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Development of Technology of Epoxy Resin Modification New Modifiers

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Abstract

In article is shown possibility of the modification of the epoxy of the mark ED-20 new phosphor containing polymers on base phosphoric acids with epichlorohydrin and methacryloilchlorid. The main regularities of the process of the modification will reveal.

Keywords: polymer; epoxy; modification; composition; toughness; adhesive; corrosion.

Abbreviations: DBP: Dibutyl Phthalate; PEPA: Polyethylene Polyamine; PECH: Polyepichlorohydrin

Introduction

To obtain polymeric materials with improved properties, modification of large-capacity industrial polymers with small additions of other polymers or oligomers is widely used [1]. The introduction of small amounts of fine crystallization nuclei [2], thermoplastic elastomers [3], oligomeric and polymeric additives [4]. The basis of the modification of polymers or oligomers by small additives laid down ideas about the significant influence of the supramolecular structure, as well as the conditions of the relaxation processes on the properties of polymers. In this case, there is a complex effect of additives on the structure and properties of polymers. A large amount of research is devoted to chemical modification of epoxy polymers and it has been shown that their modification is most effective even at the stage of mixing components when modifiers are introduced mainly with hardeners in the process of forming polymerization centers, polymer chain growth, and polymer network formation. The use of polymer modifiers is promising from the point of view of preventing some undesirable processes characteristic of low molecular weight modifiers, as well as using them in small quantities [5].

Objects and Research Methods

The compositions cured at room temperature. The samples of epoxy compositions prepared in this way were subjected to physic mechanical and chemical tests according to State Standards. The experiments used modern physicochemical research methods, such as IR, -MPR-, EPR-spectroscopy, elemental analysis. Thermogravimetry and DTA analysis, psychometry to determine the density, etc. were used to determine the heat resistance of the samples.

Results and Its Discussion

Table 1: The composition of the unmodified and modified epoxy composition.

No	Payment Order	Components Composition			
		1	2	3	4
1	Resin ED-20, %	90	92,49	92,4	91,5
2	Polyethylene polyamine, %	10	7,5	7,5	7,5
3	Phosphorus. polymer	-	0,01	0,1	1,0

In this aspect, it is of interest to develop a technology for modifying an epoxy resin synthesized by a phosphorus-containing polymer based on the interaction of phosphorous acid synthesized on the basis of the waste of JSC "Maxam-Ammophos" with epichlorohydrin (ECG), because due to its close chemical nature, as well as the thermodynamic and kinetic compatibility of components, leading to good mixing, it is possible to obtain epoxy compositions with improved Physico mechanical properties [6]. Epoxy compositions were prepared from ED-20 resin, a polyethylene polyamine hardener with the addition of a small amount of a phosphorus-containing polymer. The composition is shown in (Table 1). The compositions were cured at room temperature. The samples of epoxy compositions prepared in this way were subjected to physical mechanical and chemical tests according to State Standards, the results of which are shown in (Table 2). As can be seen from the table. 2. with the introduction of an insignificant amount of a polymer modifier con-

taining phosphorus and halogen in its composition into the epoxy composition while simultaneously reducing the amount of hardener introduced, the curing rate of the composition increases, and the physic mechanical properties are improved. High physic mechanical indicators obtained in laboratory studies in the modification of epoxy resin, confirmed by industrial tests, which were conducted at the Tashkent Production Association "Tashkentmramor", where epoxy resin of the brand ED-20 was used according to the technological regulations and TU-06-05-1082 [6] and according to the recipe given in (Table 3) for the adhesive composition. The results of physic-mechanical tests of marble slabs, obtained by standard and experienced recipes, are shown in (Table 4).

Table 2: Physical and mechanical properties of epoxy compositions.

No	Name of indicators	Composition Properties			
		1	2	3	4
1	Strength atsprains, Mpa	109,5	113,0	149,0	180,0
2	Specific impact strength, kJ / m^2	2,08	2,24	2,37	2,52
3	Chemical resistance (benzene), %	21,9	3,61	0,48	0,057
	for 24 h., %				
4	Water absorption in 24 hours, %	0,83	0,5	0,04	0,005
5	Time of ignition, sec.	6	75	120	160
6	Oxygen index, %	18,0	19,7	21,0	23,0
7	Cure time at room temperature, min.	210	160	120	75

Table 3: The composition of the unmodified and modified adhesive composition.

No	Components	Composition Number			
		Standard image	1	2	3
1	ED-20 pitch	100	100	100	100
2	PEPA	18	9,4	9,2	9,0
3	Cement	82	82	81	80
4	Phosphorus containing Polymer	-	0,05	0,10	0,15

Table 4: Physical and mechanical properties of modified epoxy resin samples.

