

THEORETICAL STUDY OF THE FORMATION OF PRIMER COATING ON THE STEEL SURFACE

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Abstract

The high efficiency of the polymer coating is achieved only by the proper choice of thermal and other conditions during the formation of its structure. The aim the work is to study only the initial stage of physical and chemical processes by the formation of the structure of polymer coating, namely, the creation of a primer adhesive layer after the application of monomer paint solution on the steel sheet before to the polymerization. In this work, the dynamic Monte Carlo method for the modified lattice Langmuir's model of adsorption was used. Time dependences of the sticking coefficient of monomers on the surface of the steel at the same and different heating rates of the metal sheet and the given values of the interaction constant of the monomers and the energy barrier are calculated. It's shown that there is an optimum temperature regime at which the adhesion of monomer coating on the surface of the metal sheet is maximal. The simulation results are confirmed by experimental data on study of adhesion strength of the primer layer from the poly-vinyl-butyril on the surface of steel sheet.

Keywords: Computer simulation, metals, polymer coatings, monomers, adhesion

1. INTRODUCTION

In recent years, the study of the surface physical-chemical properties of different polymer structures has acquired not only theoretical but also practical meaning due to their unique engineering characteristics. On the one hand, the solution of the adsorption problem of macromolecules at different interfaces creates the basis for the development of surface physical chemistry of polymers [1, 2]. On the other hand, the development of polymer coverings (polyvinylidene fluoride, polyurethane and etc.) is necessary, e.g., for the effective protection of metal production from corrosion. As it is known, the corrosion control of metals and other materials is one of the most important technical and economic problems of today's society.

The quality of polymer coating is determined, first of all, by its durability, adhesion and resistance to aggressive external environment and also by strength, which mainly depends on the degree of orientational order of macromolecules in the primer layer [3]. These properties of polymer coating depend on the method of its formation and its chemical modification [4]. High efficiency of polymer coating is achieved only by proper choice of thermal and other conditions of formation of its multilayer "sandwich" structure. Therefore, it is necessary to study in detail adhesion and orientational ordering of macromolecules in different layers of the coating. The process of formation of polymer coating on steel surface consists of the following stages:

- formation of the adhesion primer layer (the monolayer structure) after application of the monomer solution to the steel sheet before polymerization;
- polymerization of the monomer paint by special cross-linking agents;
- formation of the multilayer (macromolecular) structure during the evaporation of the solvent after polymerization.

Therefore, to predict the properties of polymer coating on the metal surface, both experimental and theoretical investigation of all the processes is necessary. In this paper, only the first stage of formation of polymer coating is under investigation.

In physics of surface there is a whole class of problems associated with the study of adsorbed atom layers on a neutral substrate [1]. The adsorbent surface, which causes "sticking" of atoms, determines a periodic

potential, and thus some “lattice” consisting of nodes possible for filling. In this case, the characteristics of the adsorbed layer on the investigated surface of three-dimensional solid must correspond to similar characteristics of two-dimensional system. Therefore, in the theory of monolayer adsorption of low-molecular substances on the surface of homogeneous neutral surface, the Langmuir’s model of lattice gas [5] may be used, in which attraction forces between adsorbed molecules and the substrate and their mobility along its surface are neglected. Further development of the model was advanced in Brunauer, Emmett and Teller’s theory of polymolecular adsorption (the BET method [6]). Hill and J. de Boer developed the theory [7], which takes into account interactions between the adsorbed molecules in Langmuir’s model.

There is a formal analogy between the model of lattice gas and the two-dimensional Ising’s model [8]. This analogy is widely used to study surface properties of ferromagnetic and ferroelectric films [9, 10]. However, to study adhesion for various materials (metals, glasses and others), more complex models should be used, which take into account interactions of atoms of the adsorbed substance, both among themselves, and with the substrate surface, specified by periodic potential, determined by the type of the substrate. It becomes difficult to calculate surface properties of the coatings in such models using analytical methods of studying, and therefore it is necessary to use computer simulation methods, such as the Monte Carlo method [10].

The aim of this work is to study the first stage of formation of polymer coating on steel surface, namely the occurrence of adhesive contact at the interface between monomers and metal, which is necessary for creation of single-layer monomer structure before polymerization. For this purpose, the dynamic Monte - Carlo method for the modified version of Langmuir’s model will be developed, which takes into account interactions between the monomers themselves and the specific form of the potential interaction of monomers with the metal surface.

