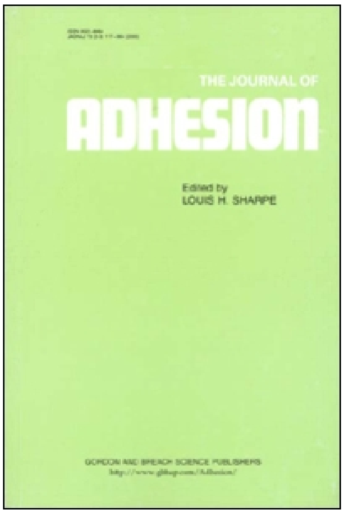

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Reconstruction of the Interface Region of Epoxy Polymer-Aluminium Coating Systems in an Aqueous Medium

V. V. Arslanov[a]
[a] Department of Polymer Adhesion, Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

To cite this Article Arslanov, V. V.(1994) 'Reconstruction of the Interface Region of Epoxy Polymer-Aluminium Coating Systems in an Aqueous Medium', The Journal of Adhesion, 44: 4, 257 — 269

To link to this Article: DOI: 10.1080/00218469408027082

URL: http://dx.doi.org/10.1080/00218469408027082

J. Adhesion, 1994, Vol. 44, pp. 257–269
Reprints available directly from the publisher
Photocopying permitted by license only

Reconstruction of the Interface Region of Epoxy Polymer—Aluminium Coating Systems in an Aqueous Medium

V. V. ARSLANOV

Department of Polymer Adhesion, Institute of Physical Chemistry, Russian Academy of Sciences, Leninskij prosp., 31, Moscow, 117915, Russia

(Received October 19, 1993; in final form April 8, 1994)

This paper reports a study of the process of reorganization of the epoxy polymer-aluminium interface during the storage of the coating systems in water. The storage in water first leads to the separation of the system components and then to the restoration of its integrity. As a result, the initial level of adhesion strength is reached or even exceeded. Of all the variable parameters (the solution composition and pH, the sign of the potential applied to the substrate surface, the method of its treatment, the type of hardener used and the conditions of deposition of oligomer from solution and the curing of the system, etc.), temperature was found to have the most significant effect on the rate of the restoration of the adhesion bonds in an aqueous medium. A mechanism of the process was proposed based on the sorption and calorimetric studies of the adhesion systems in an aqueous medium. This mechanism allows for the effect of the electrostatic interactions on the coalescence of the polymer and substrate surfaces with a thin water interlayer between them.

KEY WORDS epoxy coatings; aluminium substrate; hydration; storage in water; reconstruction of interface region; strength restoration; adhesion.

INTRODUCTION

The storage of adhesive and coating systems in water or in a humid atmosphere greatly complicates the interaction processes occurring at the polymer-metal interface.[1,2] Only after moisture tests can one draw a conclusion about the efficiency of an adhesion system, whether it is an adhesive joint, polymer coating, etc.

The existent conventional approaches to the analysis of the properties of adhesion systems during their tests in an aqueous medium consist of studies of the sorption-diffusion parameters of polymers (in a free state or on a substrate), determination of the diffusion, sorption, permeability coefficients, and their application to the description of the destruction processes in water-treated systems. The hydrolysis of the interfacial polymer-metal (oxide) bonds and oxide hydration have also been studied.[3-5] The greater part of the studies in this field are concerned with the well-studied aluminium and aluminium alloy substrates. Since the aluminium oxide hydration is thought to be a critical factor determining the system stability, attempts have been made to exclude this process or decrease its rate using organic and inorganic inhibitors, as well as chemical and electrochemical pretreatment of the metal surface.[6-8]

It is hard to agree with the opinion stated in Ref. 9 about the identity of the hydration processes occurring on a pure aluminium surface and on a polymer-coated surface. Our preliminary data[10] show quite the opposite. A polymer coating, acting as a diffusion barrier, does not only change the kinetics of the oxide hydration, but also has a significant effect on the hydration process. Being a selective membrane, a polymer film may redistribute the solution components contacting its outer surface and those resulting from the dissolution of the hydration products in the interface region. The structure of a thin water layer, different from that of a thick one, and the hydration process under the conditions of the action of the surface forces, are good prerequisites for obtaining a different hydroxide form or at least its more perfect structural organization.[10]

Our earlier data on the restoration of the epoxy polymer-aluminium adhesive strength during a long-term storage of the system in water and the results of other related studies[11–13] indicate that there is a complicated relationship between the oxide hydration and the polymer-aluminium adhesive strength. It was shown in Ref. 11 that the adhesive strength of polymers to aluminium, whose surface was stored in deionized water prior to the formation of adhesive joints, increased with storage time. Significant differences in the behaviour of the epoxy polymer-aluminium systems were observed for two anodic films on aluminium obtained in chromic and phosphoric acids.[12] In the former case, the storage in water had a weak effect on the adhesion strength, and in the latter case the adhesion strength of the system decreased during its storage in water. The possibility of restoring the adhesion strength of the polymer with aluminium alloy, the surface of which was exposed to water vapor and then dried, is related to the removal of the physically-absorbed water from the metal surface.[13] During a long-term storage of the alloy in a humid atmosphere, when aluminium hydroxide in the form of bayerite ($Al(OH)_3$) had been formed on its surface, the adhesion strength was not restored by drying.

