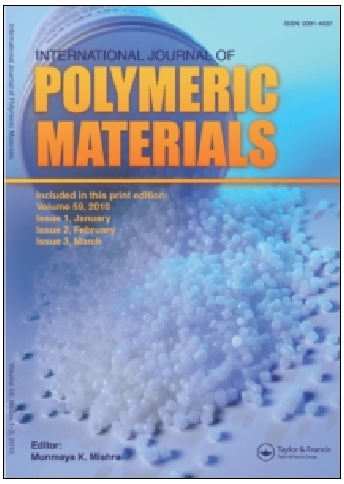

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Mechanooxidative Destruction of Polymers

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To cite this Article Saidov, D. S. , Akhrorov, D. T. , Narzulloev, N. and Zaikov, G. E.(1992) 'Mechanooxidative Destruction of Polymers', International Journal of Polymeric Materials, 17: 3, 229 — 234
To link to this Article: DOI: 10.1080/00914039208041117
URL: http://dx.doi.org/10.1080/00914039208041117

Intern. J. Polymeric Mater., 1992, Vol. 17, pp. 229–234
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Printed in the United Kingdom

Mechanooxidative Destruction of Polymers

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(Received December 7, 1991)

The mechanooxidation of polyisoprene in the cyclic loading-unloading mode is analyzed. The oxidation is shown to flow faster in the cyclic loading mode compared to that of the continuous loading. The initial strain ($\varepsilon_{\text{init}}$) acts as the stabilizing agent in the cyclic oxidation mode.

KEY WORDS Mechanooxidation, polyisoprene, cyclic loading, continuous loading.

INTRODUCTION

Studying the process of oxidation of elastomers effected by load factors the phenomenon of macromolecular splitting into small fragments called microfragments was observed.[1-3] The yield of the product was shown to be dependent on what stage of the reaction the mechanical load acts; the latter may accelerate or decelerate the process of elastomer oxidation.[4] Hence, a revision of traditional concept of the activation role of the mechanical load in the process of elastomer oxidation is needed.

The present paper provides the analysis of elastomer oxidation effected by the mechanical load.

EXPERIMENTAL

The samples of cis-1,4-polyisoprene (SCI-3) sulphur vulcanized according to standard technique provided in the form of the film of 60–120 mm thickness were used for investigation. The investigation was performed with both purified and unpurified samples. The purification was performed using CCl_4. Oxidation products in the form of C=O groups in the absorption band 1700–1740 cm^{-1} were periodically detected using the vibrational spectroscopy and the spectrophotometer Specord-75 UR.

The experiment was performed as follows. The samples were strained to some degree followed by the subsequent unloading. Both the initial $\varepsilon_{\mathrm{init}} = 0\text{–}400\%$ and the finite $\varepsilon_{\mathrm{fin}}$ strains were varied. The finite extension within the experiment had two values: 550% and 750%, i.e., a cycle comprising stages of loading and unloading was performed $[\varepsilon_{\mathrm{init}} - \varepsilon_{\mathrm{fin}} - \varepsilon_{\mathrm{init}}]_n$. The kinetics of the process was monitored through the accumulation of C=O groups by taking spectra every 10 cycles. The experiment was continued until the breakage of the sample which occurred usually after 120–150 cycles. The extension was performed using the lever unit provided for large strains.[5]

RESULTS AND DISCUSSION

Figure 1(a) and (b) show the dependence of the reduced optical density ($\Delta - \Delta_0/\Delta_0$) of the 1740 cm^{-1} band on the cycle frequency. The difference between both

