

Interrupted Plasma Treatment of EPDM-40 Rubber

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SYNOPSIS

The glow discharge plasma treatment of EPDM-40 rubber has been studied using the IR MATR spectroscopy. A mathematical model for the kinetics of rubber surface oxidation processes has been suggested. The interrupted plasma treatment was proposed as the most efficient technique of polymer surface activation. It was noted that the rubber oxidation processes occurs during the contact with air after the plasma treatment, but not during the discharge. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The glow discharge plasma is known as a technique of surface treatment of the improvement of adhesion.¹ In order to determine the mechanism of the plasma treatment effect on adhesion, it would be of interest to study the surface of a plasma-treated polymer, that is, to study the physicochemical processes that occur at the surface layer of a polymer under the action of the glow discharge plasma. Due to the complex character of the polymer as a molecular system, despite the successful development of plasma physics theory,² the theory of polymers in plasma has been insufficiently developed.³ Thus, the phenomenological theories of the plasma action upon polymers are of interest.

As was often shown,⁴ the occurrence of active oxygen-containing groups on a polymer surface is essential for adhesion, especially in the case of an epoxy-containing adhesive.⁵ The presence of oxygen-containing groups on a polymer surface, after treatment in air plasma, is recorded in spectra of XPS (X-ray photoelectron spectroscopy)⁶ and IR MATR (multiple attenuated total reflection) spectroscopy.⁷ The occurrence of these groups is related to the air oxygen residues in the discharge, as well as to the soluted oxygen in a polymer.⁸ However, the results of our preliminary experiments could not be explained by such assumptions. Therefore, the purpose of this work was to consider the process of the oxygen-containing groups occurrence on a polymer surface under the action of glow discharge plasma.

EXPERIMENTAL

The ethylene-propylene dicyclopentadiene rubber EPDM-40 (Russia), nonvulcanized and vulcanized by a radiation mechanism using ⁶⁰Co, was employed as a material. Except for the antioxidant Neoson D, the rubber did not contain any other additives.

The plasma discharge was excited by a 10 kHz generator in a spherical glass reactor, 0.1 m diameter. The discharge parameters were voltage 450 V, current 1.6 mA, and pressure 10⁻¹ torr.

IR MATR spectra were recorded using an UR-20 spectrometer (Carl Zeiss Jena, Germany), with a specially designed MATR accessory on KRS-5 crystals ($\alpha = 45^\circ$, operating number of reflections 19). The quality of the optical contact was ensured by the good elasticity of samples. Also, the normalization on the optical density of the band at $\delta(\text{CH}_2) = 1462 \text{ cm}^{-1}$ was carried out.

THEORY

The primary action of the plasma on a polymer is the formation of radicals,¹ occurring at the cleavage of chemical bonds C—H and C—C. The formation and further relaxation of radicals in polymers during the plasma treatment has been studied for many materials using the EPR spectroscopy. A specific, asymptotic dependence of radical concentration on the plasma treatment time, t_1 , was experimentally observed⁹:

$$R = R_0(1 - \exp\{-k_1 t_1\}) \quad (1)$$

The recombination of radicals, after removing the discharge, is similarly described by an exponential relationship, corresponding to the first order reaction⁷:

$$R' = R \exp\{-k_2 t_2\} \quad (2)$$

where t_2 is the storage time of a polymer, starting from the discharge removal moment, when the radical concentration was R .

It should be further assumed that in the polymer plasma treatment, even in oxygen-containing plasma, the oxidative reactions do not take place during the discharge, or they are insignificant. After the discharge removal and the air intake in the reactor, in addition to reactions of radical recombination, the oxidative reactions take place with the formation of the hydroperoxides, and then the stable oxygen-containing groups.^{6,10} Since the radical formation during the plasma treatment occurs in a sufficiently thin surface layer of the polymer,¹¹ the oxygen diffusion may be neglected. The reaction rate of oxygen-containing groups formation will then be determined by the radical concentration in the polymer surface layer.

