

PACS: 82.35 Lr

STUDY OF RADIATION-CHEMICAL STRUCTURING OF COMPOSITIONS BASED ON EPOXY OLIGOMERS

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Received November 19, 2019; revised December 5, 2019; accepted January 22, 2020

The processes of radiation-chemical structuring of modified epoxy acrylic compositions were studied depending on the nature of epoxy oligomers and modifiers. ED-20 and ED-22 grades epoxy oligomers were chosen as epoxidian oligomers; 3,4-epoxyhexahydrobenzal-3,4-epoxy-1,1-bis(hydroxymethyl)cyclohexane (UP-612 grade), 3,4-epoxycyclohexylmethyl-3,3-epoxycyclohexanecarboxylate (UP-632 grade) were chosen as cycloaliphatic oligomers; diethylene glycol diglycidyl ether (DEG) was chosen as aliphatic oligomer. To modify the epoxy oligomers, unsaturated acrylic monomers, such as acrylic acid and methyl acrylic acid ester; aromatic and aliphatic oligoester acrylates, such as α,ω -methacryl(bis-diethylene glycol)phthalate (MDP-1 grade), α,ω -methacryldi(diethyleneglycolphthalate) (MDP-2 grade), α,ω -methacryl(bis-triethyleneglycol)phthalate (MGP-9 grade) and atri-(oxyethylene)- α,ω -dimethacrylate (TGM-3 grade); condensation product of linseed oil dimerized fatty acids and polyethylenepolyamine, such as oligoamide L-20 grade; condensation product of ricinoleic acid, castor oil and maleic anhydride, such as unsaturated polyester PE-220, were used. The thermophysical and relaxation properties of cross-linked polymers, obtained under exposure to γ -radiation of Co^{60} and electrons accelerated by the absorbed radiation dose of 50–150 kGy at the beam current of 2-4 mA and electron energy of 240-300 keV, were studied. The distance from the exhaust window of the accelerator to the irradiated surface of the samples was 63-80 mm. The thermophysical properties of the cured polymers were evaluated using thermomechanical studies on a thermomechanograph with the temperature rise of 1°/min and the pressure of 0.54 MPa in the temperature range of 293-673 K, as well as the differential thermal and thermogravimetric analyzes on a system derivatograph by L. Paulik, R. Paulik, L. Erdei in the temperature range of 293–973 K with the rise rate of 7°/min. The relaxation properties and molecular mobility of the cross-linked polymers were studied by the dielectric method. The dielectric loss tangent was determined in the temperature range of 143-393K at the frequency of 1 kHz using a digital automatic bridge of alternating current R-589. The test sample temperature was measured using a potentiometer on a copper-constantan thermocouple, which was placed in the measuring cell along with the test sample. The samples were cooled by placing the cell in a vessel with liquid nitrogen. As a result of the studies, the influence of the chemical nature of epoxy oligomers and unsaturated modifiers on the processes of structure formation and molecular mobility of polymers, obtained under conditions of radiation-chemical curing, was established. It was determined, that when modifying epoxy oligomers with acrylic acid, methyl acrylic acid ester, oligoester acrylates of MGP-9 ((α,ω -methacryl(bis-triethyleneglycol)phthalate)) or TGM-3 ((tri-(oxyethyleneglycol)- α,ω -dimethacrylate)) grades, the structuring of compositions, based on the DEG-1 aliphatic epoxy oligomer and UP-612 cycloaliphatic oligomer, was more efficient than the compositions based on unsaturated ETO oligomers grade such as 2-ethylhexylepoxytallate oligomer and epoxidian oligomers of ED-20 and ED-22 grades. It was established, that the modifier oligoamide of L-20 grade, containing primary and secondary amino groups, increased the radiation sensitivity of the compositions, based on epoxidian and cycloaliphatic oligomers, and reduced the inhibitory effect of atmospheric oxygen. The optimal composition and the main technological parameters were determined, what allowed to obtain materials with high physical and mechanical properties and adhesive strength to various metals. The application of the developed materials under industrial conditions will make it possible to organize a continuous high-speed radiation-chemical process for producing polymer coatings on metals, providing improved working conditions, lower energy consumption, as compared to the thermochemical process of the coatings production, and will increase the corrosion resistance of metals.

