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STUDY OF EPOXY RESIN MODIFICATION WITH MALEIC ANHYDRIDE AND THE POSSIBILITY OF ITS APPLICATION FOR PROTECTIVE COATINGS

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Abstract. *The paper proposes a method of modifying ED-20 epoxy resin with maleic anhydride to ensure its functionalisation. IR spectroscopy confirmed the modification of ED-20 resin with maleic anhydride. Modified ED-20 resin was used for production of protective coatings of 'flexible' stone type. The proposed composition of the polymer base of the coating has the required functional properties and allows ones to substitute imported acrylic dispersion SORBUS.*

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Introduction

'Flexible' stone is a composite three-layer coating consisting of reinforcing base (e.g. glass fibre), polymer composition, and fine particles of sedimentary rocks (sandstone or marble chips), imitating the structure of natural stone [1]. Nowadays 'flexible' stone is mostly produced using acrylic dispersion SORBUS [2]. This dispersion does not fully meet the requirements of manufacturers of finishing materials. Hence, there is a need to improve the quality of the materials through ensuring import substitution for this type of materials.

In this regard, the purpose of this research was to use acrylic dispersion Akremos 121A (Dzerzhinsk, Nizhny Novgorod region, Russia) as a polymer matrix of compositions for producing 'flexible' stone. We have chosen this type of polymer matrix for protective coatings because of its chemical inertness, non-toxicity, and its good adhesion strength with the reinforcing substrate. The acrylic matrix is well combined with other polymers, i.e. with epoxy resins [3]. It provides the possibility of creating blended compositions. As a consequence, it causes a targeted change in the properties of the developed protective coatings.

Main body

We used acrylic dispersion Akremos 121A (Dzerzhinsk, Nizhny Novgorod region, Russia) as the basis of polymer matrix. Modified epoxy resin ED-20 (manufacturer OOO EPOKSID, Russia) was used as a modifier. It provided the necessary operational properties of the protective composition of the 'flexible' stone type. We modified ED-20 epoxy resin with maleic anhydride.

The chemistry of the modification process of epoxy resins with maleic anhydride proceeds according to the following scheme:

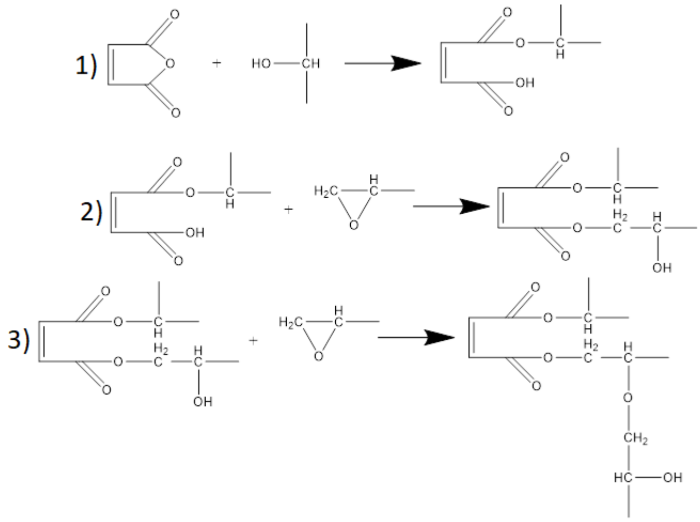

Fig. 1. Mechanism of epoxy resin modification with maleic anhydride

Modification of an epoxy resin is initiated by the interaction of its hydroxyl group with a maleic anhydride molecule (1). An intermediate compound is formed during the interaction of anhydride and resin. It reacts with epoxide groups (2). Hence, the maleic anhydride molecule binds the tails of the epoxy molecules together. The reaction can also proceed with further interaction of hydroxyl groups of the obtained compound with unreacted epoxide groups (3) to form a three-dimensional zigzag polymer [1, 4]. The reaction has a chain nature. The number of zigzags is limited by the degree of polymerisation. The final product contains a mixture of different lengths and masses of epoxy resin bonds.

The mechanism of epoxy resin modification by maleic anhydride was validated by IR spectroscopy. We identified the chemical composition and structure of PCL- and MMT-based composites, and investigated the chemical and physical bonds using a Thermo Scientific (USA) Nicolet iS10 FT-IR spectrometer equipped with a Smart iT attachment (Thermo Scientific) with a diamond crystal by the disturbed total internal reflection (TIR) method. We measured with a spectral resolution of 4 cm^{-1}, averaged over 32 scans, in the range 4000-400 cm^{-1}.

Figures 2 and 3 show the IR spectra of ED-20 epoxy resin before and after modification with maleic anhydride, respectively.

The alignment of IR spectra of modified and unmodified epoxy resin (Fig. 4) shows the formation of a new peak at 1775 cm^{-1}. It is located in the frequency of peaks of the C=O group. This confirms the assumption on the structure of the final modification product.