Taking into account the recombination reaction of radicals and their interaction with oxygen, the change in the radical concentration with time must correspond to:

$$dR' = -k_2 R' dt_2 - k_3 R' dt_2 \quad (3)$$

and the change in the oxygen-containing group concentration must correspond to:

$$dC = k_3 \alpha R' dt_2 \quad (4)$$

where α is the quantum yield of the oxygen-containing groups as a result of the radical-oxidative reactions. The joint integration of eqs. (3) and (4) yields:

$$R' = R \exp\{-(k_2 + k_3)t_2\} \quad (5)$$

$$C = \frac{k_3 \alpha}{k_2 - k_3} R [1 - \exp\{-(k_2 + k_3)t_2\}] + C_0 \quad (6)$$

where C_0 is the initial concentration of oxygen-containing groups occurring at the surface under the destructive action of the environment.

Analyzing together eqs. (1), (5), and (6), it may be noted that the oxygen-containing group concentration cannot exceed a certain value that is limited by the asymptotic character of the radical dependence at the plasma treatment and by the ratio of the velocities of radical recombination and oxidation. The concentration of oxygen-containing groups may be exceeded by the interrupted (plasma and air) treatment of the polymer.

In the n -fold treatment, the eqs. (1), (5), and (6) are transformed into a system of equations:

$$\begin{cases} \text{First Treatment} & \begin{cases} R_1 = R_0(1 - \exp\{-k_1 t_1\}) \\ R'_1 = R_1 \exp\{-(k_2 + k_3)t_2\} \\ C_1 = \frac{k_3 \alpha R_1}{k_2 + k_3} [1 - \exp\{-(k_2 + k_3)t_2\}] + C_0 \end{cases} \\ \text{Second Treatment} & \begin{cases} R_2 = R_0(1 - \exp\{-k_1 t_1\}) + R'_1 \exp\{-k_1 t_1\} \\ R'_2 = R_2 \exp\{-(k_2 + k_3)t_2\} \\ C_2 = \frac{k_3 \alpha R_2}{k_2 + k_3} [1 - \exp\{-(k_2 + k_3)t_2\}] + C_1 \end{cases} \\ (n-1)\text{th Treatment} & \begin{cases} R_{n-1} = R_0(1 - \exp\{-k_1 t_1\}) + R'_{n-2} \exp\{-k_1 t_1\} \\ R'_{n-1} = R_{n-1} \exp\{-(k_2 + k_3)t_2\} \\ C_{n-1} = \frac{k_3 \alpha R_{n-1}}{k_2 + k_3} [1 - \exp\{-(k_2 + k_3)t_2\}] + C_{n-2} \end{cases} \\ n\text{th Treatment} & \begin{cases} R_n = R_0(1 - \exp\{-k_1 t_1\}) + R'_{n-1} \exp\{-k_1 t_1\} \\ C_n = \frac{k_3 \alpha R_n}{k_2 + k_3} + C_{n-1} \end{cases} \end{cases} \quad (7)$$

if, after the n th treatment, the polymer was in air for a long time ($t_2 \rightarrow \infty$).

The consecutive solution of the system shown in eq. (7) yields an equation for the oxygen-containing group concentration after the n -fold treatment:

$$C_n = \frac{k_3 \alpha R_0}{k_2 + k_3} (1 - \exp\{-k_1 t_1\}) \times \left[\sum_{i=0}^{n-1} (n-i) \exp\{-ik_1 t_1 - i(k_2 + k_3)t_2\} - \sum_{i=1}^{n-1} (n-i) \exp\{-(i-1)k_1 t_1 - i(k_2 + k_3)t_2\} \right] \quad (8)$$

Equation (8) was obtained on the basis of the general regularities of the radical-oxidative reactions, without considering the particular type of reactions and oxygen-containing groups. It should be noted, however, that this equation refers to the oxygen-containing groups, that is, the final stage of conversion of the radical-oxidative reactions. According to the known reactions of polyolefines,¹⁰ such groups are hydroxyl, ester, carbonyl, and carboxyl groups.