KEY WORDS: radiation-chemical structuring, ionizing radiation, differential thermal analysis, macromolecule, epoxy oligomer

The operational properties of materials, as well as their physical and chemical characteristics, substantially depend on the structure of the cured polymer, the configuration and flexibility of macromolecules, their kinetic properties [1,2]. An important task of technological progress is still the development of technologies providing lower energy consumption and improved working conditions, what allows increasing the service life of products and equipment. One of the directions in the development of high-strength, heat-resistant, and chemically resistant protective materials for metal surfaces is the formation of cross-linked polymers under the thin-layer radiation-chemical structuring [3]. The properties of polymers, obtained under the radiation-chemical structuring, are studied insufficiently. Here, an important role is played by the choice of polymer compositions based on materials produced by industry, the possibility of their modification in order to increase the operational properties of the materials obtained on their basis. It is also important to establish the relationship of the service properties of the selected materials with the structure of the obtained cross-linked polymer, molecular characteristics and concentration of the starting components of the compositions under study. Besides, these properties have a significant impact on the strength and performance characteristics of products, obtained in mass production (hermetic sealing, mass production of protective coatings and products), where these structuring methods contribute to obtaining various types of products with the required set of properties. A special industry of widespread use of polymer composite material (PCM) is general instrument engineering, the manufacture of electronic equipment, where high adhesion, low residual stresses, fast curing speed in mass production, low shrinkage, and high

moisture protection are extremely important. Important indicators of a PCM, obtained under the ionizing radiation exposure, are its thermophysical properties, strength, adhesion to various substrates, and the level of residual stresses, arising at PCM quick structuring under the radiation-chemical curing [4].

The object of this study was to develop the compositions, based on epoxy oligomers, structured at low absorbed radiation doses under conditions of free access of atmospheric oxygen, which could be recommended as metal protective coatings with high adhesion and other operational properties. In this case, one of the effective ways to increase the radiation sensitivity of compositions based on epoxy oligomers, such as modification of them with various unsaturated reactive oligomers (RO) and monomers was used, and the relationship of the properties of the obtained cross-linked polymers with the chemical nature and composition of the starting components was established [5].

RESEARCH METHOD

The above mentioned set of properties was studied on the basis of thermo-mechanical research, differential-thermal and thermo-gravimetric analyzes, and of the research of macromolecules relaxation properties.

The thermophysical and relaxation properties of cross-linked polymers, obtained under exposure to γ -radiation of Co^{60} and electrons, accelerated by the absorbed radiation dose of 50-150 kGy at the beam current of 2-4 mA and the electron energy of 240-300 keV, were studied. The distance from the outlet window of the accelerator to the irradiated surface of the samples was 63-80 mm.

The thermophysical properties of the cured polymers were estimated using thermo-mechanical studies on a thermo-mechanograph with the temperature rise of 1 K/min and the pressure of 0.54 MPa in the temperature range of 293-673 K, as well as by the differential thermal and thermo-gravimetric analyzes using the derivatograph of the system by L. Paulik, R. Paulik, L. Erdei in the temperature range of 293–973 K with the rise rate of 7°/min [6].

The relaxation properties and molecular mobility of the cross-linked polymers were studied by the dielectric method. The dielectric loss tangent was determined in the temperature range of 143-393 K at the frequency of 1 kHz using a digital automatic bridge of alternating current R-589.

The temperature of the test sample was measured using a potentiometer connected to a copper-constantan thermocouple, which was placed in the measuring cell along with the test sample. The samples were cooled by placing the cell in a vessel with liquid nitrogen.

To study the properties of the obtained polymer coatings on metals, standard methods were used [7].

EXPERIMENTAL RESULTS AND DISCUSSION

Thermomechanical studies of compositions based on epoxy oligomers of various chemical nature, modified by unsaturated reactive oligomers (RO) and monomers, which are structured directly under exposure to the ionizing radiation, were carried out. The compositions were cured in bulk by γ -radiation of Co^{60} with the dose of 50-100 kGy.