Consequently, at present there is neither unanimity of views on the stability of adhesion systems during their storage in water or water vapor, nor agreement between the results of the experimental studies carried out by different authors.

As reported in Refs. 1, 2 and 10, the storage of the epoxy polymer-aluminium (or aluminium alloy) coating system in water leads to a decrease in the adhesion strength to zero followed by the restoration of the strength without drying the system. However, the reason for this effect and the possibility of controlling the strength restoration process were not clear.

To solve these problems, in this work the effects of temperature, aqueous medium pH, electrolyte, and the potential applied to the substrate on the kinetics of the restoration of the epoxy polymer-aluminium adhesion strength are studied. The kinetics of the water sorption by the systems with a different initial level of adhesion interactions at the polymer-metal interface is also determined; this level depended on the method of pretreatment of the aluminium surface.

EXPERIMENTAL

In our earlier experiments,[1,2] in which we observed the restoration of the polymer-aluminium adhesion strength during the storage of the system in water, we used epoxy enamels (manufactured in Russia and Germany) as coatings. In the present work we have used simpler lacquer systems containing Bisphenol A epoxy oligomer (E-41, M = 950) and the hardener: a 40% solution of hexamethylenediamine (HMDA) or polyethylenepolyamine (PEPA) in ethanol. The concentration of the solution of epoxy oligomer (EO) in the mixture of solvents (xylene: butyl acetate : acetone = 10:7:3) was 50 wt%. The ratios of the solutions of EO to the hardener were 50:3 and 20:1 by weight for EO/HMDA and EO/PEPA, respectively. A stepwise curing was carried out for both systems: one day at 20°C and 1 to 8 h at 90°C.

The coatings were deposited by two methods: adsorption from the solution and casting onto the rotating substrate (600 rotations/min). The thickness of the polymer coating for the two methods was 80 μm and 40 μm, respectively.

The surface of the aluminium foil (99.5% Al), with overall dimensions of 100 × 100 × 0.1 mm, was treated by three methods: 1) double degreasing with acetone; 2) degreasing with acetone and treating in a 20% aqueous solution of NaOH at 20°C for 1 min; 3) treatment by methods 1 and 2 and treatment in a solution of $K_2Cr_2O_7$ (60 g/l) in 17% sulfuric acid at 65°C followed by washing in distilled water and drying in air. The samples were allowed to stand in distilled water at 20° or 60°C and in a 0.5% aqueous solution of NaCl at 60°C. The pH values were provided using HCl and NaOH. Before the adhesion tests, the coated foil was cut into 10-mm strips. The backside of the aluminium foil with the coating was not protected during exposure of the systems to water.

To determine the effect of the size (width) of the samples exposed to water on the process of the restoration of strength, we studied the coating systems which were cut into strips before dipping them in water. However, the results obtained in this case did not differ from those for the samples prepared using the first method.

The strength of the coating systems was measured using the peeling method (180°) on an Instron 1121 testing machine at a cross-head speed of 10 mm/min and a temperature of 20°C. A schematic diagram of the experimental setup of the peel test is shown in Figure 1.

To study the effect of the initial adhesion strength on the process of its restoration, the middle part of the substrate surface was hydrophobized for 10 min in dimethyldichlorosilane vapor and dried at 90°C for 30 min. Two layers of the epoxy coating were then deposited on the substrate.

The thermograms of the coatings on the foil were measured using a DSC-7 (Perkin-Elmer) scanning calorimeter under N_2 atmosphere at a scanning rate of 10 deg/min.

The water sorption by the coating systems with a different initial level of the interphase interactions was determined in a vacuum absorbing column supplied with a beam analytical microbalance and an automated recorder. The balance sensitivity was 10^{-8} g. The 70 × 70 mm samples with a 40 μm thick coating were stored in water at 60°C for two weeks, and water was then pumped out of the samples to a constant weight. The coated substrates were placed in water at 60°C and allowed to stand for 2, 6 and 100 h. The condensed moisture was removed from the samples, and they were suspended on the analytical microbalance. Initial weight measurements were made in an atmosphere of saturated water vapor; the system was then evacuated at a constant rate and the desorption curve was recorded.

