

## INVESTIGATION OF CORROSION RESISTANCE OF STEEL WITH POLYMER COATINGS

MAKSIMOVA Olga<sup>1</sup>, DIORDIICHUK Dmitrii<sup>2</sup>, MAKSIMOV Andrei<sup>1</sup>

<sup>1</sup>*Cherepovets State University, Chair of Physics, Cherepovets, Russian Federation, og62@mail.ru*

<sup>2</sup>*OAS "Severstal", Cherepovets, Russian Federation*

### Abstract

In this paper, protective properties of polymer films on the metal surface are analyzed. The simulation is performed by means of the Monte-Carlo method on the basis of three-dimensional lattice model of polymer system with orientational interactions [1]. Initially, configuration of polymer system is calculated by the Metropolis algorithm taking into account the characteristics of the internal structure (constants of intermolecular interactions etc.), temperature regime and metal quality. Further, for the study of conductivity, the motion of charged particles within the proposed lattice model is investigated on the basis of the calculated configuration. The interaction energy of the oxygen atom with eight neighboring links of polymer chains and electric double layer on the metallic surface is accounted. The direction of movement of charged particles is calculated by the Monte-Carlo method according to the energy advantage of its position. This method allows to calculate the number of charged particles passing through the polymer film and reaching the metal sheet surface. The dependences of conductivity on temperature, film thickness, and distance between molecular layers are obtained. It is shown that there is an optimum density for the given film thickness at which it possesses protective properties. The adequacy of the developed mathematical models and calculated dependences are verified by comparison with laboratory data and production testing.

**Keywords:** corrosion, polymer coatings, conductivity, Monte-Carlo method, electric double layer

### 1. INTRODUCTION

Today, the problem of corrosion is urgent in all civilized countries. One of the most effective methods of solving this problem is application of polymer coating upon steel sheets. Currently, significant advances are achieved in the field of corrosion protection. Mechanisms of development of cracks, electrical protection, different types of inhibitors, electrochemical protection, paints are usually investigated [2, 3].

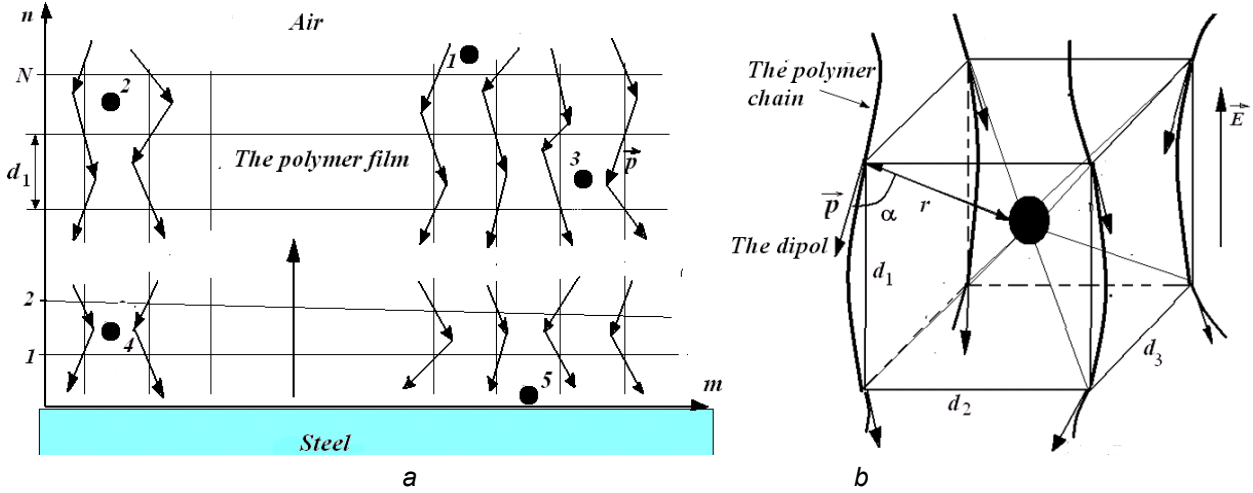
The protective polymer film is necessary to eliminate interaction of metal surface with external oxygen ions. As a rule it is assumed that a thick polymer film is an insulator. However, in recent years, the interest to investigation of transport properties of thin films has arisen [4-6]. It is shown that the change in electrical conductivity of polymer films occurs due to change in thickness, pressure, density, etc. Therefore, the study of the influence of these characteristics of polymer coatings of metal is also the topical problem for creation of protection against corrosion.

