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*H. Lavrenyuk, B. Mykhalichko***PRINCIPLES OF CONTROLLED EFFECTS ON PERFORMANCE PROPERTIES OF SELF-EXTINGUISHING EPOXY-AMINE COMPOSITES MODIFIED BY COPPER(II) CARBONATE**

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This paper reports the results of determination of tensile strength, surface hardness, water resistance and chemical resistance of polymer materials based on the self-extinguishing epoxy-amine composites modified with copper(II) carbonate. This allowed forming the basics of a new type of polymer materials with enhanced physicochemical and mechanical properties. The results of the experiments showed that the use of CuCO_3 , which is considered as a flame-retardant agent of epoxy-amine composites, not only suppresses the spread of the flame, thereby effectively reducing the fire hazard but also improves the performance characteristics of the produced polymer coatings. Due to its exceptional complexing ability, copper(II) carbonate is readily incorporated into the structure of an epoxy polymer, which ensures that the composite materials retain their performance characteristics at an appropriate level. The addition of CuCO_3 to epoxy-amine composites in the amount of 20–40 mass parts per 100 mass parts of binder increases the tensile strength and the surface hardness by 67.8–87.2% and 19.7–21.5%, respectively, in comparison with the original composition. It was also found that epoxy-amine composites with CuCO_3 additives are characterized by increased water resistance and resistance to aggressive environments.

Keywords: copper(II) carbonate, reactive fire retardant agents, epoxy-amine composites, physicochemical properties, resistance to aggressive environments.

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Introduction

To reduce the number of fires caused by the wide use of polymer materials in various industries, it is necessary to solve this important problem through targeted search for effective fire retardants. The studies [1–4] prove the high efficiency of the use of transition metal salts to reduce the fire hazard of polymeric materials based on epoxy-amine composites. The advantage of the d-metal salts to be considered as fire retardants is that these can chemically bond the components of the epoxy matrix into a chelate complex forming strong coordination bonds [5,6]. It should be noted that chelation processes play a decisive role when yielding epoxy polymer materials with reduced combustibility and moderate smoke-forming ability, that are not able to spread the flame and that self-extinguish under a condition of fire [7].

It is quite often possible to face the problem, when the introduction of additives reducing the fire hazard of polymeric materials and, in particular,

materials based on epoxy resins, results in deterioration or even loss of some physical-mechanical properties, and an increase in the cost of the material. To make competitive polymer products, it is necessary to practice a comprehensive approach to optimize operational and technical indices, apply technological requirements and introduce environmental standards to the reduced combustibility polymers [8].

Because epoxy resins are most often used as binding agents in solid composites, adhesives, compounds or protective coatings [9], first of all it is necessary to take into account the effect of the fire retardant additives on the mechanical properties (especially tensile strength) of the materials, based on epoxy resins. Other important index is a long-life, which is determined by such an important characteristic as time. This characteristic includes the following material properties: hardness, creep and aging. The aging is a change in the structure and properties of a polymer material under the

influence of the atmosphere and aggressive environment.

The specific structure of epoxy polymers is known to be characterized by low density of molecular packing, weak intermolecular interactions specifying low values of the temperatures of glass transition and melting and clearly distinct relaxation phenomena. That is why the resistance parameters to atmosphere exposure and temperature are as important as the basic strength characteristics. Therefore, apart from the strength indices, the resistance of polymer materials to the physicochemical exposure is also considered to be one of the most important parameters.

In this study, we report the effect of CuCO_3 additives on the performance properties of epoxy-amine composites. Such characteristics as tensile strength, surface hardness, water resistance and chemical resistance were measured for samples of the epoxy-amine composites modified by copper(II) carbonate. Based on these results, the most optimal ratio of components was matched to obtain the CuCO_3 -containing epoxy-amine composite with improved physicochemical and mechanical properties.

Experimental

To prepare the epoxy-amine composites, the following chemicals are used: bisphenol A diglycidyl ether (DGEBA) (ED-20 grade with almost 22% epoxy groups content) as a binding agent; polyethylenepolyamine (PEPA $\text{H}_2\text{N}[-\text{C}_2\text{H}_4\text{NH}-]_n\text{H}$, where $n=1-5$) as a curing agent; and copper(II) carbonate (CuCO_3) as a fire retardant.

