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Highly Filled Bio-Protective Epoxy Composites and Coatings, Air-Cured and Water-Cured: Comparison of Performance Properties

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ABSTRACT

A technology for obtaining epoxy composites and underwater curing coatings based on ordinary publicly available components is presented. It is shown that underwater curing composites have 2-3 times lower physical and mechanical parameters than their counterparts of normal (in air) curing. Filling epoxies with water-curing dispersions (gypsum, cement) makes it possible to enhance the strength and durability of underwater curing composites. In terms of their properties, the obtained composites turned out to be more effective than commercial analogs of comparison.

Introduction

Polymeric (in particular epoxy) compositions for underwater application and use will be increasingly relevant, given the upcoming shift of human activity to the oceans and its basins. The literary review of this topic shows the limited scientific information, closed for the sake of the commercial interests of the developer firms. Therefore, the available literature is limited and is predominantly advertising or commercial [1-6]. There is not much scientific literature on this issue [1-3]. There are also practical video-recommendations on the Internet on the issue of underwater coating [4-6] and creating imitation underwater epoxy coatings [7]. The aim of the work was to find compositions for underwater application without using hard-to-find or expensive components. Therefore, ordinary conventional\cheap cold-hardening epoxy-dian resins (Figure 1), were chosen as the polymer base for these compositions.

Pre-Experimental Part. Reagents and Methods, Visual Data

A standard epoxy composition was used: Epoxy520 (Czech analogue of Russian ED20) and PEPA in a ratio of 6:1 (Composition 1). It was filled (2/3 by weight of the polymer phase) with sifted micro dispersed powders of commercial white-cement (Composition 2), ordinary grease cement (3) and gypsum (4). For comparison, samples with commercial underwater coatings are made epoxy (TM EDMOK, Ukrainian prod. - Composition 5) and non-

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epoxy (Russian prod. - Composition 6). After mixing the resin with the hardener, the composition was applied by coating, adhesive or poured into molds under normal conditions. After special exposure and processing (the essence of the process is patent information), similar procedures with this composition were carried out under water. After aging for 1-2 months, samples and coatings were pulled for testing. The hardening mass was held until it lost fluidity and was used as a coating or molding compound. Tests for adhesion (GOST 14760-69) with normal tearing were carried out on cylinders 5 cm2 (Figure 2). For compression tests (GOST 4651-2014, ISO 604:2002), cylindrical samples d=6.5 mm, h=12+-1 mm was taken, compressed on a press-machine Louis Shopper until complete destruction. Based on the results of the tests, the strength was calculated: f = P\s (P is the load in KGF, s is the area equal to 0.332 cm2) and the modulus E: E=f\e (e is the relative elongation). Brinell microhardness (GOST 9012-59, ISO 6506-1: 2005) was measured as resistance load when a steel hemisphere (d=3 mm) was immersed in a sample-plate (b=1.5 mm) to 10-60 μm. Abrasion was performed by passing composite cylinders (diameter 6.5 cm) on the emery P60 surface 40 times at a distance of 20 cm. Weight & matter loss (in mg & mm) was determined. Abrasion resistance was calculated as the inverse of the abrasion mass of the sample - by empirical (derived from experiments) formula $W = 1 \times (m / mH) / P = m / mH \times P$, where mH / m characterizes the increase in mass (density) of the sample after filling. Working with compositions under water has a number of inconveniences and difficulties. The composition does not adhere well to the surface, washes out and changes color during the curing process (Figures 3 & 4).

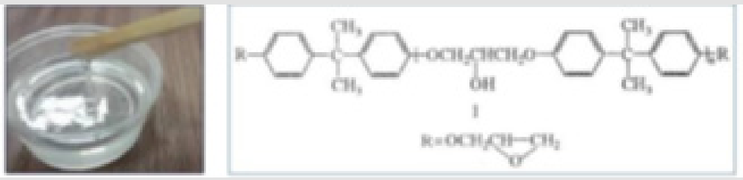

Figure 1: Epoxy-resin, typical shape and formula.

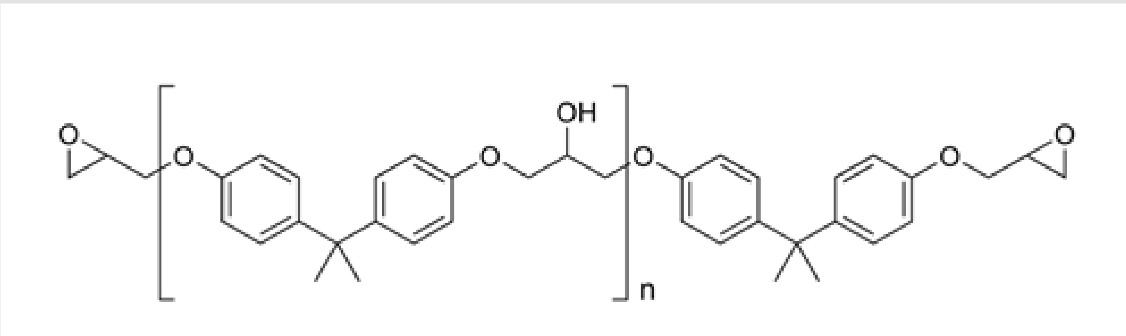

Figure 2: Epoxypolymer typical structure.