RESULTS AND DISCUSSION

Figure 1 shows the IR MATR spectra of the vulcanized rubber surface after the plasma treatment. The spectrum contains the bands at the 3500–3200 cm^{-1} region, where the $\nu(\text{OH})$ absorption of peroxide, hydroxyl, and carbonyl groups is manifested. The intensity of bands is increased at the 1600–1750 cm^{-1} region, which bands are assigned to the vibration of C=C and C=O bonds. The bands at 1605, 1634, 1643, and 1661 cm^{-1} may be tentatively attributed¹² to the absorption of unsaturated carbon-carbon bonds, and the bands at 1690, 1712, 1728, 1745, and 1760 cm^{-1} may be attributed to $\nu(\text{C}=\text{O})$ vibrations in carbonyl, carboxyl, and aldehyde groups. Moreover, a wide background is observed at the 1100–1400 cm^{-1} region, which is caused by the absorption of C—O bonds of various oxygen-containing groups.

Except for the adhesion, the most important groups are carboxyl groups on the rubber surface.^{4,5} The determination of carboxyl groups by the IR spectrum is more appropriately made by the intensity of (C=O) absorption, because the peak extinction coefficient of this band is the largest.

In order to assign the bands recorded in the $\nu(\text{C}=\text{O})$ region more accurately, the surface of oxidized rubber was treated with the 10% NaOH solution in ethanol. After treatment (Fig. 1), the in-

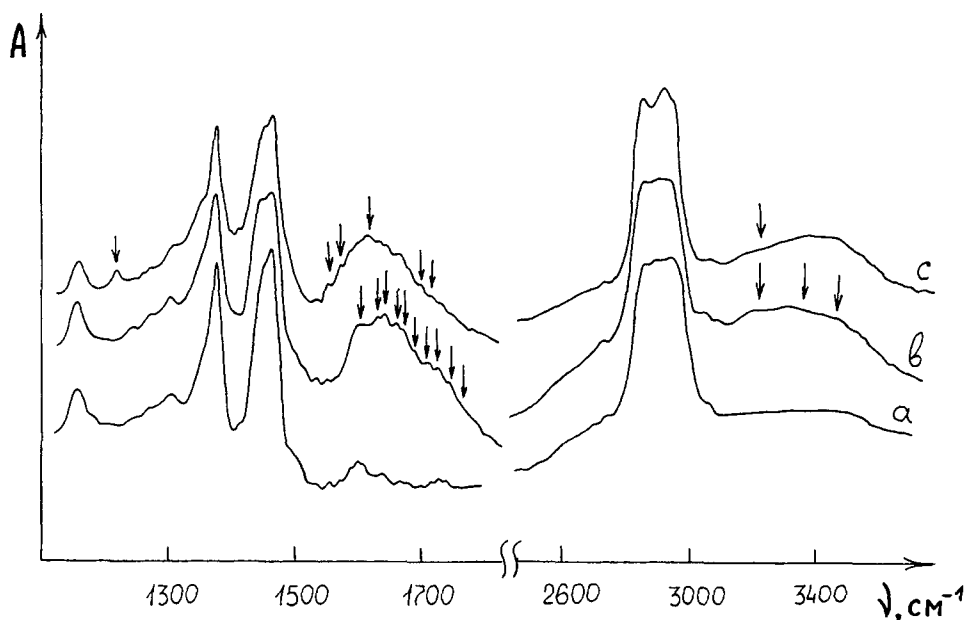


Figure 1 IR MATR spectra of vulcanized EPDM-40 rubber: (a) initial, (b) after plasma treatment, (c) after plasma and NaOH treatment.

