Composite protective coatings. Resistance to acid penetration of coatings based on epoxy resins

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Abstract

A complex of diffusion–sorption methods is used to study the effect of the chemical nature of the curing agent and polymer epoxy matrix on the solubility and diffusion of corrosive acid media and also to test the possibility of decreasing the acid penetration into laminated composite coatings. A significant effect of the chemical nature of the curing agent and polymer matrix composition on the solubility of corrosive media is observed. This is manifested as a fundamental difference in the behavior of epoxy materials cured by amines and acid anhydrides: lower solubility (5–10-fold) and lower acid penetration rate constants (2–10-fold) are typical of anhydride-cured epoxy binders. It is shown that both amine (polyethylene polyamine (PEPA)) and anhydride (succinic anhydride (SA)) aliphatic curing agents form more permeable epoxy matrices with higher acid solubility as compared to aromatic curing agents, such as metaphenylene diamine (MPDA) and phthalic anhydride (PA). It is also important that a pronounced mechanism of sorption with binding is realized in the case of amine-cured resins with residual and reduced amino groups in the case of acid penetration. This principally allows ion-selective properties to be imparted to the cured resin. It is suggested that materials containing not only residual but also functional acid groups can be used for the development of laminated composite coatings. As shown for chlorosulfonated polyethylene (CSPE) as an example, the penetration depth of sulfuric acid is comparable to that in anhydride-cured epoxy resins. Moreover, data of luminescent analysis indicate that complexes are formed between CSPE functional groups and the penetrating acid. The results show that the penetration depth of mineral acids decreases considerably for laminated composite coatings with an upper layer of materials comprising functional acid groups. This effect is observed for phosphoric acid at temperatures up to 100°C and also for nonvolatile H₂SO₄ and volatile HCl in the temperature range of 20–70°C.

Keywords: *protective polymer coatings, corrosive media, composite materials.*

Received: October 2, 2020. Published: December 9, 2020

doi: [10.17675/2305-6894-2020-9-4-22](https://doi.org/10.17675/2305-6894-2020-9-4-22)

Introduction

Epoxy composites are widely used as protective polymer coatings for corrosive media. Their advantages include the possibility of fast curing at low temperatures (down to –15°C) and

hot aftercure by the heat of the process medium in the course of operation; high chemical resistance in corrosive media, including the cases with pH alteration; long operation life of adhesion bonds with protected metallic or concrete supports.

At the same time, one of the topical problems for thermoplastic coatings, including epoxy coatings, is to improve their chemical resistance to acids.

Taking into account that the most important factor providing the chemical stability of thermoplastic coatings is the low and tunable permeability of the polymer matrix with respect to the corrosive medium components, the goals of this work were to study the effect of the chemical nature of the curing agent and polymer matrix on the solubility and diffusion of an acidic corrosive media and also to test the possibility of decreasing the acid penetration into laminated composite coatings.

Experimental

Objects and Methods

Research Objects

The main research objects in the work were model and industrial epoxy compounds with various curing agents. The curing agents used were aliphatic and aromatic amines and acid anhydrides: polyethylene polyamine (PEPA), succinic anhydride (SA), meta-phenylene diamine (MPDA), and phthalic anhydride (PA).

Research Methods and Techniques

A complex of well-known diffusion–sorption methods was employed: in particular, local X-ray spectral analysis [1] – analysis *via* Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS), luminescent optical spectroscopy [2], infrared spectroscopy (IR) [3], and gravimetry.

Analysis by SEM/EDS

The quantitative analysis in this experimental series was carried out without ZAF correction [4], with reference systems made of an amine-cured epoxy material with added fine elementary sulfur (extra purity grade: OSCh-16-5, TU 6-09-2546-77). Each elemental diffusion profile of sulfur S was recorded simultaneously with the minimum and maximum reference systems for the studied range of sulfur concentrations.