2. MODEL

Coupling of surfaces of the lower (primer) layer of the coating and the steel sheet occurs due to adhesion process, which is determined by intermolecular interactions. This adhesive layer can be considered as a set of monomers interacting with metal sheet surface. The dependence of potential energy of monomer on the distance to metal surface [11] is schematically represented in **Fig. 1**. By physical absorption, monomers interact with metal by means of the Van der Waals forces, characterized by average energy E_a . In this case, there is no charge transfer from the substrate to monomers or vice versa.

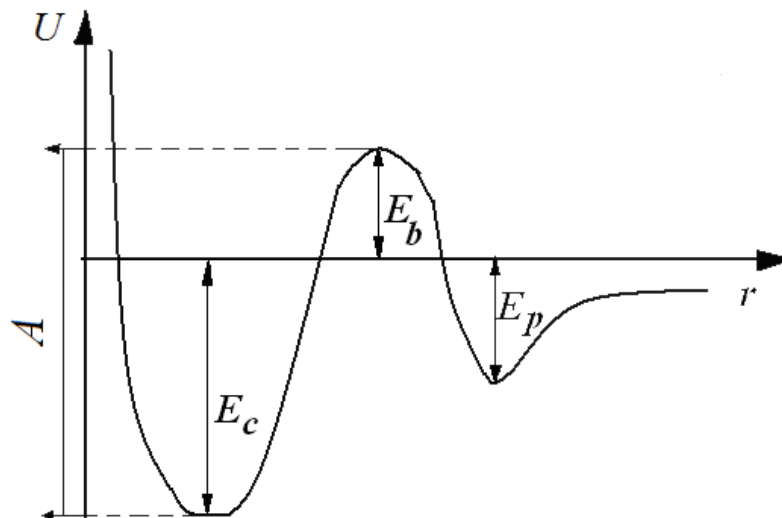


Fig. 1 The potential energy of the monomer vs. the distance between it and the metal sheet surface

At higher temperatures monomers can reach metal surface (the bottom of the potential well with the depth E_c), overcoming some energy barrier E_b . Then, electron exchange between the monomers and the metal surface is possible, it leads to sufficiently strong chemical bonds between them (i.e. to chemical adsorption [11]). The sum of energies determines the energy required for the transition of the monomer from the adsorbed state (on the metal surface) to the free state, i.e. $A = E_c + E_b$.

In this paper, the degree of adhesion of monomers to metal is calculated by the dynamic Monte Carlo method for the modified Langmuir's model of adsorption [5]. In this model, the steel sheet surface is represented as two-dimensional rectangular lattice consisting of N nodes (of adsorption) along the X axis and M nodes along the axis Y . The Langmuir's model is based on the following assumptions:

- all adsorption lattice nodes are equivalent;
- only one particle (monomer) can occupy an adsorption node;
- the influence of the adsorption forces exists only within the thickness of one monolayer.

In this model, the interaction energy between the lattice sites (monomers) has the form:

$$E = -K \sum_{i,j=1}^{N,M} n_{i,j} n_{i+1,j} - K \sum_{i,j=1}^{N,M} n_{i,j} n_{i,j+1}, \quad (1)$$

where K is the interaction constant. In the calculations by the formula (1), the interactions only between the nearest nodes are taken into account.

In this work at the initial moment ($t = 0$), it was assumed that the value was $n_{ij} = 0$ for all lattice nodes, i.e. the adsorption hasn't occurred. The calculations were performed via the computer simulation by the dynamic Monte Carlo method [10, 12], in which a random process consisting of a set of consecutive configurations of the system was generated. At sufficiently large number of configurations in the ensemble of such system, the relative adhesion degree is defined as the ratio of number of the adsorbed monomers to total number of lattice nodes, i.e.

$$\theta = (1/NM) \sum_{i,j=1}^{N,M} n_{i,j}. \quad (2)$$

3. RESULTS AND DISCUSSION

Fig. 2 shows the results of the calculation of time dependences of θ at equal heating rates of metal sheet $g = \Delta T / \Delta t$, but different values of constants of interaction of monomers ($K/k_B T_0$) and barrier energy ($E_b/k_B T_0$), where $T_0 = 300$ K. It can be seen, that with the rise of interaction constant of monomers, its adhesion degree to the metal surface increases because of the growth of the cooperative adhesion process (**Fig. 2a**). On the other hand, with the increase of the barrier height E_b the quantity θ reduces, that is, fewer and fewer monomers adhere to the metal surface (**Fig. 2b**).

Fig. 3 represents the results of the calculation of time dependence of adhesion degree θ at different heating rates g of the metal sheet for given values of the interaction constant of the monomers ($K/k_B T_0$) and energy barrier ($E_b/k_B T_0$). It is clear, that at slow heating rate of the steel sheet, the degree of adhesion of monomers to the metal surface is small (curve 1). At high heating rate and relatively high temperatures, there is some adhesion to the metal surface, but at its further heating the value of θ decreases (curve 3). In this case (after the drying process) the primer layer may peel off from the metal surface that is one of the causes of various defects of polymer coatings. It can be seen, that the optimum temperature regime is determined by curve 2 in **Fig. 3**, when the adhesion is maximal.

