UDC 678.01:537.226

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PROCESSES OF ELECTRICAL RELAXATION IN PVDF-$BaTiO_3$ COMPOSITES

Thermally stimulated polarization and depolarization currents in composite materials made of polyvinylidenefluoride (PVDF) and $BaTiO_3$ ceramics are studied experimentally. It has been found that the decrease in conductivity is related to the formation of the ferroelectric polarization. The information on parameters of the relaxation processes is obtained by the Relaxation Map Analysis (RMA) method. The experimental results are consistent with the model of the polarization formation in ferroelectric polymers.

The polymer-ferroelectric composites have some more advantages over the pure ferroelectric ceramics because of the better mechanical properties [1]. As for their applications as active elements of piezoelectric and pyroelectric devices, potential of the composites was not fully realized, partly because the electric relaxation processes were not studied enough so far.

The composite is two-phase material with small ferroelectric particle distributed uniformly into a polymer matrix. If strong electric field is applied, the spontaneously polarized dipoles in the ceramics particles are oriented along the field providing for the residual polarization of the whole sample after removing the field. This polarization is responsible in particular for the piezo- and pyroelectric activity. It is known, however, that the main part of the polarization switches back to its initial state and only 25—30% of the domains remain oriented, if the special measures are not taken [2]. Therefore, the orientation in the particles must be fixed anyhow. The similar problem exists in polyvinylidenefluoride (PVDF) and some co-polymers where ferroelectric crystallites are dispersed in the amorphous phase. This structural similarity between the composites and the ferroelectric polymers may predetermine the similarity in the electric relaxation processes too.

The important role of the space charge in control of the ferroelectric polarization in PVDF has been revealed recently and the corresponding model of the polarization formation worked out [3—8]. It was found that the formation of the ferroelectric polarization in PVDF was accompanied by deep trapping of charge carriers. The phenomenon led to abrupt decrease in the apparent conductivity, to the increased stability of the electret potential, to appearance of N-shaped current-voltage characteristics and temperature dependent current curves during the thermally stimulated polarization (TSP) [3]. Some properties of the PVDF-$BaTiO_3$ composites were studied recently [9], however any of the above-mentioned features were not studied.

In this work, PVDF-$BaTiO_3$ composite, considered as the model one, is subjected to the thermally stimulated polarization (TSP) and depolarization (TSD), as well as some other experiments are performed. The results are compared with those on pure PVDF to test the applicability to the composites of some conceptions already proved for PVDF. Some important information on the electric relaxation processes in composites is also obtained.

The samples for PVDF-$BaTiO_3$ composites of 300 μm thickness were prepared by hot pressing of the mixture containing PVDF powder and 10 μm ceramics particles with 0%, 40%, 50% and 70% of $BaTiO_3$. Two series of experiments were carried out. In the first one, the samples with 70% of $BaTiO_3$ were subjected to the thermally stimulated polarization (TSP) at a constant field of either 2 MV/m or 4 MV/m with linear heating and cooling within the range of 20...150 °C at the rate of 5 °C/min. The poling current was continuously controlled and the data were used to obtain the temperature dependence of the apparent conductivity. The poled samples were subjected to the thermally stimulated depolarization (TSD) in the short-circuit mode. Occasionally, the series capacitor of 0,3 μF was used to suppress the spurious stray currents, as it was proposed in our previous work [10]. The $I(V)$ characteristics were also obtained.

In the second series, the composites annealed at 140 °C were studied by the Relaxation Map Analysis (RMA) method by SOLOMAT 9100 Spectrometer [11]. At first, the TSC global spectra were obtained within the range from —80 °C up to +180 °C. The samples were prepoled at 150 °C under the field of 1,25 MV/m for 15 min and freezed to —100 °C with the field still applied. Then the samples were depolarized by re-heating in the short-circuit mode at constant rate of 7 °C/min. The fractional analysis of relaxation processes was also carried out by the method of thermal windows [11]. Polarization temperature was increased each time by 5 °C with the lowest and the highest temperatures set at 20 °C and 150 °C, correspondingly. The equivalent frequency of the thermal window experiments was of the order of $2 \cdot 10^{-4}$ Hz. Unfor-

tunately, all the advantages of RMA method were not fully realized, because stray currents superimposed the fractional peaks at high temperature hampering the analysis. Nevertheless, the activation energies of the relaxation processes were calculated.

RESULTS AND DISCUSSION

Results of the TSP experiments are shown in Fig. 1. The linearity of the $\log G - (1/T)$ curves is distorted at 70...80 °C, and the abrupt decrease in the rate of the apparent conductivity is observed at high temperatures. The divergence between the direct and the reversed $G(T)$ curves indicates that this change in conductivity is irreversible and probably related to the polarization formation. The sharp bend at the reversed curves appears at the temperature of 120 °C being very close to Curie point for $BaTiO_3$ [2]. The activation energy of conductivity in the paraelectric phase of composite (0,53 eV) is much smaller than that in the ferroelectric phase (0,98 eV). The phase transition is also seen at TSD curve in Fig. 2 as the splash of current during both the heating and the cooling. The control of the strong pyroelectric activity after completing the TSD experiments indicates that thermally stable component of the residual polarization exists, however, it is not disclosed in the TSD experiments.

