Cascade Model of Conduction Instability and Giant Fluctuations in Polymer Materials and Nanocomposites

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***Abstract*-A new cascade model of polymer composite materials giant current fluctuations is developed on the basis of published representable set of experimental data. This qualitative model describes the "anomalous" features of the conduction of polymer nanocomposites, in particular, conduction many orders of magnitude self-switching to the conducting state in polymer films including relatively thick up to tens of microns or more. The development is achieved by combining well known model of hopping conduction mechanism with experimental data of soft reversible electric breakdown. With much simplification the instability can be explained as follows: dividing the distance between electrodes on conducting islands (with constant potential with zero electric field) and insulating gaps (where electric field is higher than average level). In such a system we obtain "instability" - type correlation of electric field in the adjacent insulating gaps: one gap microbreakdown increases the field strength in the adjacent gaps.**

Keywords- Polymer Films; Conductivity Switching; Fluctuations

I. INTRODUCTION

Although usually the data on the conductivity of polymer films are considered with large spread (normally a few orders), this paper shows that in polymer films with thickness up to hundreds of microns giant fluctuations of resistance can be observed, which can significantly limit the accuracy of possible measuring of the electrical resistance in the all-union state standard measuring cells. Moreover, in some cases the very magnitude of the average resistivity (both volume and surface) is virtually meaningless, since the resistance of the sample begins to non-linearly (in particular, exponentially) depend on its thickness.

In a number of authors' papers [1-5] in transparent plasticized antistatic PVC films with thicknesses from tens to hundreds of microns without use of heterogeneous conductive fillers some anomalous electrical switching effects have been discovered and studied. Recently in [6, 7] similar anomalous effects were observed in PVC films whose conductivity was enhanced by creation of double conjugated bonds using thermal dehydrochlorination of PVC in solution. In such films at field intensities much lower than the level of breakdown threshold, spontaneous and stimulated by some external influences reversible transitions from the initial anti-static level to the state with high conduction (HCS) were observed. Note that the conduction jumps were 4 and more orders for the plasticized films, and up to 12 orders of magnitude in the case of thermalized PVC.

It is well known, that in thin nanoscale films conductance jumps occur in almost any dielectrics at the approach to the threshold value of the external field ("soft breakdown") and, in particular, have been widely studied in metal-insulator-metal systems, including polymer films [8 -11]. In contrast and in addition to these specific 'thin-film' phenomena, in our studies [1-7] spontaneous and stimulated jumps of conduction were observed in relatively thick films up to hundreds of microns or more. For multi-micron films of wideband polymers with relatively low voltage of units volts such behavior can be called anomalous, as in many other studies [9-11] the existence of a critical boundary thickness L_{cr} was specifically mentioned beyond which the conduction jumps were not observed, and usually thickness L_{cr} was limited to submicron and even nanometer range [11].

Since the conduction switching in polymer films is of great practical interest for new information technologies, particularly in connection with the possibility of creating new sensors and memory elements [12, 13], a lot of attention was paid in the literature in attempts to explain the physical mechanisms of the phenomena observed. However, with all the diversity and specificity of the test materials and the variety of proposed mechanisms, many experimental results did not find their explanation and, as noted by the eminent researchers, the final decision on the most probable mechanisms of switching is still not obtained (see, e.g., reviews [11-13]).

In this paper to interpret the conduction anomalies we propose a cascade type instability mechanism with respect to a composite medium, where hopping conduction is dominated. In this model the medium is treated as a row of conductive islands and isolation gaps, so it is easy to estimate that each soft microbreakdown increases the electric field in the adjacent isolating gaps, stimulating thin gaps microbreakdown. So a series of "soft" microbreakdowns implements a cascade mechanism of instabilities, which can qualitatively explain the main characteristics of spontaneous and stimulated jumps between two states of conduction in relatively thick films at the external field levels by orders of magnitude lower than the threshold, as it was observed in [1-7].

The developed model explains polymer composite electric current switching and giant fluctuations frequently observed in different experiments. The model makes use of the two well-known phenomena: electron hopping conductivity and "soft" breakdown. It is important that it is not necessary to specify the precise microscopic theory of their physical mechanisms, which even in the case of thin (nanometer) polymer films can be varied depending on the polymer material and the specific structures of electrodes, and lead to different current-voltage characteristics, observed in experiments [13]. It can be expected that the instability model considered below should be useful for understanding of other experimental results on the measurements of electrical conductivity, especially in the case of composite dielectric films containing conducting inclusions.