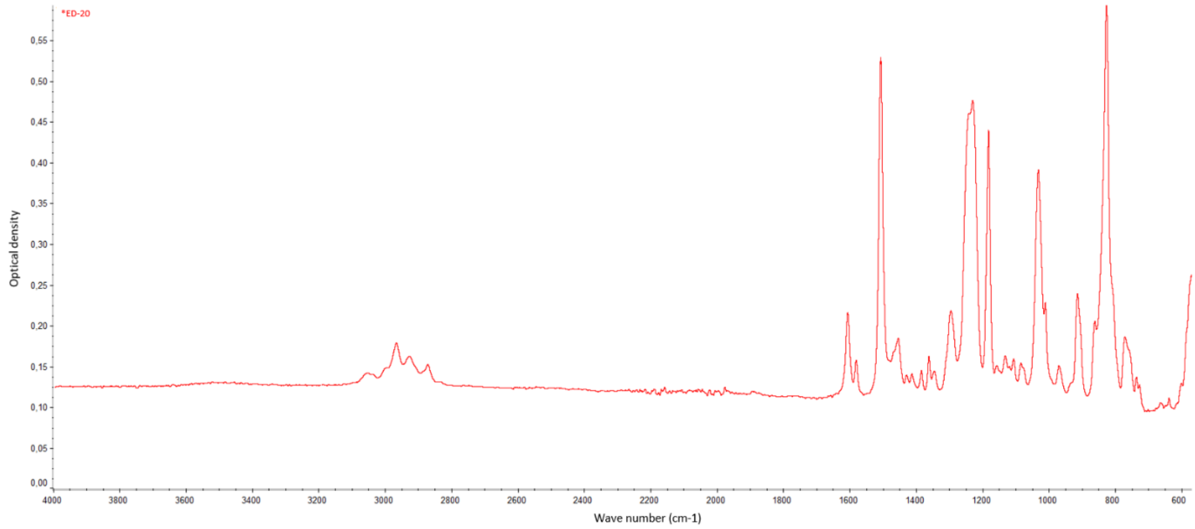

Fig. 2. IR spectrum of initial epoxy resin ED-20

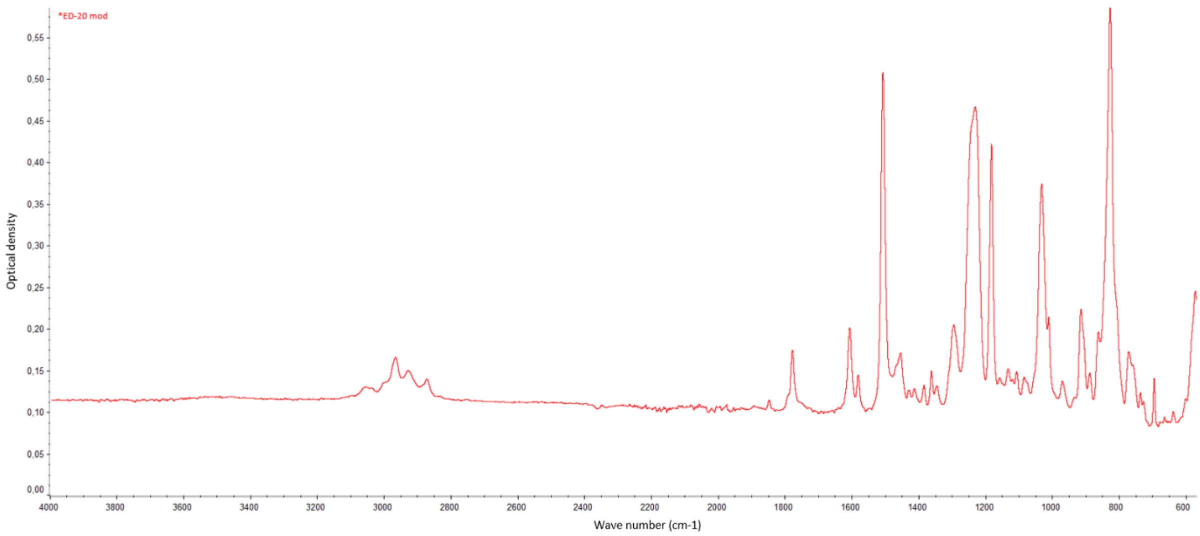

Fig. 3. IR spectrum of ED-20 epoxy resin modified with maleic anhydride

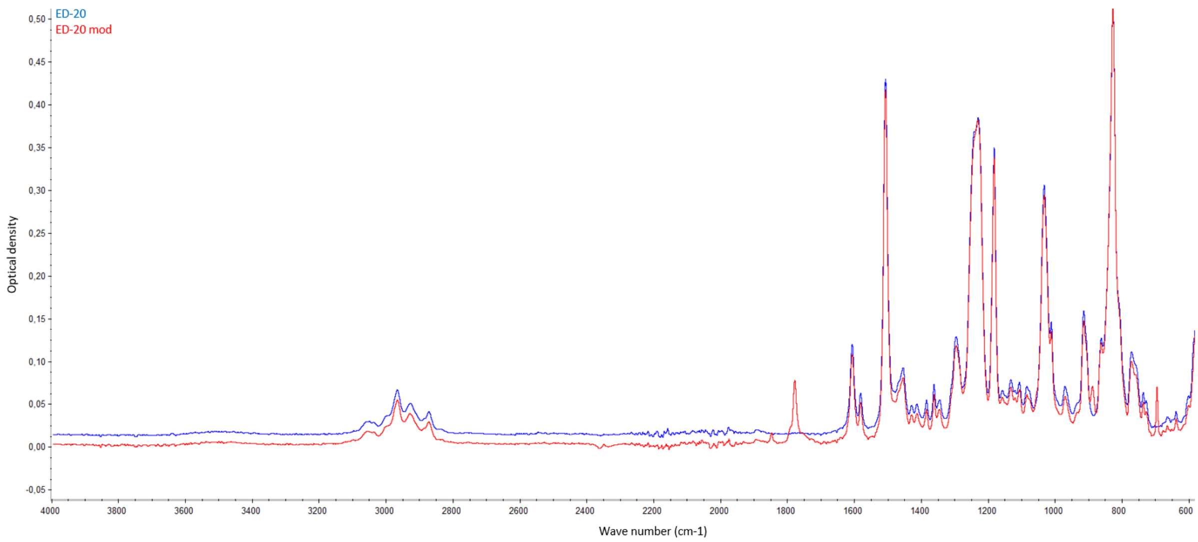

Fig. 4. Comparison of IR spectra of ED-20 epoxy resin before and after modification with maleic anhydride

The presence of the 1848 cm^{-1} peak (Fig. 4) corresponding to cyclic anhydrides shows the reaction did not proceed before the anhydride was completely consumed. However, the intensity of this peak indicates a satisfactory yield of the final reaction product.

The peak at 885.5 cm^{-1} is in the peak frequency of out-of-plane strain vibrations of the C-H bond. This is hypothesised to be due to the steric properties of the macromolecule.