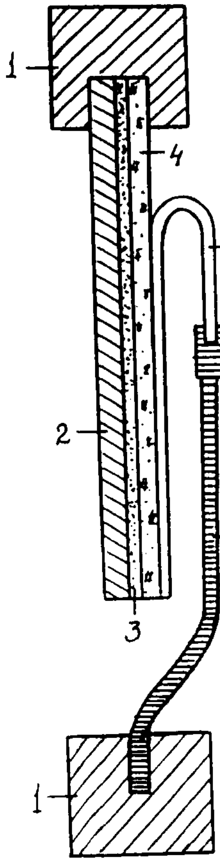

FIGURE 1 Schematic diagram of the experimental arrangement used in the peel test. 1-cross-head, 2-free backside support, 3-adhesive tape, 4-coating film, 5-aluminium foil, 6-spring clamp.

RESULTS AND DISCUSSION

Figure 2 shows the epoxy polymer (HMDA)–aluminium adhesion strength (P) *versus* time of the storage in water (t) at 20°C. At room temperature, the restoration of strength takes a long time. Whatever the decrease in P at the beginning of the process, the first increase in the adhesion strength is observed after 2–3 weeks.

This extreme dependence shows that there is a competition between two groups of processes in the system. The first group is the water diffusion to the polymer-metal interface and its accumulation in this region, as well as the hydrolysis of the interphase bonds and aluminium oxide hydration. These processes are characteristic of almost all the polymer-metal adhesion systems, and they result in the disbonding of the components at the interface.

To determine the mechanisms ensuring the increase in the adhesion strength of the systems in question during their long-term storage in water, the effect of different parameters on the behaviour of the system was studied.

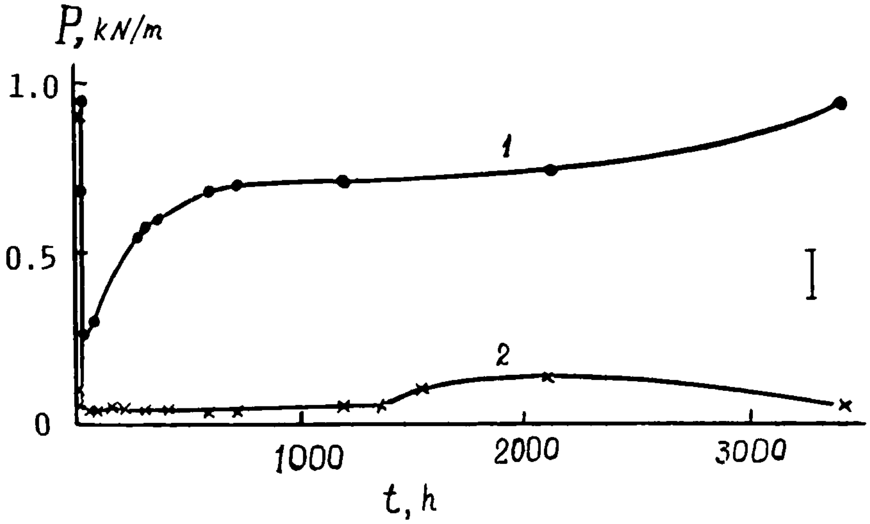

FIGURE 2 Peel Strength (P) of the epoxy polymer (HMDA)- aluminium coating systems *versus* the time (t) of the storage in water at 20°C. Pretreatment of the metal surface: degreasing and etching in alkali (1 and 3); degreasing (2). Curve 3 describes behaviour of a small group of samples whose strength was not restored. Error range indicated.

Figure 3 shows P *versus* t for the same system as in Figure 2; however, the medium in which the samples were stored at 20°C was a 0.5% solution of NaCl. A comparison of the curves in Figures 2 and 3 shows that the electrolyte does not have any effect either on the rate of decrease or the rate of restoration of the adhesion strength. This is due to a much lower diffusion rate of the ions through the polymer membrane than that of the water molecules,[14] as well as to the fact that the processes in the interface region are of a chemical, and not an electrochemical, nature, *i.e.*, they are not related to the charge transfer between the cathodic and anodic parts of the surface.

A number of characteristic features in the behaviour of the systems are noteworthy. The first increase in strength observed for all the coating systems is located rather accidentally on the time axis. This fact related to the instability of the system in the initial period of the tests also explains the presence of a small (~ 10%) number of samples whose strength has not been restored (curve 3 in Fig. 2 and curve 2 in Fig. 3). The curves in Figures 2 and 3 are characteristic of all the systems studied for either type of hardener and for any method of pretreatment of the substrate surface, as well as for formation of the coatings.

