Treatment of polymer surfaces in plasma
Part II. Qualitative analysis

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Abstract In this paper, the solutions of kinetic model are qualitatively analyzed. The model describes treatment of polymer surfaces in RF-discharge (12.56 MHz). The treating of polymer surfaces in different gases leads to alteration of surface tension of the material. The experimental bearings for wetting contact angle and work of adhesion during the time of treating are compared with theoretical results obtained from the model. As a pattern polymer material, polyethylene terephthalate (PET) is used in plasma-creating gases: argon (Ar), oxygen (O₂), Freon 14 (CF₄) and Freon 12 (CF₂Cl₂).

1. Introduction
Our theoretical model [1] describes the treatment of polymer material in gas discharge plasma. There is no data in the scientific publications for values of the rate constants which take part in chemical equations. This renders difficulty in quantitatively comparing the theoretical and experimental results. For that reason in the present paper we will compare qualitatively these theoretical results with our experimentally obtained results [2, 3], which are presented here on figure 1(a) and figure 1(b):

![Figure 1](image)

**Figure 1.** Wetting contact angle $\theta$ and work of adhesion $W_a$ as a function of the treatment time $t_{tr}$.

The solution of the system kinetic equations [1, (6)] depends on several common constants. But the stationary solution depends only on constant $\beta$. According to values of $\beta$, the polar P or non-polar N functional groups can be dominated. Therefore, in our analysis two boundary cases $\beta<1$ and $\beta>1$ will be examined. The connection of the value $\beta$ with the rest constants is:

$$\beta = \frac{k_N}{k_p}, \quad k_p = \frac{\tau_2}{\tau_4}, \quad k_N = \frac{\tau_3}{\tau_5},$$

where $\tau_1, ..., \tau_5$ are rate constants for the heterogeneous chemical reactions considered in [1].
2. Treatment in argon and oxygen plasma

Our experimental results (figure 1(a)) show monotonic decreasing of the contact angle values \( \theta \) with augmentation of the discharge time \( t_d \) in oxygen and argon plasma. We will assume that it is due to increasing of the polar \( P \) groups. The presence of oxygen is necessary for the creation of polar groups. The treatment in pure argon plasma is realized without oxygen. Therefore, the question is where that oxygen comes from. Despite that, while the hydrogen is absent as a component of the pattern gas, non-polar groups are nevertheless created, mainly with hydrogen. This problem is not completely explained in scientific publications (even in most cases it is passed over). There are three possibilities. The first is: the oxygen and hydrogen are obtained from the polymer structure. The second is: the oxygen and hydrogen are absorbed in the polymer volume. The last one is: they appear after taking out the pattern material in air environment, right after his treatment in gas discharge. These possibilities shall not be discussed in the present paper.

We will consider that there is always presence of oxygen and hydrogen molecules in the reactor, independently of the kind and the purity of the pattern gas. For that reason we will analyze together experimental results for pure argon, pure oxygen or their mixtures [2, 3]. We will use the solution of the system of differential kinetic equations under the previously mentioned conditions. These equations describe the alteration of the functional groups on the polymer surface in the course of the plasma treatment.

The solution depends on the constant \( \beta \). As we mentioned, the constant meets a condition \( \beta < 1 \) in examined gases. We can present \( \beta \) by corresponding constants and will obtain:

\[
k_p > k_N, \quad \frac{\tau_2}{\tau_1} > \frac{\tau_3}{\tau_1}, \quad \frac{\tau_4}{\tau_1} > \frac{\tau_5}{\tau_1}.
\]

Moreover, we will accept that \( \tau_2 > \tau_3 \). This inequality shows that the destruction of \( N \) functional groups is more possible by comparison with the destruction of \( P \) functional groups.

We will analyze the solution [1, (11)-(13)] at the following values of the constants defined in relation to the constant \( \tau_1 \):

\[
\frac{\tau_2}{\tau_1} = 10, \quad \frac{\tau_3}{\tau_1} = 10, \quad \frac{\tau_4}{\tau_1} = 0.01, \quad \frac{\tau_5}{\tau_1} = 0.1.
\]

These values are arbitrary selected. As it was discussed in [1], there is no data in the scientific publications about the mentioned constants. In first approximation we will give the order of alteration in relation to the constant \( \tau_1 \). We can determine the rest constants using these assumptions:

\[
k_p = 10^3, \quad k_N = 10^2, \quad k_{14} = 10^2, \quad k_{35} = 10, \quad \beta = 0.1, \quad \gamma = 11, \quad \alpha = 1,1, \quad \lambda_1 = 1, \quad \lambda_2 = 5.5 \cdot 10^{-2}.
\]