Reference systems (Figure 1) show good correlation of chemical analysis for determination of sulfur content C_S according to GOST 28644-90 (ISO 6528-1-84) (Rubber. Determination of the total sulfur content. Part 1. Method of incineration in a flask with oxygen) and elemental determination using the local X-ray analysis technique, J_{pulse} . The maximum sulfur content values in the distribution profile maximum for sulfur concentrations C_S in the polymer are presented below. They are recalculated for each measurement by

comparison with the measurements for the reference resin/curing agent formulations with added sulfur.

Figure 1. Correlation between the sulfur content in the polymer determined by SEM/EDS (J , pulses) and by chemical analysis (C_s , wt. %). Inset: the sulfur range of 3–9 wt. %.

Luminescent Optical Spectroscopy

LUMAM I-3 and ALTAMI LUM 1 LED luminescent microscopes were used to record the luminescence spectra of the polymer along the diffusion coordinate [2] in the range of 420–700 nm.

For filled compounds, the acid penetration depth was measured using the method of luminescent indicators that were applied onto a sample chip to be studied [5]. The indicator was based on Luminore orange–red 600 PT. The color of the indicator solution was initially green and became blue after interaction with the acid.

Infrared Spectroscopy

Studies were carried out in the range of 4000 to 550 cm^{-1} using a NEXUS IR spectrometer (NICOLET).

Gravimetry

A Pioneer PA214 analytical balance was used for gravimetry.

A characteristic feature of the studied systems is that there is a distinct boundary separating the acid penetration zone from the initial material [2, 6–12].

It should be noted that the position of the boundary is similar in different well-known methods, such as optical microscopy for colorless transparent systems, luminescence spectra, methods of acid–base and luminescence indicators, and the SEM/EDS technique.

It is most informative to use the SEM/EDS method for studies of the diffusant distribution profiles. However, its application implies a number of limitations related to the need for evacuation, owing to which the diffusants must be “non-volatile”.

The research object in this work that meets this requirement is sulfuric acid that is one of the most frequently used industrial corrosive media.

Results and Discussion

Let us consider the experimental data on the penetration of aqueous acid solutions into epoxy materials.

Effect of the curing agent type on diffusion–sorption properties of epoxy materials in highly corrosive acidic media

The curing agents studied in this work are amines, both aliphatic (polyethylene polyamine (PEPA)) and aromatic (metaphenylene diamine (MPDA)), as well as anhydrides of organic acids (aliphatic succinic anhydride (SA) and aromatic phthalic anhydride (PA)).

Amine-cured epoxy compounds

The SEM/EDS distribution profiles of the diffusion of sulfuric acid solutions are shown below (Figure 2, Figure 3). They represent the sulfur distribution profiles along the direction of diffusion (from the sample surface) for epoxy composites cured by amines: aliphatic PEPA and aromatic MPDA. Here and below, “m.p.” stands for “mass parts”.

Figure 1. SEM/EDS diffusion profiles for the penetration of 30% H₂SO₄ (*J*, pulses) for 384 h at 90°C into a model epoxy formulation with varied amounts of the PEPA aliphatic amine curing agent; *C*_{PEPA} = 2–10 m.p. per 50 m.p. of ED-20 epoxy resin. The arrow indicates the direction of diffusion along the *X* coordinate, μm.

Figure 2. SEM/EDS diffusion profiles of penetration of 30% H_2SO_4 (J , pulses) for 384 h at 90°C into a model epoxy composition with varied amounts of the MPDA aromatic amine curing agent; $C_{\text{MPDA}} = 4\text{--}12$ m.p. per 50 m.p. of the ED-20 epoxy resin. The arrow indicates the direction of diffusion along the X coordinate, mm.

Apparently, stepped profiles for the MPDA aromatic amine are qualitatively similar to the distribution profiles typical of the PEPA aliphatic amine.

Effect of acid concentration on the distribution profiles and penetration constants

As shown earlier [13], the concentration of the acid is the most important factor determining its penetration into the epoxy matrix.