II. EXPERIMENTAL FACTS, STIMULATING THE CONSTRUCTION OF THE MODEL

The behavior of the electrical conductance of plasticized or dehydrochlorinated PVC films was experimentally investigated in the cited papers [1-7]. Here we present only some of the experimental results, which stimulated the development of the cascade model.

First, in recent experiments [7] with a copolymer of PVC-polyacetylene, upon transition to the HCS the resistance of sample with thickness of 30 microns was less than ten Ohms. For other geometry measurements of the same sample for measuring the surface resistance with an effective thickness of the measuring gap 3 mm, in accordance with the formula for the sample resistance R through its geometry (L-length, S-sectional area) and the resistivity (ρ):

$$R=\rho L/S, \tag{1}$$

the surface resistance associated with volume currents was to increase only 10^6 times and it should be easy measured by the device with a limit of 10^{12} Ohms. Nevertheless, despite numerous attempts, the surface resistance measurement of the sample was failed because it exceeded 10^{12} Ohms. Thus, for a sample of PVC-polyacetylene copolymer the widely used formula (1) gave an error of more than six orders of magnitude, which of course required the use of additional models for interpretation. Earlier for plasticized films an exponential dependence on the thickness was obtained in [5] (see below), which is obviously contrary to the simple Formula (1).

The main mechanism involved for the interpretation of anomalous data is associated with the results obtained in [2] for PVC films, where the increase in the applied voltage gave rise to transitions in HCS when the threshold voltage E_{th} was achieved (the threshold of a "soft" breakdown). Such transitions were accompanied by the release in its original state in the form of a stochastic process, corresponding to reversible random transitions into HCS and low conductive initial state (see Fig. 1). In addition, as noted in [2], the transitions were followed by the generation of clearly distinguishable sound waves. Also the same "soft" breakdowns were observed in other plastic film, polyethylene, teflon, etc. In the standard scheme of measurements in the presence of big ballast resistance such transitions take place reversibly, without destruction of a polymeric film and materials of electrodes.

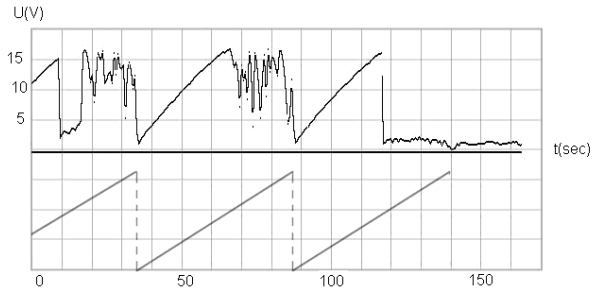

Fig. 1 Successive oscillogram for the voltage applied to measuring cell in scan cycle; the bottom picture shows the sawtooth shape of the applied voltage pulses [2]

From the Fig. 1 it is clear that at achievement of some threshold value E_{th} (Volt) the "soft" breakdown occurs rather regularly. Its reversibility is proved by recurrence of switching. In this case, after relatively rapid change due to the soft breakdown, the sample is in HCS for some time τ_m even after complete removal of the external voltage. In particular, as noted in [2], the sample could remain for days in a conducting state, then returning to the normal state with low conduction. In addition, the distribution of the conductivity on the film surface was very inhomogeneous [2], and in fact, realized at several points on the surface of the sample (conducting channels similar to those observed in other studies, see, for example, [14]).

The dynamics of single spontaneous and stimulated switching in HCS for plasticized PVC samples was illustrated in [3, 5]. Fig. 2 (based on the papers [7, 8]) shows the oscillogram of the single spontaneous transition to a HCS for dehydrochlorinated PVC sample. On Fig. 2 a relatively rapid jump is seen to be followed by some interval of time τm (in the example in Fig. 2 - some seconds), when the sample is in HCS, and then - return to an initial state which happens more smoothly, and completely initial conduction is restored only through tens of seconds that allow estimating τm .