It was found that the thermal stimulation during poling was necessary, because the polarization is not formed at room temperature even under high electric fields of the order 20 MV/m. This was proved by absence of TSD current after poling at room temperature. Moreover, the $I(V)$ characteristic at 20 °C was super-linear and typical for the space charge limited currents [12], but not *N*-shaped as in the case of PVDF [3].

The similarity in the character of TSP curves of PVDF-$BaTiO_3$ composites presented in Fig. 1 and those of PVDF [3] indicates that the mechanism of correlation between the polarization formation and the decrease in conductivity is the same in both cases. The charge carriers are probably trapped at the boundaries of the polarized particles, compensating the depolarizing field and providing for the subsequent stability of the ferroelectric polarization [6, 8].

As for the compensating charge, the sufficient density of the charge carriers in PVDF can be provided not only by thermal activation, but also through injection of carriers in the bulk at high fields. The latter, however, is not possible in the case of PVDF-$BaTiO_3$ composites.

The well-defined low temperature peak around —40 °C is observed at the TSD curves in all samples, including pure PVDF (Fig. 3). The peak is located near the glass transition temperature of the amorphous phase in PVDF and is usually attributed to β-relaxation related to the micro-Brownian motion of molecular fragments

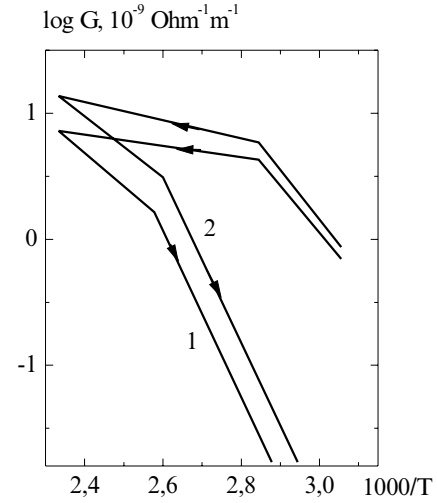

Fig. 1. Apparent conductivity during the TSP experiments. Poling field is 2 MV/m (*1*) and 4 MV/m (*2*)

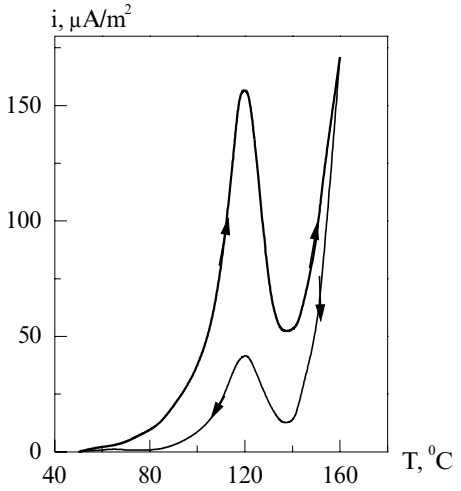

Fig. 2. Direct and reversed TSD currents after poling at the field of 4 MV/m

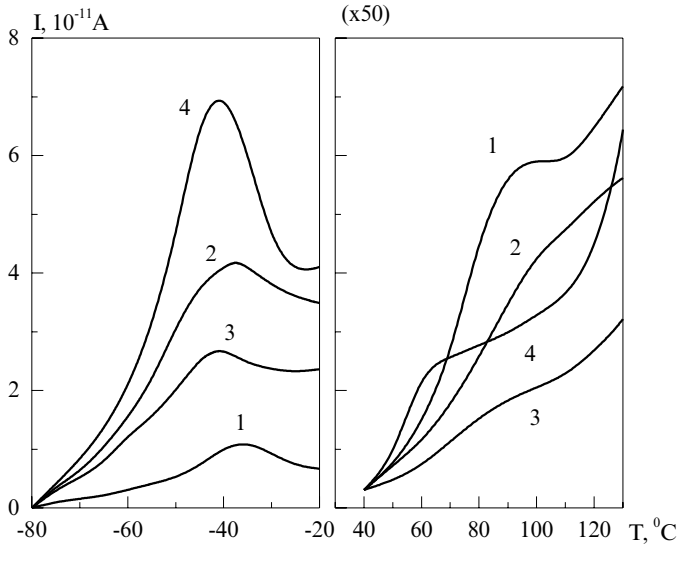

Fig. 3. Global TSD curves of the composites containing 0% (*1*), 40% (*2*), 50% (*3*) and 70% (*4*) of $BaTiO_3$

in the amorphous regions [1]. Neither temperature of the peak, nor its maximum value correlates with the quantity of the filler in the composite. Thus, it is exclusively related to properties of the polymer. The other peak in the region of 80—120 °C is well structured only in pure PVDF, but suppressed in composites by the exponentially increasing spurious current of the unknown origin. To suppress stray currents, we suggested to connect a capacitor in series with the sample [10]. But even in this case, the unambiguous interpretation of the peaks is difficult, because the theory of TSD currents in composites has not been developed so far.

