DEVELOPMENT OF COMPOSITE PROTECTIVE COATINGS FOR METAL SURFACES

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ABSTRACT: In order to increase the lifespan of epoxy coatings, the purpose of this work was to create a composite coating material, based on commercially available components, with high cohesion and a high degree of scratch resistance, which provides anti-corrosion protection for the metal support material, correlated with a method of pre-treatment of the support material.

KEYWORDS: epoxy, protective coating, metal surface, composite material

1. INTRODUCTION

Metals are favoured in many industries due to their long lifespan and superior mechanical properties. Some examples of such industrial applications are represented by the oil and gas industry, marine transport, construction area (bridges, railways, other civil constructions) or aerospace and automotive. However, exposure to environmental conditions like variations in external temperature or pressure, the presence of water or corrosive substances [1-3], makes them susceptible to corrosion, potentially reducing their lifespan and altering their appearance [4-6].

As a solution to increase the lifespan of metals, protective coatings help prevent corrosion by isolating of the support material against exterior factors [7]. The effectiveness of such materials are in strong corelation with the intrinsic properties of the coatings, their composition [8-10], surface pretreatment [11], and the presence of other anti-corrosion additives.

The global market for industrial coatings represents a permanently growing market (i.e., from USD 73.8 billion in 2016 to USD 105.5 billion in 2022 [12]). Epoxy resin coatings dominate this market due to their excellent corrosion protection, water resistance, and durability [13]. They are often used alongside other coatings for enhanced protection.

Epoxy-based coatings, a type of organic coating, typically contain five main components: binders, pigments, solvents, fillers, and additives [14]. Binders, such as epoxy and epoxyphenolic resins, form a continuous film on the substrate surface, ensuring adhesion [15]. Pigments provide colour and opacity, while solvents adjust the coating's viscosity for application [14]. Fillers and diluents, like talc and silica, enhance properties such as hardness and abrasion resistance. Additives, including surfactants and UV absorbers, impart specific properties and prevent defects, with some serving as corrosion inhibitors [16, 17].

In most cases, hardening agents are required to rapidly cross-link epoxy resin, forming a protective coating (cross-linked film) to guard against corrosion. However, in certain applications, epoxy monomers may not react swiftly enough with hardeners, necessitating the use of additives as catalysts to speed up the curing process. Typical epoxy curing agents include amine-based, anhydride-based, polyamide, aliphatic, and cycloaliphatic types, while common curing additives are phenol, carboxylic acid, and tertiary amine [18].

Highly cross-linked epoxy polymer resins are inflexible and brittle with poor tear strength, limiting their use in applications such as building materials. To improve the mechanical and chemical properties of epoxy resins, extensive research has focused on incorporating various inorganic and organic compounds, including polymers or nanomaterials [19, 20]. Epoxy coatings with nanoparticles exhibit significant enhancements due to their large specific surface area and small size, which help block micropores and boost anticorrosive performance [21-23]. Nanomaterials have been found to increase the corrosion resistance of waterborne coatings more efficiently than conventional micro-sized materials, even at lower weight percentages [24]. Inorganic compounds are often added to epoxy resins (ERs) to increase fracture resistance. The addition of inorganic fillers enhances properties such as modulus, strength, fire resistance, elastic stiffness, optical characteristics, and crack resistance. A range of inorganic

compounds, including ZnO [25], TiO_2 [26], SiO_2, carbon nanotubes [27], and graphene oxide [19], are incorporated into the epoxy matrix to further improve its mechanical and chemical properties [28, 29].

To extend the lifespan of epoxy coatings, this work aims to develop a composite coating material using commercially available components. The resulting material will offer high cohesion and scratch resistance, providing anti-corrosion protection for metal substrates, in conjunction with a method for pre-treating the substrate.

The practical issue addressed by this work is represented by the creation of a stable, easy-to-apply material that offers both high cohesion and scratch resistance. This material is specifically designed for steel-carbon substrates and provides effective anti-corrosion protection.

2. MATERIALS AND METHODS

2.1 Materials used

The composite material was obtained using a commercially available two-component water-based epoxy resin (as base material, Top Epoxy Amorsa, SC Europlastic SRL, Bucharest, Romania), having as functional fillers quartz sand (Merck KGaA, Darmstadt, Germany), zinc oxide (Merck KGaA, Darmstadt, Germany) and magnetite (Fe_3O_4, Merck KGaA, Darmstadt, Germany).