Moreover we will accept somewhat arbitrarily that:

\[
X_0 = 0.7, \quad Z_0 = 0.3, \quad V_0 = 0.
\]

Then the solution of the system in [1, (6)], using the constants (3) and (4) is:

\[
X = 0.7 e^{-\tau_0} \\
Z = -0.333 e^{-\tau_0} - 0.276 e^{-5.5 \cdot 10^{-2} \tau_0} + 0.909 \\
V = -0.367 e^{-\tau_0} + 0.276 e^{-5.5 \cdot 10^{-2} \tau_0} + 0.091
\]
The solution (5) shows that the components \( X \) and \( Z \) are monotonous functions. The first component decreases, while the second increases in the dimensionless time. The component \( V \) has maximum at \( t_n = 3.01 \) where the value \( V_{max} = 0.307 \). The dependences of the components \( Z \) and \( V \) as a function of dimensionless time \( t_n \) are shown on figure 2. The component \( X \) decreases rapidly and at values of \( t_n = 5 \) already it has values near zero. Comparing the theoretical results (5) with the experimental ones (figure 1(a) and figure 1(b)) is obvious that the component \( Z \) (representing the number of the polar molecules \( P \)) can qualitatively describe the change of \( \cos \theta \) as a function of the time of treatment \( t_0 \).

![Figure 2. Polar Z and non-polar V relative concentrations as functions of the relative time \( t_n \) for oxygen and argon plasma.](image)

### 3. Treatment in Freon plasma

The presence of two gases as a chemical active (oxygen) and organic (Freon 12 and Freon 14) shows complicate development of the polymer surface morphology (figure 1(a) and figure 1(b)). At the beginning an increase in the polar component is shown. After that non-polar \( N \) groups (for example \( \text{CF}_3 \), \( -\text{CCIF}_2 \), etc.) start to grow. It is obvious that rate constants should correspond to the condition \( \tau_5 < \tau_4 \). Moreover, \( \beta \) cannot be less than one.

In order to analyze the solution of the system \([1, (6)]\), we will consider the following values of the constants defined in relation to \( \tau_1 \):

\[
\frac{\tau_3}{\tau_1} = 10 \quad \frac{\tau_3}{\tau_1} = 10 \quad \frac{\tau_4}{\tau_1} = 0.01 \quad \frac{\tau_5}{\tau_1} = 0.001
\]

These values are arbitrary chosen defining the order of the alteration (in relation to \( \tau_1 \)). We can determine the rest constants under the mentioned assumptions:

\[
k_P = 10^3 \quad k_N = 10^4 \quad k_{14} = 10^5 \quad k_{15} = 10^3 \quad \beta = 10 \quad \gamma = 0.1 \quad \alpha = 1
\]

We will consider that

\[
X_0 = 0.7 \quad Z_0 = 0.3 \quad V_0 = 0
\]

Then, the solution of the system \([1, (6)]\), which describes the treatment of polymer material in Freon plasma is:
The solution \( (9) \) shows that the components \( X \) and \( V \) are monotonic functions. The first function decreases, while the second increases in time \( t_n \). The component \( Z \) increases to maximum value \( Z_{\text{max}} = 0.618 \) \( (t_{\text{max}} = 5.033) \) and after it begins to decrease. The dependences of the components \( Z \) and \( V \) as a function of the dimensionless time \( t_n \) are shown on figure 3. When we compare these results with experimental (figure 1(a) and figure 1(b)) we see that the solution \( (9) \) qualitatively well describes the experimental results.

It is necessary to vary the constants \( \tau_1...\tau_5 \) to achieve better quantitative coincidence of the experimental results. The other way is to obtain the values of some constants by processing of the experimental results.

![Figure 3. Polar Z and non-polar V relative concentrations as functions of the relative time \( t_n \) for organic plasma.](image)

4. Conclusion
The analysis shows that the examined solution describing the alteration of the functional groups as a function of time illustrates the treatment of polymer material in gas discharge plasma. The plasma is created in different kind of plasma-creating gases, which are representatives of a wide range of gases as inert, electronegative, chemical active and polymer-creating ones.

If we want to obtain better quantitative coincidence of the theoretical with experimental results, it is necessary to vary constants \( \tau_1...\tau_5 \). But from other aspect, similar theoretical results can be used as fitting functions for the treatment of experimental results. Using similar approach we can obtain experimentally the constants, which describe the process of treatment in gas discharge plasma.

References
[1] Tabaliov N A and Svirachev D M (Part I, this conference).
[2] Svirachev D M and Tabaliov N A 2005 *Bulg. J. Phys.* 32 22
[3] Svirachev D M and Tabaliov N A 2005, *Bulg. J. Phys.* 32 32