It is assumed in the thermal-windowing method that each resolved peak represents the single Debye relaxation process. Therefore, the analysis of the peaks gives the value of the temperature dependant relaxation time $\tau(T)$ that can be fitted in the Arrhenius equation

$$\tau(T) = \tau_0 \cdot \exp(Q/kT),$$

where τ_0 — is pre-exponential factor, Q is activation energy and k is Boltzmann constant.

The activation energy, as one can see in Fig. 4, slightly decreases within the range of 20...80 °C from 1,17 eV to 1,09 eV independently on composition of the samples. Then Q increases abruptly reaching the highest values of 1,23...1,55 eV at 105...110 °C. The magnitude of the energy correlates with the concentration of ceramics filler, being 1,23 eV at 40%, 1,40 eV at 50% and 1,55 eV at 70% of $BaTiO_3$ in the composite. Moreover, the temperature of the peak in Fig. 4 is very close to Curie point for $BaTiO_3$, proving that the relaxation behavior of the composite near this temperature is governed by the ceramics.

It has been found that the temperature for the maximum current intensity of the thermal window peak was about 15 °C higher than the temperature of polarization for all fractions not depending on composition of the sample.

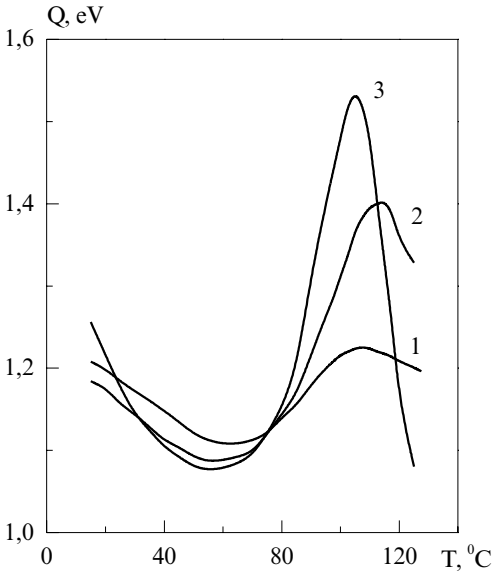

Fig. 4. Activation energy of the relaxation processes in composites containing 40% (*1*), 50% (*2*) and 70% (*3*) of $BaTiO_3$

The dielectric strength of the composites increased with temperature and correlated with the percentage of the filler, being 20...250 at 40%, 30...400 at 50% and 40...1100 at 70% of $BaTiO_3$ in the composite. It is known that the dielectric constant of pure PVDF is about 10...12, while that of the $BaTiO_3$ is 1500...7000 [2]. The polarization field applied to the composite in RMA experiments (1,25 MV/m) was higher than the coercive field of pure $BaTiO_3$ estimated as corresponded to 0,3 MV/m [2], but it is doubtful that the ferroelectric polarization appeared in this case, because the resistivity of the polymer matrix was much higher than that of the ceramics.

CONCLUSION

It is shown that processes of polarization formation and electrical relaxation in PVDF-$BaTiO_3$ composites are very similar to those already known for the ferroelectric polymers. This can lead to the development of the generalized model capable to interpret and even predict the electrical properties of polymer-ceramics composites.

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ПРОЦЕСИ ЕЛЕКТРИЧНОЇ РЕЛАКСАЦІЇ В КОМПОЗИТАХ ПВДФ-$BaTiO_3$

Експериментально вивчені струми термостимульованої поляризації (ТСП) і деполяризації (ТСД) композиційних матеріалів на основі полівініліденфториду (ПВДФ) і порошку $BaTiO_3$. Встановлено, що зменшення провідності композитів пов'язано з формуванням в них сегнетоелектричної поляризації. Методом термічних вікон (МТВ) отримані дані про параметри релаксаційних процесів. Експериментальні результати знаходяться у відповідності з моделлю формування поляризації в сегнетоелектричних полімерах.

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ПРОЦЕССЫ ЭЛЕКТРИЧЕСКОЙ РЕЛАКСАЦИИ В КОМПОЗИТАХ ПВДФ-$BaTiO_3$

Экспериментально изучены токи термостимулированной поляризации (ТСП) и деполяризации (ТСД) композиционных материалов на основе поливинилиденфторида (ПВДФ) и порошка $BaTiO_3$. Установлено, что уменьшение проводимости композитов связано с формированием в них сегнетоэлектрической поляризации. Методом термических окон (МТО) получены данные о параметрах релаксационных процессов. Экспериментальные результаты находятся в соответствии с моделью формирования поляризации в сегнетоэлектрических полимерах.