The rate of restoration of the adhesion strength increases significantly with increasing temperature of the water in which the coating system is stored. As seen in Figure 4, the left-hand branches of the P *versus* t curves for the identical systems stored at either 20° or 60°C are similar. However, the difference in the time of the beginning of the P increase (the first increase for 20°C, Figs. 2 and 3) is equal to hundreds of hours and the time of the attainment of the highest degree of the restoration is equal to thousands of hours (Figs. 2 and 4). It should be noted that the initial strength was restored or

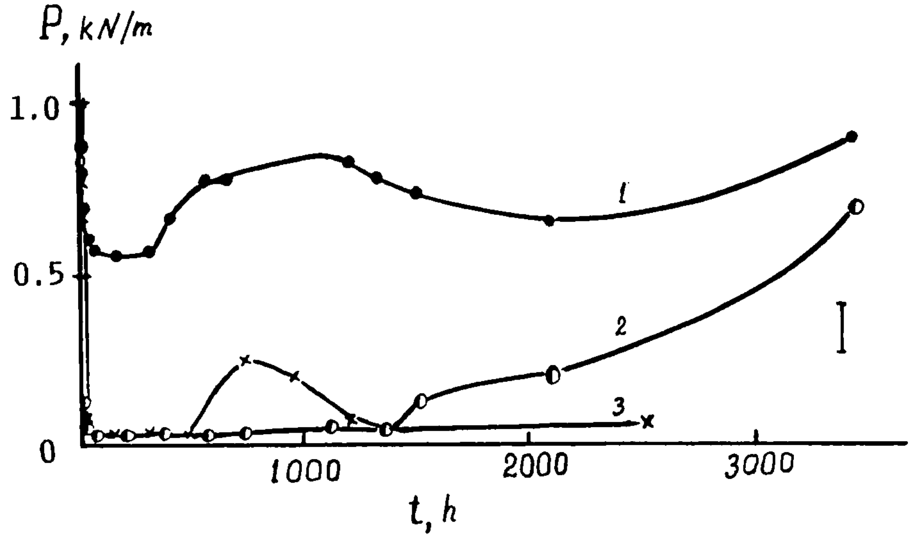

FIGURE 3 Peel strength of the epoxy polymer (HMDA)- aluminium coating systems *versus* the time of the storage in a 0.5% aqueous solution of NaCl at 20°C. Pretreatment of the metal surface: degreasing and etching in alkali (1); degreasing (2). Curve 3 describes behaviour a small group of samples whose strength was not restored. Error range indicated.

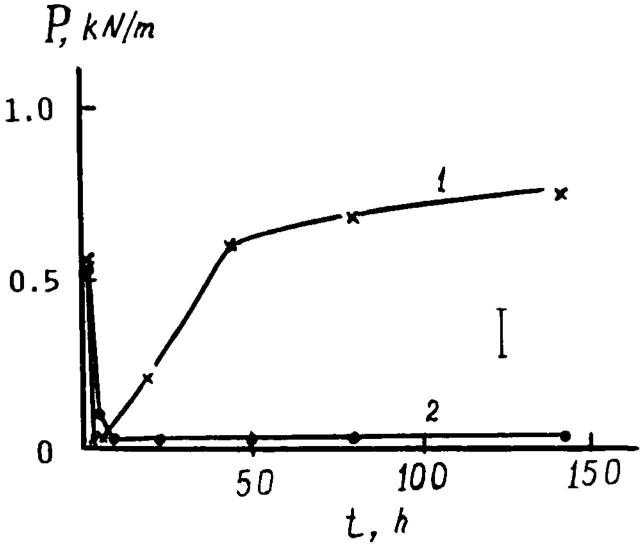

FIGURE 4 The *P-t* dependence for the epoxy polymer (PEPA)-aluminium coating systems. Water temperature: 60° (1) and 20°C (2). Error range indicated.

exceeded in all the samples stored at 60°C, and there was only one minimum in the *P versus t* curve.

Of particular importance is the result in Figure 5 showing the *P versus t* dependence for pH 3.0 and 12.0. It was shown in Ref. 15 that a local change in pH due to the

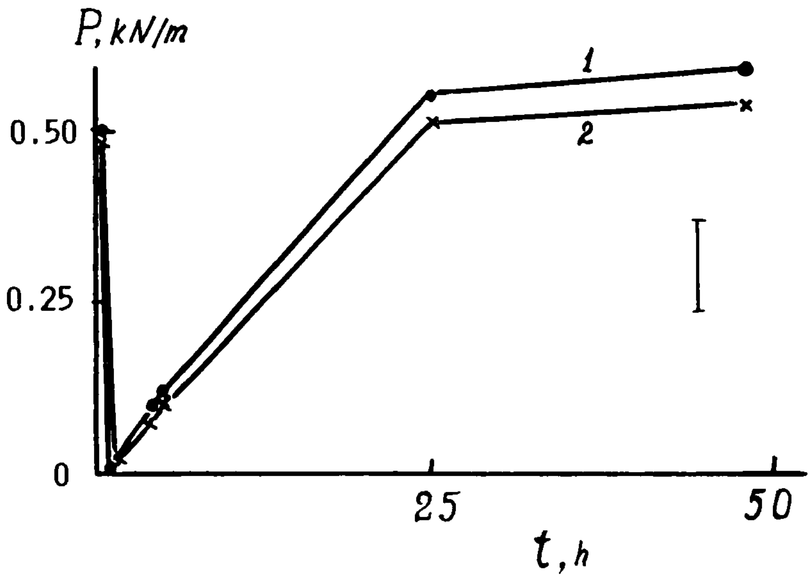

FIGURE 5 The *P*-*t* dependence for the epoxy polymer (PEPA)-aluminium coating systems. Water temperature: 60°C, pH 3(1) and 12(2). Error range indicated.