The diffusion profiles obtained can be divided into three groups corresponding to acid solutions with different concentrations:

- Smooth S-type Fickian profiles observed in the range of dilute H_2SO_4 solutions with concentrations up to 10%;
- Pronounced stepped profiles observed in the medium H_2SO_4 concentration range (10–30%); they are characterized by a small concentration gradient of the penetrating acid (at the step);
- Stepped profiles with signs of surface degradation observed in solutions with H_2SO_4 concentrations above 50%. Such solutions are known to manifest oxidative activity at elevated temperatures.

Effect of the content of the amine curing agent

As one can see in Figure 4, the diffusion–sorption properties depend considerably on the support/curing agent ratio.

Summarized results on the penetration rate constant (Figure 4) show acceleration of acid penetration into the polymer after the resin/curing agent ratio passes the stoichiometry point (7 m.p. MPDA per 50 m.p. of ED-20 resin).

Figure 3. Dependence of penetration rate λ (SEM/EDS) of 30% H_2SO_4 solution for 384 h at 90°C into a model epoxy composition on the weight content of the MPDA curing agent. The scatter of experimental point for several experiments is shown.

At the same time, the concentration plots of the weight gain *vs.* the curing agent amount per stoichiometric value for aliphatic (PEPA) and aromatic (MPDA) amines are qualitatively similar (Figure 5).

Figure 4. Dependence of gravimetric weight gain *P* of the epoxy material in 40% HF (OSCh-27-5) at 20°C on the type and content of PEPA and MPDA curing agents. The exposure times were 2088 and 4968 h.

Thus, it is found in the studies of systems containing different amounts of amine curing agents that:

- S-shaped “Fickian” distribution profiles are observed in the case of a low amine content, below 60% of the stoichiometric amount for aliphatic amines and below 80% for aromatic compounds, in the case of a low solubility of the medium. A similar shape is characteristic of the distribution profiles in the case of diffusion of dilute, low-activity acid solutions;
- from this perspective, the diffusant (acid) distribution in undercured epoxy materials approaches the distribution typical of inert hydrophobic polymers where there are no conditions for chemical interaction between the penetrating acid and the inert polymer matrix;
- one can assume that a certain fraction of polar sorption- and chemically active epoxy polymer groups in undercured systems can be inaccessible under certain conditions for the diffusing acid molecules;
- the stepped character of the distribution profile becomes very pronounced if the amine content is increased above the stoichiometric amount and residual unreacted amino groups appear in the system.

IR and Luminescence

The above results and conclusion allow assuming that the diffusion process is accompanied by a specific interaction between a chemically active diffusant (acid) and the polymer matrix containing residual amino groups.

As shown by IR spectroscopy data, penetration of 30% H_2SO_4 into an amine-cured epoxy resin is characterized by significant changes in the spectrum [14]. The assignment of analytical bands [15, 16] in an amine-cured epoxy resin after penetration of 30% H_2SO_4 at an elevated temperature of 90°C is shown below (Table 1).

Table 1. Assignment of IR bands to functional groups in an amine-cured epoxy resin (ED-20/PEPA 50/5 m.p.) after penetration of 30% H_2SO_4 at 90°C.

No.	Band, cm^{-1}	Functional group, range, cm^{-1}	Band intensity, a.u.	
			Initial polymer	Polymer + acid
1	3390	NH_2 val. 3500–3300; NH val. 3450–3300	30	0
2	2965–2962		25	40
3	2931–2927	NH_3^+ , NH_2^+ , NH^+ val. 3000–2000	22	38
4	2872–2870		31	48

No.	Band, cm ⁻¹	Functional group, range, cm ⁻¹	Band intensity, a.u.	
			Initial polymer	Polymer + acid
5	1720	C=O val. (aldehyde) 1765–1645; C=O val. (ketone) 1775–1650; C=O val. (amide I) 1740–1630	0	71
6	1608		24	49
7	1510	NH ₃ ⁺ , NH ₂ ⁺ , NH ⁺ def. 1600–1460	5	22
8	1462–1461		26	42
9	1402		0	34
10	1295		0	42
11	1244		0	25
12	1183	SO ₂ val. 1420–1000; S=O val. 1225–980	0	20
13	1116		0	16
14	1041		0	30
15	1011		0	38
16	620	S–O val. 879–690	0	48

