Experimental Study and Numerically Supported Approach to Interpretation of Spontaneous Transitions into a State of High Conductivity in Poly(vinyl chloride) Composite Films

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Abstract: The results of experimental studies of conductivity anomalies are analyzed for film samples of specially synthesized PVC and polyacetylene copolymer, in which polyene conjugated bonds are built in PVC macromolecules. In such samples spontaneous and stimulated conductivity jumps by 12 orders of magnitude take place, and the lifetime of each of these states can be very large - minutes, hours and more. The nonlinear model is considered which describes the anomalous behavior of conductivity as a result of percolation transition associated with reversible thermal "shorting" of insulating gaps between conductive regions.

Keywords: Polymer composite films, PVC, conductivity, switching effects.

1. INTRODUCTION

Modern applications of polymer materials stimulate investigations of electrical properties specifics for polymers, both conductive, containing conjugated double bonds [1,2], and wide-band [3], and also for most promising polymer-based composites [4,5], which are widely represented now in market and industry. Among the last, nano-composites form a new class of materials with a wide potential range of different useful properties, including unusual type of conductivity, changing from almost perfect metal to a perfect insulator. Unlike the ordered conductors, polymer composites exhibit high specificity of conductive properties. In particular, the film samples of such composites can manifest radical change of electrical conductivity under external influences, which opens a wide perspectives for the creation of new devices of polymeric electronics like memory cells, sensors and circuit design polymeric elements (see e.g. [4-7]). Nevertheless, today many characteristics of polymer composites are investigated insufficiently. This is related primarily to the fact that they have complex, usually random fractal supramolecular structure [8,9], in which physical processes, such as conductivity and chemical structure are closely bound.

Such complex phenomena include switching of conductive states in relatively thick film samples of PVC plasticates investigated in a number of our publications [10,11], which can be important, e.g., at research of losses reduction ways in PVC based insulators of power cables. The absolute value of spontaneous switching effects are illustrated by the considered bellow example of copolymer of vinyl chloride and polyacetylene [12], where jumps of conductivity on 12 orders of magnitude were found. Such phenomena require further development of existing polymers conductivity theories that do not describe the possibility of jumps.

Among the most popular models it is possible to note numerous researches of polymeric conductivity due to formation of charge-transfer complexes [13], polymeric donor-acceptor complexes providing semiconductor conductivity level. Another physical mechanism of conductivity in disordered media is hopping conductivity, which was developed and investigated in detail for weakly doped semiconductors. It arises due to the "jumps" of charge carriers between impurity atoms (extrinsic conductivity and the Mott transition metal-insulator) [14], and is applicable to describe some cases of polymer conductivity (the discussion of hopping conduction theory in relation to transfer of electrons in organic materials and comparison with band theory is given in [15]). The "jumps" can be associated with thermal activation ("incoherent" heat mechanism [16]), and with the sub-barrier tunneling ("coherent" quantum mechanism [17]). There are also many theories of conductivity mechanisms in thin nanometer films, where in the first place are the contact effects associated with carrier injection and space charge limited currents [18,19], and also various mechanisms of conductivity switching, which was observed in thin wideband polymer films (see review [3]).

Usually anomalously high conductivity of amorphous semiconductors films is associated with the emergence of thin conducting channels arranged

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perpendicular to the film surface [20-23] (analogous channels were studied in detail also for thin film of inorganic amorphous semiconductors, such as chalcogenide glasses [24]). In many studies the existence of some critical thickness L_{cr} was specifically mentioned beyond which the conductivity jumps were not observed, and usually the thickness L_{cr} was limited to submicron or even nanometer range [3]. Unlike it, in our works rather thick films, with thickness from tens to hundred microns were investigated.

Nevertheless, in our opinion, the existing theoretical models are constructed mostly *ad hoc* and do not describe the abnormal phenomena of spontaneous conductivity switching observed by us, stability, and long lifetime of states with high conductivity (HCS), and relatively fast switching of conductivity states in polymer composites based on PVC. This case is of particular interest, since PVC is one of the most widely used in practice polymers, and the thermal dehydrochlorination used below in a sense simulates natural thermal aging of this polymer.