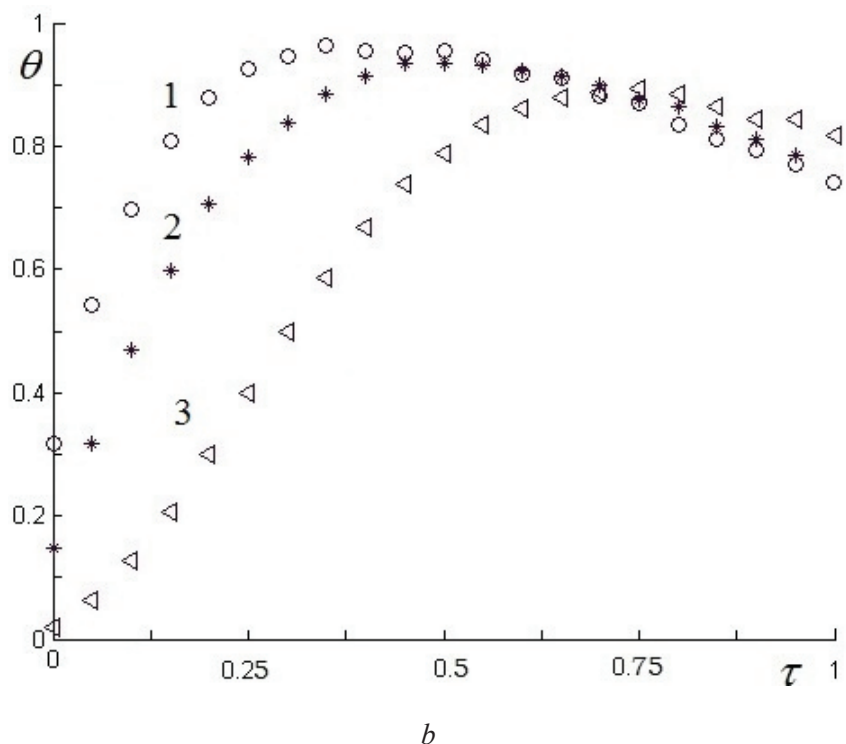
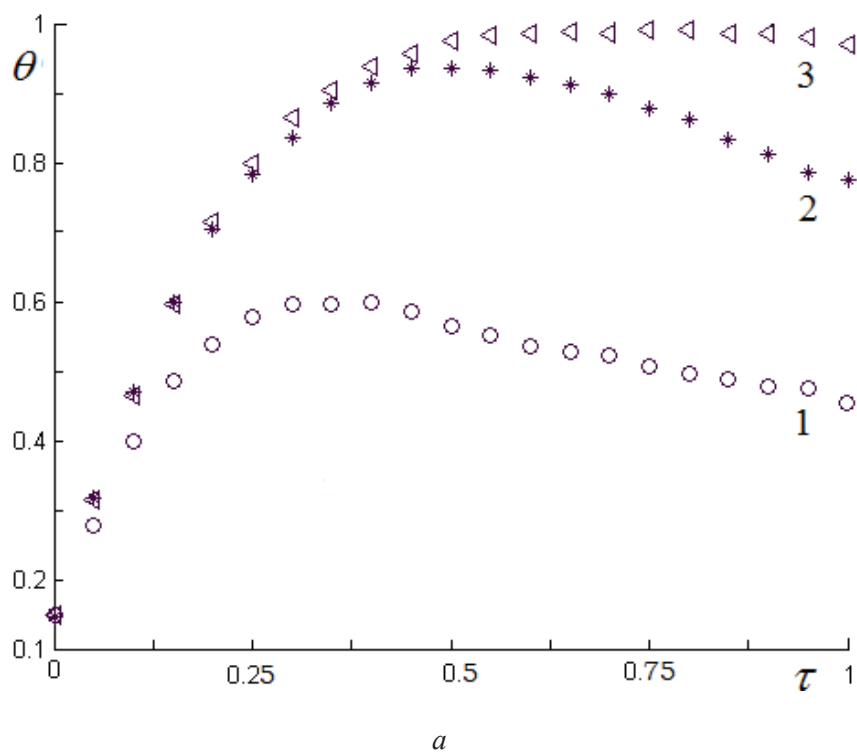