amine-bearing coupling agent in the epoxy coating-aluminium interface had a significant effect on the aluminium oxide hydration. The absence of the relationship between the restoration of the adhesion strength and the external pH of the aqueous medium is determined, on the one hand, by the decrease in the diffusion rate of the hydrogen ions through the polymer membrane charged positively due to the amine-containing hardener and, on the other hand, by the local increase in pH in the interface region decreasing the driving force of the diffusion of hydroxyls to the surface. These processes and the possible water counterflow as a result of the coalescence of the charged polymer and metal surfaces prevent the change in pH in the interface region and, consequently, the change in the oxide hydration conditions. Also, the *P versus t* dependence is not sensitive to the sign of the potential applied to the substrate on which the coating was deposited (± 1.5 V with respect to the electrode in contact with the free coating surface).

The following experiment illustrates the effect of the initial level of the interface interactions on the restoration of the adhesion strength and simulates the parts of a real mosaic surface[16] with a high and low adhesion capacity.

Figure 6 shows the *P* values for different parts of the substrate surface situated at a distance *l* from the edge. For a degreased aluminium surface (region I), the strength decreases to zero in the first hours of the storage in water and is then restored; moreover, a long storage in water leads to a 50% increase in the adhesion strength compared with its initial level. For a surface with a low adhesion capacity (region II), the strength is restored by 65%. Consequently, the restoration effect is observed even for a surface coated with an antiadhesion layer.

This experiment allows one to understand the reasons for the effect of the restoration of the adhesion strength for nonactivated surfaces subjected only to degreasing. This

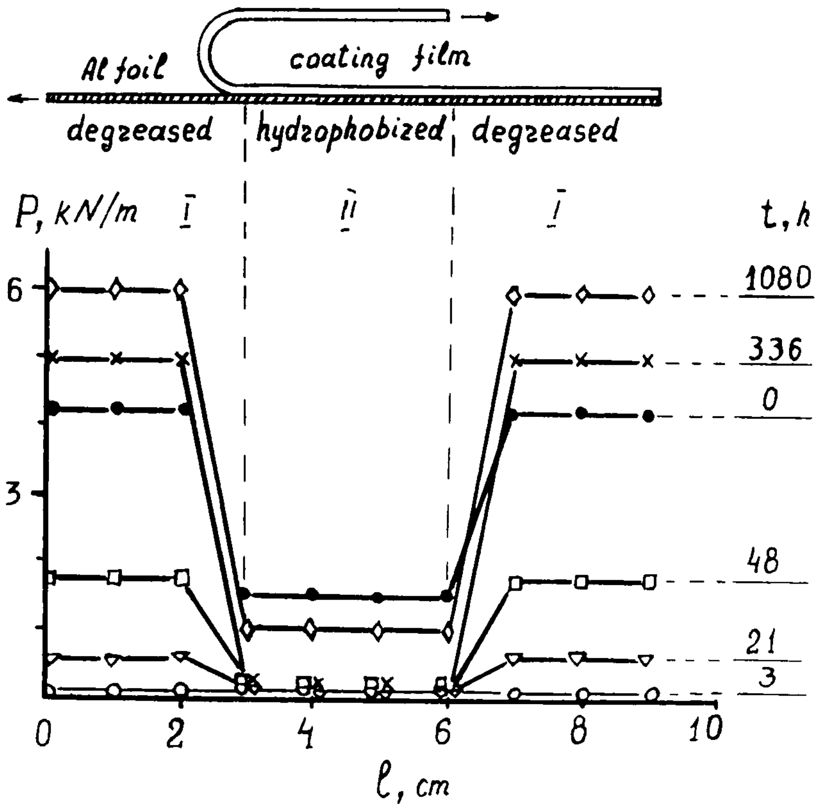

FIGURE 6 The effect of the pretreatment method of the aluminium surface on the kinetics of the restoration of the adhesion strength. Peel strength for parts of the strip with the two methods of surface pretreatment. Time of the samples storage in water is shown on the right side of the figure.

surface contains the parts with adsorbed impurities preventing the formation of strong bonds between the polymer and substrate functional groups. The oxide hydration and the dissolution of the surface layer lead to compulsory purification of the surface followed by its activation due to the newly formed hydroxide.