The method of preparation of samples of epoxy polymers containing various quantities of CuCO_3 is described in detail elsewhere [2]. To study physicochemical and mechanical properties, the polymer samples with different contents of copper(II) carbonate were fabricated. In five obtained epoxy-amine composites that have *DGEBA/PEPA-CuCO₃* general formula, the salt content was 0, 5, 20, 40, and 80 mass parts of CuCO_3 per 100 mass parts of *DGEBA*.

The physicochemical properties of the composites were studied by measuring surface hardness, tensile strength, water absorption, and chemical resistance. The samples surface hardness was measured on the Höppler's consistometer by indentation of a steel cone at an angle of $53^{\circ}08'$ and at a load of 50 N for 60 s.

Uniaxial tensile tests were performed on the samples according to all-Union State Standard 11262-80 at room temperature using a P-0.5 tensile testing machine. Rectangular samples with

dimensions of $250 \times 10 \times 3$ mm were used. A displacement rate of $100 \text{ mm} \cdot \text{min}^{-1}$ was adopted. The tensile properties were averaged from the results obtained from a minimum of three samples.

The water absorption or chemical resistance was studied by gravimetric method. A weight change of the polymer films was measured after their immersion into distilled water or corrosive medium for a certain time.

Results and discussion

The strength is one of the performance properties determining the life-time of polymer materials; it depends on the presence of defects and their number in the structure [10]. As a rule, the use of inert fire retardants results in structural inhomogeneity of the material, which, in turn, negatively affects hardness, strength and specific impact strength. There is an insignificant influence of the character of inert fire retardant agent on the properties of the composites. Here, the more essential role plays the surface area of the interphase boundary. Therefore, the use of inert additives in most cases is defined by a number of factors of an interaction of phases. The superposition of all these factors often results in the extremal dependence between the strength of polymer material and the inert fire retardant content.

In this study, we used the reactive fire retardant agents instead of inert ones. This type of fire retardant agents is able to actively take part in the polymer forming processes, changing thereby the polymer network topology, the molecular packing density and the intermolecular interaction energy. However, all changes in the topology of the polymer network are closely related to changes in their chemical structure which ultimately affects the strength of the polymer.

The results of the tensile strength measurement presented in Fig. 1 showed that copper (II) carbonate significantly affects this index. It was found that the tensile strength achieved the maximum value for those *DGEBA/PEPA-CuCO₃* composites, in which the salt content was from 20 to 40 mass parts of CuCO_3 per 100 mass parts of *DGEBA*. It can be assumed that when the content of copper(II) carbonate is the highest (80 mass parts), only a certain part of CuCO_3 will chemically bond to the polymer matrix; the rest of this salt will act as an «inert» filler. Adding more copper(II) carbonate to the system (>40 mass parts of CuCO_3 per 100 mass parts of *DGEBA*), we thereby overfill the epoxy-amine composite with a flame retardant additive. Undoubtedly, an excess of CuCO_3 will negatively affect the structuring processes of the polymer composite and, as a result, worsen the mechanical properties of polymeric materials.

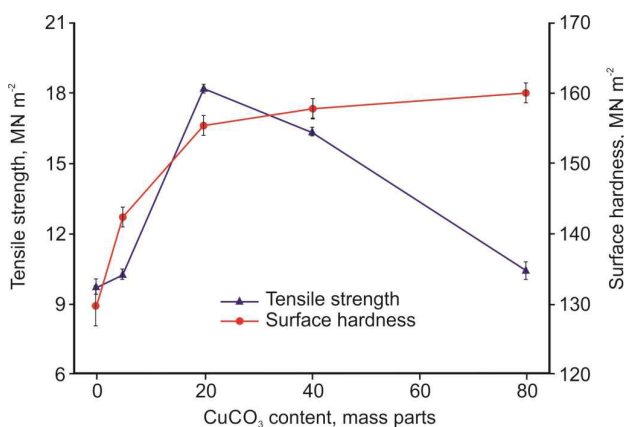


Fig. 1. The tensile strength and the surface hardness as a function of the CuCO_3 content in the modified epoxy-amine composites

Apparently, the interaction conditions of macromolecules of a binder with filler worsen and, hence the thickness of the boundary interlayers decreases [11]. This prevents the formation of the lattice structure of the filler in the composite and, accordingly, reduces the cohesive strength. In addition, the amount of polymer phase in such composites is insufficient for even envelopment of all grains of the filler as well as for polymer inclusion in surface layers of the material. It eventually causes a decrease in the polymer strength.

