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## INFLUENCE OF ELECTRIC CURRENT ON THE OXIDATION PROCESS OF CONDUCTIVE POLYMER COMPOSITIONS

*Ключевые слова:* электропроводящая полимерная композиция, окисление, искусственное старение.

*Показано влияние электрического тока на окислении проводящих полимерных составов. Создана программа, которая описывает математически процесс окисления изученных материалов в различных условиях старения.*

*Keywords:* conductive polymer composition, oxidation, artificial ageing.

*The papershows influenceof electric current onthe oxidationof conductivepolymer compositions. A program, that describes mathematicallythe oxidation process of the studied materials in differentaging conditions, has been created.*

Recently conductive polymer materials (CPM) have obtained a wide usage in different branches of industry. It takes place due to combination of performance characteristics, availability and low cost. Conductive polymer materials have conductivity specific to metals, and such advantages of the plastics as corrosive resistance, high processing quality, low density, elasticity. Nowadays the most perspective method of conductive polymer compositions generation is introduction of conductive materials (such as metal powder, graphite, soot) topolymer dielectric [1].

Advantages of charged CPM in comparison with high molecular semiconductors include the possibility of controlling of their conductivity, technological, physical and chemical, and performance properties in accordance with actual practical problems. Variation of performance properties of CPM in a wide range is possible due to rational choosing of the polymer binder and the conductive filler as well as due to optimum ratio polymer –filler [2].

At the present time the demand for conductive materials used as heating elements, antistatic coatings, and electrode circuits is increasing. Ever increasing production line gives importance to the problem of functional endurance of such products.

In the process of storage and operation conductive polymer compositions undergo chemical and physical changes resulting in the loss of performance properties. These processes are caused by different factors. One of the key factorsreducing efficiency of the products is the process of chemical interaction of polymer materials with atmospheric oxygen. However, in the process of exploitationproducts of conductive polymer materials undergo exposure to not only atmospheric oxygen, but such factors as temperature, electric current, humidity, mechanic loading. All of it can result inacceleration of oxidation process of conductive polymer materials and loss of performance characteristics. It has been observed that oxidation process strongly effects CPM properties; thus, in the process of oxidation changing of electrical parameters and reducing of physical and mechanical characteristics

take placedue to destructive processes taking place during the oxidation of CPM at thesimultaneous exposure to stress and temperature [1, 3, 4].

Thus, the aim of this work was the study of electric current effect on the oxidation process and properties of CPM as well as development of the model of materials oxidation process under different conditions of ageing.

### Experimental

Compositions based on synthetic polyisoprenorubber (SKI-3) and polypyromeltitimide(PPMI) have been studied. Conducting carbon black used as a filler were Technical carbon (TC) P-234, P-514, P-803 [1, 5].

For the experiment technique of quick ageing of CPM was chosen [1]. Oxidation temperature range of CPM based on SKI-3 used was 60°C to140°C, and of CPM based on PPMI 120°C to 240°C. Oxygen pressure in the system was 300 mm Hg. Electrical voltage range 0 to 60V.

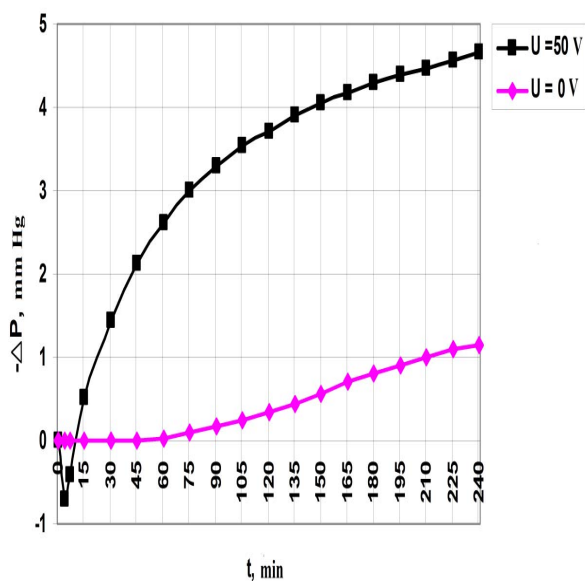
### Results and discussion

In Fig. 1 pressure variation in the system and ageing time of CPM based on SKI-3 containing carbon black P-234 dependence is given.