The formation (growth) of the aluminium hydroxide in the interface region may occur both on the metal and polymer surfaces. Moreover, the change in the hydroxide modification under these conditions compared with that during crystallization from the bulk of the solution may be related not only to the limited water supply or its structuring in a thin layer, but also to the induction effect of an organized polymer surface. This fact follows from work[17] in which it has been shown that an organized monolayer of stearic acid on the surface of an oversaturated aqueous solution of bicarbonate induces the growth of oriented modification of $CaCO_3$ in the form of vaterite, whereas the growth of the calcite modification was observed under normal conditions.

These and our electron diffraction data for the aluminium hydroxide modifications growing on a free metal surface and under epoxy enamel[10] allow us to explain why the

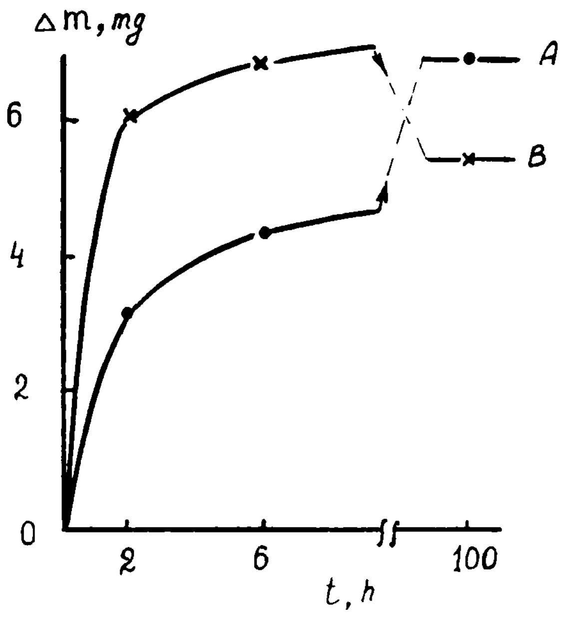

FIGURE 7 The equilibrium water sorption by the epoxy polymer (PEPA)-aluminium coating systems (Δm) *versus* the time of the storage in water (*t*) at 60°C for the substrate surface subjected to chemical pretreatment (A) and degreasing (B).

initial strength of the coating systems is exceeded after their storage in water. It was shown in this work[10] that the aluminium hydroxide modification in the form of boehmite with a perfect structural organization grew under the polymer coating, and loose bayerite was formed on a free aluminium surface.

Thus, changing the temperature at which the adhesion system is stored in water is the most effective method of restoring the strength of coating systems. The other methods that can change the rate of the process do not have the desirable effect because of the selectivity of the barrier properties of a polymer coating with respect to the particles diffusing through it.

Based on the results obtained, we can reach some conclusions about the mechanisms underlying the separation of adhesion systems in an aqueous medium and the reasons determining the final state of these systems with the restored adhesion strength. However, these data do not give an answer to the question of which of the possible mechanisms of reaching this state operates in the system. The change in the thickness and mass of the water layer in the interface region is a parameter that may serve as an indicator of the mechanism of the restoration of the adhesion strength. During the peeling-off of the samples stored at 20°C for the times corresponding to the first minimum in the *P versus t* curves, one can observe a thin (thousands of angstroms) water layer. Nevertheless, this extreme change in the thickness of the water layer does not allow one to reveal the mechanism of the process.

The measurement of the thickness of ultrathin water layers under a polymer coating stored in water being a difficult task, we have measured the water sorption by the

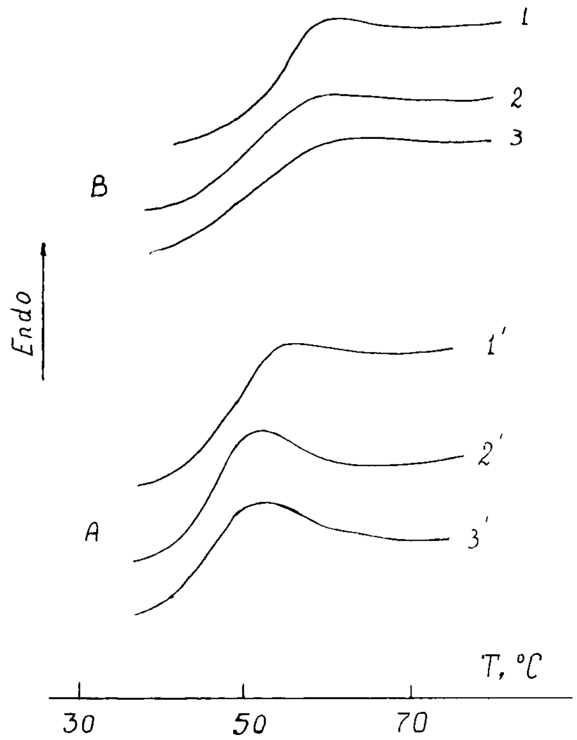

FIGURE 8 The thermograms of the epoxy polymer (PEPA)-aluminium coating systems for different times of storage in water: 30 (1, 1'), 160(2, 2') and 420 (3, 3') min at 60°C. A—chemical pretreatment of metal surface; B—degreasing.

