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MODIFICATION OF EPOXY POLYMERS WITH METALORGANIC COMPLEXES

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A new type of epoxyamine composition containing a copper (II) metalorganic complex has been created. The mechanism for obtaining the complex is developed. The structure and properties of the modified materials have been explored and analyzed, as well the relationship between them has been determined. A copper (II) chelate complex has been obtained and applied as a hardener for epoxyamine compositions. It has also been found that the complex mentioned reduces the flammability of materials during the structuring.

Keywords: modification, chelate complex, hardener, epoxy composition, burning, organometallic complex.

Introduction

A key feature of the thermal decomposition and burning of polymer materials, including epoxy resin-based composites, is the intensive release of gaseous products and toxic compounds. The ignition ability, composition of burning products, and volume of gas emissions formed as a result of the combustion and smoldering of polymers are determined by a number of factors. The chemical structure of macromolecules is of primary importance among these factors.

For example, aliphatic polymers emit a minimal amount of gaseous compounds during burning despite their high flammability. In contrast, polymer materials containing halogen atoms in their structure are characterized by low flammability, but their burning is accompanied by significant formation of gaseous products [1].

The formation of thermal decomposition products is influenced by the conditions of the burning process. In particular, the intensity of the heat flux acting on the polymer material surface, the volume of oxygen entering the burning zone, and the pressure, humidity, as well as the composition of the environment are important factors. Predicting the burning process, as well as the composition and volume of gaseous emissions, is not always a linear dependence, as a result.

The literature [2, 3] states that a significant range of toxic compounds is released into the environment during the burning of epoxy-containing materials. These compounds include carbon oxides (II) and (IV), various organochlorine compounds (epichlorohydrin, chlorobenzene), aromatic hydrocarbons (benzene, toluene, phenols and their derivatives), as well as hydrogen chloride, formaldehyde and nitrogen oxides. Even insignificant concentrations of these chemical substances have a negative impact on both the ecological state of the environment and human health. Statistics show that 70–75 % of fatalities during fires are caused by toxic emissions intoxication. Therefore, the development of new, effective compounds with reduced flammability and minimal toxic combustion product content that meet modern safety requirements is becoming extremely relevant.

Such additives include complex metal compounds, among which copper (II) attracts special attention. Its attractiveness lies in its ability to significantly improve a number of fire hazard indicators of materials. These include increasing the ignition temperature and self-ignition, as well reducing the flame spread rate and maximum temperature of gaseous burning products [3–6].

The aim of this work is to create new epoxyamine compositions modified with the copper (II) metal-organic complex in order to obtain materials with improved structural and functional properties.

Materials and research methods

Epoxy resin ED-20 is a transparent, viscous liquid manufactured by Brilux (Germany). Charac-

teristics: minimum working temperature – 10 °C; maximum working temperature – 60 °C; dynamic viscosity – 17 Pa·s; gelatinization time makes not less than 8 hours; hardening to maximum hardness is 7 days; mass fraction of epoxy groups is 21%; volatile substances: not more than – 0.2 %; hydroxyl groups: not more than 1.7 %.

Polyethylenepolyamine (PEPA) is a liquid ranging in colour from light yellow to dark brown. (Ukraine). Density at 25 °C is 1.017 g/cm^3. Viscosity value is 900 MPa·s. Consists of several fractions. Temperature: melting 30 °C, boiling over 350 °C, flash point – 104 °C. Curing ability is not more than 1.5 hours.

Crystalline hydrate of copper (II) chloride ($CuCl_2 \cdot 2H_2O$) is green crystals, very hygroscopic, melt in crystallization water at 110 °C. Well soluble in water (77 g/100 ml), ethanol (53 g/100 ml), methanol (68 g/100 ml), and acetone as well. Easily reduced to Cu^{1+} and Cu^0 and is toxic. When water is added, the complex is destroyed. In nature, dihydrate of copper(II) chloride $CuCl_2 \cdot 2H_2O$ occurs in the form of the rare mineral ernochalcite (blue crystals).