Analysis of IR spectra shows:

- disappearance of band no. 1 with wavenumber 3390 cm⁻¹ corresponding to neutral amino groups;
- enhancement of bands nos. 2, 3, 4, 6, 7, 8 for charged amino groups interacting with the acid;
- appearance of bands nos. 9–16 corresponding to various sulfur-containing groups of sulfuric acid derivatives; bands nos. 9–15 are also characteristic of ethers that may be formed with the hydroxy groups of the resin under exposure to sulfuric acid;
- appearance of band no. 5 with wavenumber 1720 cm⁻¹ corresponding to the C=O group appearing upon formation of amides, ketones, aldehydes under exposure to sulfuric acid at an elevated temperature.

Analysis of the IR spectra of the same epoxy material under exposure to the same 30% sulfuric acid solution, but at a low temperature of 70°C also allows making a conclusion about the presence of a number of sulfur-containing groups in the polymer, mainly in the

form of HSO_4^- (590 and 880 cm^{-1}) and SO_4^{2-} (620 and 1130 cm^{-1}). A negligible amount of SO_3 groups (650 cm^{-1}) appear at prolonged exposure to the acid (more than 600 h).

The above IR spectral features at temperatures of 70 – 90°C are also preserved for the studied range of 5 – 70% H_2SO_4 solutions and for formulations based on ED-20 epoxy resin with a PEPA content of 2 – 10 m.p. of the resin and with an MPDA content of 4 – 12 m.p. per 50 m.p. of the resin.

It is crucial that sulfur-containing groups do not disappear completely after washing the ground epoxy material (dispersion degree $\delta < 5\text{ }\mu\text{m}$) at temperatures of 70 – 100°C for 30 h .

The results obtained confirm the assumption about the presence of predominantly chemisorption interactions of acids with the amine-cured epoxy matrix.

The conclusion about the specific interaction agrees with the results of studying the luminescence spectra (Figure 6).

The absolute values of the spectral intensity after exposure to the acid, J_{acid} , are lower than that of the initial polymer with no penetrated acid, J_{poly} , but the spectra are normalized to the same J/J_0 value for the wavelength of 468 nm for convenience of comparison.

Figure 5. Luminescence spectrum of the composition of 50 m.p. ED-20/ 5 m.p. PEPA before and after exposure to 50% H_2SO_4 at 70°C for 138 h . Luminescence: blue (excitation at 340 – 380 nm and recording at 420 – 500 nm); green (360 – 440 and 480 – 700 nm); red (530 – 570 and 600 – 700 nm).

When an epoxy material is conditioned in solutions of mineral acids (hydrochloric, sulfuric, phosphoric, and phosphonic), changes in the spectral maxima are observed in all the three studied luminescence ranges: “blue”, “green”, and “red”.

The most characteristic changes in the fluorescence intensity of luminescence centers of epoxy resins under exposure to acids (Figure 5) correspond to the wavelengths of 422 nm and 468 nm in the “blue” range; 540 nm and 574 nm in the “green” range; 615 nm and 637 nm in the “red” range.

Similar changes in the spectra are observed for all the acids; here, a new band appears, *e.g.*, at 540 nm and 574 nm, and/or the band intensity increases, particularly that of the 615 nm and 637 nm bands in the longwave (above 520 nm) spectral region.

A longwave shift in the luminescence spectra is typical of oxidative processes [17, 18] and correlates with the appearance of IR band no. 5 (Table 1) with a wave number of 1720 cm^{-1} corresponding to the C=O group formed upon resin oxidation under exposure to sulfuric acid.

