Influence of Electric and Mechanical Forces on the Oxidation Kinetics and Electroconductive Polyisoprene Composition Properties

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ABSTRACT: The investigation results of the simultaneous effect of electric current and tensile deformation on the oxidation processes and electroconductive polyisoprene composition (EPIC) properties are presented in the study. The effects of the EPIC oxidation process under the conditions of complex factor action, consisting of the gaseous product emission and decrease of the oxidation rate at the final stage of the experiment, were disclosed. It was found out that the change in the electric resistance

INTRODUCTION

When using articles of polymer materials, the reactions of the air oxygen interaction are of a great significance for holding their operational characteristics. These reactions are to a great measure affected by the service temperature and action of various forces, chiefly, mechanical and electric. In particular, articles of electroconductive polymer compositions are subjected to such actions.

At present, the demand for electroconductive polymer materials applied as various kinds of heating elements, antistatic coatings, electrode circuits, grounding devices, etc. is increasing. The continuously increasing range of the articles attaches a particular importance to the problem of their serviceability maintaining.

One of the primary factors limiting the articles' serviceability is the process of the chemical interaction of a polymer composition with air oxygen. In addition, the articles are exposed to the action of factors such as temperature, electric current, and mechanical loads that affect to a certain measure the oxidation processes of the polymer matrix.

The previous studies^{1,2} investigating the electric current influence on the oxidation of electroconduc-

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tive polymer compositions demonstrated the increase in the rate of the oxidation process upon electric current flowing. However, these studies took no account of mechanical effects. Therefore, this study is devoted to the investigation of the simultaneous influence of electric current and tensile deformation on the oxidation process and electroconductive polyisoprene composition (EPIC) properties.

EXPERIMENT

The object of the investigation was synthetic polyisoprene rubber-based composition SKI-3 (GOST 14925-79) containing commercial carbon of the II-367- \ni grade in the amount of 50 mass parts. The polyisoprene composition comprised the following components: sulfur, sulfenamide II, zinc oxide, and stearic acid.

The process of the specimen manufacture was performed in several stages: mixture preparation, component blending, and curing. Blending was performed in the laboratory mixer of the "Banbury" type. Upon emerging from the mixer, the mixture was squeezed between rolls. Curing was carried out in the steam-heated hydraulic press at a curing temperature of 143°C.

The plant for accelerated polymer aging was used as the method to investigate the oxidation process under the effect of temperature, electric current, and deformation. The plant's principle of operation consists of registering a pressure change in the system



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Figure 1 Change of pressure in system from time of aging at T = 373 K, U = 60 V and a different degree of deformation.

where the specimen is tested. Since this plant² was previously used to study the thermoelectrooxidation destruction of electroconductive polymer compositions without any mechanical effects, some changes were made enabling the oxidation process to proceed under the simultaneous effect of current and deformation. In compliance with the task to be solved, the design of the reaction dish and clamp-furnished base for specimen securing was changed.

The electric resistance was measured by means of a digital versatile instrument C0234 with the specimen being not removed from the reaction dish. The following methods were also applied in the study: gas chromatography and electronic microscopy.

RESULTS AND DISCUSSIONS

In the process of EPIC oxidation, the pressure change in the system was registered during the experiment period. Since the oxidation was to be performed under the multiple-factor action, the investigations were conducted under the conditions of both the separate factors' action and also of their combination. That allowed us to note some features of these factor's effect on the oxidation processes.

The investigations of the EPIC oxidation process at various extents of the tensile deformation demonstrated that under the conditions of the electric current flow through the composition specimens (Fig. 1), the original area of the kinetic oxidation curves was characterized by an area of the gaseous product emission (not absorbed by absorbents). This area is unavailable for the oxidation process performed under the same conditions, but without any current (Fig. 2). Under these conditions an induction period is observed in the curves' initial area. The performed analysis of the gaseous substances emitted at the initial stage (as a result of oxidation under the electric current flow) showed the presence of methane, hydrogen, and hydrocarbon mixture.



Figure 2 Change of pressure in system from time of aging at T = 373 K, U = 0 V and a different degree of deformation.

It was found out as a result of this investigation that with the increase of the deformation extent the gaseous product emission time decreased and the maximum value of the oxidation rate and pressure change in the system increased. That is accounted for by the action of mechanical load, in particular, tensile deformation that contributes to the intensification of the oxidation process. A similar regularity was observed in EPIC oxidation without any current; however, in this case the induction period decreased.

It is reasonable to point out that the maximum rate of the oxidation process without current increases with deformation to a lesser extent than for the aging process under current that is caused by its direct effect. The maximum value of the pressure change in the system is higher for current-aged specimens.

In the final area of the curves, the EPIC specimen deformation stable values of the pressure change in the system are observed. The observed effect of the oxidation rate decrease is not related to the electric current influence since it was revealed without it as well if the specimen was subjected to deformation in this case. It was found out that the time of this effect manifestation depended on the deformation extent and experiment temperature. For instance, the time of the gaseous product emission decreases with the temperature, the oxidation rate increase, and pressure stabilization effect is observed later. At sufficiently high temperatures (140°C), this effect within the testing time interval was absent, that is related to the formation of additional active centers that assist in intensifying the oxidation processes.

For the purpose of forecasting, the time of the composition serviceability holding the electric characteristics were investigated under the conditions of the complex factor effect. Figure 3 shows the results of the electric resistance change depending on the EPIC aging time.

At the commencement of the experiment, a considerable decrease in the electric resistance is observed. That is related to the electric current flow since when conducting the experiment on EPIC aging under the same conditions, but without current, a negligible decrease in R values was noted. The electric current flow during the oxidation process causes the current-conducting path reformation that is a result of an abrupt decrease in the electric resistance. This assumption is confirmed by the experiments conducted using the method of the electronic microscopy.

The decrease in the electric resistance of the electroconductive polymer composition is also affected by the tensile deformation. For instance, the value of the electric resistance decreases with the deformation that is related to the orientation of the soot structure elements along the tensile axis. The values of the electric resistance behind the area of the electric resistance decrease in curves log R = f(t) do not in practice change in the case of 20 and 50% deformation, and upon the 100% deformation the increased values of the electric resistance in the final area of the experiment is noted.

The area of the electric resistance increase with the temperature was also observed at other deformation degrees and it occurred at a shorter aging time. For instance, at a temperature of 140°C it was observed under all the deformations extents and even without it. That is explained by the fact that the destruction processes that are accompanied with the current-conducting path destruction intensify with temperature.

The electric resistance increase can further result in loss of the electroconductive polyisoprene-based



Figure 3 Change of electric resistance from time of aging at T = 373 K, U = 60 V and a different degree of deformation.

article serviceability. Therefore, the theoretical service life was computed on the basis of the data obtained using the mathematical description programs. The results of the performed serviceability computation found practical application in choosing a composition for the anode grounding system: rustprotection element for gas pipelines.

A design of the reusable device for heating packed foodstuff was developed by the results of the oxida-

tion investigations under conditions of the complex factor action (electric current, deformation, and heating), and the period of its safe operation was established.

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