

The improvement of adhesion of the polymeric materials by modification of metallic surfaces with the high molecular surfactants

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The modification of steel (St3) surface by the copolymer of styrene with maleic acid (CSMA) and its ammonium salts with next drawing of double-layer polymeric film from high density polyethylene and the copolymers of ethylene with vinylacetate, is shown the possibility of obtaining polymeric coating which stable in the conditions of high temperature and humidity. Found that for non-polar polymers by the conformational structure of the adsorbed molecules PSAS and consequently by hydrophobicity of the modifying surfaces. In the case of polar polymers, beside the chemical bonds, which creating by amphiphilic macromolecules of modifier the contribution to the adhesion make also the functional polar groups of the polymer adhesive.

1. Introduction

One of the most important purposes of the anti-corrosion protection of metals by polymeric materials is to create a stable adhesion connection at the interface between a metal and a polymer and insure its stability in usage conditions.

The easiest way to achieve this purpose is covering with polymeric surfaces at high temperature causing oxidation of the adhesive's surface and enhanced interaction with a metal. However a high temperature process induces usually deterioration of the polymer surface' solid properties due to activation of degradation processes. That is why polar and reactive groups are attached to the polymer. Often the positive results are obtained due to the addition of modified components to polymer composition. Unfortunately these methods do not always lead to the necessary solid properties and stability of a surface especially under high temperature and humidity conditions.

In the process of applying a protective layer particular interests are the various means of metallic surface' preparation and particularly its adsorption modification by surface active substances (SAS) which decreasing surface energy of a metal and convergence of molecular properties of the surface of the polymer and substrate [1, 2]. Remarkable is the fact that bipolar molecules of surfactants insure creation of the stable adhesion connections between the substrate and the adhesive not only by influence of surfactants on intermolecular interaction and confirmation of polymeric chains but due to the solubilisation of water and other admixtures by the micelles of surfactants. This is definitely lead to the strengthening of the adhesive strength of the coating [3].

Anionic polymeric surface active substances (PSAS) or polysoaps exceed the low molecular soaps by their surface

activity. In the aqueous solution every molecule of a polysoap may be considered as an associate of usual surfactants, interlaced by the covalent connections maintaining hydrophobic radicals in the form of hydrophobic fields isolated from water by the hydrophilic groups [4]. Taking into account the polymer nature and ability to the conformational changes of polysoaps is reasonable to expect that the deployment of macromolecules and increased contact of hydrophilic carboxylate groups with a metal surface and hydrophobic hydrocarbon chains of the polymer will increase the density of adhesive connections between the adhesive and the substrate. In combination with the surface activity it must promote an improvement of the water stability. In order to verify these hypothesis the copolymer of styrene with maleic acid (CSMA) and its ammonium salts were studied.

2. Experimental

The aqueous solution was made by hydrolysis of copolymer of styrene with maleic anhydride in the deionized water at 65 °C. Polysoaps of the required degree of ionization were made by dissolving of a copolymer of styrene with maleic anhydride in a certain volume of the titrated ammonium solution at room temperature [4]. The concentration of the required solutions was checked by potentiometric titration.

Steel (St3) specimen was used as a substrate, and a double-layer film was created by coextrusion – as a polymeric surface. The defensive layer of this film is made of thermo stabilized and light stabilized low density polyethylene and the adhesion layer was made of polyethylene with a melt index of 15–20 gr/10 min and also of the copolymers of ethylene with vinylacetate (CEVA) containing 4, 6, and 12 percent of vinyl acetate groups.