A hardener is required after continuous mechanical mixing of the components to give them a solid structure. We used polyethylene polyamine (PEPA) as a hardener. The curing of polymer compounds with PEPA hardener is well studied and described in the literature [3, 4].

Fig. 5 shows the curing mechanism of maleic anhydride-modified ED-20 epoxy resin.

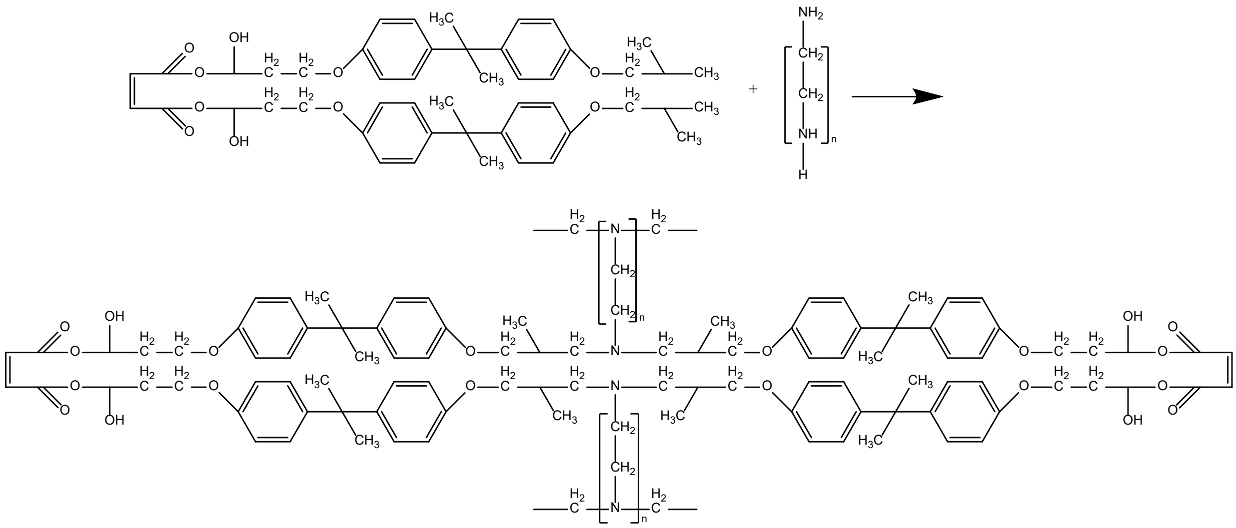

Fig. 5. Curing mechanism of modified ED-20 resin

The epoxy molecules modified with maleic anhydride react with the hardener. The reaction is conducted by a polyamine group with polymer chain extension and cross-linking of the modified resin molecules.