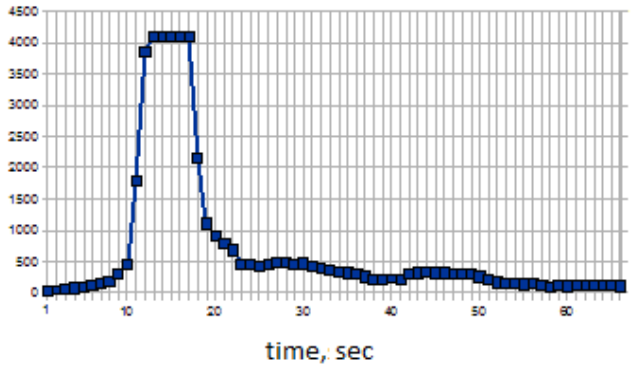

Fig. 2 Spontaneous transition to HCS for PVC- polyacetylene nanocomposite film

Thus, PVC composites films, like many other polymers and dielectrics (insulators) films have a clearly defined sustainable threshold of "soft" breakdown or, in other words, a reversible, non-destructive transition in HCS. The return from HCS after removing of the external field is not instantaneous, and can be characterized by the time τm that depends on many parameters.

III. THE CASCADE MODEL OF TRANSITIONS IN HCS

In the case of thermal dehydrochlorination of PVC the cleavage of hydrogen chloride results in origin of copolymer PVC-polyacetylene, ie chains of conjugated double bonds, which have high electrical conductivity, and are embedded in PVC macromolecules. The magnitude of this conductivity can be close to that of metals, if present in the PVC chlorine atoms act as dopants (as is known, doping can significantly - by 7-10 orders - raise the conductivity of conjugated polymers, see, e.g., [15]). With this in mind, to describe the electrical conductivity of dehydrochlorinated PVC samples in the above relatively thick films we adopt a model of composite consisting of highly conductive areas separated by dielectric layers (native PVC). We assume that the single electron tunneling with a noticeable probability induces the appearance of a "soft breakdown" of the gap, so it is a limiting factor for the transition to the HCS.

For the probability of electron tunneling through a potential barrier U (x) the WKB approximation gives the well-known expression [16]:

$$W = \exp\left(-\frac{\sqrt{8m}}{\hbar}\int\sqrt{U(x)-\varepsilon}\,dx\right), \quad (2)$$

where U(x)= U0 -qEx barrier potential, the q-electron charge, ħ - Planck constant, m and ϵ - the mass and energy of the electron, respectively, and in our case ϵ ~ κT<<U0 . This shows that the dependence of the barrier on its thickness is generally exponential, but it also depends on the external field, and increases exponentially with its increase. Thus, in the simplest approximation U0 >>ϵ + qEx for rectangular barrier with width Δx for the tunneling probability (2) gives

$$W(\Delta x, U0) = \exp(-\Delta x/ld), \quad (3)$$

where $1/ld = \sqrt{8mU_0}/\hbar$, *ld* - characteristic length, depending on the barrier height U0. Note that by the mean value theorem the Relation (3) can be used in general case, but in general the characteristic length *ld* in complex manner dependent on the shape of the barrier and the field strength.

In a more detailed consideration the insulating barrier is lower under the influence of an external field, and in the Fowler-Nordheim approximation the probability of sub-barrier electron tunneling in the field strength E obtained exponential form ~ exp (-E0 / E) (here E0 - a characteristic value of the field, see, for example. [16]). So, the probability of "soft breakdown" will exponentially decay with increasing thickness of the insulating gap Δx at a fixed potential difference Δφ ~ E Δx.

In the proposed model the probability of tunneling through two adjacent barriers will be determined by a simple product of the probabilities (3) (as the events are independent). The probability is again determined by the exponential, and the exponents (3) are added. When calculating the total probability of hopping from one electrode to the other in the above assumptions, we obtain the full length of the potential barrier equal to the sum of all lengths, Lv = ΣΔxi. Thus, the total probability of tunneling from Electrode A to Electrode B is expressed by the exponential with the total width of the potential barriers. Analyzing all possible trajectories of the charge from A to B, it can be expected that for most of the trajectories of electron tunneling probability is exponentially small, though in a set of random trajectories there is a trajectory with a certain minimum value of L. It is obvious that really has a chance to "work" only path with minimum Exponent (3). Along such a path from A to B, we can write

$$L = L_в + L_C, \quad (4)$$

where L - the distance between the electrodes and the L C -full length of the conductors. Then, the average field strength, with the equipotential conductive elements can be estimated as:

$$E = UАБ/ Lв=UАБ/ (L - LC). \quad (5)$$

This simple expression shows that with decrease in the total length of the barrier Lв, the local field strength at the barriers increases. In particular, for using the percolation theory [17] in the considered problem from this simple formula it follows that at the growth of conductive impurities concentration and thus closer to the formation of an infinite cluster, the local field strength can be significantly higher, and (up to the percolation threshold) the system due to tunneling of the charge will go to the conducting state and can make transitions similar to those shown in Fig. 1.

