real part) and (b) dielectric-loss (imaginary part) plots measured on a P(VDF-TrFE-CFE) terpolymer film as functions of temperature at frequencies between 10 mHz and 10 kHz.

Figure 2. 3D dielectric-loss plot (imaginary part of the permittivity) measured on a P(VDF-TrFE-CFE) terpolymer as a function of frequency and temperature.
At lower frequencies, processes A and B are superimposed by a strong increase of the dc-conductivity-induced loss (only partly shown). In the frequency range from 1 to 100 Hz, both processes A and B become clearly visible. At higher frequencies (typically $10^3$ and $10^4$ Hz), the intensity of process B increases, and finally process B merges with process A, and they form one combined peak.

Figure 3 shows the dielectric loss of a P(VDF-TrFE) film as a function of frequency and temperature. There are three processes in the loss plot at $10^4$ Hz (front edge of 3D plot): process A′, process B′ (corresponding to the similar processes in the terpolymer) and process C. Process B′ appears between $-40$ and $+20$ °C and shifts to higher temperatures with increasing frequency, corresponding to the $\alpha$ relaxation which is associated with the glass transition [13]. Process A′ manifests itself as a loss peak in the temperature range from 120 to 140 °C and is independent of frequency. Its corresponding permittivity peak is more clearly seen in the 2D plot of $\varepsilon'$-versus-temperature [9] and can be assigned to the F-P (Curie) transition [10, 16]. In comparison to the copolymer P(VDF-TrFE), it appears to be down-shifted in temperature [13, 14], which may be explained by the random incorporation of CFE groups into the main chain of P(VDF-TrFE) leading to a size reduction of ferroelectric domains from a micro- to a nano-scopic level [8, 11]. In case of the terpolymer, the temperature ranges of the glass transition and the Curie transition are not well separated. Therefore, processes A and B overlap—leading to one combined loss peak at higher frequencies (figure 1(b)).

3.2. Thermally stimulated depolarization currents

Figure 4 shows the TSDC thermograms of the terpolymer and the copolymer poled at $T_p = 40$ °C under a field $E_p = 30$ MV m$^{-1}$ for $t_p = 10$ min. On the terpolymer thermogram, three TSDC peaks can be identified: The first peak is found between 0 to 10 °C with a shoulder around $-16$ °C. This peak is supposed to be caused by the onset of segmental motions of the polymer chains in the amorphous phase and is usually called the $\alpha$ (or $\alpha_a$ subscript $a$ for amorphous) relaxation. Consequently, it should be related to relaxation process B as seen in DRS. The shoulder indicates that the glass transition is probably a two-step process. It becomes visible due to the very low

Figure 3. 3D dielectric-loss plot (imaginary part of the permittivity) measured on a P(VDF-TrFE) copolymer as a function of frequency and temperature.
equivalent frequency ($< 10^{-2}$ Hz) which allows for a higher resolution as in the $\varepsilon'$-versus-$T$ (dielectric-loss) plot—in accordance with the two-step glass transition found in DSC experiments before [9]. Such a non-uniform glass transition may arise from the different components of the terpolymer, showing more than one $T_g$ similar to the situation in a polymer blend. The dielectric process A does not manifest in the TSDC thermogram; it should have appeared at about 20 °C where a local minimum is seen. The peaks above 20 °C may arise from excess charges accumulated on internal boundaries (amorphous-crystalline or polymer-electrode interfaces). An interface polarization is commonly observed in semi-crystalline polymers such as PVDF [17]. Because these processes do not represent distinct molecular motions, they are not further considered here.

Considering the TSDC thermogram of the copolymer, there are marked differences to the terpolymer, such as a peak at about −40 °C, indicating the glass transition in accordance with the results from DRS measurements. Furthermore, a shoulder of unknown origin appears around 5 °C. Previously, for a similar VDF/TrFE composition of 75/25 mol%, in addition to a $T_g$ peak at −36 °C, a shoulder at 10 °C associated with an ‘upper’ $T_g$ was reported [14]. Thus, the copolymer also exhibits a non-uniform glass transition. The peak around 46 °C, slightly above the poling temperature, may again correspond to interface charges (cf [18]), and the sharp peak at 128 °C indicates the F-P or Curie transition.

The area under the TSDC curve is proportional to the induced dipole polarization. Figure 5 shows the polarization as a function of the poling field obtained by numerical integration of the respective dipolar-relaxation peak (upper integration limit 24.5 °C as indicated by the dashed line in figure 4) for spin-coated and drop-cast terpolymer films. The polarization shows a non-linear dependence on the poling field with a strong tendency to saturate. At first glance, the polarization values of the drop-cast and the spin-coated samples agree with each other, and they also agree with the values obtained in the dielectric-hysteresis measurements. In addition, the saturation polarization of 44 mC m$^{-2}$ obtained at a field strength of around 190 MV m$^{-1}$ from the TSDC measurement (spin-coated sample) is comparable to values found by other authors from hysteresis curves on P(VDF-TrFE-CFE) terpolymers with similar composition [8]. Thus, TSDC is also a reliable method for determining electric polarization in polymer films. Moreover, an advantage of TSDC is that contributions stemming from excess charges can be separated from the dipolar polarization [18].

More precisely, the polarization obtained from TSDC experiments should agree with the initial polarization curve obtained during the first poling cycle of the hysteresis measurement, where the applied electric field induces a finite polarization in the material—starting from an initial zero value, then increasing non-linearly, and finally reaching a saturation value. So, the TSDC-related curve is expected to fit inside the hysteresis loop shown in the figure. The slightly higher polarization values obtained here may be due to the higher poling temperature of 40 °C for the TSDC measurements, whereas all hysteresis experiments were performed at room temperature.
4. Conclusions

In this study, dipolar relaxations and structural transitions occurring in a relaxor-ferroelectric VDF-based terpolymer were investigated in detail by means of DRS and TSDC experiments. Annealed free-standing as well as spin-coated films of a 55.5/37.2/7.3 mol% VDF/TrFE/CFE terpolymer were examined, and P(VDF-TrFE) copolymer samples with a 75/25 mol% VDF/TrFE composition were used as reference. The dielectric spectra revealed two processes (processes A and B) which superimpose at higher frequencies. Process A corresponds to a low-temperature shifted ferro-to-paraelectric phase transition occurring at a temperature which is determined by the terpolymer composition and which does not show a frequency dependence. Process B has its origin in the glass transition in the amorphous phase, giving rise to a so-called \( \alpha \) relaxation. TSDC measurements indicate a non-uniform glass transition as previously observed on polymer blends as well. The dipolar-relaxation TSDC peak was used to calculate the polarization in the terpolymer as a function of applied electric field. The polarization values calculated from TSDC measurements agree well with those obtained from the polarization- versus- electric-field hysteresis. Consequently, TSDC experiments may be used to determine polarization values in relaxor-ferroelectric polymers (and possibly also in ferroelectric polymers).

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