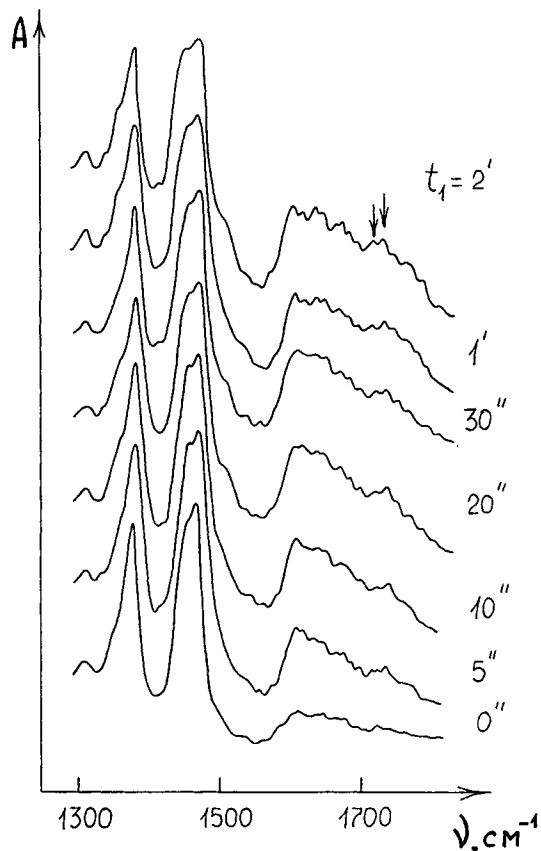


Figure 2 IR MATR spectra of nonvulcanized EPDM-40 rubber with various times of plasma discharge treatment. The air treatment time is 3 min, $n = 5$.

tensity of bands at 1712 and 1728 cm^{-1} was decreased, and a set of bands at 1570, 1585, 1615 cm^{-1} , assigned to $\nu(\text{C}=\text{O})$ of sodium carboxylate, appeared. At the same time, the intensity of $\nu(\text{OH})$ of the carboxyl group is decreased in the 3200–3300 cm^{-1} region. The band that appeared at 1218 cm^{-1} may be assigned also to $\nu(\text{C}-\text{O})$ of sodium carboxylate, but it is difficult to determine accurately.

Therefore, from the entire set of $\nu(\text{C}=\text{O})$ bands, the lines at 1712 and 1728 cm^{-1} are to be assigned to carboxyl groups of the rubber oxidized layer, and their occurrence is to be analyzed as a consequence of the plasma treatment.

In order to find the parameters of the plasma treatment process, the rubber was treated in ultimate conditions. According to eq. (8), the ultimate conditions are the case of $t_1 = \infty$ and $t_2 = \infty$ at constant parameters of the discharge. For correct measurements of the optical density of analyzed bands, the five-fold interrupted treatment of rubber was sufficient.

The case $t_2 = \infty$ was realized in the air treatment, with 3 min between the periods of the discharge treatment. Figure 2 shows the IR MATR spectra of the nonvulcanized rubber surface at various times of the discharge treatment. The changes in the spectrum in the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ region, analogous for vulcanized rubber, are observed. Figure 3 shows the dependence of normalized optical density of analyzed bands on the time of the rubber

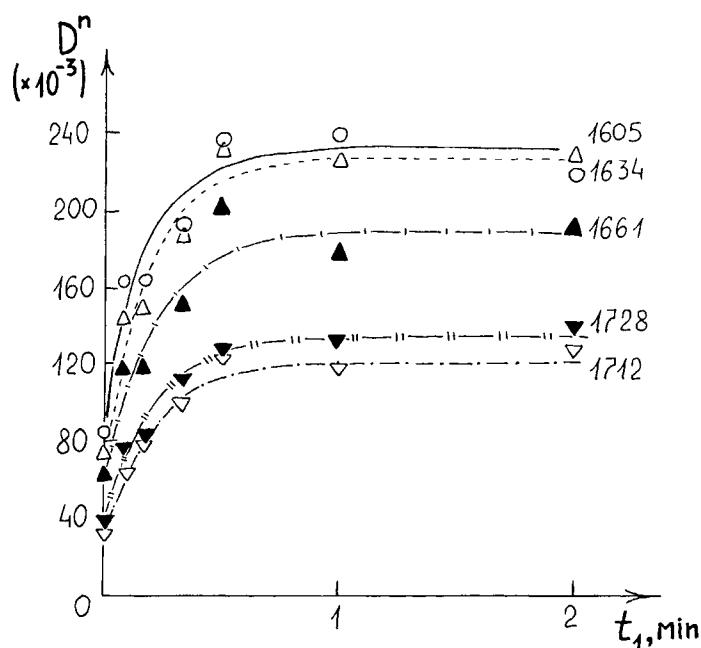


Figure 3 Normalized optical density of IR MATR spectrum bands as a function of the time of rubber plasma treatment. (O) $\nu(\text{C}=\text{C}) = 1605$, (Δ) $\nu(\text{C}=\text{C}) = 1634$, (\blacktriangle) $\nu(\text{C}=\text{C}) = 1661$, (∇) $\nu(\text{C}=\text{O}) = 1712$, (\blacktriangledown) $\nu(\text{C}=\text{O}) = 1728 \text{ cm}^{-1}$.