At the initial stage of ageing of CPM under exposure of current a period of gaseous products evolution is observed. This period is absent in case of oxidation without current exposure.

Similar patterns of CPM oxidation were obtained for other compositions SKI-3 filled with carbon blackP-514, P-803as well as for compositions based on PPMI. It should be noted that with an increase of ageing temperature,evolution of gaseous productsincreases; in case of simultaneous exposure of electrical current and oxygen oxidation rate increases. In case of artificial ageing without exposure to electrical current with increasing of the temperature induction period of oxidation reduces and oxidation rate increases; at the

same time CPM samples oxidation rate without current exposure is lower than for samples oxidized at electrical current exposure.



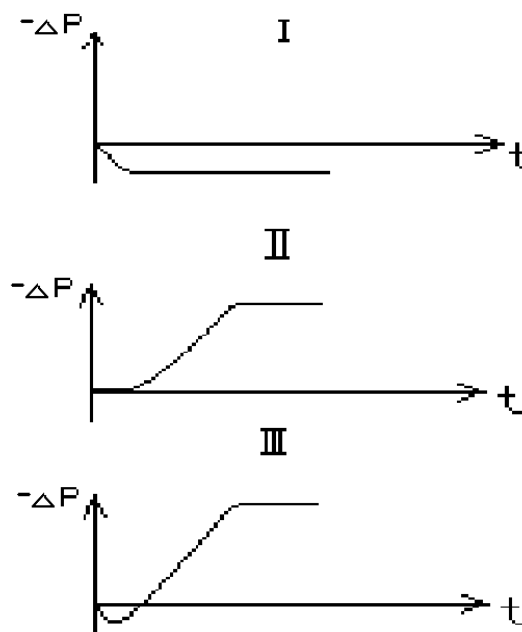
**Fig. 1 - Pressure variation in system and ageing time of CPM based on SKI-3 containing technical carbon P-234 dependence. Ageing conditions:  $P_{O_2} = 300$  mm Hg,  $T = 100^\circ\text{C}$**

Mathematical treatment of kinetic curves of CPM oxidation at different temperatures was carried out. At the curves for CPM samples under exposure to electrical current critical points were chosen: amount of gaseous products, time of evolution. For the curves of the samples without current exposure induction period was marked.

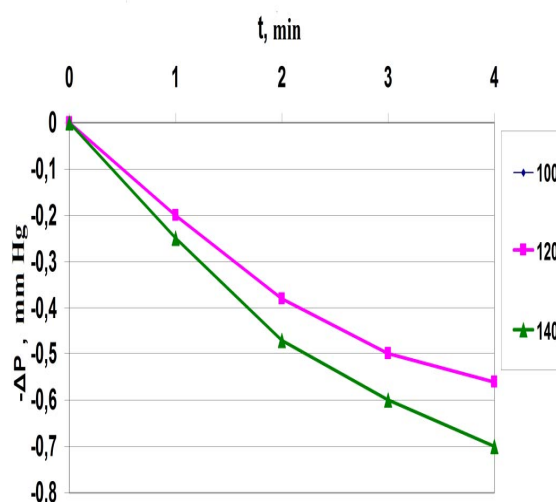
General view of kinetic curve (Fig. 2) is described by the following processes: first type of process (I) is evolution of gaseous products, second type (II) is absorption of the oxygen by the sample, third type (III) supposes two phenomena: evolution of gaseous products and oxygen absorption.

Based on the undertaken study a model of CPM oxidation process was proposed. This model allows to divide a view of kinetic curve into two segments: first segment is a period of gaseous products evolution, reflected on the curve from the beginning of the running time to the point of minimum. This segment is typical only for CPM under exposure to current, because without application of voltage on the sample this segment is absent, and induction period is marked on the curve. Second segment was distinguished from the minimum point in the negative area of kinetic curve to the end point of CPM oxidation time.