IR spectrometric studies were conducted applying a PerkinElmer Spectrum Two FTIR spectrometer in the frequency range of 4000 – 500 cm^{-1} with a resolution of 2 cm^{-1}. IR measurements were carried out both with solid-phase samples (chelated amino-cupro complexes and polymer compositions) pressed into granules with spectroscopically pure KBr, and with samples in the liquid state (pepa) using a cuvette made of KBr [7].

The thermal behavior of flame retardants (inorganic salts of d-metals), hardener (pepa), flame retardant hardeners (chelated aminocoupro complexes), and metal-coordinated epoxyamine compositions obtained on their basis was studied via the derivatography method. Using this method, the mass loss of the sample (TG thermogravimetry), the mass change rate (DTG differential thermogravimetry), and the thermal effects accompanying the processes of thermooxidative destruction (DTA differential thermal analysis) were determined. Thermograms were recorded on a Q-1500D derivatograph of the F. Paulik, J. Paulik, L. Erdey system with registration of the analytical signal of mass loss and thermal effects using a personal computer. The study was carried out in a dynamic mode in an air atmosphere. The samples were heated at a rate of 5 ºC/min. The sample weight was 100 mg. The standard substance was aluminium oxide [8, 9].

Results and discussion

The synthesis of epoxyamine compositions modified with copper (II) chloride is carried out using two methods that differ in the way and form of adding the flame retardant to the polymer matrix [4].

The traditional method involves sequentially mixing components in the following order: binder, flame retardant, hardener.

Instead, we have proposed a method based on the application of a pre-synthesised crystalline flame retardant-hardener complex, which is added directly to the binder.

To prepare the ED/PEPA-$CuCl_2$ composition, green-blue $CuCl_2 \cdot 2H_2O$ crystals were dried in a thermo-oven at 110 ºC to obtain a yellow-brown $CuCl_2$ powder. The appropriate amount of the PEPA hardener and the $CuCl_2$ flame retardant were added to the epoxy resin alternately and mixed until the composition was homogenised [10].

The second method of obtaining the ED/pepa-$CuCl_2$ composition foresees mixing a certain amount of ED-20 epoxydian oligomer with a flame retardant hardener, which in the ED – PEPA – $CuCl_2$ system being formed two chelate aminocouper complexes – $[Cu(eda)_2(H_2O)(Cl)]Cl$ and $[Cu(deta)_2]Cl_2 \cdot H_2O$. Complete hardening of the composition occurred within 24 hours at room temperature. The stoichiometry of the derived compositions is given in Table 1.

Table 1

Stoichiometry of ED/PEPA-$CuCl_2$ compositions

Compo-sitions	Mole ratio of ED -20: PEPA:$CuCl_2$	Compositions content, wt. %		
		ЕД-20	PEPA	Cu Cl_2
ED/PEPA - $CuCl_2$(7)	2.5 : 1 : 0.5	100	12	7
ED/PEPA - $CuCl_2$(14)	2.5 : 1 : 1	100	12	14
ED/PEPA - $CuCl_2$(40)	2.5 : 1 : 3	100	12	40
ED/PEPA - $CuCl_2$(60)	2.5 : 1 : 4,5	100	12	60
ED/PEPA - $CuCl_2$(80)	2.5 : 1 : 6	100	12	80

To confirm the participation of both chelate complexes $[Cu(eda)_2(H_2O)(Cl)]Cl$ and $[Cu(deta)_2]Cl_2 \cdot H_2O$ as flame retardants-hardeners in the structuring

of the epoxy composition, IR spectroscopic studies were carried out (Fig. 1) [11–13]. The derived IR spectra testify to the interaction of chelate cupric chloride amino complexes with the binder (ED-20), resulting in the disappearance of the N–H bonds in the amino groups. Instead, N–C bonds are formed, and new O–H bonds appear. It is worth noting that the coordination site occupied by the water molecule in the $[Cu(eda)_2(H_2O)(Cl)]Cl$ complex can be occupied by an OH group after curing.

