



Effect of chemical interactions in the metal–F system on the electric properties of fluoroelastomers

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The characteristics of low-frequency dielectric relaxation at high temperatures in poly(vinylidene fluoride) (PVDF) and copolymers of VDF with hexafluoropropylene HFP are discussed; this relaxation is localised near the melting temperatures, characterised by a giant strength of relaxation and attributed to the accumulation of spatial charge (presumably H^+ and F) at electrode boundaries. For Al electrode, dispersion is controlled by the concentration of CF_3 groups in the polymer; this fact should be related to formation of specific fluorine-aluminium compounds and the capacitance of the double electric layer is considerably controlled by formation of AlF_3 groups at the boundary of the polymer melt with the electrode.

Poly(vinylidene fluoride) (PVDF) and its copolymers are soft-chain crystalline polymeric dipole ferroelectrics,^{1,2} which have high piezo- and pyroelectric constants. Considering the specific properties of the plastics, this class of polymers may be recommended for various piezo- and pyrosensors.^{1,3} Upon special modification of their structure, these polymers show huge electrostriction.⁴ The high chemical stability and low glass transition temperatures T_g of these polymers allow them to be used as components of gel-polymer electrolytes for lithium current sources and in fuel cells with protonic conductivity.⁵

In this work, the high-temperature electrical properties of VDF copolymers with a high content of hexafluoropropylene (HFP) were studied. Films with 7 and 14 mol% HFP⁶ were obtained by extrusion; X-ray diffraction shows that they crystallise in the α -polymorphic modification.⁷ To measure electrical properties, an Al layer 100 nm thick was applied to the films using vacuum deposition. The dielectrical properties of copolymers were studied in isothermal mode using a Novocontrol spectrometer in the frequency range 10^{-1} – 10^7 Hz at 100–150 °C.⁸ The melting transition of the polymers was studied using dif-

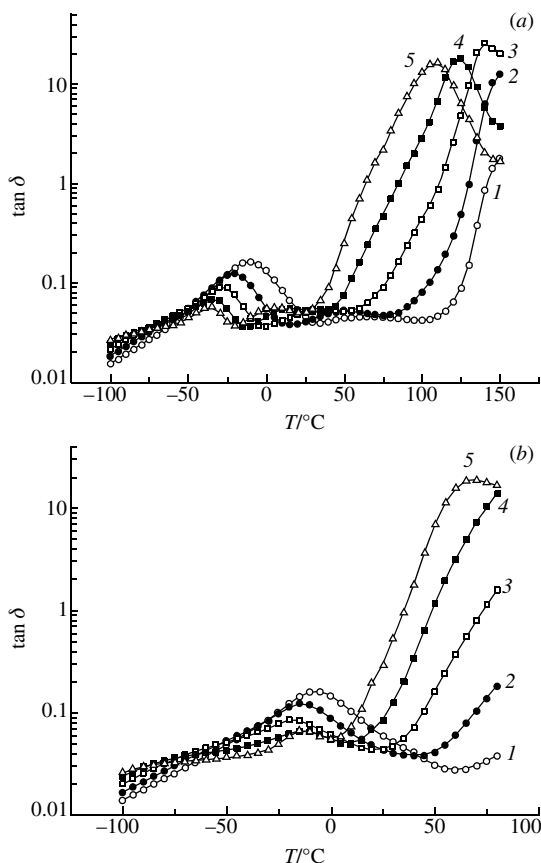


Figure 1 Temperature dependence of dielectric loss angle tangent in the films of VDF/HFP copolymers with compositions (a) 93:7 and (b) 86:14; (1) 10^4 , (2) 1.3×10^3 , (3) 1.2×10^2 , (4) 10 and (5) 1.3 Hz.⁸

ferential scanning calorimetry. The thermal effects were measured using a Perkin-Elmer DSC-7 calorimeter at a heating rate of 20 K min⁻¹.