In this paper, we give some results of experimental studies of conductivity anomalies associated with transitions between states with low conductivity (LCS) and HCS for the film samples of specifically synthesized copolymer, which can be treated as polymer composite with conductive linear fragments of polyacetilen macromolecular segment. We discuss also an explanation of the obtained results, given by one of the authors [25] on the base of percolation transition associated with reversible thermal "shorting" of insulating gaps between conductive regions.

2. EXPERIMENTAL

To study the effects of conductivity switching we have synthesized film samples of copolymer containing conjugated double bonds (CCDB) on the basis of dehydrochlorinated (DHC) PVC [12]. In such composite polyene conjugated bonds are built in PVC macromolecules with variable concentration.

For preparation of copolymer samples the initial solutions of pure PVC (grade C-7085M) in acetophenone was exposed to the process of thermolysis in solution to a level of conjugated double bonds concentrations at which for formation of film samples it was possible to use a watering method on glass substrates [12] (that is limited by a technological possibility of obtaining continuous, removable and smooth films of identical thickness). In a test tube with chemically pure acetophenone (boiling point 202 ^{o}C) pure PVC granules was added in the ratio 100ml acetophenone: 4g PVC. Further dissolving PVC occurred by mechanical stirring with a magnetic stirrer for 12 hours at a temperature of 22 ^{o}C. As a result, a homogeneous transparent solution PVC was obtained. The tube with the resulting solution was placed in a thermostat, where thermolysis process was conducted at a temperature t = 190 ^{o}C. As a result, a set of solutions of PVC in acetophenone was received, different timing of the thermolysis. The obtained solutions was poured into a Petri dish with a diameter d = 10 cm and subjected to drying at t = 95 ^{o}C for 48 hours. Thus, a series of dehydrochlorinated PVC samples were obtained in the form of thin circular films with thickness 10 ± 1 micrometers, differing by timing of thermolysis and, as showed optical measurements, conjugated double bonds concentrations.

At the initial stage of DHC process an insulating material is a classic wideband polymer. As the concentration of conjugated double bonds grows, depending on the degree of DHC, conductivity of the samples increases, and it can be treated in the frame of a model of composite with conductive inclusions and insulating gaps.

Indeed, the chemical structure of dehydrochlorinated PVC macromolecules is well known, as the DHC process is actually equivalent to one of the known mechanisms of thermal aging of insulating PVC materials [26]. During heat treatment of PVC solution the HCl molecule is split off from the macromolecule of PVC, resulting in a chain link of macromolecule containing a double bond - C = C - . At continuation of the process of allocation of HCl, chains of conjugated double bonds of type ..... -C = C-C = C-...... with random lengths are built in PVC macromolecules, which have relatively weakly bound π-electrons and under certain conditions can actually turn into nanowires.

Note also that the addition of fragments with conjugated double bonds in the DHC process of PVC led to the appearance of certain plastic properties in the films obtained by casting, so that there was no need for any additional use of plasticizers for manufacturing film samples (from 10 to 200 microns) flexible enough for experimental measurements. In our experiments such copolymers have demonstrated the highest level of conductivity in HCS compared with other previously studied PVC composites, in which the initial level of conductivity was increased by introducing a special plasticizer-modifier A [10,11].

Studying of the conductivity states in the received films was carried out by technique described earlier in [10,11] for the case of plasticized PVC films.

The observed transitions between states of conductivity could be both stimulated (i.e., occur under the influence of various external factors that was investigated earlier in the literature), and first observed in our studies spontaneous, i.e. under constant external macroscopic parameters. As an example, we present the results of stimulated transitions typical changes in resistance of the samples with different degrees of dehydrochlorination occurring with increasing temperature and shown in Figure **1**.