Fig. 2 The adhesion degree of monomers at equal rates of heating of the metal sheet vs. the reduced time τ :
 a - at different values of the interaction constants of monomers ($K/k_B T_0 = 0$ (1), 1(2), 2(3)) for the given energy barrier ($E_b/k_B T_0 = 1$); b - at different values of the energy barrier $E_b/k_B T_0 = 0.5$ (1), 1(2), 2(3) for the given value of the interaction constant of monomers ($K/k_B T_0 = 1$), where $T_0 = 300$ °K

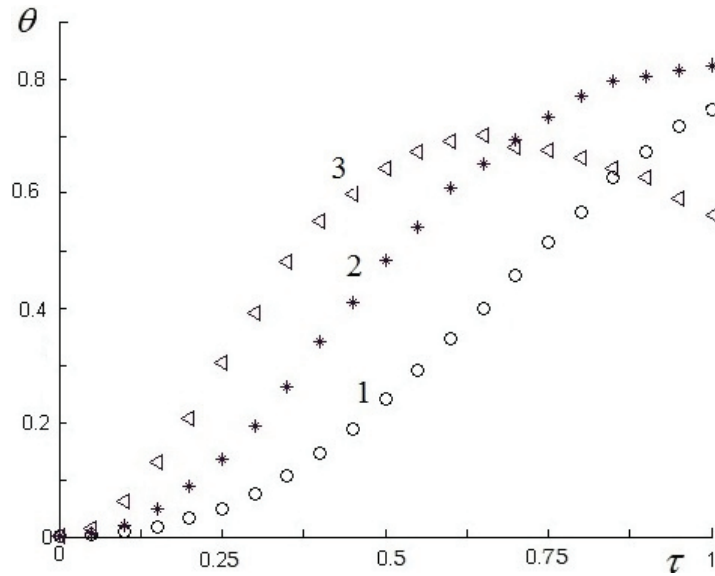


Fig. 3 The adhesion degree of monomers vs. the reduced time τ at different reduced heating rates of the metal sheet $g_0(1)$, $2g_0(2)$, $3g_0(3)$ for the given values of the interaction constant of monomers ($K/k_B T_0 = 1$) and the barrier energy ($E_b/k_B T_0 = 3$), where $T_0 = 300$ K.

Despite of well-known analogy of statistical properties of the lattice Langmuir's model and the two-dimensional Ising's model [9], the calculated temperature dependence of the adhesion degree, determining the adhesive strength of the polymer coating is non-monotonic function (**Fig. 2** and **3**). Initial increase of the value θ in this model can be explained by the growth of kinetic energy of the monomers, it results in overcoming the energy barrier E_b (**Fig. 1**), that prevents the formation of absorbed state of monomers on the metal surface. At further rise of temperature, adhesion degree of the monomers, conversely, decreases as well as magnetization in the two-dimensional Ising's model due to the growth of thermal fluctuations in the system. This result is consistent with the experimental data [13] from the study of temperature dependence of the adhesion strength of primer poly-vinyl-butiral adhesive layer on the steel surface (**Fig. 4**).

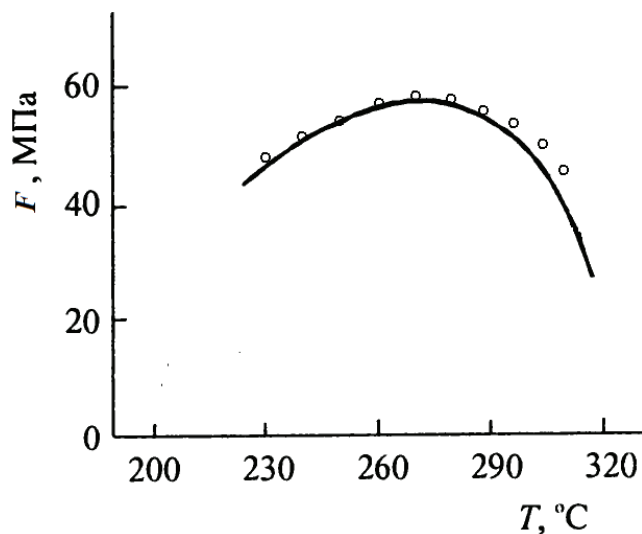


Fig. 4 Adhesion strength of primer poly-vinyl-butiral film vs. temperature of its formation on the steel surface: solid curve - experimental data [13], symbols (o) - results of simulation by the dynamic Monte Carlo method

4. CONCLUSION

Thus, in this paper we propose the model of absorption of monomers for the study of one of the most important stages in the process of forming the polymer coating, namely, the formation of single-layer structure from monomers on the surface of the metal sheet. It is shown that there is an optimum temperature regime at which there is the greatest adhesion of monomers to metal sheet surface.

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