system for different storage times. The measurements were made for samples of two types. High adhesion strength was provided in the reference sample (A) by a chemical pretreatment of the aluminium surface (see EXPERIMENTAL, method 3). This pretreatment allowed us to exclude the disbonding of the system for a normal time of the experiment (100–200 h) on restoring the strength. In that case, water was absorbed only by the bulk of the polymer coating. For the samples of the second type, in which the metal surface was not subjected to any special pretreatement (B), water was concentrated in two parts of the system: in the bulk of the coating (as in the reference sample) and at the polymer-metal interface. The dependence of the equilibrium sorption for samples A and B on the time of the storage in water are shown in Figure 7. A higher rate of sorption of water in sample B was due to water accumulation in the interface region. The decrease in the water content in system B during long-term storage in water is followed by the restoration of the adhesion strength. This is the key result of the experiment. For sample A, the water sorption increased monotonically over the entire storage time range. The water diffusion coefficients for samples A and B calculated from the Fickian kinetic curves of desorption were equal to 5.5×10^{-14} and 1.2×10^{-13} m^2/s, respectively.

The difference in the interphase interactions in samples A and B reflect their thermophysical properties. Figure 8 shows the thermograms of these samples for different times of storage in water. For the samples with a high (A) and low (B) level of adhesion interactions, the thermograms obtained at the beginning of the process, when the interface region of both systems are not disturbed, show a small endothermal peak due to the physical ageing of the polymer after its devitrification. When the storage time is increased, the endothermal peak in sample B disappears, but the peak persists in sample A with a high adhesion. The long-term water sorption and annealing of the coating systems at a temperature (60°C) close to the vitrification temperature of the polymer matrix activate the reconstruction processes. However, for sample A, the rate of the ageing process slows down because of the decreased rate of relaxation due to the adhesion interactions between the system components, whereas, in sample B, which is not under these restrictions, the relaxation is soon over after the detachment of the polymer from the substrate.

The results reported allow us to distinguish between the mechanisms of the restoration of the adhesion strength. It is more convenient to carry out their analysis in terms of the water layer thickness changing in the course of the storage of an adhesion system in water.

Figure 9 shows the schemes of the transformations in the polymer (EP)/aluminium interface for two mechanisms. Positions a and b show the initial state and that with a water interlayer, respectively. A competition between two processes is further observed in both cases (position c); these processes both increase (water diffusion) and decrease (the growth of the hydroxide) the free water content in the interface region. If the growth rate of the hydroxide consuming the diffused water is higher than that of the water supply (mechanism I), the interlayer thickness will decrease (position d). The water diffusion will stop (position e) as a result of the restoration of the hydroxide-polymer bonds. In the case of this mechanism the dependence of the water layer thickness on the storage time will be described by the curve with a maximum, and the kinetic curve of water sorption by the system would reach the saturation value. The second, electrostatic mechanism, additionally involves the charging of the polymer and metal surfaces (mechanism II, position c). At some moment of time determined by the critical value of the surface charge density and the interlayer thickness (position d), the polymer and metal (hydroxide) surfaces coalesce (position e). The excess water displaced from the interface region would lead to an abrupt change in the kinetic curves of the interlayer thickness and sorption. It should be noted that the second mechanism is more universal than the first one, because it also works in the case when the rate of the water supply to the interface region is higher than that of the growth of the hydroxide. At this ratio of the rates of the processes and in the absence of the assumption about the charging of the surfaces, the coating systems should fail without further restoration, which is usually observed for the majority of adhesion systems stored in water for a long time.

The data in Figure 7 for sample B, whose sorption in the time range corresponding to the restored strength decreases significantly, show that the process of restoration of the adhesion strength occurs in the system in question by mechanism II.

Thus, the experiments performed allowed us to determine the conditions under which the process of the restoration of the epoxy polymer-aluminium adhesion strength may be increased by several orders of magnitude. The mechanism of the process was specified using the data on the coalescence of the polymer and substrate surfaces with the water interlayer between them. The quantitative description of the mechanism will be given in further publications.