Such approach made it possible to determine mathematical formulation of the segment of gaseous products evolution. With a probability of 0.99 shape of curve stays within quadratic dependence  $-\Delta P = at^2 + bt + c$ , where  $a$ ,  $b$ ,  $c$  – coefficients of the equation,  $\Delta P$  – pressure change in the system,  $t$  – time of artificial ageing of the CPM. (fig. 3).



**Fig. 2 - Stages of CPM oxidation process**



**Fig. 3 - Dependence of pressure change on ageing time for segment of gaseous products evolution for CPM based on SKI-3 filled with P-234. Conditions of ageing:  $P_{O_2} = 300$  mm Hg,  $U = 60\text{V}$**

Based on experimental data coefficients  $a$ ,  $b$ ,  $c$  were calculated.

Temperature has a specific impact on the initial period of gaseous products evolution during CPM oxidation under exposure of electrical current. In table 1 some values of pressure change in the lowest point of the kinetic curve  $-\Delta P_{min}$  and time of products evolution  $t_{min}$  is given.

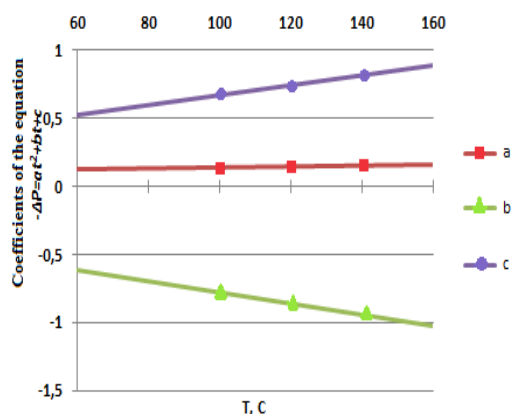
As it is seen from given data, with increasing of the oxidation temperature amount of gaseous products increases and period of their evolution reduces. On the basis of these facts dependences between pressure change in the lowest point of kinetic curve and

temperature  $\Delta P_{min} = f(T)$  and between time of evolution and time were plotted.

In fig. 4 dependences between the calculated coefficients and CPM oxidation temperature is given.

**Table 1 - Amount of evolving gaseous products resulting from CPM ageing**

Composition	Temperature, °C	Pressure change in the lowest point- $\Delta P_{min}$ , mm Hg	Time of gaseous products evolution $t_{min}$ , min
PPMIP-234	200	0,24	30
	300	0,7	27
PPMI P-514	200	0,49	32
	300	0,8	28
PPMI P-803	200	0,46	45
	300	1,35	30
SKI 3 P-214	120	0,7	4
	140	0,56	4,2
SKI 3 P-514	120	0,42	12
	140	0,56	6
SKI 3 P-803	120	0,35	7
	140	0,56	4



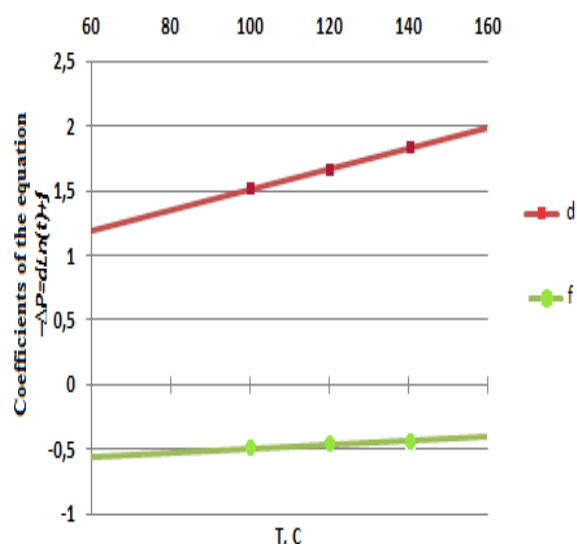
**Fig. 4 - Dependence of coefficients  $a$ ,  $b$  and  $c$  of the gaseous products evolution equation  $-\Delta P=at^2+bt+c$  on temperature for CPM based on SKI-3 filled with P-234. Conditions of ageing:  $P_{O_2} = 300$  mm Hg,  $U = 60V$**