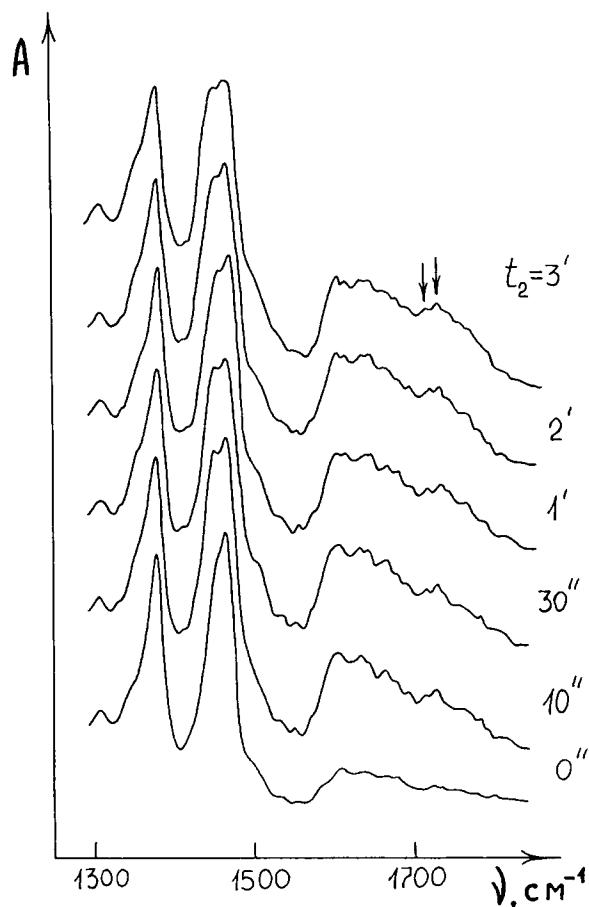


Figure 4 IR MATR spectra of nonvulcanized EPDM-40 rubber with various times of air treatment. The plasma treatment time is 1 min, $n = 5$.

discharge treatment. Equation (8), at $t_2 = \infty$ and $n = 5$, is converted to

$$C_5 = 5 \frac{k_3 \alpha R_0}{k_2 + k_3} (1 - \exp\{-k_1 t_1\}) + C_0$$

or, taking into account the Lambert-Beer law and the optical density normalization,

$$D_5^n = 5A(1 - \exp\{-k_1 t_1\}) + D_0^n \quad (9)$$

where D_0^n is the optical density of the bands of untreated rubber spectrum. Here

$$A = \frac{k_3 \alpha R_0}{k_2 + k_3} \frac{\epsilon_j}{\epsilon_{CH} C_{CH}}$$

where ϵ_j is the extinction coefficient of an analyzed band, ϵ_{CH} is the extinction coefficient of the band $\delta(\text{CH}_2) = 1462 \text{ cm}^{-1}$, and C_{CH} is the concentration of the methylene groups. The determined parame-

ters of eq. (9), from the experimental dependence (Fig. 3), are given in Table I.

In addition to the $\nu(\text{C}=\text{O})$ bands at 1712 and 1728 cm^{-1} , the optical densities of $\nu(\text{C}=\text{O})$ bands at 1605, 1634, and 1661 cm^{-1} were also analyzed. The preexponential factor, k_1 , refers to the radical formation process and must be independent on the type of the analyzed groups, just as it was observed in the calculated results. Factor A is different for various types of groups. Apparently, the difference is due not only to the extinction coefficients of different bands, but also to the quantum yield of these groups.