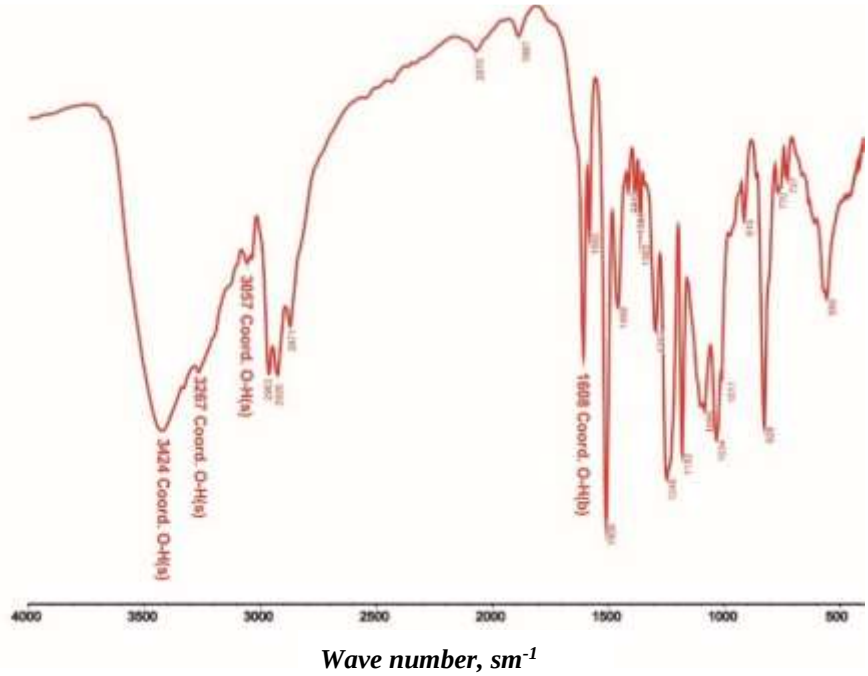

Fig. 1. IR spectra of the ED/PEPA-$CuCl_2$ composition

The absorption bands characterizing the stretching vibrations of the coordinated NH_2 and NH groups (3315, 3266, and 3187 cm^{-1}) appear at 3324, 3267 and 3057 cm^{-1}, respectively, and describe the stretching vibrations of the OH group, which is significantly weakened due to Cu(II)–OH coordination. This may indicate a chemical interaction between the epoxy groups of the epoxydiane oligomer and the coordinated Cu^{2+} ion of the PEPA, which proceeds during the structuring of the epoxyamine composition [14].

The thermal-oxidative degradation of the ED/PEPA-$CuCl_2$ composition sample occurs within five stages, as shown in Fig. 2. At the first stage of thermal-oxidative degradation, in the temperature range of 20–138 °C, a slight loss of sample mass (Δm = 2.27 %) is observed, which corresponds to the release of volatile products that do not participate in the formation of the spatial grid of the epoxyamine composition. An endothermic effect appears on the DTA curve in the mentioned above temperature range.

In the temperature range of 138–216 ºC, at the second stage of thermolysis, the partial thermooxidative destruction of the coordinated amine hardener PEPA occurs. This process is accompanied by an exothermic effect on the DTA curve with a maximum at a temperature of 199 ºC and a slight loss of sample mass (Δm = 1.59 %).

At the third stage of thermolysis, in the temperature range of 216–326 °C, complete thermal decomposition of the complex is observed, which is significantly complicated by thermo-oxidative processes in the epoxy resin. This process corresponds to a loss of sample mass of 18.48 %. An exothermic effect appears on the DTA curve at a temperature of 266 ºC. It is worth noting that the destructive processes of the ED/PEPA-$CuCl_2$ composition sample, compared to the ED/PEPA composition sample, begin at lower temperatures. This is most likely due to the course of destruction in the complex, Table 2. The thermo-oxidative processes of destruction of the epoxy component containing a flame retardant, in contrast to the ED/PEPA composition proceed less intensively, as evidenced by the appearance of a less intense exoeffect on the DTA curve.