Figure 1 shows the temperature–frequency plots of dielectric loss angle tangent $\tan \delta$ for both of the copolymers. At high temperatures, there is an α relaxation process, which corresponds to the melting region as a comparison with DSC data shows. Its intensity is more than an order higher than that for other (lower-temperature) transitions. This is untypical of dipole relaxation processes; therefore, there is a reason to relate it to a spatial charge that may be formed by ionic admixtures. Published data show that a transition with similar characteristics was also observed previously for PVDF.^{9,10} This process was related to electrode polarisation involving the formation of a double electrical layer at the electrode interface. According to the theory, the ionic contribution to the real (ϵ') and imaginary (ϵ'') components of the complex dielectric constant has the forms:^{9,10}

$$\epsilon'_i = \frac{2\nu_0 q^2}{dkT\sqrt{\pi}} \left(\frac{D_0}{f} \right)^{3/2} \exp \left[- \left(\frac{3E_d}{2} + \frac{W}{2\epsilon_0} \right) / kT \right]; \quad (1)$$

$$\epsilon''_i = \frac{2\nu_0 q^2}{kT} \left(\frac{D_0}{f} \right) \exp \left[- \left(E_d + \frac{W}{2\epsilon_0} \right) / kT \right], \quad (2)$$

where ν_0 is the concentration of mobile ions with charge q_0 , d is the specimen thickness, D_0 is the diffusion coefficient, f is the electric field frequency, E_d is the diffusion activation energy for the ion, and W is the dissociation energy of admixture molecules. Since the test process involves the accumulation of charges at the polymer–metal interface, its characteristics change when electrodes are blocked.¹⁰ For our data, it is necessary to introduce the ‘electrode blocking factor’ concept. In crystalline polymers, a part of the volume is occupied by crystals. They have denser packing, hence the carriers will move through the amorphous phase. The mobility of free charges will be determined by the character of dynamics in amorphous polymer regions.

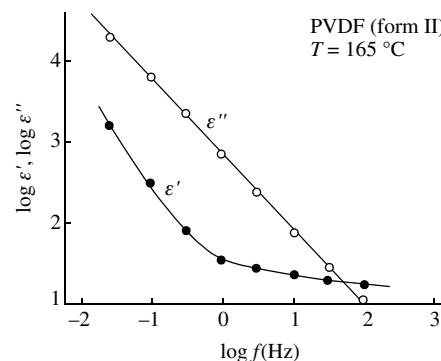
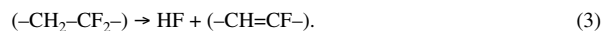


Figure 2 Low-frequency dependence of the real (ϵ') and imaginary (ϵ'') components of dielectric constant in a PVDF film crystallised in the α (form II) polymorphic modification.¹⁰

Clearly, this mobility will be intensified above the glass transition point T_g where cooperative motion is characterised by high amplitudes of reorientation of chain segments. In this case, an increase in temperature will favour an increase in the mean frequencies of such motions. This should increase the mobility of extrinsic carriers. At temperatures $T_g < T < T_m$ (where T_m is the melting point), a part of the crystals contacts the electrode; hence, at first approximation, the degree of its blocking equals the degree of crystallinity. The crystallinity decreases on melting and hence a decrease in electrode blocking should be expected. Polymers are usually characterised by a broad melting range, and the degree of blocking will decrease in this range with temperature. It is the reason of the increase in the electrode surface where the double electric layer can form at the metal–polymer interface. In the problem of interest, the nature of extrinsic carriers is of importance. According to published data,^{9,10} these are Na, Ca, Al, S and Cl ions. In our opinion¹² and according to other data,¹¹ the carriers in the polymers of interest should involve H^+ and F^- ions formed upon dissociation of HF molecules, which are generated at elevated temperatures by the reaction:



A goal of this study is to compare the quantitative characteristics of the α -transition in the homopolymer^{9,10,13} and the VDF/HFP copolymers. Figures 2 and 3 show the dispersion curves recorded at similar temperatures in the α -relaxation region. A comparison shows that the low-frequency values of ϵ' are much lower for PVDF than for copolymers. What is more, as follows from Figure 3, an increase in the fraction of HFP (increasing concentration of CF_3 groups) in the copolymer increases considerably the ϵ' values. Presumably, this occurs due to the abstraction of a fluorine atom under the effect of the electrode metal (Al). The possibility of this abstraction was confirmed by XPS in a study¹⁴ of interactions between metals

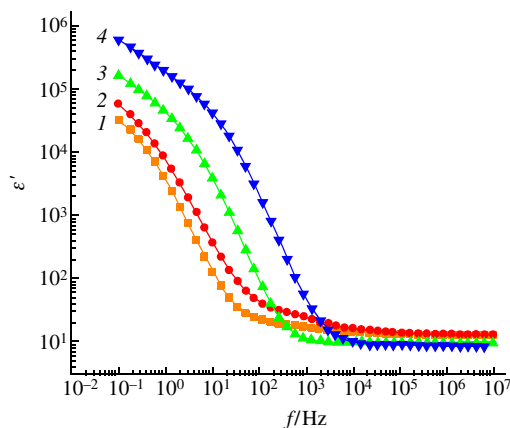


Figure 3 Low-frequency dependence of the real (ϵ') component of dielectric constant in (1), (2) PVDF and (3), (4) VDF/HFP copolymers with compositions (3) 93:7 and (4) 86:14 films crystallised in the α -polymorphic modification; $T = 140^\circ\text{C}$.^{12,13}