### 2. MODEL

Properties of polymers cannot be described by equations of continuum mechanics. Therefore, development of specialized discrete models which are based on molecular structure of polymers is necessary [7]. Peculiarities of macroscopic characteristics of different polymers are primarily related to geometric anisotropy of constituting macromolecules. The theory describing the behavior of macromolecules with different mechanisms of flexibility in ordered polymer systems of finite size (layers, domains, etc.) with developed segmental mobility should correctly take into account intermolecular interactions, particularly, of orientational type. For the study of this problem, the Gotlib - Maksimov's models [8] of ordered polymer systems are used,

in which, on the one hand, an individual polymer chain with bending rigidity is chosen, and on the other hand, local interactions of the dipole type are taken into account.

In these lattice models, the links of the polymer chains are localized in the nodes  $(n, m, l)$  of three-dimensional cubic “quasi-lattice”. Fig. 1a shows one of the planes  $(n, m)$  of the model. The position of a node is characterized by the set of three numbers  $n, m$  and  $l$ . Every node is related to a dipole (flexible or rigid kinetic unit of polymer chain); its orientation is determined by angles in the spherical coordinate system.



**Fig. 1** *a* - the movement of oxygen ion within the polymer film: ● - oxygen ion,  $\vec{p}$  - dipole moment of a link of the polymer chain,  $\vec{E}$  - strength of the external electrical field. *b* - the location of the ion within the unit cell.

The potential energy of interaction of dipole type in the lattice model of polymer system has the form [9]:

$$V = - \sum_{n,m,l} K_1 \cos(\Phi_{n,m,l,n+1,m,l}) - \sum_{n,m,l} K_2 \cos(\Phi_{n,m,l,n,m+1,l}) - \sum_{n,m,l} K_2 \cos(\Phi_{n,m,l,n,m,l+1}) + pE \sum_{n,m,l} \cos(\phi_{n,m,l}), \quad (1)$$

where  $\Phi_{n,m,l,n',m',l'}$  is the spatial angle between the dipoles located in the neighboring nodes  $n, m, l$  and  $n', m', l'$  of the lattice,  $p$  is the module of the dipole moment of the polymer chain link,  $E$  is the strength of the external electric field, that creates an electric double layer of the metal surface,  $\phi_{n,m,l}$  is the angle between

the vectors  $\vec{p}$  and  $\vec{E}$ . The energetic constant  $K_1$  along the longitudinal curved direction  $X$  of the “quasi-lattice” describes intrachain orientational interactions; it is related to the chain bending rigidity, which determines the persistence length. The constant  $K_2$  characterizes interchain orientational interactions in the “transverse” directions  $m$  and  $l$  of the “quasi-lattice”. Its value can be estimated, for example, from the multipolar expansion of the interaction energy of two identical dipoles  $p$  in neighboring chains:

$$K_2 = \frac{1}{4\pi\epsilon_0} \frac{p^2}{r^3}, \quad (2)$$

where  $r$  is the mean distance between neighboring chains,  $\epsilon_0$  is dielectric constant.

The energetic constants are determined by the chemical structure of the polymer coating and its density. For example, by the density  $\rho = 1.78 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$  the constants for poly (vinylidene fluoride) (PVDF) are equal to  $K_1 = 5.3 \times 10^{-22} \text{ J}$  and  $K_2 = 2.1 \times 10^{-20} \text{ J}$ .