Let us now consider in more detail the model chain, ordered along the optimal route tunneling along the applied uniform external field, and consisting of conductive areas separated from each other for simplicity identical gaps Δx (Fig. 3). The field strength E in each of the gaps for estimating can be considered as the same, so that the differences between potentials φ_i of Conductors 1, 2 and 3 are equal, $\Delta\varphi = \varphi_2 - \varphi_1 = \varphi_3 - \varphi_2$. In the case of "soft breakdown" of the Gap 12 potentials of the Conductors 1 and 2 are equalized (for a time τ_m), and the potential difference in the Gap 23 is doubled, resulting in increased probability of breakdown of the gap. In turn, the breakdown of the Gap 23 increases the potential difference between the 3 and the adjacent conductive area to the right, located at a higher potential, thus increasing the probability of the next breakdown, etc.

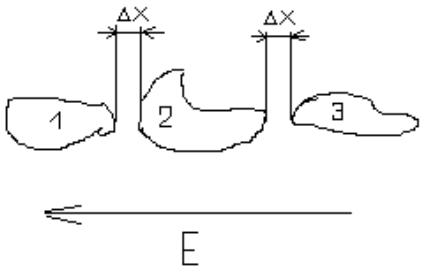

Fig. 3 Chain model of conducting regions with insulating gaps

Thus, taking into account the threshold of soft breakdown and the finite lifetime of the conductive micro-channel, we can speak of a cascade mechanism of the instability along the applied external field or along the most likely trajectory of tunneling (channel).

Conversely, if in some gap of the soft breakdown channel restores insulating properties, the field in adjacent gaps decreases, respectively, the probability of return to the original state increases. Thus, it can spontaneously develop instability, both in the emergence of HCS, and to return to its original state. Note that in the simplest version of the model (the same height of the potential barriers) it predicts an exponential dependence of the total thickness of the insulating gaps, ie at a fixed concentration of the conducting phase on the thickness of the sample.

IV. ON THE MECHANISM OF SPONTANEOUS TRANSITION IN HCS ("SWITCHING")

It is known that even pure polymer has a complex (in some cases fractal) distribution of density, a large number of specific defects, crystallite, etc. with the free volume, which largely determines the physical properties of polymers. When placing the polymer or polymer composite in a uniform external electric field strong voltage fluctuations can occur in the polymer volume. Such fluctuations can appreciably exceed the average value of the applied field, and reach the point where the "soft" reversible breakdown of thin layer of insulator can occur causing transition to HCS.

Very rough estimate of such fluctuations can be obtained by considering a macroscopic model of the rounded tip of radius r at a distance d from a conductive surface, which gives the enhancement factor ~ $(d/r)^2$. If we take d as the average distance between the conductive areas, treating r as the characteristic size of the "bulge" on the border of conducting region, already at r ~ d / 3 (that is quite admissible in strongly inhomogeneous media) we obtain an order of magnitude gain compared to the average value of the field.

Note that much larger gains (about 10^5 or more) are obtained in the models of so-called methamaterials - metal-insulator composites in the presence of plasmon resonances [18], but in polymer case it is difficult to expect the presence of such collective effects associated with negative effective permittivity of metallic regions.

Along with the fluctuations of the field it is reasonable to assume that in the plastic polymer medium insulating gaps can fluctuate also (among other factors even in weak mechanical vibration), increasing the strong fluctuations of local fields, in particular, with the excess of the threshold of soft breakdown. In this case, the transition to the HCS starts from "soft breakdown" of one of the thin gaps between the conductive areas in which there are free charges or the largest local values of

the electric field (we leave aside the question of the details of the microscopic mechanism of the breakdown). In the case of thin gaps it is natural to consider electron tunneling through a gap as an initiating factor of such breakdown.

On the other hand, switching can also be stimulated by cosmic particles, which ionize molecules and create free charges, which facilitate the soft breakdown of insulating gaps and the development of instability, especially near the percolation threshold. Similarly, switching to the conducting state can be influenced by light and the appearance of photo-electrons in the insulating gap, micro-displacement when applied to a sample of external pressure and other effects. The experimental results confirming these transitions were obtained in our experiments [1-7] and many others [11].

V. AREA OF APPLICABILITY OF THE CASCADE MODEL

Thus, the cascade model of soft breakdown at qualitative level allows explaining the observed in composite medium (PVC-polyacetylene copolymer) anomalous switching of conduction in rather thick films and absolute inapplicability of the Formula (1) for calculation of resistance of a sample through the volume specific resistance.