The composite material was obtained in two stages. In the first stage, the mixture used as filling is obtained, by sieving the quartz sand to reach the maximum particle size of 150 μm. The sand thus separated is heated to 80°C for 2 hours, using a laboratory oven. During this time, the other components of the filling (zinc oxide and magnetite) are mortared separately in agate mortars until reaching particle sizes below 100 μm, in the case of zinc oxide (determined by sieving on a 100 μm mesh sieve), respectively until obtaining particle sizes below 500 μm, in the case of magnetite (determined by sieving on a 500 μm mesh sieve).

After heating the quartz sand, the three components are mixed in weight ratios of 2:1:4 (magnetite:zinc oxide:sand), thus obtaining the filling composition.

In the second stage, the composite material is obtained, by mixing the epoxy resin with the hardener, adding water and finally filling. The materials used are in a weight ratio of 1.66/1/1.33/4.66 (resin/hardener/water/filler), and the mixing is done with a mixer (rotation speed 350 revolutions/minute), for 1 minute (for the resin/hardener mixture), followed by the gradual addition of water and then the filler, under continuous stirring, until a homogeneous composition is obtained (3 minutes). The resulting coating was encoded as CC.

Two control samples were also obtained, for comparison purposes: epoxy resin with the addition of quartz sand having variable particle sizes, below 2 mm (encoded as BC1) and epoxy resin with the addition of filler containing only quartz sand with a size below 150 micrometers, heated to 80°C for 2 hours (encoded as BC2), using the same resin/hardener/water/filler ratios.

The coatings were applied by direct casting on the surface of metal samples (7 cm x 15 cm) made of carbon steel with medium carbon content, previously treated by shot blasted with metal balls.

2.2 Characterisation methods

The developed materials were tested in terms of physical properties (workability time, drying time), coating cohesion, scratch resistance and anti-corrosion properties.

The workability time was determined as the maximum time the composite remains workable before it begins to harden.

Drying time refers to the time it takes for the surface of the resin to dry to the touch.

The cohesion of the composite was determined by using the ISO 16276-2:2007 standard [30], the X-cut method. Briefly, the method involves the application of an X-cut through the coating with sharp blade, followed by the application of adhesive tape (to remove the loosely attached layer). The test result is expressed according to the damage observed. Each cut is 40 mm long and the angle between the cuts is 40-45°. Using pressure-sensitive adhesive tape, a 75 mm long piece is firmly applied to the cut which is peeled off within 5 minutes.

The tests to determine the scratch resistance were performed with a Rockwell indenter with a diamond tip, having an angle of 120° and a contact radius of 200 μm, according to the ASTM G 171 – 03 standard [31]. The test parameters are:

- Normal penetration force - Fz = 25 N
- Relative speed - v2 = 0.5 mm/s;
- Length - Y = 10 mm.

Scratch resistance is calculated according to the formula:

$$\boldsymbol{HSp = \frac{8P}{\pi w^2}} \qquad \textbf{(1)}$$

where HSp = scratch hardness number (Pa), P = normal force (N) and w = scratch width (m).

Corrosion resistance was determined in accordance with ASTM D1654-08 [32], the specimens being exposed for 240 hours to the corrosion resistance test by salt spray (using 5% NaCl solution). Corrosion

resistance is presented by scoring according to the ASTM D1654-08 standard.
An electron microscope Hitachi TM4000plus II (SEM), equipped with an energy dispersive spectroscopy accessory (EDX) was used to evaluate the morphology of the coatings.

3. RESULTS AND DISCUSSIONS

The physical characteristics of the coating material, compared with the two control samples, are presented in Table 1.

Table 1. Physical properties of the composites, determined by direct observation

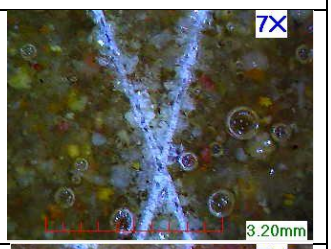
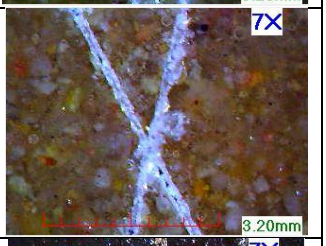
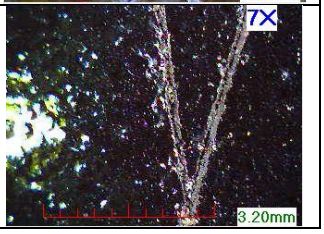
Encoding	Filler composition	Working time (min.)	Drying time (min.)
BC1	Quartz sand (variable dimensions)	80	28
BC2	Quartz sand, particle size <150 µm, heated to 80°C for 2 hours	65	20
CC	Quartz sand (as BC2)/ZnO/ Fe_3O_4, ratio = 4/1/2	60	18

A sharp decrease in the drying time is observed in the case of the experimental variant (CC), in the presented working conditions.