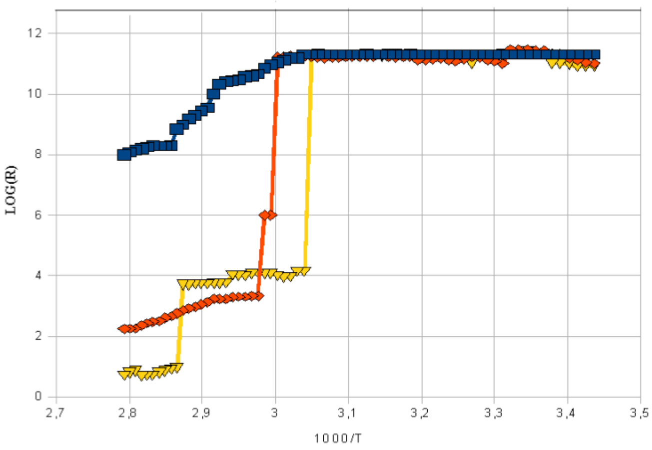

Figure 1: Temperature dependence of copolymer resistance for pure PVC film –squires dots, rhombus -20 min of DHC process, triangles - 240 minutes of DHC process.

In this figure one can observe well known relatively small changes of resistance for pure PVC material during all the range of temperature changing. Yet for DHC samples situation differs very much. For small temperatures, resistance changes very slowly, up to some threshold temperature, where resistance changes for many orders of magnitude. It was observed also that the more is the DHC time (and, as a consequence, concentration of conjugated double bonds) the lower is the temperature needed for giant jump to occur. For higher double bonds concentrations, spontaneous jumps appears quite often starting from lowest temperature range, so well defined and reproducible curves as shown on Figure **1** are not observable.

So, the appearance of spontaneous transitions between states with different levels of conductivity occurred only for samples with a sufficiently high level of DHC. This fact is illustrated in Figure **2**, which shows (in logarithmic scale) typical dependence of the resistance of CCDB film samples from thermolysis time. The shaded area in the figure corresponds to samples for which the spontaneous transitions between two unstable states of the conductivity were observed. This graph shows that the resistance of the samples from some level of DHC reveals a tendency to spontaneous transitions in HCS with the change in resistance by 12 orders of magnitude. The term "spontaneous" refers here to the transition to the HCS "without visible external effects", i.e. while keeping the applied voltage, temperature, pressure, light, etc.

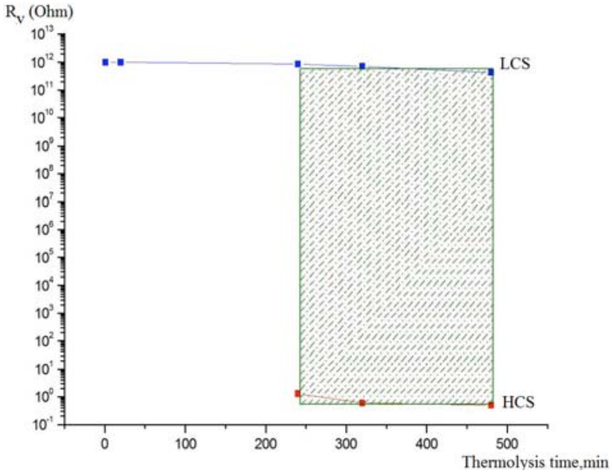

Figure 2: A typical dependence of the resistance R_V of the copolymer sample from the degree of DHC of PVC solution at a temperature of 190°C. The shaded is zone of instability on the transition between the high (HCS) and low conductivity states (LCS).

An important feature of the conductivity jumps in PVC composites considered here is a wide spread duration of HCS lifetimes. Figure **3** shows one of the realizations of random spontaneous transition from LCS to HCS, and after some time (in this case about ten seconds) reverse transition to the LCS. It is clearly seen that the HCS is unstable which lifetime significantly exceeds times of transitions between states.