In the model developed in this paper, the oxygen ions are initially at the interface “polymer– air” (ion 1 in Fig. 1a). It is assumed that the motion of the charged particles in this lattice model is carried by leaps in localized states in the centers of the cells (ions 2-4 in Fig. 1a). Similar approach has been used previously in the ref. [10]. For example, it has attributed the increase of conductivity of the layer by increasing the temperature

and the frequency of the external electric field. The number of oxygen ions that pass through the polymer film and reach the metal surface (ion 5 in Fig. 1a) is calculated to determine the protective properties of the film. The interaction potential between the oxygen ion and the dipole is determined by the formula [11]:

$$V_{ion} = -\frac{qp \cdot \cos \alpha}{4\pi\epsilon_0 r^2}, \quad (3)$$

where  $q$  is the charge of oxygen ion ( $q = -2e$ , where  $e$  is the charge of electron),  $p$  is the module of the dipole moment of the polymer chain link. The distance  $r$  and the angle  $\alpha$  are shown in Fig. 1b. The ion interactions with more than eight links of the polymer chains and the field of the electric double layer of metal are taken into account in the simulation process of corrosion-resistance.

### 3. SIMULATION METHOD

The simulation algorithm of the full configuration of the polymer chains on the metal surface and the motion of charged particles, takes into account consists of two stages:

Stage 1. The calculation of polymer chain links configuration depending on temperature, its inner structure (energetic constant of intermolecular interactions), and influence of the metal substrate is performed by the Monte Carlo method. The calculated values of the orientational order parameter ( $\mu = \langle \cos(\phi_{i,j,k}) \rangle$ ) coincide with the experimental data on the investigation of thermal depolarization of the poly (vinylidene fluoride) [12]. Calculations of heat capacity, susceptibility and other macroscopic characteristics of polymer systems show that all of them have abnormal behavior at the same temperature, namely in the point of phase transition [1]. Stage 2. The study of the movement of oxygen ions within the simulated polymer system is also carried also by the Monte Carlo method. The selection criterion of the direction of the ions motion is based on checking the energy advantage of its position in each of six neighboring lattice places. The new position of the ion is determined by the following algorithm:

1. The ion energy  $V_{ion0}$  is determined if it is located at the point O.
2. The virtual displacement of the ion into each of the points  $O_s$  ( $s = 1, 2...6$ ), i.e. in six neighboring cells, is produced. The energy of the ion is calculated in each of these positions by the formula (3).
3. The transition probability of the ion from the point O to each of the points  $O_s$  is calculated by the formula:

$$W_s = \exp\left(-\frac{V_{ion s} - V_{ion 0}}{k_B T}\right). \quad (4)$$

4. A unit segment is divided into six parts. The length of each segment is equal to the value  $W_s / \sum_{s=1}^6 W_s$ .

Further, a random number  $R$  in the interval  $[0; 1]$  is selected by a uniform distribution. Its number determines the new position of the ion.

To characterize the anticorrosive properties of the coating, the corrosion parameter is introduced as

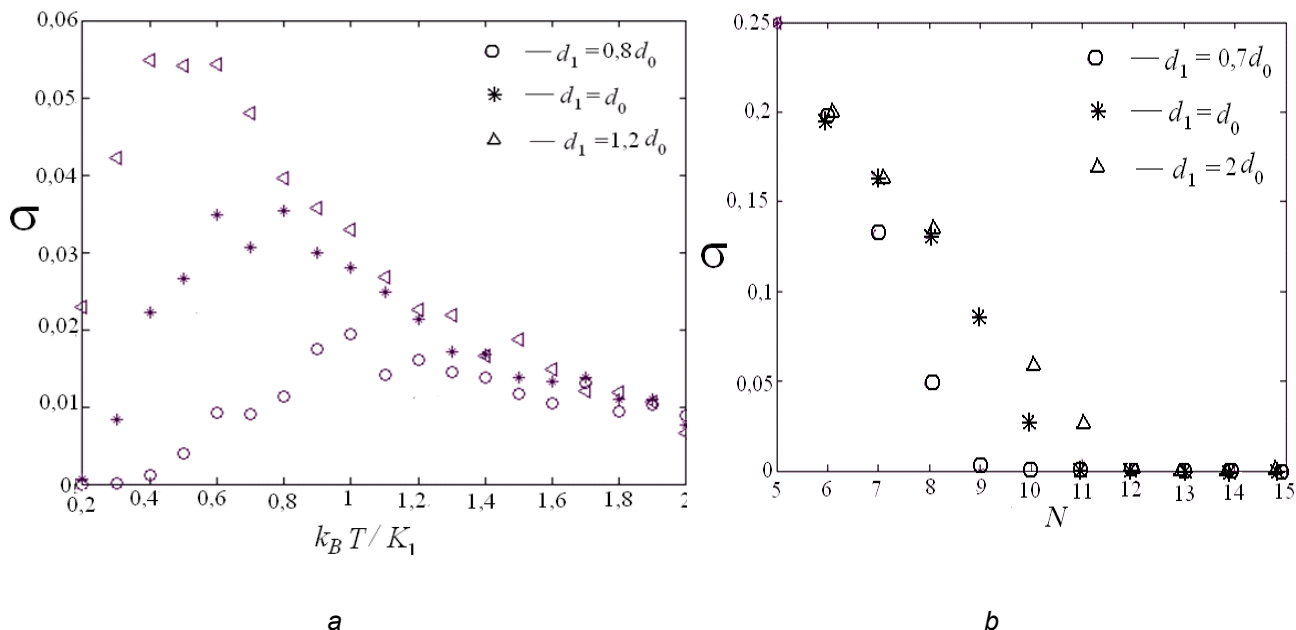
$$\sigma = \frac{N_{cor}}{N_{MC}}, \quad (5)$$