The CC composite was applied on metal samples, as previously presented, and, after drying, the cohesion of the coating is determined using the ISO 16276-2:2007 standard, the X-cut method [30].

The results obtained are presented in Table 2 compared with those obtained for the two control samples.

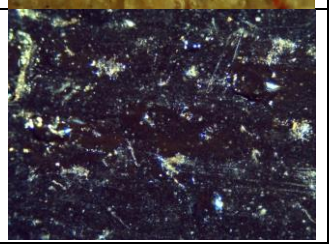
Table 2. Coating cohesion results

Composite	Classification (according [30])	Images of the observed effect
BC1	Level 3	
BC2	Level 2	
CC	Level 1	

The scratch resistance of the material coatings (according to example 2) was determined according to the ASTM G 171 – 03 standard [31], using a Rockwell indenter with a diamond tip, having an angle of 120° and a contact radius of 200 µm.

The results obtained are presented in Table 3 compared to those obtained for the two control samples.

Table 3. Scratch resistance results

Composite	Scratch resistance (GPa)	Representative images after testing scratch resistance
BC1	0.02980	
BC2	0.05495	
CC	0.55203	

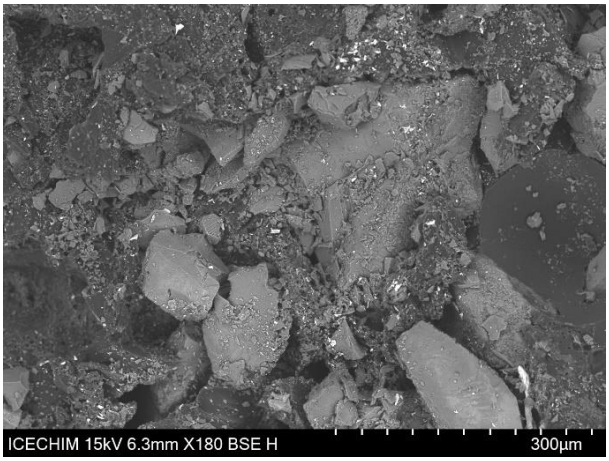
According to Table 3, there is a significant increase in scratch resistance in the case of CC sample, compared to BC1, correlated with a self-regenerating effect of the composite.The corrosion resistance of the coated materials was determined according to ASTM D1654-08 [32], the specimens being exposed for 240 hours to the corrosion resistance test by salt spray (using 5% NaCl solution), the results being presented in Table 4 (according to scoring system presented in the ASTM D1654-08 standard), compared to those obtained for the two control samples.

Table 4. Corrosion resistance results

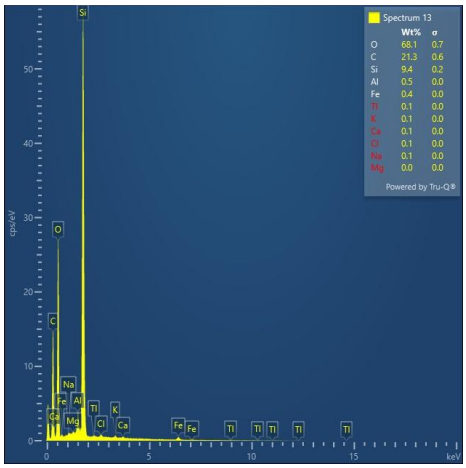
Composite	Corrosion resistance (rating acc. ASTM D1654-08)
BC1	5
BC2	5
CC	9

According to Table 4, there is a significant increase in corrosion resistance in the case of CC sample, compared to the control variants. Finally, the obtained coatings were characterized in terms of morphological appearance using Scanning Electron Microscopy (images are presented in Figure 1)

(a)



(b)



(c)

Figure 1. SEM images of BC1 (a), BC2 (b), CC (c, left), and EDX spectra of CC (c, right)

4. REFERENCES

In order to increase the lifespan of epoxy coatings, the purpose of this work was to develop a composite coating material, based on commercially available components, with high cohesion and a high degree of scratch resistance, which provides anti-corrosion protection for the metal support material, correlated with a method of pre-treatment of the support material. The obtained results supports the application of the proposed recipe for industrial applications.

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