This fast spontaneous switching to HCS and wide spectra of decay times of conductive state, from seconds to hours and more, can be understood in the frame of some type of conductivity instability, which develops under the influence of thermal fluctuations. High resistance difference and good reproducibility of the spontaneous transitions modes, as well as known from the literature [26] chemical structure of the material, produced during DHC of PVC, make it possible, at least on a qualitative level, to analyze the physical mechanisms of the observed spontaneous conductance jumps and to suggest a possible mechanism for the onset of instability (see Sect. 3).

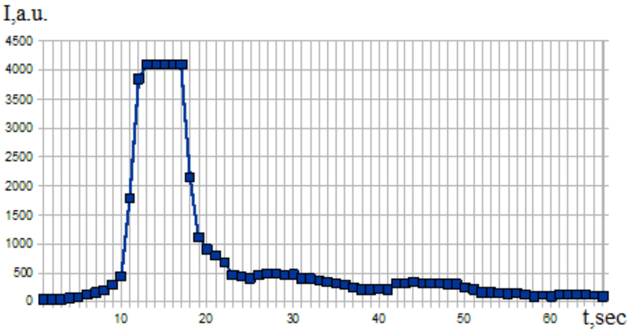

Figure 3: Oscillogram of spontaneous transition of copolymer sample to HCS and its spontaneous return to the LCS (flat top - ADC limit) [31].

Specifics of giant conductance jumps in the copolymer samples is reflected in the fact that the measured conductivity of the copolymer "through" the film falls to a fraction of Ohm, but at the same time, an attempt to measure the resistance along the film in HCS showed no change in the surface resistance of the film (more than 10^{12}Ohm), which is similar to that observed in plasticized PVC composites [10,11]. In this case, the expression for the resistance $R = \rho l / S$, where ρ, l and S are volume resistivity, length and cross-section of the sample, respectively, at a reasonable choice of parameters gives for estimation R_s about 10 kOhm, which obviously does not correspond to the experimental data (in the experiment> 10^{12}Ohm) and the evidence in favor of the strong in homogeneity of the current distribution in the sample.

In fact, in contrast to the "normal" conductivity, the observed conductivity jumps are one-dimensional and directed perpendicular to the film surface, i.e., HCS has strong anisotropy (more than 10^9) at the molecular level and is associated with the directed micro channels of conductivity. Note that in the case of plasticized PVC in almost all results of papers [10,11] the surface resistance always exceeded the upper limit of the possible value of the instrument, that is > 10^{12} Ohm.

The presence of conducting channels in the transition to HCS in CCDB samples we observed experimentally. Wherein at room temperature (24^{o}C) a special transparent electrode (ITO layer on a glass substrate) with a conductivity of 100 Ohms per square was used. Upon transition to HCS on a sample of CCDB at special darkening it was possible to observe through a transparent electrode several weak shining points, which in our opinion are associated with narrow conductive channels and similar to observations, described in other publications on the electrical conductivity in different cases of thin polymer films [20-23]. The intensity of light points was different and changed over time, and in some channels short to 10 seconds intense glow was developed, the magnitude of which was sufficient for reliable camera records.

3. MODEL AND SOME CALCULATION RESULTS

In typical schemes of conductivity measurements for insulators with a large ballast resistance the transition to HCS with increasing voltage is always realized. In our experiments [10,11] such reversible transition, which we call “soft breakdown", was observed in all PVC samples at voltages of the order of 30V/μm, and for all other polymer samples (polyethylene, teflon, etc.) This effect is universal and is not dependent on the type of polymer, and can be described by numerous theories of dielectric breakdown [26], i.e. release of electrons from the impurity atoms, shallow traps and defective assemblies of macromolecules, and energy gain in an external field with further ionization of the molecules of the main matrix. The term "soft" breakdown we have applied to the process of breakdown when the current resulting in breakdown is essentially limited by ballast and the breakdown energy is insufficient to change the structure of the material or the formation of irreversible changes in the molecular structure. Therefore, a "soft" breakdown is non-destructive and reversible, unlike a real breakdown, where there are irreversible changes in the sample structure at the expense of heat release and spark discharge.