Polymer materials based on epoxy-amine composites in the operation process are exposed to external mechanical influences (impacts, scratches and abrasion). In this case, the destruction of the material always begins with damage to the surface. Thus the long service life of materials, in fact, will directly depend on the strength of the surface layer of products, including products based on epoxy-amine polymers.

The surface hardness of composites is known to be one of the most important indices to assess the strength of a polymeric material. This index characterizes both the mechanical stability of the polymer material and its resistance to any type of external influences. It should be noted that the structure and properties of the surface layer of the polymer differ from those in its bulk. The mechanical properties of the surface layers depend mainly on their molecular structure, temperature-time processing conditions and the physical state of the medium in contact with polymers during their formation.

Insufficient hardness of the surface layer results in the loss of the protective and decorative functions

of products during operation. A less hard surface layer is less resistant to abrasive wear. Dents and other damage due to the low hardness of the surface layer significantly reduce the aesthetics of the products. On the other hand, the formation of a very hard surface layer, followed by the formation of a rigid structure with significant internal stresses, reduces the elasticity of the polymeric material. Therefore, only materials with a balanced combination of hardness and elasticity, resistance to shock load and adhesion strength can be long-life and reliable.

The breakdown of the samples of polymeric materials (for example, during the stretch) always begins from the surface. Therefore, we can assert that the condition of the surface layer predetermines the strength of polymeric materials. Surface defects are the main source of over stresses. These cause the formation and propagation of main cracks in polymeric materials [12]. In the surface layers of a polymeric material, the level of potential energy in micro-grains increases due to over stresses. This excess energy provides the decay of the inter-boundary surfaces of neighboring micro-grains, thereby initiating the complete breakdown of the composite material.

It has been experimentally found (Fig. 1) that epoxy-amine polymers modified by copper(II) carbonate are characterized by higher values of surface hardness than the unmodified epoxy-amine polymers. In particular, the introduction of copper(II) carbonate into the epoxy-amine composite in the amount of 5 mass parts of CuCO_3 per 100 mass parts of DGEBA results in the growth of surface hardness by almost 10%. But, an increase in the fire retardant content in the composite (>20 mass parts of CuCO_3 per 100 mass parts of DGEBA) does not essentially affect the surface hardness value. That is, the value of the surface hardness for composite samples containing 40 mass parts of CuCO_3 per 100 mass parts of DGEBA increases by only 1.56% as compared with the composites containing 20 mass parts of CuCO_3 . The highest value of the surface hardness (159.65 MPa) was detected for composites containing 80 mass parts of CuCO_3 per 100 mass parts of DGEBA.

When forming a three-dimensional structure of an epoxy-amine composite modified with copper(II) carbonate, Cu^{2+} ions firmly bond the molecules of the nitrogen-containing hardener of epoxy resins, thereby compacting the polymer framework. As a result, the kinetic mobility of the chemical particles inside such a framework decreases which results in an increase in the surface hardness

value.

Since epoxy polymers are mainly used as protective coatings, compounds and composites for various purposes, their operational capabilities largely depend on the diffusion permeability of water and aqueous electrolyte solutions [13]. Water is the most active and easily penetrating agent. Water molecules are small; their polar molecules readily bond to similar polar groups in the polymer matrix. That is why water is considered an excellent sorbate and diffusant. In an aqueous medium, polymer samples first adsorb H₂O molecules by the surface. Then water diffuses inside the polymer, where it forms unstable chemical bonds with the low-molecular constituent parts of the polymer, washes out and dissolves the non-bond particles. In the medium of aqueous solutions of electrolytes, polymers first absorb the solvent molecules (i.e. the H₂O molecules) and only then these absorb the corrosion-active ions.

The ability of polymeric materials to absorb water with their surfaces, as a rule, depends on the qualitative and quantitative composition and the structure of a polymer. Certain amounts of residual amine or epoxy groups may be present in the polymer frameworks of the tested epoxy-amine composites, which could not react due to stereo-chemical or diffusion limitations. Intercalated hydroxyl groups resulting from epoxy-amine polymerization are also present in these epoxy-amine polymers. These polar hydroxyl groups can attract water molecules, which, in turn, affect the water resistance of the polymer. However, the epoxy-amine composites under study include copper(II) carbonate, which, besides being water-insoluble, forms strong bonds of Cu(II)–N with PEPA. That is why one of the important characteristics for assessing the performance properties of such polymers should be considered the change in mass (Δm) of epoxy-amine composite samples after exposure to water.