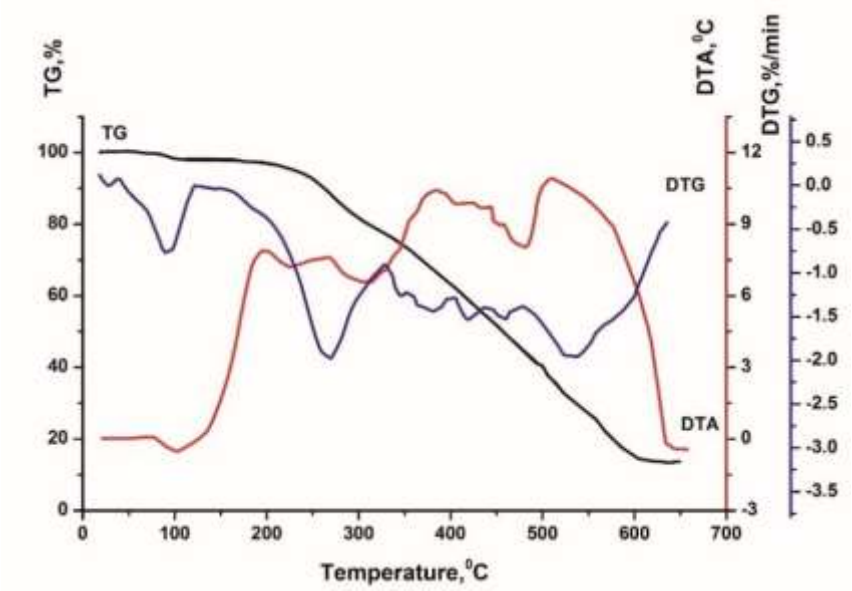

Fig. 2. Thermogram of ED/PEPA-$CuCl_2$

Table 2

Results of thermolysis of the ED/PEPA-$CuCl_2$ sample

Sample	Stage	Temperature range, ºC	Weight loss, %
ЕД/*PEPA*-$CuCl_2$	1	20 – 138	2.27
	2	138 – 216	1.59
	3	216 – 326	18.48
	4	326 – 480	33.33
	5	480 – 640	30.83

At the fourth stage of thermolysis, in the temperature range of 326–480 ºC, deep thermo-oxidative processes occur in the epoxy resin and combustion of the products of the organic component destruction of the sample. According to the TG curve data, this process is accompanied by an intensive weight loss of 33.33 % in the sample, and an exothermic effect appears on the DTA curve, reaching a maximum at a temperature of 385 ºC.

At the fifth stage, in the temperature range of 480–640 ºC, burning of the pyrolytic residue of the sample is observed, which corresponds to an intensive loss of the sample mass of 30.83 % and the appearance of an exothermic effect on the DTA curve with a maximum at a temperature of 511 ºC.

Burning of the carbonized residue of the unmodified composition occurs at a temperature of 900 ºC. For the ED/PEPA-$CuCl_2$ composition, it proceeds at a temperature of 650 ºC. This demonstrates the self-extinguishing effect of burning of a composition containing a flame retardant [14, 15].

Conclusions

Based on the conducted research, a new type of epoxyamine compositions, containing a metalloorganic complex based on copper(II) was created. Within the work, the synthesis of a chelate cuproamine complex was developed, which performs the role of both a flame retardant (a substance that slows down or prevents burning) and a hardener as well. Analysis of the structure of the flame retardant-hardener allowed us to predict its effective effect on the moisture resistance of materials, and a deep analysis of the chemical processes in the system including ED-20 resin, copper chloride and hardener, confirmed that our flame retardant-hardener actively participates in the formation of a strong polymer grid. The aforementioned allows us to believe that the application of transition metal salts, such as copper sal,t reduces the flammability of epoxyamine materials.

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МОДИФІКАЦІЯ ЕПОКСИДНИХ ПОЛІМЕРІВ МЕТАЛООРГАНІЧНИМИ КОМПЛЕКСАМИ

Створено новий тип епоксиамінних композицій, що містить метаолорганічний комплекс на основі купрум (II). Розроблено механізм одержання комплексу. Вивчено та проаналізовано структуру та властивості модифікованих матеріалів, встановлено зв'язок між ними. Отримано хелатний комплекс на основі купрум (II), який використовували як отверджувач епоксиамінних композицій, а також виявлено, що він у процесі структурування забезпечує зниження горючості матеріалів.

Ключові слова: модифікація, хелатний комплекс, отверджувач, епоксидна композиція, горіння, металоорганічний комплекс.