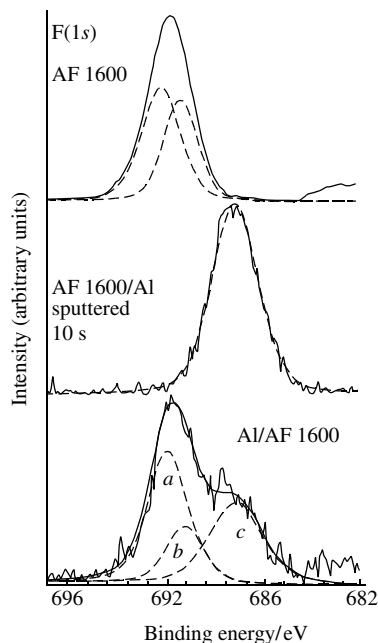
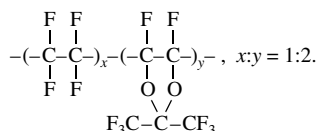


Figure 4 XPS F(1s) spectra of pure AF 1600 elastomer films and films with vapour-deposited Al (3 nm thick).¹³

and the amorphous fluoroelastomer AF 1600, the structure of which is the following:



Specific compounds are formed in the area where a contact with Al exists. Figure 4 shows the F(1s) spectra for the pure elastomer and its combination with Al. The upper diagram shows the spectrum of pure AF 1600, where the two peaks correspond, in the order of decreasing energies, to the absorption of CF₃ and COF, CF₂ groups, respectively. After vapour deposition of Al (3 nm thick) onto AF 1600, the original spectrum contains three components, one of which (c) is associated with AlF₃. After the layer of AF 1600 was sputtered away from this combined system, only one component remains, which is responsible for AlF₃ formed. A similar conclusion follows from Al(2p) spectra demonstrated in Figure 5. It shows the spectra of the Al–AF 1600 system, where the fluoroelastomer was spin-deposited onto the metal. The spectrum was monitored as the polymer layer was gradually removed. At short exposure times, the spectrum contains the c component, which is believed to be due to AlF₃. This compound disappears on long exposures, and only line a responsible for pure Al remains. The free energy decrease due to the formation of AlF₃ from Al and fluorine from CF, CF₂ or CF₃ groups amounts to –15.9, –58.1 and –135.4 kcal mol^{–1}, respectively.¹⁴ This means that Al mainly reacts with CF₃ groups.

These results suggest that interpretations of high-temperature relaxation processes in metal-coated fluoropolymers should take into consideration that new chemical compounds can be formed in the surface layer. It follows from the above data that reactions involving fluoropropylene groups are of importance in the case of an aluminium electrode. As noted above, the low-frequency dielectric α -dispersion increases abruptly on changing from PVDF to VDF/HFP copolymers (Figures 2, 3). This effect should be attributed to CF₃ groups, as one can see in Figure 3. It follows that an increase in the molar fraction of fluoropropylene groups in the copolymer increases the intensity of the observed relaxation region. Taking into account the above,

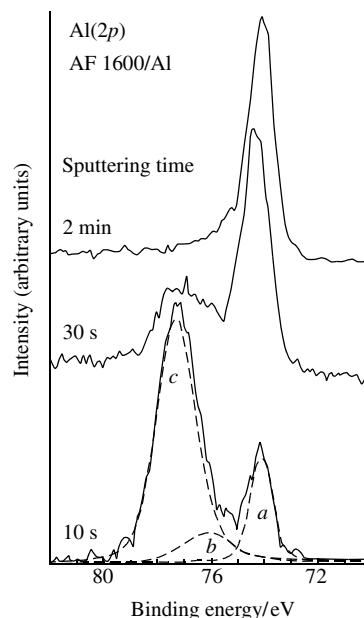


Figure 5 XPS Al(2p) spectra for the two-layered AF1600/Al system at different exposures of the fluoroelastomer.¹³

it may be concluded that the formation of AlF₃-type compounds at the electrode surface increases the capacitance of the double electric layer that is formed near the surface at high temperatures.

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