No	Test Title	Composition Number			
		Std Sample	1	2	3
1	Ultimate strength at statistical bending,	44,5	85,78	119,3	148,0
	kgf / cm^2				
2	Water absorption, %	0,19	0,0098	0,008	0,0062
3	Chemical resistance (diesel oil), %	0,3	0,018	0,012	0,012
4	Full cure time, min.	35-40	20	15	20

From Table 4 it follows that the introduction of a small amount of phosphorus-containing polymer in the composition leads to a significant improvement in the physical and mechanical properties, reducing the time for complete curing. By increasing the strength of glued art marble slabs (2.7 times), the number of substandard products decreases. It should be noted that the modification of the epoxy composition leads to a decrease in the injected hardener by 2 times (the corresponding acts of experimental tests were obtained). The chemical nature of the polymer modifier introduced has a significant effect on the structure and properties of the cured epoxy composition. In addition, the factor of chemical and thermodynamic compatibility of the modifier and the polymer, leading to the formation of a homophasic system, influences the strength characteristics of the modified composition. The introduced modifying additives are sorbed on the defective areas of the resulting spatial grid and, due to the compatibility of the systems; a more dense structure is formed.

Acknowledgement

One of the effective methods of corrosion protection of process equipment and structures is the development and use of composite polymer coatings. In this regard, the role of quality control and prediction of the long-term strength of such coatings is increasing. Increasing the service life of coatings can significantly reduce the consumption of scarce and expensive polymers, more efficiently use production facilities, as well as improve the environmental situation in enterprises using aggressive media in their units. In this regard, the use of epoxy film-forming with active plasticizers modifiers as well as fillers containing metal oxides. Their use allows to increase the operational and deformation, strength characteristics, to reduce the diffusion permeability of metal-polymer structures. Thus, it was of interest to study the effect of synthesized polymers based on the interaction of phosphorous acid with epichlorhydrine and methacryloylchloride as modifiers on the physic mechanical and anticorrosive properties of polymer composite coatings [7].

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ED-20 epoxy diane resin was used as a binder, dibutyl phthalate (DBP), hardener-polyethylene polyamine (PEPA) - as a plasticizer. The results of the study of the effect of the content of the synthesized polymers on the deformation-strength properties (flexural strength, micro hardness of coatings, adhesive strength) of composite coatings show that the strength characteristics increase with the introduction of polymers into the composition (compared to the control sample - based on the composition without polymers) by 25-35%, and adhesive properties by 50-60%. The optimum combination of properties is achieved, depending on the content of polymers, up to 3.0 parts by weight. Similar results were achieved in the study of the electro physical properties of the obtained composite coatings. With the introduction of polymers (the optimum content is 3.0 mph), the dielectric constant (ε) of the coatings increases (by 15–20%), the specific surface resistance of the coatings increases by several orders of magnitude. The required physic mechanical properties of the composition, their stability during operation can be ensured only with a combination of high adhesive strength in the modifier-substrate system and the formation of an optimal spatial structure of the polymer. The increase in the strength characteristics of the composition with the introduction of a polymer modifier can be explained according to the adsorption theory, which considers adhesion as the result of the manifestation of the forces of molecular interaction between the concentrating phases. In this case, all varieties of Wander-Waals forces (orientation, inductive, and dispersive) can occur. It is important that the adhesive and substrate have functional groups that can interact.

Molecular interaction, according to the adsorption theory of adhesion, is preceded by the formation of contact between the adhesive and substrate molecules. Temperature increase the introduction of the modifier, the pressure increase, the use of solvents - all these factors facilitate the flow of the first stage of the process and contribute to achieving a more complete contact. Wetting and cracking of the adhesive on the substrate surface are accompanied by surface diffusion, migration of adhesive molecules on the surface. It is this circumstance, as well as the flexibility of polymer macromolecules and their ability to make the micro-Brownian motion, were taken into account in the adsorption theory of adhesion. When adhesive failure does not always require the breaking of chemical bonds, and with cohesive destruction of the network adhesive, breaking of chemical bonds is inevitable. When loading the adhesive connection due to the different elastic constants of the adhesive and the substrate, an additional stress concentration occurs. Under these conditions, a gap along the interfacial surface is more likely than in the array of adhesive and substrate, even if the bonds are equally strong, since the durability of the adhesive bonds decreases with increasing voltage. Finally, in many cases, the adhesive compound is affected not only by mechanical loads, but also by moisture, various chemical agents, and an elevated temperature. It is the phase boundary that is most affected by these factors. One of the ways to increase the durability of a composite material and adhesive compounds is to facilitate relaxation processes in the zone of contact of the polymer with the substrate, with a dispersed or fiber-like filler. These processes can be changed by regulating the intensity of the interfacial interaction, as well as by applying elastic layers. Adhesive compounds possess optimal properties, along with strong chemical bonds, in the contact zone, less durable, but easily recoverable, labile polar bonds occur, characterized by a low value of activation energies. Such bonds are characteristic of groups containing a mobile hydrogen atom, as well as heteroatoms with non-generalized electrons. A rare mesh of strong chemical bonds in combination with a sufficiently large number of easily regenerated less strong bonds creates favorable conditions for relaxation of overvoltage's and sticking of defects. The role of hinged groups with low potential for rotation is also very important. It is shown that in systems containing not only strong interfacial covalent bonds, but also hydrogen bonds characterized by low recombination energy, more favorable conditions arise for the redistribution and variation of the voltages of stabilizing defects.