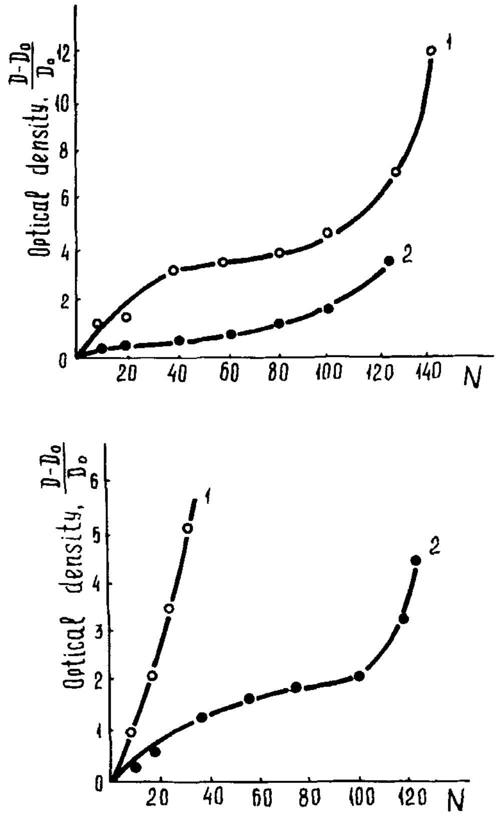

FIGURE 1 The plot of the reduced optical density of 1740 cm^{-1} band vs cycle frequency. The rest period between cycles: a) 1 sec.; b) 10 sec. The finite strain $\varepsilon_{\mathrm{fin}}$ in the loading-unloading cycle: (1) 750%; (2) 550%.

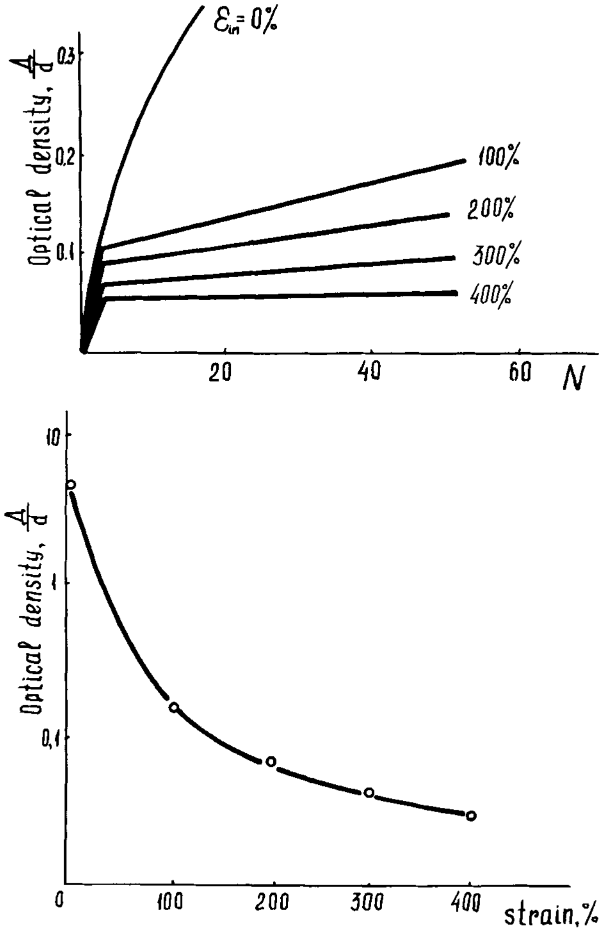

FIGURE 2 The plot of the reduced optical density of 1740 cm band vs the number of loading-unloading cycles (N) in samples with different degrees of the preliminary strain (a); (b) the yield of oxidation groups (Δ/d; C=O) versus the preliminary strain during the continuous loading-unloading cycle (N = 30).

curves appears due to strain hence, at $\varepsilon_{\text{fin}} = 750\%$ the yield of oxidation products of the reaction is more significant compared to samples with the degree of finite strain $\varepsilon_{\text{fin}} = 550\%$. In this case significant strains seem to accelerate the oxidation process. In cases of the increase of the initial extension ($\varepsilon_{\text{init}}$) from 0–400% the deceleration of the oxidation kinetics is observed (Figure 2). The initial strain acts here as the stabilizing agent.

The experiments further show that the kinetics of oxidation is effected mainly by the durability of the loading state rather than the value of the maximum loading (Figure 3). The reduced optical density of 1740 cm^{-1} band seems to be increasing with the loading period. This is explained in terms of the thermoactivated processes according to which the concentration of free radicals in strained samples is increas-

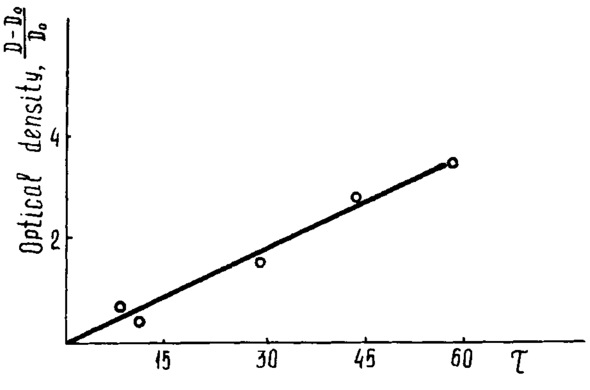

FIGURE 3 The plot of the reduced optical density $\left(\Delta - \Delta_0/\Delta_0;\ \rangle C{=}O\right)$ vs the durability of the loading state.

