Treatment of polymer surfaces in plasma
Part I. Kinetic model

N A Tabaliov and D M Svirachev
Sofia University, Faculty of Physics, 5, J.Bouchier Blvd., Sofia, Bulgaria
E-mail: niki_tabaliov@yahoo.com, svirach@phys.uni-sofia.bg

Abstract. The surface tension of the polymer materials depends on functional groups over its surface. As a result from the plasma treatment the kind and concentration of the functional groups can be changed. In the present work, the possible kinetic reactions are defined. They describe the interaction between the plasma and the polymer surface of polyethylene terephthalate (PET). Basing on these reactions, the systems of differential kinetic equations are suggested. The solutions are obtained analytically for the system kinetic equations at defined circumstances.

1. Introduction
The treatment of polymer surfaces in gas discharge is still very topical for numerous causes, [1-3]. First, that is the wide putting into practice in many branches of the industry and life standard. Second, that is the insufficient knowledge of the processes with respect to the chemical and physical kinetics, as well as with respect to a given plasma. The creation of the theoretical models can extend our knowledge in that field of science.

The inert and molecular gases, which interact with solid material, very rarely interact with atoms of the solid material in non-excited state by chemical reactions. Therefore, the gas should be in atomic state in order for a homogenous or heterogeneous reaction to be realized.

Plasma-chemical modification of the polymer surfaces is accomplished thanks to created gas discharge plasma in the plasma reactor. The surface layer of the polymer materials is modified as a result of complicated homogenous and heterogeneous reactions. A main mechanism of the plasma-chemical modification is accepted to be the alteration of the functional groups. These functional groups are created by heterogeneous chemical reactions, which are realized on the dividing line of both phases – solid and gaseous. The reactions are between chemical active particles (free atoms and radicals), created in the plasma and active centers (atoms on the surface with free valence) of the material. When the polymer is in the zone of the plasma, such as our case, the processes are significantly complicated. Towards the components of the processes, the radiation of the plasma with electron and ion flows is added too. This leads to stimulation of the heterogeneous reactions and very often leads to changing of the kinetic mechanism.

Our studies [4,5] are made in RF-discharge (12.56 MHz) for the following plasma-creating gases – argon (Ar), oxygen (O2), Freon 14 (CF4) and Freon 12 (CF2Cl2). The argon is a typical representative of the inert gases, and oxygen of the electronegative gases. The freons are organic gases, which can develop polymer chain at certain circumstances. As a pattern polymer material we used polyethylene terephthalate (PET).

The modification of the polymer surface in non-equilibrium plasma is tracked by changing of the wetting contact angle. The sessile drop method is used with bi-distilled and de-ionized water. The changing of the contact angle on certain surface means a changing of its free surface energy. That energy typically is presented as a sum of two components: disperse and polar compound. It is due to creating or destroying of polar functional groups as hydroxyl (OH), carbonyl (CO), carboxyl (COOH) and hydroxide (OOH). In that case, the disperse component of the surface energy is unchangeable or little it is changed. The polar component increases with the growing of surface concentration of polar groups and its respective component decreases with reducing of the concentration.
The creation or destruction of non-polar or on small-scale polar functional groups, leads to low alteration of the disperse compound, as well the polar compound. These groups are: carbon-hydrogen (CH, CH2, etc.), carbon-fluorine (CF, CF2, etc.) and carbon-fluorine-chlorine (CCl, CFCl, CF2Cl, etc). Despite that, the non-polar groups can be tracked, since they have a definite proportion with polar groups for each state of the surface.

2. Chemical reactions
We will analyze the following heterogeneous chemical reactions to make qualitative and quantitative analysis of the bearing of treated polymer surface in plasma:

\[
\begin{align*}
M + A & \xrightarrow{k_1} M^* \\
M^* + B & \xrightarrow{k_2} P \\
M^* + C & \xrightarrow{k_3} N \\
P + A & \xrightarrow{k_4} M^* \\
N + A & \xrightarrow{k_5} M^*
\end{align*}
\]

where the values \(k_1, \ldots, k_5\) are rate constants of the respective reactions, \(M\) is a part of the polymer molecule, which is on the surface; \(M^*\) is a radical, which is a chemically active center on the polymer surface; \(P\) and \(N\) respectively are polar and non-polar groups formed over of the existing active centers \(M^*\); \(A\) is an activating component from the plasma (radiation, electrons, ions, etc.); \(B\) is a gaseous component of the plasma containing oxygen, leading to the obtaining of polar functional groups; \(C\) is a gaseous component of the plasma leading to obtaining of non-polar groups as: \(H_2, CH_4, CF_4\), etc. Unfortunately, the value \(M\) cannot be defined accurately, which in itself leads to inaccurate defining of its surface concentration. We shall assume that this is a repeated section in the polymer chain.