All experimental results on the conductivity jumps, considered in our papers, were obtained at voltages of at least an order of magnitude below the thresholds of soft breakdown, and below in this paper we discuss only spontaneous transitions, while usually studied stimulated transitions occur under the influence of controlled external influences (electric field [10,28], pressure [22,29], light [30], etc.).

For the CCDB material consisting of conductive elements (on nano-level), separated by insulating gaps, the conductivity is anyway connected either with tunneling, or with hopping of electrons between the conductive elements of composite. Unlike "classical" hopping conductivity, in which charge carriers are "jump" from atom to atom, in the case of a composite such jumps occur between the conductive elements, whereas along the conductive element charges propagate almost freely. This point is similar to Sheng model [18], where, however, switching effects were not considered. This raises the first difference to which attention should be paid in this case, namely, a significant increase in effective local values of the electric field due to the introduction of conductive elements.

These fields, in turn, can lead to the appearance of strong mutual dependence of the conductivity states in adjacent insulating gaps. As a result, a models in which the conductivity state in a single (average) gap is considered independently of the neighboring gaps may be insufficient to adequately describe the switching effects, as the "shorting" of a single gap increases the probability of "shorting" for neighbors. These simple heuristic arguments have been used previously in [31] in the construction of the qualitative cascade model to account for the occurrence of correlations between states of different gaps.

In the development of the approach of [31], in [25] a model was proposed that relates the observed spontaneous transitions of the samples conductivity states with similar transitions in single gaps caused by joint Joule heating and cooling (which, in fact, is the cause of the appearance of correlations in this model). Omitting the details of the calculations [25], we give the main results obtained in this model.

We assume that the current-voltage characteristic of a single gap is given by simple "step" similar to that observed in macroscopic transition temperature dependence (Figure **1**). In other words, the gap is in the LCS at $T < T_0$, and in HCS at $T > T_0$, where T_0 is some characteristic transition temperature. In the case of PVC such behavior can be explained by local reversible thermal dehydrochlorination, leading to the formation and destruction of conjugated double bonds, so T_0 can be called a dehydrochlorination temperature.

The heat conduction equation is taken as starting point, in which the source term is associated with the Joule heat generated in weakly conducting gaps. In the case of a cylindrical conducting channel in the simplest model [25], the problem reduces to the solution of a nonlinear integral equation depending on the number of taken into account gaps. Considering the nonlinear term as "small", this equation can be solved by iterations. The results of such solution are illustrated in Figures **4** and **5**.

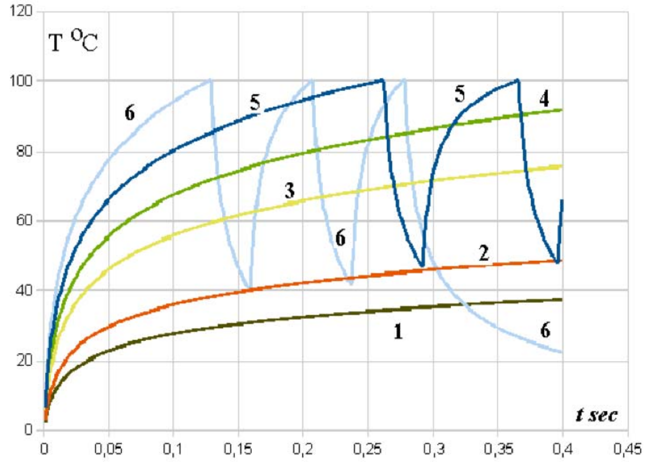

Figure 4: Variation of temperature on one element of resistance - one insulating gap at various levels of "measuring" current.

