



Negative dielectric permittivity of poly(acrylic acid) pressed pellets



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ABSTRACT

Spontaneously formed temperature-frequency zone of negative dielectric permittivity $\epsilon' < 0$ was found in polymer-water system “poly(acrylic acid) + 3 wt% of moisture”. Nucleation and evolution of the zone is demonstrated on $\epsilon'(f,T)$, $\epsilon''(f,T)$ and $\text{tg}\delta(f,T)$ 3D plots. Bound water release at $T > 65$ °C is thought to be the reason of this phenomenon. The frequency width of the zone steadily increases with temperature up to $T = 83$ °C, and then sharply increases at low-frequency side. This effect might be related to the anomalies in temperature dependencies of thermodepolarization currents in water at 83 °C. Spontaneous manifestation of $\epsilon' < 0$ phenomenon indicates that one can expect it in natural materials, including biopolymers, i.e. in living organisms.

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1. Introduction

The possibility of creation of optical materials with negative dielectric permittivity and magnetic susceptibility was demonstrated as early as in 1968 [1]. Later it was shown that physical realization of negative values of dielectric permittivity $\epsilon' < 0$ in the expression for complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ does not contradict principles of causality and dispersive Kramers-Kronig relations [2,3]. In other words, counter motion of similar charges in dynamic systems is possible.

At the same time, USA National Bureau of Standards developed a new technique for measurements of complex dielectric permittivity at radio frequencies [4]. Measurements on series of strong electrolytes showed that negative dielectric permittivity is observed at certain frequencies. This phenomenon was explained using the following physical mechanisms: (i) there is an out-of-phase portion of the conductivity which appears as a negative dielectric permittivity; (ii) the carriers have inertial properties in contrast to the restoring force usually associated with dielectric polarization phenomena.

The first mechanism was found in nanostructures [5,6]. It induced the researchers to investigate solid state metacomposites including polymers with negative dielectric permittivity (see the review [7]). In the recent paper [8] negative dielectric permittivity is explained by oscillations of delocalized electron plasma. Different models of the phenomenon were presented in earlier papers [9–12]. The investigations are stimulated, on the one hand, by attempts to create non-wire inductivities, and, on the other hand, by searches for the new ways to control the properties of electrolytes, colloids and to control

biomembrane performance [6]. Since there are still no examples of natural polymers with negative dielectric permittivity, they were artificially made by incorporation of conductive ligands into polymer matrix [10] and development of nanocomposites [11].

In spite of progress in development of polymers with $\epsilon' < 0$, the second physical mechanism (ii), which is well studied in metals [2,3], was not observed and studied in polymer dielectrics.

This problem could be solved by investigations of spontaneous appearance of the effect of negative dielectric permittivity in dielectrics with known composition and consecutive studies of conditions of its appearance. This would allow to discover the mechanisms of the phenomenon and to find the ways to control it.

In our experiments we observed spontaneous nucleation and evolution of the process of formation of negative dielectric permittivity during investigations of dielectric properties of Poly(acrylic acid) (PAA) samples with different amount of absorbed atmospheric moisture. As far as we know, such peculiarities of dielectric properties of PAA haven't been observed and discussed earlier [13–18].

2. Materials and methods

2.1. Sample preparation

Poly(acrylic acid) powders (Aldrich, $M_w = 450,000$) with different moisture content were pressed in pellets with diameters of 13 mm and thicknesses of 1–1.5 mm at room temperature under pressure ~ 8 tons. To avoid effects of repolarization of surface layer, Toray carbon paper was used as electrodes. No traces of carbon diffusion into the surface of the samples were detected during the experiments. Shrinkage of the powder during the process of pressing indicates that there are deformations, mutual slip and internal friction of the powder grains at pressing. These processes inevitably lead to formation of

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tribo- and mechanoelectret state in the sample [19,20]. Measurements showed the existence of 1.5 V DC voltage on the electrodes. The analysis of the pellets' surface by scanning probe microscopy (SPM) revealed their porous structure (1–100 pores per $1 \mu\text{m}^2$) with typical pore size 50–100 nm and pore depth 1–15 nm

Three types of samples were investigated: dehydrated (sample 1), sample with 3 ± 1 wt% of moisture (sample 2) and sample with 8 ± 2 wt% of moisture (sample 3). The amount of moisture was determined by thermogravimetric analysis (TGA).