where  $N_{cor}$  – the number of ions reached the metal surface and trapped by it,  $N_{MC}$  is the number of Monte Carlo steps. The calculations show that the value  $\sigma$  does not depend on the simulation parameters (initial conditions and the number of Monte Carlo steps). At sufficiently large number of steps, the corrosion parameter is determined only by the constants of the interaction potential and the value of the electrical field of double layer on the metal surface. Therefore, in this paper, the criterion  $\sigma = 0$  (when corrosion is absent) is accepted as the main indicator of the polymer coating quality.

#### 4. THE SIMULATION RESULTS

Fig. 2a demonstrates the dependences of parameter of corrosion  $\sigma$  on the renormalized temperature (the value  $k_B T / K_1$ ) at different values of the distance  $d_1$  between the layers of the polymer coating. It is shown, that the number of the oxygen ions that have passed through the polymer film and have reached the metal surface, increases with the rise of temperature up to a certain critical one. The same behavior of the conductivity of polymers has also been observed experimentally, for example, in ref. [13]. The comparison of the simulation results with the data obtained in the ref. [1] show, that the temperature at which the value  $\sigma$  reaches its peak, is the point of structural phase transition. Beyond it all properties of the coating dramatically change (e.g., strength and hardness reduce). However, it should be noted, that this model has great restrictions for the study of macromolecular systems at temperatures above the phase transition point  $T_c$ , because the mobility of segments of sufficiently large chains cannot be considered in this model.

Fig. 2b shows the dependences of the corrosion parameter  $\sigma$  on the polymer film thickness  $N$  at different values of the distance  $d_1$  between the layers of the polymer coating. The value of the parameter  $\sigma$  drops till zero with the increase of the polymer film thickness. At every value of the distance  $d_1$ , there exist the minimum number  $N_{\min}$  of the coating layers, at which the oxygen ions stop to penetrate to the metal surface. In this case, the polymer film with thickness  $N > N_{\min}$  becomes a corrosion protective barrier.



**Fig. 2** The parameter of corrosion  $\sigma$  vs. the renormalized temperature  $k_B T / K_1$  (a) and the number of layers in the polymer film  $N$  (b) at different values of the distance  $d_1$  between the layers.

#### 5. RESULTS OF EXPERIMENTAL STUDY

The test samples were selected to investigate the corrosion properties of the coated metal (polyester enamel). Two incisions at 90 °C were made on each test sample. Further, the test samples were placed into saline mist chamber for a certain time. The results of corrosion resistance of the coating after 240, 360 and 500 hours are shown in Fig. 5.

The test sample № 1. The coating thickness is 18.3 mkm. Result: the polymer film is a protective coating.

The test sample № 2. The coating thickness also is 18.3 mkm, but the density of the polymer film is decreased by 1.5% (the distance between the molecular layers is slightly increased). According to computer simulation, this value of density of the polymer film is optimal. Result: at further decrease of the polymer film density it is not a protective cover.