Kinetic curves describing the dependence of water absorption on the duration of water exposure to samples with different CuCO₃ contents are shown in Fig. 2. The experimental data obtained show that in the first 3 days of water exposure of polymer samples, Δm increases reaching its largest value and

is from 0.07 to 0.09 wt.% per day. Over the next few days, the water absorption rate of epoxy-amine composites decreases, and after 50 days the value of Δm does not exceed 0.002 wt.% per day. After next 55–60 days of exposure, a state of equilibrium absorption occurs.

Water absorption of film samples of epoxy-amine composites with and without copper(II) carbonate is a one-step process which indicates the phase homogeneity of these polymer samples. Despite a different content of CuCO₃ in the composites under study, their water absorption curves have a similar character and are numerically close (Fig. 2). However, the sorption curve for a sample of an epoxy-amine composite that does not contain CuCO₃ is located above all other curves. This means that this composite has the lowest water resistance. Composites containing 20 mass parts of CuCO₃ per 100 mass parts of DGEBA reveal improved water resistance.

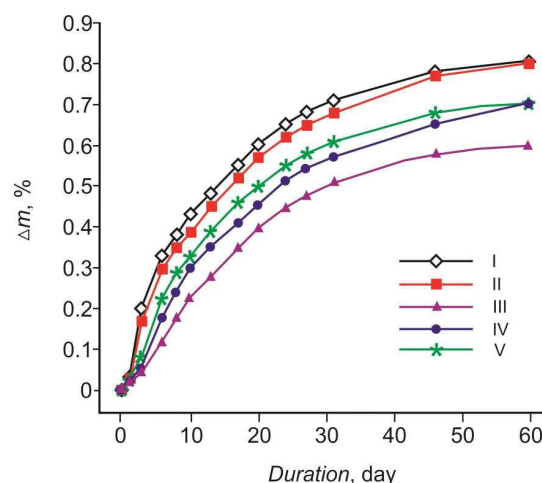


Fig. 2. Water absorption of film samples of the epoxy-amine composite containing a different quantity of CuCO₃ (mass parts): I – 0, II – 5, III – 20, IV – 40 and V – 80

The above becomes clearer if we analyze the effect of the amount of added CuCO₃ on the equilibrium water absorption (Table). As can be seen, the equilibrium water-absorption for a composite

Sorption properties of polymer films based on the CuCO₃-containing epoxy-amine polymers

Properties	CuCO ₃ content in polymer, mass parts				
	0	5	20	40	80
Water absorption for a day, %	0.026	0.024	0.018	0.023	0.023
Equilibrium water absorption, %	0.8	0.8	0.6	0.7	0.7
Equilibrium swelling in 10% H ₂ SO ₄ , %	1.2	1.1	0.8	1.0	1.0
Equilibrium swelling in 10% NaOH, %	1.4	1.2	0.7	0.9	1.1

containing 20 mass parts of CuCO_3 is 0.6%. This is 0.2% less than for a composite without CuCO_3 .

The results showed that copper(II) carbonate is not washed out of the cured polymer by water. The main reason for this is the water-insolubility of this inorganic salt. On the other hand, copper(II) carbonate is directly involved in the formation of a three-dimensional structure of the epoxy-amine composite under its curing process. At that, the strong Cu(II)–N bonds are formed. It facilitates the compaction of the polymer networks, thereby preventing free penetration of water into the polymer bulk.

Prolonged stay of epoxy-amine composites in 10% aqueous solutions of H_2SO_4 and NaOH showed that polymer samples containing copper(II) carbonate differ only slightly from the equilibrium absorption value of the initial unmodified composite (Table).

The sorption abilities of epoxy-amine composites in acidic and alkaline solutions and in water are close. However, compaction of the spatial lattice of polymer composites results in an increase in their chemical stability. The least equilibrium absorption values are characteristic of the most compact epoxy-amine composite, i.e. containing 20 mass parts of copper(II) carbonate. With decreasing or increasing the mass parts of CuCO_3 , the stability of the polymer samples decreases.