Based on these data dependences between coefficients of the equation  $a$ ,  $b$  and  $c$  and temperature were obtained:

$$a = 0,0115T + 0,1247$$

$$b = -0,081T - 0,732$$

$$c = 0,0695T + 0,6073$$



**Fig. 5 - Dependence of coefficients  $d$  and  $f$  of the equation of the oxygen absorption segment  $-\Delta P=dLn(t)+f$  on temperature for CPM based on SKI-3 filled with P-234. Conditions of ageing:  $P_{O_2} = 300$  mm Hg,  $U = 60V$**

Based on these data dependences between coefficients of the equation  $d$  and  $f$  and temperature were obtained:

Then mathematical analysis of the second segment of the kinetic curve (segment of oxygen absorption by CPM) was performed. In this case it was determined that this process is most likely described by logarithmic equation  $-\Delta P = dLn(t) + f$ . In the Fig. 5 dependences between calculated coefficients of this equation and CPM oxidation temperature are shown.

$$d = 0,158T + 1,3487$$

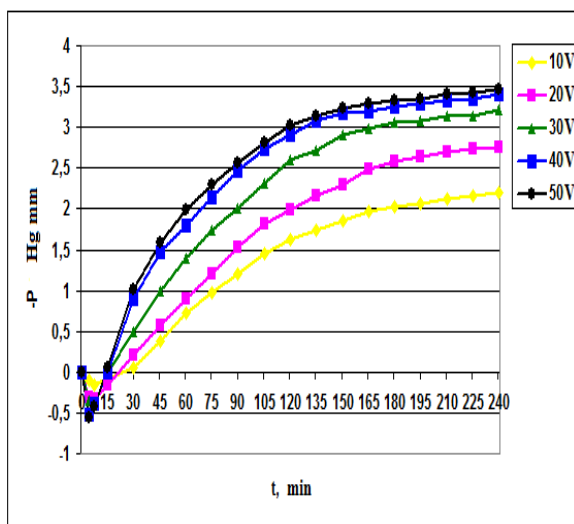
$$f = 0,0293T - 0,528$$

Undertaken studies of the artificial ageing of CPM have allowed determining that with increasing of the voltage, amount of gaseous products and CPM oxidation rate increase (fig. 6).

Because kinetic oxidation curves of CPM oxidation at different conditions of voltage exposure (range 10 to 50V) on the sample looks alike, we performed similar operations to obtain experimental data for CPM aged in the conditions of simultaneous exposure to current and temperature. Equations for the segment of gaseous products evolution and oxygen absorption segments, coefficients of the equations and their dependences on the voltage for these segments have been determined.

On the basis of these data the program which is aimed at selection of the major oxidation factor for material and allows plotting kinetic oxidation curve for CPM in different conditions of ageing has been developed.

The program is carried out after introduction at it is start of two aging factors – temperature and voltage. In the table values of pressure change in the system and CPM oxidation time necessary for plotting are output.



**Fig. 6 - Dependence of pressure change on ageing time for CPM based on SKI-3 depending on voltage. Conditions of ageing:  $P_{O_2} = 300$  mm Hg,  $T = 100^\circ\text{C}$**

This program allows to obtain graphic plot of kinetic oxidation curve  $-\Delta P = f(t)$  under exposure to the voltage and temperature in the range 0 to 60V and 60 to 160°C after entering two oxidation factors (temperature and voltage) for CPM based on SKI-3 and PPMI.

This program can be used for calculation of the amount of evolving gaseous products and time of their evolvment, as well as parameters of oxidation process such as maximum oxidation rate.

## Conclusions

On the basis of the performed experiments influence of the voltage and temperature on the CPM based on PPMI and SKI-3 oxidation process has been determined. Program for data processing allowing simulation of CPM oxidation process with demonstration of the process has been developed.

*This paper is dedicated to the memory of the teacher, honoured worker of science and technology of RSFSR doctor of science, professor Gul' Valentin Evgenievich.*

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