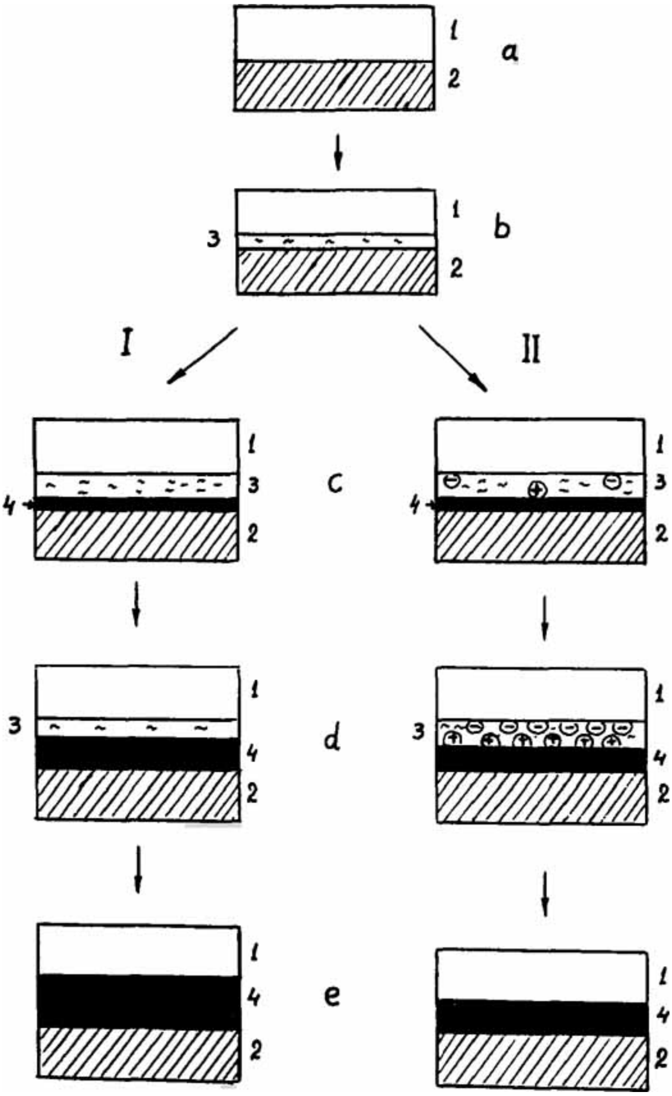

FIGURE 9 The schemes of the transformations in the interface region of the epoxy polymer-aluminium coating system for two mechanisms of the restoration of the adhesive strength: epoxy polymer (1), aluminium (2), water (3) and aluminium hydroxide (4). See the text for explanation.

CONCLUSIONS

The effect of various parameters on the kinetics of the adhesion strength restoration of epoxy polymer-aluminium coating systems exposed to water was studied. The temperature was found to have the most significant effect on the rate of the restoration process. The suggested mechanism of the strength restoration is based on the aluminium oxide hydration process, water diffusion to the interface and electrostatic interactions between the surfaces of the system separated by a thin water layer.

Acknowledgement

The author wishes to thank A. V. Lobanov, P. Sh. Vartapetyan, and D. A. Ivanov for carrying out the experiments and for discussion of the results.

References

1. V. V. Arslanov and W. Funke, *Progr. Org. Coat.* **125**, 355 (1988).
2. V. V. Arslanov and W. Funke, *Zashita Metallov* **24**, 950 (1988).
3. D. A. Hardwick, J. S. Ahearn and J. D. Venables, *J. Mater. Sci.* **19**, 223 (1984).
4. J. S. Ahearn and G. D. Davis, *J. Adhesion* **28**, 75 (1989).
5. W. Brockmann, O. D. Hennemann and H. Kollek, *Int. J. Adhesion Adhesives* **6**, 115 (1986).
6. D. A. Hardwick, J. S. Ahearn, A. Desai and J. D. Venables, *J. Mater. Sci.* **21**, 179 (1986).
7. Q. Yang and Q. Zhou, in *Adhesive Chemistry–Developments and Trends*, L.-H. Lee, Ed. (Plenum, New-York, 1984), p. 799.
8. P. Poole and J. F. Watts, *Int. J. Adhesion Adhesives* **5**, 33 (1985).
9. G. D. Davis, *Surf. and Interf. Anal.* **17**, 439 (1991).
10. V. V. Arslanov, *Reports of the* 1st *Finnish-Soviet Corrosion Symposium*, M. Tavi, Ed. (Helsinki, 1988), p. 125.
11. E. Isoyama, M. Hasegava and T. Uchiyama, *Aluminium* **63**, 1151 (1987).
12. J. F. Watts, R. A. Blunden and T. J. Hall, *Surf. and Interf. Anal.* **16**, 227 (1990).
13. N. A. Thorne, P. Thuery, A. Frichet, P. Gimenez and A. Sartre, *Surf. and Interf. Anal.* **16**, 236 (1990).
14. H. Leidheiser, Jr. and W. Wang, *J. Coat. Technol.* **53**, 77 (1981).
15. S. L. Selector, V. V Arslanov and V. A. Ogarev, *Int. J. Adhesion Adhesives* **10**, 99 (1990).
16. V. V. Arslanov, Dissertation, Doct. Sci. (Chem), Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, 1989.
17. S. Mann, B. R. Heywood and S. Rajan, 197th ACS Nat. Meet. Dallas, Tx, USA, Abstr. Pap. (Am. Chem, Socy., Washington, 1989), paper no. 116.