The systems studied are characterized by a relative increase in the intensity of the 422 nm band for the amine-cured epoxy resin under exposure to the acid. This correlates with the shortwave shift [19] at acidic pH in the fluorescence spectrum for nitrogen-containing fluorescent centers, *e.g.*, derivatives of aromatic nitrogen-containing indole $\text{R-CH}_2\text{-C}_6\text{H}_4\text{-C}_2\text{H}_2\text{=NH}$.

For the HSO_4^- and SO_4^{2-} ions, the effect of the nitrogen-containing group on fluorescence occurs at $\text{pH} < 1.7$, in particular, at a sulfuric acid concentration of about 60% or 9.4 M. A similar effect of acidity on the luminescent properties is observed for aromatic moieties of a macromolecule, including amine-cured epoxy resins, such as the benzene moiety $\text{R-CH}_2\text{-C}_6\text{H}_5$ or phenolic one $\text{R-CH}_2\text{-C}_6\text{H}_4\text{-OH}$ with a hydroxy group. Fluorescence quenching of all the above macromolecule moieties occurs if the pH of the medium is below the pK_a of the acid.

Dimethylsulfoxide: an individual diffusant with a sulfur-containing SO group

As shown above, the interaction of mineral acids, including sulfuric acid, with amine-cured epoxy resins is characterized by irreversible binding.

It was of interest to study the regularities of diffusion for diffusants with residual acid groups incapable of irreversible sorption. Dimethylsulfoxide $(\text{CH}_3)_2\text{SO}$ (DMSO) is an example of such a diffusant that is a strong solvating agent containing SO groups with reversible sorption. Figure 7 below shows the results of studying the sulfur distribution profiles (SEM/EDS) for diffusion of anhydrous DMSO.

Analysis of the sulfur distribution profiles shows that the DMSO distribution in an amine-cured system is stepped; there is an abrupt boundary between the DMSO penetration region and the non-swollen core of the sample.

Interpretation of the results should take into account that though DMSO is a high-boiling solvent with $T_{\text{boil}} = 189^\circ\text{C}$, it has rather a high vapor pressure under the measurement conditions (more than 0.4 mmHg at 20°C). Therefore, desorption in the course of preparation and evacuation during the electron microscopy study is unavoidable.

It is significant to note that DMSO is a highly efficient solvent for many polar polymers, as it has a strong solvation ability for organic compounds containing cationic groups, hydroxy compounds, or sulfonic groups [20]. It is also known that $2\text{DMSO}\cdot 3\text{H}_2\text{O}$, $\text{DMSO}\cdot 2\text{H}_2\text{O}$, and $\text{DMSO}\cdot 3\text{H}_2\text{O}$ exist in the DMSO/water system [21] and that the diffusion activation energy of DMSO is lower than that of H_2O [22].

Figure 6. Diffusion profiles of DMSO penetration at 20°C for 40 and 187 min into a model epoxy formulation based on ED-20 resin cured by an aliphatic curing agent, polyethylene polyamine PEPA, and modified by butadiene–acrylonitrile rubber SKN-26-1A with terminal carboxy groups.

One should point out that no abrupt diffusion step is observed in the case of DMSO diffusion into weakly structured biological polymers, namely proteins containing amino groups of different nature [23, 24]. The diffusion profiles are smooth and qualitatively close to S-shaped Fickian profiles.

An anomalous feature of DMSO penetration into amine-cured epoxy systems is that the weight gain P and linear size L are directly proportional to the exposure time t rather than to the square root of time $t^{0.5}$ as is the case with other diffusants (Figure 8). This argues for a complex mechanism of penetration with a relaxation component due to the high plasticizing ability of DMSO with respect to amine-cured epoxy resins.

Figure 7. Kinetics of weight gain P and thickness increase ΔL of a sample of a model epoxy formulation upon swelling in DMSO at 20°C.

Thus, one can state the effect of anomalous diffusion of DMSO, which is characterized by weak acidic properties but is an efficient plasticizing agent for epoxy materials, into amine-cured epoxy matrices.