The case $t_1 = \infty$ was realized in the five-fold rubber discharge treatment for 1 min. The IR MATR spectra of the nonvulcanized rubber surface at various times in air are given in Figure 4. The changes in the spectrum coincide with the preliminary experimental results with vulcanized and nonvulcanized rubbers. Figure 5 shows the dependence of the normalized optical density of analyzed bands on the air treatment time. Equation (8), at treatment conditions $t_1 = \infty$, $n = 5$, may be written as:

$$C_5 = \frac{k_3 R_0}{k_2 + k_3} [5 - 4 \exp\{-(k_2 + k_3)t_2\}] + C_0$$

or, taking into account the Lambert-Beer law and the optical density normalization:

$$D_5 = A[5 - 4 \exp\{-(k_2 + k_3)t_2\}] + D_0^n \quad (10)$$

where the symbols of eq. (9) are retained. The determined parameters of eq. (10) are given in Table I.

The sum $(k_2 + k_3)$ was found to be independent of the type of these groups. If the coefficient k_2 , associated with the radical recombination, must be independent of the type of the group, then the coincidence of coefficient k_3 suggests that the rate of the unsaturated carbon-carbon bond formation is determined by the same rates of processing the rubber radical-oxidative reactions as the formation of oxygen-containing groups. Good agreement of coefficient A of corresponding bands obtained in this experiment with the previous results is observed.

Thus, eq. (8) describes the change in the rubber surface during the interrupted plasma treatment at ultimate conditions. From eq. (8), it becomes evident that the maximum oxidation of rubber is achieved when $t_1 = \infty$ and $t_2 = \infty$. In this case, the eq. (8) transforms into the expression:

$$C_n = \frac{k_3 \alpha R_0}{k_2 + k_3} n \quad (11)$$

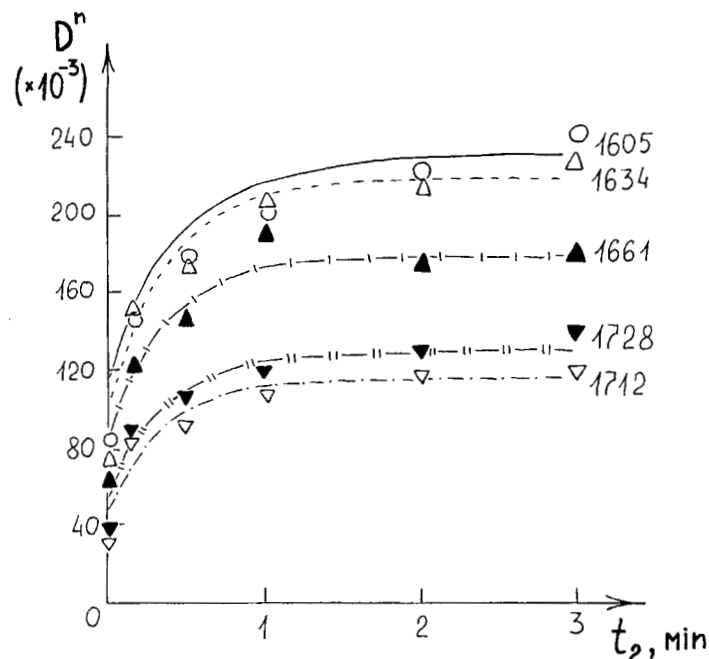


Figure 5 Normalized optical density of IR MATR spectrum bands, as a function of the time of rubber air treatment, between periods of plasma treatment. (○) $\nu(\text{C}=\text{C}) = 1605$, (Δ) $\nu(\text{C}=\text{C}) = 1634$, (\blacktriangle) $\nu(\text{C}=\text{C}) = 1661$, (∇) $\nu(\text{C}=\text{O}) = 1712$, (\blacktriangledown) $\nu(\text{C}=\text{O}) = 1728 \text{ cm}^{-1}$.

where n is the period number of the treatment in discharge and in air.