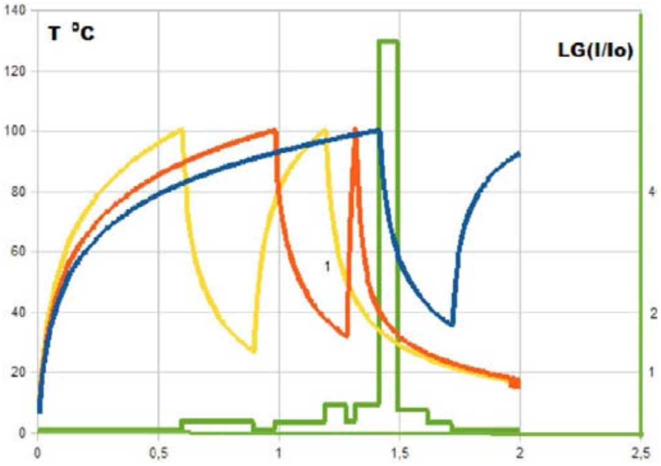

Figure 5: Self-synchronization of temperature oscillations in the current channel (green shows the peak current on the right scale).

Figure **5** shows the temperature versus time at very low measuring currents, on the level of nA. Since the channel itself has a small cross-sectional dimensions of about 10 nm, insulating element in the channel actively reacts to the applied voltage. For vanishingly small currents there is simply smooth heating, but even at units of nA may occur oscillations associated with the cycles of heating and cooling due to the transitions from LCS into HCS and back.

As noted above, upon transition of one of the isolating gap to the conductive state heating of the others increases. Thus, the phases of nonlinear fluctuations (Figure **4**) "are tied" and to a greater or lesser extent there is their self-synchronization. Figure

5 shows the calculation results of oscillations for three gaps in a series (divided by conductive areas), which are synchronized on an interval of 1.3 sec, at the same time pass into the conductive state (due to DGH), which leads to the release of the current (decrease in the resistance).

Thus, in general, in a narrow current channel the temperatures of elements can self-synchronize, and at some, according to our experimental data, an arbitrary moment, the channel can as if "spontaneously", pass into the HCS.

Using these calculations it is easy to predict that self-synchronization "easily" occurs at a small amount of insulating gaps. On the contrary, with increasing the number of conductive inclusions (in particular, with increasing the thickness of the film samples) nonlinear synchronization weakens and jumps should disappear.

4. CONCLUSIONS

In this paper we have presented some experimental results on stimulated and spontaneous switching between conductivity states arising in film samples of partially dehydrochlorinated PVC, associating these transitions with local thermal nonlinear effects arising near the percolation threshold.

Such a model can qualitatively explain the basic features of reversible transitions from low to high conductivity states with amplitude of jumps to 12 orders of magnitude, found earlier in film samples (thickness of 10 microns, and more). To this end the cascade model of the composite material developed previously [31] is extended, and possible mechanisms of instability providing relatively rapid transitions of the sample from LCS into HCS and back is proposed.

The difference of cascade model from classical percolation theory is that in the first the main attention is paid to nonlinear effects leading to closure of the insulating gap, whereas percolation theory focuses on the dependencies of the averaged medium characteristics on the concentration of conductive phase, and the presence of gaps is totally ignored, i.e. all small gaps are considered as closed. In this case, the conductive elements in percolation theory are considered as random and uncorrelated. In contrast, in cascade model conductivity of a gap in each chain is dependent on the state of adjacent gaps, which substantially complicates the development of a quantitative theory that must take into account the respective nonlinear and non-local effects.

For PVC composites (and the like, for example, polyvinyl bromide) within the same cascade model the mechanism of transition in HCS is considered, with more low threshold as compared to a soft breakdown. The structural-chemical mechanism is proposed, that explains the relatively long lifetimes of HCS in PVC composites, and is based on the fact that near the percolation threshold in this case conspicuous local heating of insulating gaps occurs, which activate in isolated element of free volume the reversible reaction of local DHC.

From a practical point of view, taking into account the developed model, a more thorough study of the distribution of the lifetimes of the HCS can be used to study the structure and properties of the free volume in PVC composites, in addition to or instead of expensive and complicated electron-positron method [32].

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