Anhydride Curing Agents

As shown above, one of the significant factors affecting acid diffusion is the composition of the thermoplastic matrix that to a large extent determines the possibility of specific interaction between the diffusant and the residual groups or impurity components of the thermoplastic matrix.

In this connection, it was of interest to study the sorption–diffusion process in epoxy thermoplastic materials cured by agents that differ fundamentally from amines, that is, acidic (anhydride) curing agents.

Sorption in Anhydride Systems

Figure 8 further presents SEM/EDS data on the sulfur concentration upon penetration of sulfuric acid into epoxy compounds cured by various amounts of different curing agents with respect to the stoichiometric ratio.

Figure 8. Dependence of sulfur content C_s , % in the surface layer of samples after their conditioning in 30% H_2SO_4 at 90°C on the curing agent amount ($C/C_{stoichio}$) in the ED-20/curing agent system: 1. PEPA, 2. MPDA, 3. SA, 4. PA.

As one can see in Table 2, anhydride curing, as opposed to amine curing, results in a much lower sulfur content in the diffusion zone, i.e., lower sulfuric acid solubility in epoxy compounds.

Table 2. Sulfuric acid content in the diffusion zone of an epoxy polymer cured by amine and anhydride curing agents.

No.	Curing agent	Content at a curing agent concentration of $C/C_{\text{stoich.}} = 1\%$	
		Sulfur C_S	Sulfuric acid $C_{\text{H}_2\text{SO}_4} = C_S \times M_{m\text{H}_2\text{SO}_4} / M_{mS}$
1	PEPA	1.80	5.5
2	MPDA	1.50	4.6
3	SA	0.45	1.4
4	PA	0.20	0.6

Distribution profiles

Figure 10 below shows comparative profiles of sulfur distribution upon diffusion of H_2SO_4 into systems cured by amine and anhydride curing agents. Here, the H_2SO_4 diffusion profile in the case of anhydride curing is not stepped, as opposed to amine curing. It should be noted that this type of profiles is observed in the entire studied range of the curing agent concentrations.

Figure 9. Comparison of diffusion profiles in terms of penetration depths and the maximum sulfur content on the profile “shelf” for different curing agents in the case of 30% H_2SO_4 diffusion at 90°C for 384 h. The stoichiometric amounts of the curing agents are: 5 m.p. (PEPA), 7 m.p. (MPDA), 26 m.p. (SA), 38 m.p. (PA) per 50 m.p. of ED-20 resin. The arrow indicates the direction of diffusion.

One should point out that despite the higher profile “shelf” of MPDA (Figure 1) as compared to the PEPA profile, the actual sulfur content values correspond to Table 1. This is due to the fact that each profile was recorded together with recording a reference sample

and the J_{pulse} value for the reference differed in each experiment, so the calculated value of $C_{\text{S.sample}} = C_{\text{S.reference}} / J_{\text{pulse.reference}} \cdot J_{\text{pulse.sample}}$ also differed. Therefore, in this case, higher J_{pulse} values for MPDA as compared to PEPA correspond to lower C_{S} values than for PEPA.

Comparison of SEM/EDS results obtained in this work using sulfur-containing reference systems and using ZAF correction [7] shows their good agreement.

Conclusion on diffusion profiles and solubility of acids in epoxy matrices

Analysis of the entire data set obtained allows stating that the chemical nature of the curing agent significantly affects the solubility of corrosive media observed as a fundamental difference in the behavior of epoxy materials cured by amines and acid anhydrides:

- The sulfur content C_{S} in the diffusion zone of amine-cured materials is 5–10 times higher than in the case of anhydride-cured ones; moreover, the sorption of sulfuric acid $C_{\text{H}_2\text{SO}_4}$ is higher for aliphatic PEPA and SA as compared to aromatic MPDA and PA.
- The curing agent type considerably affects (by a factor of 2–10) the rate of acid penetration into epoxy compounds; here, the aliphatic curing agents, both amine PEPA and anhydride SA, are more permeable than similar aromatic curing agents, MPDA and PA.
- At the same time, in the case of amine-cured resins with residual and reduced amino groups, penetration of acids occurs *via* the mechanism of sorption with binding, which allows implementing ion-selective properties of a cured resin.