For preparation of dehydrated sample 1, thin layer of PAA powder was heated in muffle oven up to 120°C during 30 min, then kept for 1 h under this temperature, cooled down to 50°C and immediately pressed into pellets. According to literature, glass transition temperature of PAA powder is $T_g = 106^\circ\text{C}$. DSC measurements showed that the glass transition process begins at 104.5°C .

Moistened samples (2, 3) were pressed from powder that absorbed atmospheric moisture during storage. Some moisture might be lost during the process of pressing. No moisture absorption or moisture loss was detected during dielectric measurements.

2.2. Experimental methods

Dielectric measurements were performed on heating using broadband dielectric spectrometer Novocontrol Concept 40 in the frequency range 0.1 Hz–10 MHz and in the temperature range 2 – 140°C (with temperature steps 2 – 3°C). Dielectric parameters were measured with 1% accuracy. The voltage of the measuring field was 1 V. During the measurements the sample was kept in thermostat in dry nitrogen atmosphere. Each temperature point was stabilized with 0.02°C accuracy during ~ 10 min in order to reach the equilibrium state of the sample.

3. Experimental results

3D surfaces of three basic dielectric parameters (real ϵ' and imaginary ϵ'' parts of complex dielectric permittivity, dielectric loss tangent $\text{tg}\delta$) describing the evolution of dielectric properties of PAA samples at increasing moisture content are presented below. Fig. 1 presents temperature–frequency dependencies of basic dielectric parameters for dehydrated PAA sample 1.

Absolute values of dielectric parameters of PAA sample 1 at $f > 1$ Hz are typical for organic dielectrics: small value of dielectric permittivity in wide frequency and temperature ranges and small values of dielectric loss which increase only at infralow frequencies. The results are typical for polyacrylic polymers [15–17] and demonstrate weak dependence on the electrode material [21].

We assign the peculiarity on Fig. 1a at $T = 120^\circ\text{C}$ to the glass transition temperature T_g , which corresponds to reorganization of polymer structure. This value differs from the T_g value mentioned above for the PAA powder. It is well known that the T_g value depends on the polymer composition, thermal history, moisture content [15,16,22] and preceding mechanical influence, which, on our opinion, is the cause of the difference. At the same time, the samples with the molecular weight as in our samples demonstrate increased glass transition temperature [17].

Structural reorganization of polymer at glass transition is accompanied by sudden increase of ϵ' , ϵ'' and $\text{tg}\delta$ at $T > T_g$, as shown on Fig. 1. The extremum of dielectric properties at $f < 100$ Hz and 30 – 45°C is clearly seen on Fig. 1. We relate this peculiarity to the presence of cross-linked PAA.

polymer chains with glass transition temperature $T_g = 38^\circ\text{C}$ which is assigned to the delocalized cooperative molecular mobility of the main chain [23].

From the analysis of temperature positions of β -relaxation peaks (Fig. 1b) activation energy values in different temperature intervals were determined. Accurate determination of frequency positions of the β -peak (f_{max}) was difficult because of the presence of several