Figure 3: Image of epoxycomposite samples, coatings and glued steel plates and cylinders.

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Figure 4: The method of applying epoxy-coating under water.

Experimental Results

Under normal conditions, epoxy polymers are characterized by high strength and moduli in compression (about 100 MPa), bending, microhardness, resistance to abrasion and scratching. According to experiments, exposure to water worsens all parameters for all studied compositions (Table 1). The compressive strength is especially affected, for which a 2-3-fold drop is observed. Flexural strength, scratch resistance, abrasion resistance, and microhardness are also somewhat reduced. Qualitatively, the indicators of the obtained underwater coatings are clearly visible from Table 2. All of them give a shiny (in normal conditions) or matte (under water) coverage. Composites hardened "in normal conditions" have very good scratch resistance (up to 4 on the Mohs scale, i.e., almost at the level of glass). But when cured and exposed "under water", scratch resistance is greatly weakened, and differences appear: Unfilled polymer - has poor resistance; the rest of the samples are acceptable or even good (Table 2). So, filling in all cases softens the decline in abrasion resistance when moving from normal conditions to underwater conditions. The introduction of the taken water-hardening fillers as a rule gives an increase in all characteristics during underwater curing. The nature of the destruction of samples during compression depends on exposure to water. Non-watered composites almost always fail elastically. With a clear diagonal Chernov-Luders crack, without breaking apart and generally retaining its shape. The watered ones scatter fragilely into small parts, or they are destroyed along longitudinal cracks (Table 3).

Table 1: Parameters of composites with 66 wt % filler obtained in water (and in air).*-estimated.

	Underwater			Normal conditions		
	Wear, resistance	Scratching, resistance	Shape	Wear, resistance	Scratching, resistance	Shape
1. (unfilled)	Poor	Weak	Matte, solid	Good	Good	Matte-glossy
2. (Wh. Cem.)	Good	Good	Matte, solid	Excellent	Excellent	Glossy
3. (Cement)	Good	Medium	Matte rough	Excellent	Excellent	Glossy
4. (gypsum)	Good	Medium	Matte rough	Good	Good	Matte-glossy
5. (Edmok)	Medium	Weak	Matte, solid	Good	Excellent	Glossy
6. (non-epoxy.)	Good	Good	Matte, solid	Excellent	Good	Matte-glossy

Table 2: Some practical indicators of coatings.

	Properties in water (in normal conditions – in air at 20oC)				
	Compression, kgf on 0,33 cm2	Microhardness, , X.F.	Scratching, estimation	Wear, mg(mm) & wear-resistance	Adhesion, kgf
1. (unfilled)	100 (330)	65 (70)	Good (Excellent)	11 (2) & 0.16	50 (250)
2. (wh.cem.)	150 (350)	72 (77)	Excellent (Excellent)	10 (1,8) и 0,18	130 (300)
3. (cement)	160 (370)	73 (80)	Excellent (Excellent)	10 (1,8) и 0,18	70 (350)
4. (gypsum)	120 (350)	70 (75)	Good (Excellent)	8,5 (1,7) и 0,23	75 (375)
5. (Edmok)	95 (130)	75 (80)	Good (Excellent)	-	120 (-)
6. (non-epox.)	90 (100)	63 (70))	Good (Excellent)	-	70 (250)

Table 3: Adhesion parameters (* - estimated) of composites obtained in water (measured by tearing off a cylindrical sample glued in water from an unprepared steel or copper metal) surface.

	Shift Adhesion, kgf on 3 cm^2 area	Tear Adhesion, kgf on 5 cm^2 (≈ MPa)
1. (unfilled)	95 (≈ 3 MPa)	120 (≈ 2,4 MPa)
2.(wh.cem.)	90 (≈ 3 MPa)	130 (≈ 2,5 MPa)
3. (cement)	150 (≈ 5 MPa)	50 (≈ 1 MPa)
4. (gypsum)	85 (≈ 3 МПа)	-
5. (edmok)	90 (≈ 3 МПа)	40 (≈ 0,8 MPa)
6.(non-epox.)		

Conclusion

The possibility of creating effective underwater compositions based on ordinary Epoxy Dian resin filled with standard water-hardening binders is shown. With an optimal curing regime (including 2-3 hours of exposure before use), it is possible to obtain very cheap import-substitute underwater coatings and compounds that do not require high skill in their use.

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