The reaction (1) essentially represents the destruction of the polymer. The radicals \(M^*\) are created by that process. Depending on the agent following destruction is observed: photo destruction (radiation influence of the plasma) and local thermal destruction (electron or ion bombardments of polymer surface). Part of the polymer chain is excited on defined vibration and electrical levels at the photo destruction, as well at the thermal destruction. It leads to disassociative processes. The reactions (2) and (3) idealistically present the formation of the polar \(P\) and non-polar \(N\) functional groups. These groups are formed where the defined bond is destructed and the radical \(M^*\) is created, i.e. in the end of the new polymer molecule. It is possible the creation of the radical \(M^*\) to be realized at other places along to the polymer molecule without its destruction.

The reactions (4) and (5) idealistically represent the destruction of the polar \(P\) and non-polar \(N\) functional groups too and the active center is formed again. In contrast to the reaction (1), with these two reactions destruction of the polymer chain is not obtained, because the bond between \(P\) and \(N\) groups and the polymer chain is attacked directly. This hints that, the rate constants \(k_4\) and \(k_5\) have small values in comparison with the other reactions.

The qualitative analysis, which we will suggest, has not a purpose to select (or determine) the possible channels of the plasma treatment in details. Because of that, the rate constants \(k_1, \ldots, k_5\) should be examined as constants, which describe commonly the processes of the same character.

3. System of kinetic equations
The equations of the heterogeneous chemical reactions from (1) to (5), which describe the plasma modification of the polymer surface, can be with of different kinetic order (first, second etc.). That means that the system of differential kinetic equations with reactions from (1) to (5) is non-linear. The analytical solving of similar system is rarely possible. We will consider that, all flows toward the surface are unchangeable and their amplitudes do not depend on the kind of the chemical reactions. The flows respectively are radiation, electrons, ions and the rest plasma components. In this way, the concentration of these particles can be included in the rate constant so that all chemical reactions from
(1) to (5) may be examined as reactions of first order. Then the system of differential equations describing chemical reactions from (1) to (5) becomes linear:

\[
\begin{align*}
\frac{dX}{dt} &= -\tau_1 X \\
\frac{dY}{dt} &= \tau_1 X - (\tau_2 + \tau_3)Y + \tau_4 Z + \tau_5 V \\
\frac{dZ}{dt} &= \tau_2 Y - \tau_4 Z \\
\frac{dV}{dt} &= \tau_3 Y - \tau_5 V
\end{align*}
\]

(6)

where \( X = [M], Y = [M^*], Z = [P], V = [N], \tau_1 = k_1[A], \tau_2 = k_2[B], \tau_3 = k_3[C], \tau_4 = k_4[A] \) and \( \tau_5 = k_5[A] \).

The values \( \tau_1, \tau_5 \) have dimension \( s^{-1} \) and present the rate constants for the reactions in first order. They are proportional to constants \( k_1, k_5 \) and concentrations of the particles in the volume too.

The system (6) will be solved at initial conditions \((t=0)\):

\[
\begin{align*}
X(0) &= X_0 = [M_0] \\
Y(0) &= Y_0 = [M_0^*] \\
Z(0) &= Z_0 = [P_0] \\
V(0) &= V_0 = [N_0]
\end{align*}
\]

(7)

where \([M_0], [M_0^*], [P_0]\) and \([N_0]\) are the initial surface concentrations. We will assume that only one radical \( M^* \) is obtained from the section \( M \) of the polymer molecule. The following condition is always fulfilled:

\[
X + Y + Z + V = \text{constant}
\]

(8)

where the constant is defined from the initial conditions:

\[
\text{Constant} = G = X_0 + Z_0 + V_0,
\]

(9)

The initial surface concentration \( Y_0 \) is equal to zero, because we presume that there are no radicals \( M^* \) on the untreated material.