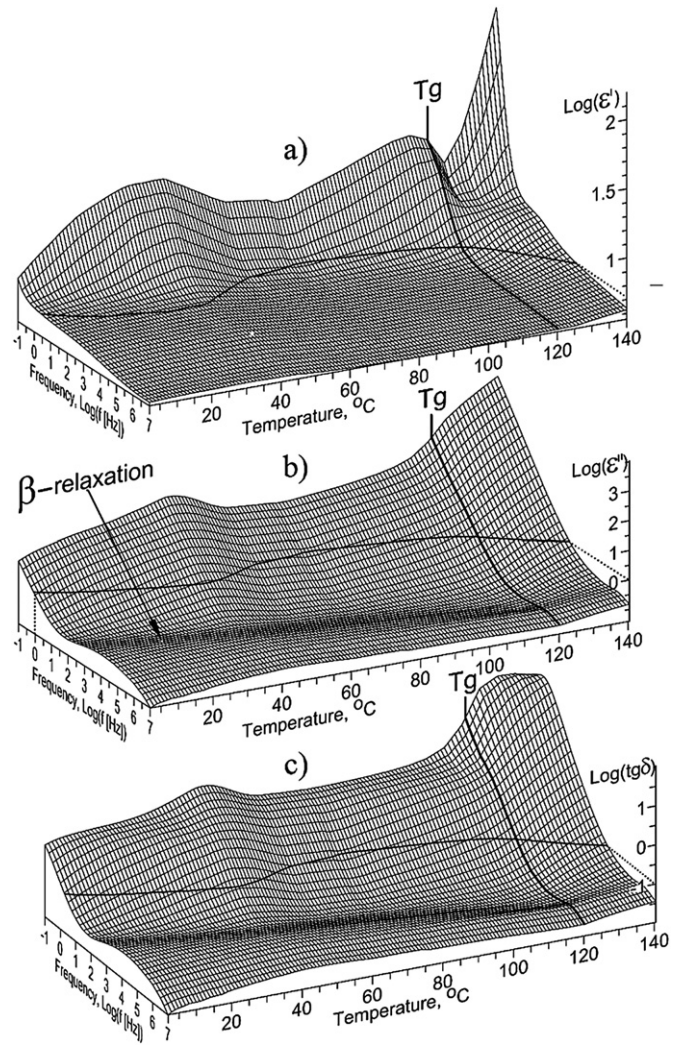


Fig. 1. Dielectric properties of dehydrated PAA sample (1): (a) $\log \epsilon'$ ($\log f, T$), the line is for $\log \epsilon' = 0.72$ ($\epsilon' = 5.25$); (b) $\log \epsilon''$ ($\log f, T$), the line is for $\log \epsilon'' = 0$ ($\epsilon'' = 1$); (c) $\log(\text{tg}\delta)$ ($\log f, T$), the line is for $\log(\text{tg}\delta) = -1$ ($\text{tg}\delta = 0.1$).

mechanisms involved in formation of $\epsilon''(f, T)$ dependence. This leads to deviations from classical Arrhenius law [17]

$$f_{\text{max}} = f_0 \exp(-E_a/kT) \quad (1)$$

where E_a is the activation energy, k is the Boltzmann constant, f_0 is the pre-exponential factor.

As seen from the Fig. 2, four temperature regions with constant activation energies were found. At $T = 120^\circ\text{C}$ (which is the T_g value obtained from the Fig. 1a) there is a transition to the region with minimal activation energy $E_a \sim 0.008$ eV.

We will take the dielectric properties of the dehydrated PAA sample as a reference for further comparison with properties of samples with increased amount of moisture.

Moistened PAA samples were studied at temperatures from 2 to 90°C in order to avoid active vaporization of water from the sample.

In comparison to dehydrated PAA sample 1, sample 2 which contain ~ 3 wt% of moisture demonstrates totally different dielectric behaviour (Fig. 3): peak values of ϵ' and ϵ'' increase by two orders of magnitude and in certain frequency–temperature region ($f, T > 65^\circ\text{C}$) they are negative.

Dielectric properties of sample 2 are similar to those of sample 1 at $T < 65^\circ\text{C}$ and $f \geq 10$ Hz: they demonstrate low values of ϵ' (Fig. 3a) and clearly seen β -process. However, dielectric properties at $T > 65^\circ\text{C}$

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