Permeability of materials with acidic functional groups

As the rate constant λ of sulfuric acid penetration into anhydride-cured epoxy materials is 1.8–2.1 times lower than into amine-cured compounds, one can conclude that the presence of residual ester groups in anhydride-cured resins is preferable to acid-resistant coatings.

In view of this, materials containing not only residual but also functional acid groups, *e.g.*, chlorosulfonated polyethylene (CSPE), can also be promising for the development of composite coatings.

In this work we studied the solubility and penetration of sulfuric acid into a number of CSPE-based materials. Figure 11 below shows data on the kinetics of 30% H_2SO_4 penetration into CSPE at 70°C obtained by recording the moving boundary X of luminescence variation under exposure to the penetrating acid.

As follows from the presented data, the penetration constant λ in CSPE is $1 \mu\text{m}/\text{h}^{0.5}$, which is much smaller than the penetration depth of 30% H_2SO_4 into amine-cured (PEPA) system ($\lambda = 4.6 \mu\text{m}/\text{h}^{0.5}$).

As opposed to epoxy systems cured by amines and containing cation-forming $-\text{NH}_x$ groups, chlorosulfonated polyethylene CSPE contains anionogenic $-\text{SO}_2\text{Cl}$ groups. Therefore, CSPE forms other fluorescent centers and shows specific spectral features of polymer matrix luminescence quenching under exposure to acids.

Figure 10. Kinetics of the depth (X) of 30% H₂SO₄ penetration into CSPE-20 vs. the square root of time ($t^{0.5}$) at 70°C.

Luminescence spectra of CSPE upon penetration of sulfuric acid

The luminescence spectra of CSPE upon penetration of 30% sulfuric acid are shown in Figure 12. For convenience of comparison, the spectra are normalized to the intensity at the wavelength of 468 nm, like in the case of the epoxy compounds described above.

Figure 11. Blue luminescence spectrum of CSPE before and after exposure to 30% H₂SO₄ at 70°C for 642 h. Excitation at 340–380 nm. Recording at 420–500 nm.

One can see that a decrease in the intensity of the bands at 422 and 433 nm and an increase in the intensity of the bands at 484 and 502 nm are observed in the blue luminescence spectrum of CSPE after exposure to sulfuric acid.

The observed suppression of the bands at 422 and 433 nm can be evidence of the formation of complexes between acid molecules and $-\text{SO}_2\text{Cl}$ groups and fluorescence quenching, similarly to the interaction of the acid with $-\text{OH}$ groups of a luminescence center like $\text{R}-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$ at $\text{p}K_a = 2.45$ [7].

This allows us to conclude that spectral luminescence data agree with the known models of diffusion of aqueous electrolyte solutions in polymers [2, 25, 26].

The second important point is the observed spectral shift to the longwave region, which may indicate that concurrent CSPE oxidation occurs under exposure to 30% sulfuric acid.

From the methodic viewpoint, the results obtained confirm that the luminescence method is quite informative [27] and can be used for studying the penetration of highly corrosive media into the polymers and coatings of various nature.

Thus, there are results in the case of CSPE that indicate that complexes with a penetrating acid can form and that the penetration and solubility of sulfuric acid are lower than in epoxy materials.

Study of the permeability of composite coatings

As shown earlier [13], a considerable decrease in acid penetration into protective polymer coatings can be achieved by using a laminated composite structure. Here, the inner coating layers should have acid-binding centers, while the outer layer should be inert and hydrophobic. However, it is rather difficult to implement all advantages of such a structure in practice and the main problem is to provide long-term adhesion stability of the interlayer “thermoplastic material–hydrophobic inert layer” contact.

