APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Acid–Base Interactions and Adhesion Capacity in the System Constituted by an Epoxy Coating and a Metal

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Abstract—Free surface energy and acidity parameter of solid surfaces of polyepoxides used as anticorrosive coatings were measured. Formulations of epoxy resins with various curing agents were studied. The adhesion capacity of epoxy films to various metallic surfaces was evaluated.

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The presently widely used three-layer (epoxy primer, polyolefin-based thermoplastic melt-adhesive, and polyethylene) anticorrosive coatings (ACC) for steel pipes combine high adhesion properties of polyepoxides with good mechanical properties and high chemical resistance of polyolefins. As, however, the temperature is elevated and working time made longer, the adhesion capacity of ACC decreases. The performance of these coatings can be markedly improved by varying the composition of an epoxy formulation and the set of design elements of a three-layer ACC. This type of anticorrosive coatings is an interesting object of study and matter for further development, because a high adhesion between the constituent layers is to be achieved.

As is known, the phenomenon of adhesion consists in various kinds of interaction between molecules of the contacting phases. For an adhesion interaction to occur, it is necessary that bonds between molecules of the adhesive and active centers on the substrate surface should be formed. The existing thermodynamic approaches are based on the results obtained in studying the energy of interphase tension, wetting angles at the substrate–adhesive interface, and adhesive spreading angles at phase boundaries, with account of various contributions of intermolecular forces [1].

Recently, the approach according to which an important role in bonding between the contacting phases is played by acid–base interactions has gained wide acceptance [2]. In this context, the best properties should be observed for an adhesion joint in which one side shows acidic (by Lewis) properties, and the other, basic properties. In view of the aforesaid, a study of surface characteristics of all components of a coating is a matter of strong current interest. Further purposeful modification of the layers, aimed to enhance their acid–base interaction, could improve the properties and extend the service life of ACC.

The surface characteristics that allow prognostication of the capacity of a material for adhesion interaction include, in the first place, the surface energy with two components, dispersion and acid–base (previously named polar), and the acidity parameter [3], or reduced acidity parameter [4], which is the difference of the acidity parameters of the adhesive and substrate. The acidity parameter gives information about the acid–base properties of a surface under study and, consequently, about its capacity for an acid–base interaction in an adhesion joint.

The aim of our study was to reveal and assess the relationship between the above-mentioned characteristics and the adhesion capacity in the system constituted by an epoxy coating and a metal, which is highly important for a multilayer coating and ensures its adhesion to the metal and resistance to cathode flaking.

EXPERIMENTAL

We used in the study ED-20 epoxydiane resin and PEF-3A low-molecular weight epoxyurethane
caoutchouc. The formulation was cured with diethyl-
enetriamine (DETA), polyethylenepolyamine (PEPA),
AF-2M aminophenol, and DTB-2 curing agent, which
is formed in the reaction of diethilenetriamine and
butylmethacrylate in the presence of a catalyst,
a solution of boron trifluoride in diethylene glycol.
The curing agent was taken in the stoichiometric
amount with respect to the epoxy resin.

Copper, titanium, brass, steels (St.10, St.20,
EP696, and Ya1T brands), and duralumin alloys
(D16T, D16ATV, and D16AM brands) served as met-
thallic substrates.

To evaluate the surface properties, film samples
of epoxy formulation were formed on glass substrates
and cured in air at room temperature (cold method)
and in an oven at 80°C for 2 h (hot method).

We evaluated the components of the free surface
energy (FSE) by measuring the wetting angles for
test fluids on the sample surface with a KM-6 cath-
etometer and calculated them graphically, with pro-
cessing by the least-squares method with the use of
Microsoft Excel software.

As test fluids served water, aniline, phenol, form-
amide, glycerol, dimethylformamide, dimethyl sul-
f oxide, saturated aqueous solution of K_2CO_3,
methylene iodide, and α-bromonaphthalene. Their param-
eters are listed in Table 1 [1, 3].

Table 1. Free surface energy \( \gamma_s \) of model fluids and its
acid–base (\( \gamma_{ab} \)) and dispersion (\( \gamma_d \)) components

<table>
<thead>
<tr>
<th>Model fluid</th>
<th>( \gamma_d )</th>
<th>( \gamma_{ab} )</th>
<th>( \gamma_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>22</td>
<td>50.2</td>
<td>72.2</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>32.4</td>
<td>4.9</td>
<td>37.3</td>
</tr>
<tr>
<td>Glycerol</td>
<td>33.9</td>
<td>29.8</td>
<td>63.7</td>
</tr>
<tr>
<td>Formamide</td>
<td>31.8</td>
<td>25.7</td>
<td>57.5</td>
</tr>
<tr>
<td>Aniline</td>
<td>41.2</td>
<td>2.0</td>
<td>43.2</td>
</tr>
<tr>
<td>Phenol</td>
<td>37.8</td>
<td>2.6</td>
<td>40.4</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>34.9</td>
<td>8.7</td>
<td>43.6</td>
</tr>
<tr>
<td>Saturated aqueous</td>
<td>34</td>
<td>70.9</td>
<td>104.9</td>
</tr>
<tr>
<td>solution of K_2CO_3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Bromonaphthalene</td>
<td>44.6</td>
<td>0</td>
<td>44.6</td>
</tr>
<tr>
<td>Methylene Iodide</td>
<td>49.8</td>
<td>2.4</td>
<td>52.2</td>
</tr>
</tbody>
</table>

We calculated the acidity parameter by the Berger
method [3], which consists in the following. If we use
the known Owens–Wendt equation [5]

\[
\gamma_{lv}(1 + \cos \Theta)/2 = (\gamma_d + \gamma_{ab})^{1/2} + (\gamma_p + \gamma_p)^{1/2},
\]

which can be brought to the form

\[
W_d/2(\gamma_{lv})^{1/2} = (\gamma_{ab}^{1/2} + (\gamma_p + \gamma_p)^{1/2}/(\gamma_{lv})^{1/2}
\]

\( \gamma_d \) and \( \gamma_{ab} \) are the acid–base and dispersion
components of the FSE of the test fluids; \( W_d \) thermo-
dynamic work of adhesion of a fluid on the surface
under study; \( \gamma_s \) and \( \gamma_{ab} \), dispersion and acid–base
components of the FSE of the surface under study) and
plot, using a linear approximation, a curve in the
coordinates \( \gamma_{ab}^{1/2} - W_d/2(\gamma_{lv})^{1/2} \), then the co-
ordinate of the intersection point of the curve and the
ordinate axis will be \( (\gamma_{ab})^{1/2} \) and the slope of
the straight line, \( (\gamma_{ab})^{1/2} \). The sum of the values of
\( \gamma_s \) and \( \gamma_{ab} \), graphically found in this way, is the geo-
metric-mean approximation of the free surface energy of
the material.

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Fig. 1. Determination of the geometric-mean approxima-
tion of the FSE of a PEF-3A film cured with PEPA. Test
fluid: (1) α-bromonaphthalene, (2) methylene iodide,
(3) aniline, (4) phenol, (5) dimethylformamide, (6) di-
methyl sulfoxide, (7) formamide, (8) glycerol, (9) satu-
rated aqueous solution of K_2CO_3, and (10) water. For explana-
tions see text.