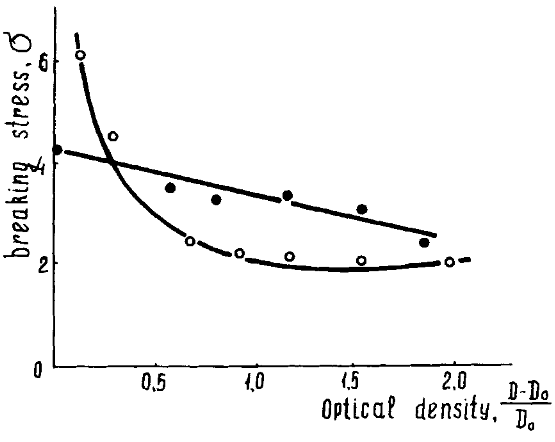

FIGURE 4 The variation of the breakage stability (σ_{br}) of polyisoprene with the accumulation of C=O groups: (1) inhibited samples; (2) purified samples.

ing with time and transforms into stable C=O groups due to chemical reactions of oxidation.

The dependence of the breaking stress σ_{br} on the concentration of C=O groups was studied to compare breaking microprocesses with the macroscopic σ_{br} parameter (breaking stress). The results are shown in Figure 4.

This dependence drops abruptly for purified samples at low concentrations of C=O groups followed by the deceleration. Further seems to be independent of the concentration of C=O groups. As for inhibited samples the $\sigma_{br} - \Delta - \Delta_0/\Delta_0$ $\left(\rangle C{=}O\right)$ dependence of the elastomers is monotonously decreasing with the accumulation of C=O groups.

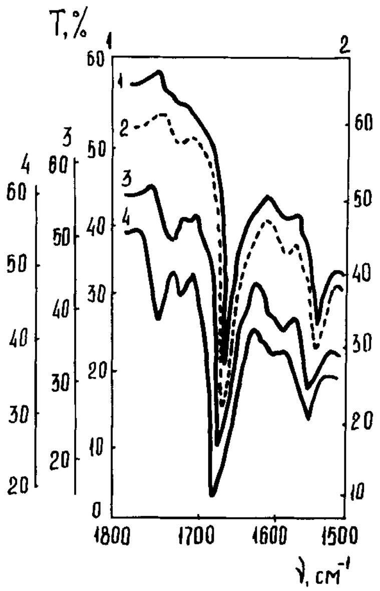

FIGURE 5 IR-spectra of polyisoprene in 1900-1500 cm^{-1} band: (1) initial; (2) after the appearance of the 1710 cm^{-1} band; (3) after 20-hr storage.

Thus, the analysis of the above experiments confirms that for polyisoprene samples (irrespective of whether they are purified or not) the breaking stress σ_{br} (and hence, the durability) drops with the concentration of C═O groups.

These data are certainly needed to plot the correlation function of macro- and microprocesses of polymer destruction.

The experiments on polyisoprene oxidation show that for the cyclic loading-unloading process in some samples along with 1740 cm^{-1} band additional 1710 cm^{-1} band are observed (Figure 5). After recording the 1710 cm^{-1} band the oxidation in the cyclic loading-unloading mode was stopped and the time variation of the band position was traced. The intensity of the band appeared to drop while the band completely disappeared within 18–22 hr. Along with the decrease of the 1710 cm^{-1} band the increase of the 1540 cm^{-1} band was observed. The same picture was observed both for samples after the breakage and those under indoor conditions. The appearance and disappearance of the 1710 cm^{-1} band in various conditions (effected by the mechanical loading, during the storage) remains to be understood, since no additional effect was used apart from small dosages of IR-irradiation.

Thus, the following may be concluded on the basis of obtained experimental data on the elastomer oxidation in the cyclic mode. 1. The kinetics of the oxidative polymer destruction depends on the loading mode. The process flows faster in the cyclic mode compared to that in the continuous loading model. 2. At oxidative destruction a new 1710 cm^{-1} band appears together with aldehydes (1740 cm^{-1}) disappearing with time and with the simultaneous increase of the 1540 cm^{-1} band intensity.

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