The modification of the surface of steel samples was

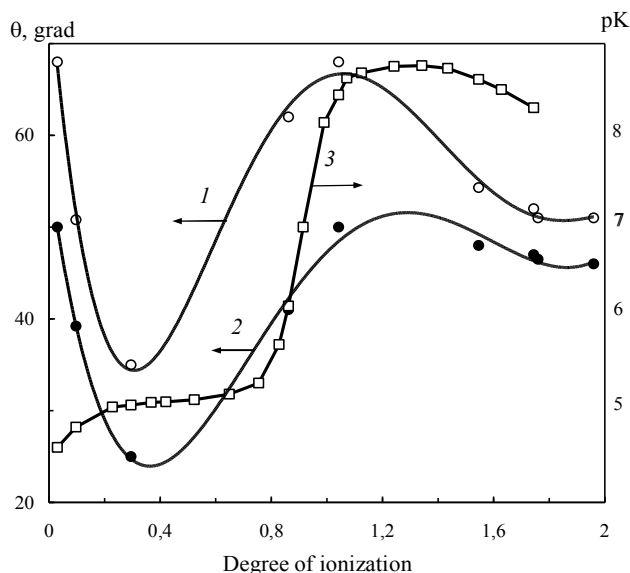


Fig. 1. Dependence of the negative logarithm of an ionization constant pK (3) and of a watering angle θ of St3 surface modified by CSMA (2, 1) of the degree of its ionization α

carried out at normal temperature by adsorption of the CSMA and its ammonia salt from aqueous solution with the concentration of 1 g/l during 10 min. The saturation time of the adsorption layer by molecules of PSAS was defined by kinetic curves of adsorption and the concentration was chosen in the area of the indices which were lesser than an inverse of the characteristic viscosity what means an absence of the molecules aggregation [2, 5].

The covering of the samples St3 sized $(2 \times 20 \times 100) \cdot 10^{-3}$ m with a double-layer polymeric film was accomplished by the thermal pressing. By the results of differential thermal analysis the degradation temperature of the studied PSAS exceeds 180 °C and its definition was based on the adhesive's melt index. This temperature was reached 150 °C for polyethylene and 160–180 °C for CEVA as to the content of the vinylacetate groups.

Determination of the adhesion strength of the metal - polymer systems was carried out by peeling at the angle of 180 °C with the speed of peeling of 3 m/h.

Water stability of an adhesion joint was defined by measuring the adhesion strength by the end of its 200 hour test in water at 80 °C.

3. Results and Discussion

During the research it was affirmed that adsorption of PSAS on the surface of St3 has a mixed character. This follows from the fact that a part of them connected physically can be eliminated by hot water while the macromolecules which are maintained due to chemical interaction are invariably adsorbed and remain stable in the vacuum in the temperature up to 180 °C. The stability of the chemisorbed layer of a surfactant has been checked by measuring of an edge angle watering the modified surface with distillate water.

The singularity of CSMA adsorption from aqueous so-

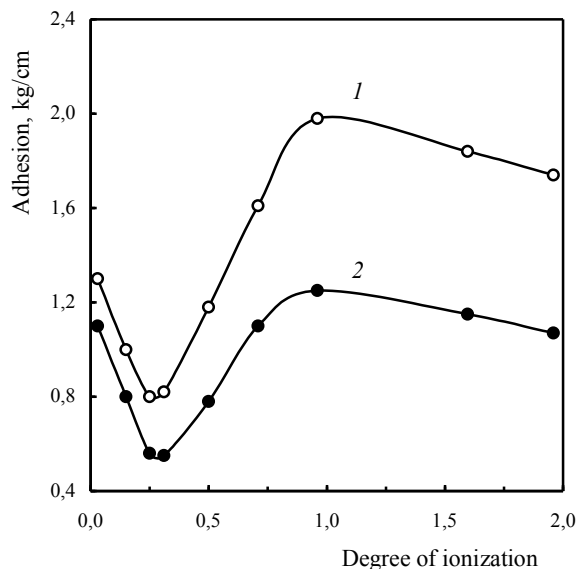


Fig. 2. Dependence of adhesion strength of the system St3 - polyethylene of the degree of ionization α of CSMA. 2 - general absorption, 1 - chemisorption

lutions is a possibility to get different conformations due to the degree of ionization of macromolecules [4]. The comparison of these changes with an edge angle of the watering θ the surface of St3 modified by the CSMA of different ionization degree (α) is illustrated on fig. 1.