The structural formula of the final polymer under the condition of reaction termination at stage 2 (Fig. 1) is as follows:

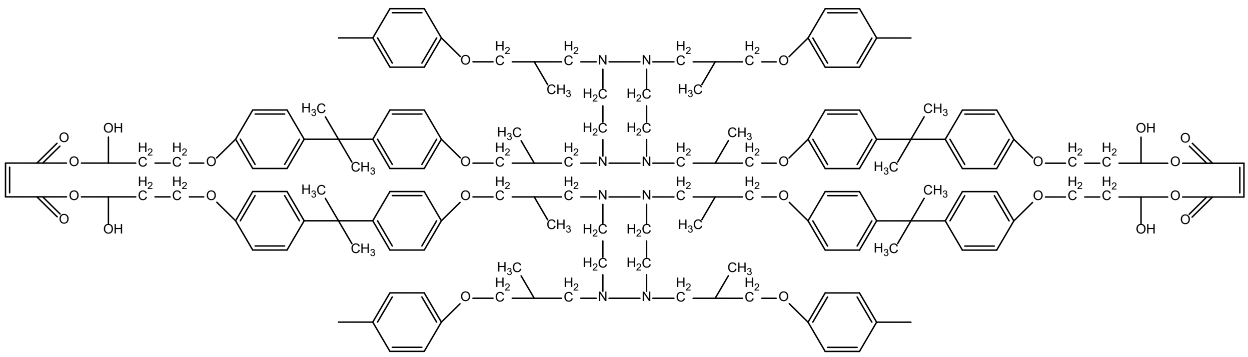

Fig. 6. Structural formula of modified ED-20 resin after curing

The presence of a structured component in the heterogeneous polymer matrix [5, 6] increases its resistance to external media and provides an increase in the durability of the developed coatings.

Mixing of acrylic dispersion and modified ED-20 resin was conducted using a high-speed stirrer for 30 min at a temperature of 23±1°C. The obtained compositions were used for the production of films and reinforced samples modelling the ‘flexible’ stone. We obtained compositions both containing hardener (polyethylene polyamine) and without hardener.

We applied the polymer composition after preparation to a Teflon plate and incubated at 23±1°C for a day. We then visually inspected the composition and tested it.

We used 30 g/m^2 glasswool (PRC manufacturer) as a load-bearing substrate for the fabrication of reinforced samples.

The coating elasticity under bending on a 5 mm diameter rod (GOST 6806-2024 [7]) and resistance to static water exposure for 24 h at 20±2°C (GOST 9.403-2022, method A [8]) were used as criteria for assessing the quality of the developed coating compositions.

We evaluated the obtained properties from the perspective of possible application as a marketable product and grouped them as good (+), satisfactory (±) and unsatisfactory (-) ones. Tables 1 and 2 present the results of the tests.

Table 1. Basic properties of polymer compositions samples

Qualitative data	Acrylic dispersion	Composition acrylic latex + modified epoxy resin ED-20 (without hardener)					Epoxy resin ED-20 (without hardener)	SORBUS dispersion
		80/20	70/30	60/40	40/60	20/80		
Without reinforcement								
Bending elasticity of the coating	+	+	+	+	+	+	+	+
Resistance to static water impact	±	±	–	–	–	–	–	+
Glass fibre reinforcement								
Bending elasticity of the coating	+	+	+	+	+	+	+	+
Resistance to static water impact	±	±	–	–	–	–	–	+

Table 2. Basic properties of polymer composite samples

Qualitative data	Acrylic dispersion	Composition acrylic latex + modified epoxy resin ED-20 (with hardener)					Epoxy resin ED-20 (with hardener)	SORBUS dispersion
		80/20	70/30	60/40	40/60	20/80		
Without reinforcement								
Bending elasticity of the coating	+	+	±	±	±	–	–	+
Resistance to static water impact	±	+	+	±	±	±	+	+
Glass fibre reinforcement								
Bending elasticity of the coating	+	+	+	±	±	–	–	+
Resistance to static water impact	±	+	+	±	±	±	+	+

According to Tables 1 and 2, the modified resin allows ones to increase the resistance of acrylic dispersion-based compositions to static water exposure while maintaining the elasticity of the coating. The developed composition - acrylic latex + modified epoxy resin ED-20 (with hardener) - allows ones to replace SORBUS dispersion for production of ‘flexible’ stone.

Conclusions

Hence, the compound containing 80 wt. % of acrylic dispersion and 20 wt. % of ED-20 epoxy resin modified with maleic anhydride is the composition allows ones to replace SORBUS dispersion in the production of 'flexible' stone products.

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