Confirmation of the above results was obtained according to the corrosion tests according to GOST 9.083-78 in a 30% HCl and HNO_3 solution and a 30% H_2SO_4 solution. The coatings showed high corrosion resistance. The weight loss of the coatings was no more than 0.3% for 30 days of exposure to aggressive media. However, the resulting coatings have sufficient heat resistance and fire resistance, which are important performance characteristics, and do not require a long time for curing. The introduction of a small amount of phosphonium polymers enhances the physicochemical properties of epoxy composite coatings, as well as increases their heat and flame-retardant properties. As studies have shown, with the introduction of polymers, the process of curing epoxy resin is significantly accelerated. The curing time of the control composition (without a modifier), determined according to a known method [8], is more than 200 minutes at room temperature, in the presence of polymers it is reduced to 118-140 minutes. When using polyepichlorohydrin (PECH), which does not contain phosphorus-nitrogen fragments, as well as terminal unsaturated bonds, the induction period of curing is longer than in the case of polymer modifiers, indicating a greater efficiency of phosphorus-containing polymers with an end double bond compared to model oligomers (PEHG) not containing it. With the introduction of an insignificant amount of polymer modifiers containing phosphorus halide into the epoxy composition with a one-time decrease in the amount of hardener introduced (PEPA), the curing rate of the composition increases (by 65-70%), and anti-corrosion properties are improved, water absorption - by 70- 80%, benzine resistance by 50-60% (Table 5). Apparently, the chemical nature of the polymer modifiers introduced has a significant effect on the structure and properties of the cured epoxy composition. In addition, the anticorrosive properties of modified composite coatings are also affected by the factor of chemical compatibility of high molecular weight modifiers and polymer, leading to the formation of a homophasic system. In addition, in all likelihood, the polymer modifiers synthesized by us, in addition to the modifier, also act as a structurant for the polymer matrix, contribute to the ordering of macromolecules near its surface, and this leads to a decrease in the entropy of the system. Synthesized phosphorus-containing polymers based on the interaction of phosphorous acid with epichloro-

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hydrine, methacryloylchloride can be used as an effective modifier and accelerator for curing epoxy composite coatings.

Note: in the denominator - the data for the polymer (FC + ECH); in the numerator - data for the polymer (FC + MAX).

Table 5: The main Physico mechanical and other characteristics of epoxy compositions (PEPA-10).

Indicators	Standard Samples	Content of Modifier, %			
		0,5	1,0	3,0	5,0
Strength at static bending, MPa	102,3	108,5	114,6	121,0	126,3
		106,4	118,0	132,5	136,4
Specific impact strength, kJ / m2	2,15	2,29	2,33	2,39	2,44
		2,16	2,16	2,24	2,39
Water absorption in 24 hours, %	0,94	0,71	0,54	0,32	0,16
		0,65	0,65	0,54	0,29
Chemical resistance for 24 h, %	24,5	12,8	10,2	8,6	3,44
		16,8	16,8	8,9	5,32
Cure time, min	35,4	20/18	16/13	11/9	8/6
Oxygen index, %.	18,0	20,5	22,4	24,3	26,0
		19,6	21,8	23,9	25,6

The factor of chemical compatibility of high-molecular modifiers and a polymer, leading to the formation of a homophasic system, also influences. In addition, in all likelihood, the polymer modifiers synthesized by us, in addition to the modifier, also act as a structurant for the polymer matrix, contribute to the ordering of macromolecules near its surface, and this leads to a decrease in the entropy of the system. Synthesized phosphorus-containing polymers based on the interaction of phosphorous acid with epichlorohydrine, methacryloylchloride can be used as an effective modifier and accelerator for curing epoxy composite coatings. Such modifiers are non-volatile, non-toxic, easily combined with epoxy resin; the technology for their preparation is simple, which makes it possible to use them widely.

Summary

The laboratory and industrial tests of the polymer obtained from the interaction of phosphorous acid based on the waste of "Maxam-Ammophos" OJSC with ECG and MAX as a flame-retardant modifier for epoxy compositions indicate the promise of the phosphorus-containing polymers synthesized by their possible industrial realization and us.

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