The system kinetic equations (6) can be made dimensionless by using relative concentrations and time, defined as:

\[
\begin{align*}
x &= \frac{X}{G}, \quad y &= \frac{Y}{G}, \quad z &= \frac{Z}{G}, \quad v &= \frac{V}{G} \quad \text{and} \quad t_\tau = \tau t
\end{align*}
\]

(10)

In that case, the condition (9) is:

\[
x_0 + z_0 + v_0 = 1
\]

Using the method of the stationary concentrations for the radical \( M^* \), following solution to the system (6) is obtained:

\[
x = x_0 e^{-k_1 t_\tau}
\]

(11)
\[ z = -\frac{1}{1+\alpha} x_0 e^{-\lambda_1 t} + \frac{1}{1+\beta} \left[ \beta z_0 - v_0 + \beta \frac{1-\gamma}{1+\alpha} x_0 \right] e^{-\lambda_2 t} + \frac{1}{1+\beta} \left[ x_0 + z_0 + v_0 \right] \] 
\[ v = -\frac{1}{1+\alpha} x_0 e^{-\lambda_1 t} + \frac{\beta}{1+\beta} \left[ -z_0 + \frac{1}{\beta} v_0 - \frac{1-\gamma}{1+\alpha} x_0 \right] e^{-\lambda_2 t} + \frac{\beta}{1+\beta} \left[ x_0 + z_0 + v_0 \right] \] 

where

\[ \lambda_1 = 1, \quad \lambda_2 = \frac{k_P + k_N}{k_{15} k_P + k_{14} k_N} \]  
\[ \alpha = \beta \gamma \]  
\[ \beta = \frac{k_N}{k_P} \]  
\[ \gamma = \frac{k_{14} - 1}{k_{15} - 1} \]  
\[ k_P = \frac{\tau_3}{\tau_4}, \quad k_N = \frac{\tau_3}{\tau_5}, \quad k_{14} = \frac{\tau_1}{\tau_4}, \quad k_{15} = \frac{\tau_1}{\tau_5} \]  

Unfortunately, there is very little published data about the values of the surface rate constants, related to PET and gas discharge plasma. Thus it is impossible to examine the obtained results directly from (11) to (13) and to interpret the experimental results. For that reason we shall attempt to do some qualitative conclusions and comparisons. The solutions from (11) to (13) show that the bearing of heterogeneous reactions in the time \( t \) follows exponential alteration at the plasma treatment of polymer surface. The bearing is proportional to common dimensionless rate constants \( \lambda_1 \) and \( \lambda_2 \), which are dimensionless in the relation to the rate constant \( \tau \). The stationary values of the components are equal to

\[ x_{st} = 0, \quad z_{st} = \frac{1}{1+\alpha}, \quad v_{st} = \frac{\beta}{1+\beta} \]  

Expressions (19) are determined by the coefficient \( \beta \), which is related to both coefficients \( k_N \) and \( k_P \). Coefficients \( k_N \) and \( k_P \) can be interpreted as the equilibrium constants respectively for reactions (3), (5) and (2), (4). If polar \( P \) and non-polar \( N \) groups dominate over \( M \) radicals, then reactions (2) and (3) prevail over reactions (5) and the following condition is fulfilled

\[ k_2 > k_4 \quad \text{and} \quad k_3 > k_5 \]  

This is to be expected, because it is known that radicals have very high chemical activity. The following cases are possible depending on the value \( \beta \):

1) \( \beta = 1 \) \quad \( z_{st} = v_{st} = \frac{1}{2} \)
2) \( \beta < 1 \) \quad \( z_{st} > v_{st} \)
3) \( \beta > 1 \) \quad \( z_{st} < v_{st} \)

It is obvious that in order to observe the increasing of the polar \( P \) groups, the condition \( \beta < 1 \) should be fulfilled. This is possible when the polymer surface is treated in oxygen and argon plasma. When the
treatment is conducted in plasma-creating gases (as in the case of freon14 and freon12) the condition reads $\beta > 1$, which means increasing of non-polar $N$ functional groups on the treating pattern.

References
[1] Coburn J W 1991 IEEE Trans. Plasma Sci. 19 1048
[2] Egitto F D 1990 Pure Appl. Chem. 65 1699
[3] van Oss C J 1995 Colloids and Surfaces B: Biointerfaces 5 91
[4] Svirachev D M and Tabailov N A 2005 Bulg. J. Phys. 32 22
[5] Svirachev D M and Tabailov N A 2005, Bulg. J. Phys. 32 32