It is shown that in the whole range of α the character of the curves practically doesn't depend on degree of the surfactants' adsorption: in the domain if $0 < \alpha < 0,25$ the angle of watering decreases and then if $0,25 \leq \alpha \leq 1,0$ increases and if $\alpha > 1,0$ falls again remaining stable in the domain if $\alpha > 1,5$. However in the entire range studied ionization degrees after having the physically adsorbed part of CSMA (fig. 1, curve 2) eliminated, hydrophobicity of the metal's surface is lower. Evidently, that is connected with the creation of polymolecular layers of a modifier. This fact is proved by the result of research of the adhesion strength of modified polyethylene (fig. 2). As we can see in the case of chemisorptions modification, adhesion strength is higher in the whole α interval. It is natural that in the case of a mixed adsorption the formed polylayers lead to the lessening of the system's adhesion strength. In connection with that the following researches were only carried out with the specimens modified by the irreversibly adsorbed PSAS.

Analyzing the above-mentioned results in the context of the titration curve (fig. 3, curve 1) we discover a complete similarity of the polarity changing the metallic surface and adhesion of CSMA to the conformational mood of its molecules.

It is known [4] that if there is no ionization, CSMA is situated in a conformation of a compact folded ball stabilized by the phenyl radicals, located in the interior of the ball and maintained by COOH-hydrophilic groups dissolved in water. When the steel specimens were placed into the aqueous solution the CSMA macro-molecules were

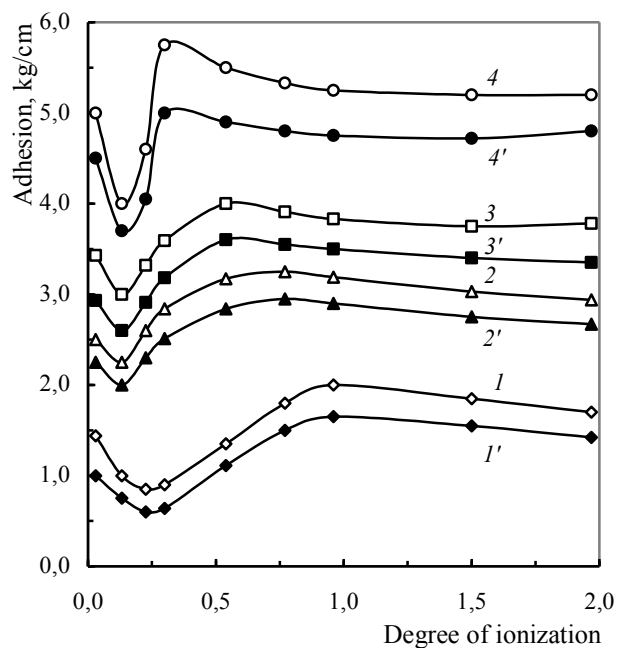


Fig. 3. Dependence of adhesion solidity (*I*, *2*, *3*, *4*) and water stability (*I'*, *2'*, *3'*, *4'*) of the system St3 – polymeric surface of the degree of ionization α CSMA: *I*, *I'* – polyethylene, *2*, *2'* – CEVA (4 % VA), *3*, *3'* – CEVA (6 % VA), *4*, *4'* – CEVA (12 % VA)

connecting through their hydrophilic groups with the active centres at the metal's surface in the conformation characterizing it in an aqueous solution.

With an increasing of ionization degree of a CSMA up to 0,25 an increase of the number of carboxylate groups improves the hydrophilicity of macromolecules. It makes metal surface hydrophilic which is proved by a rather sharp decrease of the angle of watering. The same reason together with low density of molecules is for decreased adhesion strength and water stability of polymeric surfaces in the field of α (fig. 3).