Moreover, despite the fact that the model is formulated for composite medium like conductor-insulator, which is the most reasonable in the case of dehydrochlorinated PVC containing highly conductive chains with double bonds, many of the results, which it explains and predicts can be applied to describe the anomalous effects of flexible plasticized PVC films studied previously [1-5]. This may indicate the presence in the plasticized PVC of areas with high conductivity. In particular, in such plastic compounds spontaneous and stimulated transitions to HCS, and also transitions to HCS under the influence of pressure were observed. Fig. 4 shows the exponential dependence of the resistance on the sample thickness measured in [5].

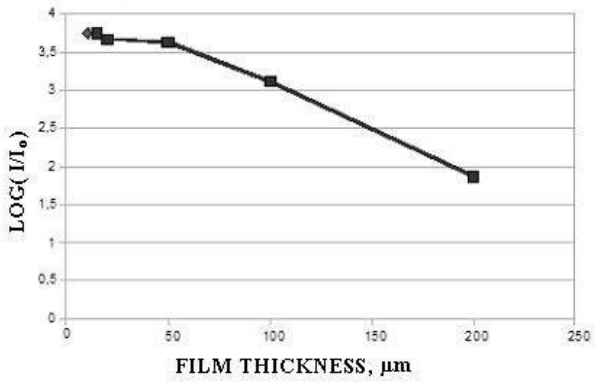

Fig. 4 Experimental dependence of the current on the thickness of the plasticate sample at a fixed voltage (the x axis represents the polymer film thickness, y axis - logarithm of current [5])

Exponential dependence of resistance on sample thickness completely explains any deviation from the standard formula of calculation of average resistance (1) in case of transition to HCS, and small informational content in this case in relation to polymers (and to composites on the basis of polymers) concepts of specific resistance. As another example of the inadequacy of (1) in relation to polymeric materials is possible to give the results of work [9], in which a more complex exponential dependence of the measured resistance on the sample thickness was observed.

VI. ON ANALOGUES OF THE MODEL

Earlier, in [2] the similarities were noted between soft breakdown of polymer films and avalanche breakdown of transistors, which also comes under a certain threshold E_{th}, repeatedly invertible for sufficiently large load resistance and has a characteristic lifetime τ, significantly greater than the time of the actual breakdown.

Avalanche breakdown is often used in electronics for generating short (typically a nanosecond) fronts. In this case, if you want to get a pulse of high amplitude, much more then E_{th}, transistors are connected in series, so that N series-connected transistors give the breakdown threshold $N \cdot E_{th}$ (thus for alignment of voltage the resistor divider is used).

In such scheme the cascade mechanism of breakdown also is realized, which is completely similar to described above: at voltage increase in one of transistors avalanche breakdown is realized, thus voltage on others sharply increases and they almost instantly pass to conductive state providing at the exit a powerful impulse of current and voltage.

Significant difference from the above model of polymer medium is that the analogue of “transistors” in the polymer medium, ie, insulating gaps between the conducting regions are random, so the “transitions” in HCS may occur at different voltages, including spontaneous, because the shortest gaps-insulators can pass in HCS at very low relative E_{th} voltages. Thus, prepared in a special way polymer composite films can already be used in circuits cascading pulse generators instead of avalanche transistors.

Note also that the appearance of non-linearity, even in weak external fields, accompanied by a sharp change in resistance

observed in polymer composite films, and the presence of the delay time τ_m , which can be significant, indicate the possibility of creation on the basis of considered polymeric composites of new passive elements — memristors (see, e.g., [20]).

VII. CONCLUSIONS

The presented model of transitions to high conduction state (and swithcing) in rather thick films in polymer composite was considered. This model is based on cascade development of instability, which is connected with tunneling of electrons through insulating gaps between the neighbouring conductive areas with formation of soft breakdown that is relatively long living conducting channel. Taking into account experimentally established threshold of soft breakdown (reversible transition to a high conductive state) and finite lifetime of conductive channels, such model allows explaining at qualitative level the main dependences of conductivity switching in PVC polymer composites.

In particular, the model explains conductive instability which leads to the observed spontaneous and stimulated by various external influences switching of conductivity, the conductivity returns to its original state, the exponential dependence of the resistance of the sample thickness. We believe that future development of the model will allow quantifying the behavior of the conductivity switchings not only for PVC composites, but also for other polymer nanocomposite films.

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