One can assume from the observed regularities that anhydride-cured polymer materials with acidic functional groups, *e.g.*, SO_2Cl , or reduced acid groups can be of interest as a base for the upper layer of composite coatings. Their potential advantage can lie in a strong interlayer adhesion to thermoplastic materials.

In view of this, this work includes a study on the penetration of inorganic acids into model laminated composite coatings based on CSPE and its derivatives.

The penetration depths X in the case of 30% H_2SO_4 diffusion into an epoxy material under the surface layer of chlorosulfonated polyethylene CSPE and materials developed on its basis were measured by recording the luminescence intensity along the acid penetration coordinate with luminescent drop indicators. As pointed out previously [5], this method can be used for recording the penetration of both nonvolatile and volatile acids.

The efficiency of application of surface layers together with the ROCOR-793-TRIO industrial epoxy compound is presented in Table 3.

Table 3. Comparison of penetration depths of mineral acids into the ROCOR-793-TRIO compound and a composite coating based on this compound with a 25–50 μm thick surface layer with acidic functional groups.

Acid	Temperature, °C	Exposure time, h	Penetration depth, μm	
			ROCOR-793-TRIO compound	Composite coating
30% H_3PO_4	100	1872	1575	115
30% H_3PO_4	70	2520	300	<5
30% H_3PO_4	70	42	90	<5
30% H_2SO_4	70	42	200	<5
20% H_2SO_4	20	70128 *	825	<5
5% H_2SO_4	20	70128 *	550	<5
36% HCl	70	42	188	44
20% HCl	70	42	100	<5
20% HCl	20	70128 *	250	63
5% HCl	20	70128 *	150	38

Note: * exposure for 8.2 years

The results show that surface modification of materials with acidic functional groups prevents phosphoric acid penetration even at 100°C and decreases the penetration depth of the corrosive medium by at least an order of magnitude, namely, $1575/115 \approx 13$ -fold. Surface modification is similarly efficient in the case of penetration of nonvolatile H_2SO_4 and volatile HCl in the temperature range of 20–70°C.

Conclusion

- A significant effect of the chemical nature of the curing agent and polymer matrix on the solubility of corrosive media is observed. It is manifested in the fundamental difference between the behavior of epoxy materials cured by amines and by acid anhydrides: lower solubility (5–10 fold) and lower penetration rate constants (2–10 times fold) of acids are typical of anhydride-cured epoxy binders.
- It is shown that the aliphatic curing agents of both amine (PEPA) and anhydride (SA) types form more permeable epoxy matrices with a higher acid solubility compared to curing agents of the same type based on aromatic MPDA and PA. It is also important that in the case of amine-cured resins with residual and reduced amino groups, penetration of acids is characterized by a pronounced mechanism of sorption with binding, which basically allows implementing ion-selective properties of the cured resin.

- The effect of anomalous diffusion into amine-cured epoxy matrices of DMSO is found. DMSO is characterized by weakly acidic properties, but it is an efficient plasticizing agent for epoxy materials. A particular feature of such penetration is that it shows stepped a distribution profile with a pronounced penetration boundary, similarly to other acids, but the sorption value is directly proportional to time and therefore follows the Fickian kinetics. This allows concluding that even in the case of densely cross-linked thermoplastic materials, one should take into account the possibility of relaxation contribution to the penetration mechanism for some compounds.
- It is suggested that materials containing not only residual but also functional acid groups can also be promising materials for the development of laminated composite coatings. Penetration of sulfuric acid into CSPE has been studied. It has been shown that the penetration rate in the case of sulfuric acid is comparable with anhydride-cured epoxy resins and that luminescent analysis indicates the formation of complexes between CSPE functional groups and the penetrating acid.
- The results show that laminated composite coatings with an upper layer of materials containing functional acid groups provide a significant decrease in the mineral acid penetration depth. The effect is observed for phosphoric acid at 100°C and also for nonvolatile H₂SO₄ and volatile HCl in the temperature range of 20–70°C.

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