Thus, the sorption ability of epoxy-amine composites modified with copper(II) carbonate in water and alkaline or acidic solutions is lower than that of unmodified epoxy-amine composite. A decrease in the diffusion permeability of the samples is governed by a decrease in the defects resulted from the original internal stresses. The CuCO_3 –PEPA chelation and, consequently, the chelate complex participation in the polymer network structuring, reduce the permeability of polymer coatings in corrosive solutions. The obtained data indicate that a more compacted structure of the polymer is formed in the case of modified composite. At that, the optimal amount of CuCO_3 is in the range of 20 to 40 mass parts.

Conclusions

The physical and mechanical properties of the DGEBA/PEPA- CuCO_3 polymer samples were determined by considering surface hardness, tensile strength, water absorption and chemical resistance. The influence of different amounts of CuCO_3 on the performance properties of epoxy-amine composites modified with copper(II) carbonate was considered. It has been found that the CuCO_3 –PEPA chelation, which triggers the formation of the

Cu(II)–N coordination bonds within the polymeric framework of the epoxy-amine composites containing copper(II) carbonate, results in the compaction of spatial lattices of the polymer, which predetermines their mechanical strength and the chemical resistance to corrosive agents (acids, alkalis, solvents, etc.).

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ПРИНЦИПИ РЕГУЛЮВАННЯ ЕКСПЛУАТАЦІЙНИХ ВЛАСТИВОСТЕЙ САМОЗГАСАЮЧИХ ЕПОКСІАМІННИХ КОМПОЗИЦІЙ, МОДИФІКОВАНИХ КУПРУМ(II) КАРБОНАТОМ

О. Лавренюк, Б. Михалічко

Визначені міцність на розрив, поверхнева твердість, водостійкість і хімічна стійкість полімерних матеріалів на основі самозгасаючих епоксіамінічних композицій, модифікованих купрум(II) карбонатом. Це дало змогу сформувати основу нового типу полімерних матеріалів з покращеними фізико-хімічними і механічними властивостями. Результати експериментів показали, що використання CuCO_3 , який розглядається як антипірен у епоксіамінічних композиціях, полягає не тільки в здатності цієї солі пригнічувати поширення полум'я, тим самим ефективно знижуючи пожежонебезпечність, але і покращувати експлуатаційні характеристики виготовлених полімерних покриттів. Купрум(II) карбонат завдяки своїй винятковій здатності до комплексоутворення легко включається в структуру епоксидного полімеру, що забезпечує композиційним матеріалом збереження експлуатаційних характеристик на належному рівні. Введення до складу епоксіамінічної композиції 20–40 мас.ч. купрум(II) карбонату на 100 мас.ч. зв'язуючого підвищує міцність на розрив на 67,8–87,2%, а поверхневу твердість – на 19,7–21,5% порівняно з вихідною композицією. Також було виявлено, що епоксіамінічні композиції з добавками CuCO_3 характеризуються підвищеною водостійкістю і стійкістю до агресивних середовищ.

Ключові слова: купрум(II) карбонат, хімічно активні антипірени, епоксіамінічні композиції, фізико-механічні властивості, стійкість до агресивних середовищ.

PRINCIPLES OF CONTROLLED EFFECTS ON PERFORMANCE PROPERTIES OF SELF- EXTINGUISHING EPOXY-AMINE COMPOSITES MODIFIED BY COPPER(II) CARBONATE

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This paper reports the results of determination of tensile strength, surface hardness, water resistance and chemical resistance of polymer materials based on the self-extinguishing epoxy-amine composites modified with copper(II) carbonate. This allowed forming the basics of a new type of polymer materials with enhanced physicochemical and mechanical properties. The results of the experiments showed that the use of CuCO_3 , which is considered as a flame-retardant agent of epoxy-amine composites, not only suppresses the spread of the flame, thereby effectively reducing the fire hazard but also improves the performance characteristics of the produced polymer coatings. Due to its exceptional complexing ability, copper(II) carbonate is readily incorporated into the structure of an epoxy polymer, which ensures that the composite materials retain their performance characteristics at an appropriate level. The addition of CuCO_3 to epoxy-amine composites in the amount of 20–40 mass parts per 100 mass parts of binder increases the tensile strength and the surface hardness by 67.8–87.2% and 19.7–21.5%, respectively, in comparison with the original composition. It was also found that epoxy-amine composites with CuCO_3 additives are characterized by increased water resistance and resistance to aggressive environments.

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