If $0,25 \leq \alpha \leq 1,0$ because of prevaluation of an electrostatic opposition of the identically charged COO^- -groups, the macro-molecules are unrolling and the pK sharply increase (fig. 1, curve 3). Relished hydrophobic phenyl groups will increase hydrophobicity of the metal's surface (fig. 1, curves *1* and *2*). This kind of orientation of the molecules with an unrolled structure in an adsorptive layer promotes improved interaction of hydrophobic groups with polymeric matrices what results in increasing of adhesion strength and water stability of the surface (fig. 3).

On further neutralization of the carboxyl groups ($\alpha > 1$) the unrolled conformation of macromolecules does not

change much. Consequently the adhesion strength and water stability of metallic polymeric system (fig. 3, curves *I* and *I'*) do also slightly modify. This is allow to make conclusions that for non-polar adhesives, adhesion strength and water stability of polymeric surface is in a direct dependence of conformational mood of the modifier and of hydrophobicity of the substrate.

With an increase of polarity of the adhesive at the passage from polyethylene (fig. 3, curves *I* and *I'*) to the copolymer of ethylene with vinylacetate where the number of VA-groups is increasing from 4 to 6 and 12 %, the adhesion strength (fig. 3, curves *2*, *3*, *4*) and water stability (fig. 3, curves *2'*, *3'*, *4'*) increase. Due to this the maximums of dependencies clearly decline to the side of lesser α . That experimental fact can be explained, so that if $0,25 \leq \alpha \leq 1,0$ the lack of adhesive bonds formed by the insufficiency of the surface's hydrophobization of a metal due to the uncompleted confirmative passage of molecules PSAS and insured by adhesive's functional polar groups.

4. Conclusions

Taking all this in consideration we can affirm that during modification of St3 by CSMA, the quantity of adhesion and stability of polymer covering in the conditions of high temperature and humidity, is defined for non-polar polymers by the conformational structure of the adsorbed molecules PSAS and consequently by hydrophobicity of the modifying surfaces. In the case of polar polymers, beside chemical bonds, creating due to amphiphilic the macromolecules of modifier, its contribution to the adhesion make also the functional polar groups of the polymer.

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Was received to the editorial office 03.12.2013.

Підвищення адгезії полімерних матеріалів модифікацією металевої поверхні високомолекулярними поверхнево-активними речовинами

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Показана можливість отримання стабільного в умовах високої температури і вологості полімерного покриття шляхом модифікації сталі (Ст3) співполімером стиролу з малеїновою кислотою і його амонійною сіллю з подальшим нанесенням двошарової плівки з поліетилену високої щільності і співполімеру етилену з вінілацетатом. Установлено, що для неполярних полімерів адгезійна міцність і водостійкість визначаються конформаційним станом адсорбованих макромолекул поверхнево-активного модифікатора і, відповідно, ступенем гідрофобності поверхні металу. У разі полярних полімерів, поряд з хімічними зв'язками, утвореними амфільними макромолекулами модифікатора, внесок у адгезію вносять функціональні полярні групи полімеру.

Повышение адгезии полимерных материалов модификацией металлической поверхности высокомолекулярными поверхностно-активными веществами

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Показана возможность получения стабильного в условиях высокой температуры и влажности полимерного покрытия путем модификации стали (Ст3) сополимером стирола с малеиновой кислотой и его аммонийной солью с последующим нанесением двухслойной пленки из полиэтилена высокой плотности и сополимера этилена с винилацетатом. Установлено, что для неполярных полимеров адгезионная прочность и водостойкость определяются конформационным состоянием адсорбированных макромолекул поверхностно-активного модификатора и, соответственно, степенью гидрофобности поверхности металла. В случае полярных полимеров, наряду с химическими связями, образованными амфифильными макромолекулами модификатора, вклад в адгезию вносят функциональные полярные группы полимера.