The test sample № 3. The coatings thickness is 18.7 mkm. The density is decreased by 3%, i.e. it is less than the optimal one. Therefore, though this coating is thicker, it is not a protective coating.

a)



b)



c)



**Fig. 3** The images of the samples №1 (a), № 2 (b) and №3 (c) after the experiment on saline mist.

## CONCLUSION

The thickness of the polymer coating can be increased by its drying temperature. This reduces the cost of production. However, anti-corrosion properties of the polymer coating decrease if the temperature or the distance between the molecular layers increases. Simulation model is developed that allows to calculate the number of oxygen ions that penetrate through the protective film. For the given value of intermolecular distance there is an optimal number of layers, by which the film becomes a protective coating.

***This work was supported by the Ministry of Education and Science of the Russian Federation, project №1715 (contract № 2014/267)***

## REFERENCES

- [1] PETROVA T., MAKSIMOVA O., MAKSIMOV A., NASTULJAVICHUS A., BARUZDINA O., BAIDGANOV A. Computer Simulation of Phase Transition, Orientational Order and Mobility in Low- and Highmolecular Ferroelectric Nano-Systems. In NSTI-Nanotech: NSTI Nanotechnology Conference and Expo, Washington, 2013, pp. 611-614.
- [2] BELETSKAYA I., TYURIN V.S., TSIVADZE A.Y., GUILARD R., STERN C. Supramolecular Chemistry of Metalloporphyrins. Chemical Reviews. Vol. 109, No. 5, 2009, pp.1659-1713.
- [3] BARTENEV V.V., GRIGOREV V.P., BARTENEVA O.I. Acid Corrosion of ATSE Cyrillic SIGN-1M Aluminum Alloy during Contact Ceposition of Cadmin. Protection of Metals and Physical Chemistry of Surfaces, Vol. 34, No. 2 1998, pp.253-257.
- [4] SHIRAKAWA H. The Discovery of Polyacetylene Films. The Dawning of a New Era of Conducting Polymers. Synthetic Metals, Vol. 125, No. 1, 2002, pp. 3-10.
- [5] HILL I.G., KAHN A., COMIL J., DOS SANTOS D.A., BREDAS J.L. Occupied and Unoccupied Electronic Levels in Organic Conjugated Molecules: Comparison between Experiment and Theory. Chem. Phys. Lett., Vol.317, No.3 2000, pp.444-450.
- [6] NABER R.C.G., TANASE K., BLOM P.W.M., GEIINCK G.H., MARMAN A.W., TOUWSLAGER F.J., SETAYESH S., LEEUW DE D. M. High-Performance Solution-Processed Polymer Ferroelectric Field-Effect Transistors. Nature Materials, Vol. 4, No. 3, 2005, pp. 243-248.
- [7] LIFSHITZ I.M., GROSBERG A.Yu, KHOKHLOV A.R. Some Problems of the Statistical Physics of Polymer Chains with Volume Interaction. Reviews of Modern Physics, Vol. 50, 1978, pp. 683-701.
- [8] GOTLIB Yu.Ya., MAXIMOV A.V. A Theory of Orientational Ordering in Two-Dimensional Multichain Polymer Systems with Dipole Interaction. Polymer Science, Vol. A 34, No.11, 1992, pp. 902- 907.
- [9] MAKSIMOVA O.G., PETROVA T.O., MAKSIMOV A.V. Modeling of the Processes of Repolarization in Ferroelectric and Antiferroelectric Polymer Systems. Ferroelectrics, Vol. 444, No.1, 2013, pp.111-115.
- [10] KAUSCH H.H. Polymer Fracture. Springer: New York, 1978.
- [11] KLEMAN M., LAVRETOVICH O.D. Soft matter physics. Springer: Berlin, 2003.
- [12] PETROVA T.O., MAKSIMOVA O.G., GERASIMOV R.A., MAKSIMOV A.V. Application of Analytical and Numerical Methods to Simulation of Systems with Orientation Interactions. Physics of the Solid State, Vol. 54, No 5, 2012, pp. 937-939.
- [13] ILYASOV V.K., LACHINOV A.N., MOSHELEV A.V., PONOMAREV A.F. Estimation of the Parametes of Charge Carriers in Polymers in the Vicinity of the Threshold of Thermally Stimulated Switching. Physics of the Solid State, Vol. 50, No. 3, 2008, pp. 568-572.