Figure 6 presents the dependence of the optical density of $\nu(\text{C}=\text{O})$ bands of carboxyl groups on the overall time of discharge treatment. The continuous and interrupted treatments, with parameters $t_1 = 1$ and $t_2 = 3$ min, were used. The bands denote the graphical solution of eq. (8) and (11), using the parameters determined (see Table I). In the case of the interrupted treatment, the initial portion of the dependence agrees well with the theory. Disagreement is observed at long treatment times. This is due to the fact that the concentration of oxygen-containing groups becomes so high that the pro-

cesses of the carbon-oxygen bond destruction begin to be manifested, which lowers the oxygen-containing group concentration.

CONCLUSIONS

1. The agreement of experimental results with the model suggested by polymer plasma treatment has confirmed the initial assumption that the oxidative reactions in the surface layer of a treated polymer occur during contact of the polymer with a sufficient

Table I Parameters of Eqs. (9) and (10)^a

| Treatment Conditions | ν (cm^{-1}) | 1605 C=C | 1634 C=C | 1661 C=C | 1712 C=O | 1728 C=O |
|----------------------|-----------------------------------|-------------|-------------|-------------|-------------|-------------|
| Without treatment | D_0^n | 0.084 | 0.075 | 0.063 | 0.032 | 0.038 |
| $t_2 = \infty$ | A | 0.030 | 0.031 | 0.026 | 0.018 | 0.019 |
| t_1 varied | k_1 (min^{-1}) | 5.9 | 5.0 | 4.5 | 4.5 | 4.7 |
| $t = \infty$ | A | 0.029 | 0.029 | 0.023 | 0.017 | 0.018 |
| t_2 varied | $k_2 + k_3$ (min^{-1}) | 2.3 | 2.5 | 2.7 | 2.7 | 2.6 |

^a Explanations are in the text.

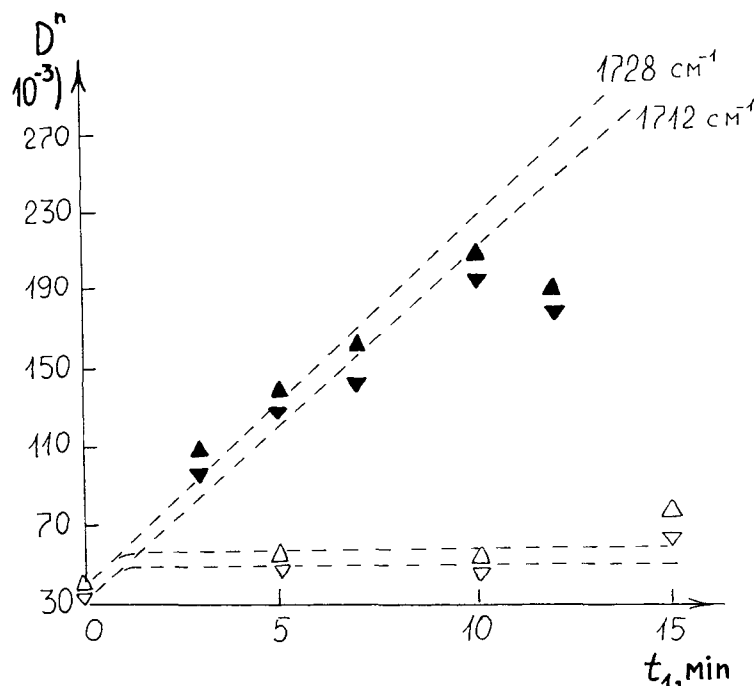


Figure 6 Normalized optical density of IR MATR spectrum bands as a function of the total time of plasma treatment at continuous (open triangles) and interrupted (closed triangles) treatment. The lines are the theoretical dependences. (∇) $\nu(\text{C}=\text{O}) = 1712 \text{ cm}^{-1}$, (Δ) $\nu(\text{C}=\text{O}) = 1728 \text{ cm}^{-1}$.

amount of oxygen (e.g., with air), but not during plasma discharge.

2. The radical-oxidative reactions in the surface layer of a polymer and the occurrence of stable oxygen-containing groups may be described using the known equations of polymer radiation chemistry.
3. As follows from the polymer theory in air plasma, the most efficient technique of polymer surface activation is the interrupted plasma treatment with recurrent air intake into the reactor.

It should be noted that the theory suggested was confirmed only for the EPDM-40 rubber, but there are no visible limitations for other polymers.

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