The nature of the thermomechanical curves of the cured epoxy oligomer – acrylic acid (AA) compositions (the absorbed radiation dose was 63 kGy) (Fig.1) indicates, that the cured products have high rigidity, low deformation (8-15%) and sufficiently high heat resistance (the samples are destroyed at 593 K) [8,9].

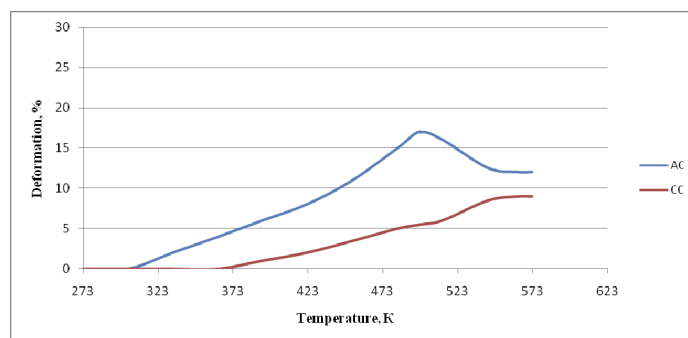


Fig. 1. Thermomechanical curves of polymers based on compositions AC, CC

The composition containing a cycloaliphatic epoxy oligomer CC (cycloaliphatic composition) is structured to form a more rigid structure (the glass transition temperature of the polymer based on this composition is 403 K, which is 80 K higher than that of the composition based on the aliphatic oligomer of DEG grade (AC - aliphatic composition), which is 323 K).

When heating the samples obtained under irradiation with the dose of 420 kGy, some decomposition of polymers with gas release is observed, what indicates to the polymer destruction.

The composition, containing the unsaturated aliphatic epoxy oligomer 2-ethylhexyl epoxytallate of the ETO grade and AA, is not cured with the dose of 100-150 kGy under the effect of both γ -radiation and accelerated electrons.

The compositions, containing the diene epoxy oligomer of ED-20 grade and AA, modified with the PE-220 oligoester, are cured at the dose of 100 kGy to form sufficiently brittle blocks, that are destroyed at mechanical treatment. It is impossible to obtain from them the samples for thermomechanical studies.

The thermomechanical studies of the cured compositions, containing an aliphatic oligomer as an epoxy oligomer, in the presence of modifying components (Fig. 2), showed that the presence of acrylic acid methyl ester (AM) in the composition provides a more elastic polymer composition AC-MM (aliphatic composition - acrylic acid methyl ester modified). The value of deformation in the highly elastic state of the cured composition, containing AM, is 5-7% higher than that of the cured compositions without it (AC-N – aliphatic composition - not modified). In this case the glass transition temperature remains unchanged.

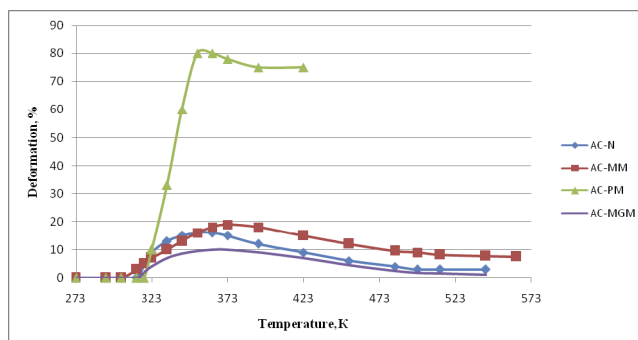


Fig. 2. Thermomechanical curves of polymers based on compositions AC-N, AC-MM, AC-PM

The heat resistance of the composition in the presence of AM is also higher. The destruction temperature is 613 K, while for the composition without it is 555 K.

Modification of the compositions with oligoester PE-220 (PE-220 – polyester) (AC-PM – aliphatic-polyester modified composition) provides samples with lower heat-resistant (destruction at 423 K), with the values of highly elastic deformations higher, than those, when modified with MGP-9 grade oligomer (Fig. 2, AC-MGM (aliphatic composition – methacryl glycol modified), what confirms the conclusion, that PE-220 does not participate in the formation of the cross-linked polymer, but plays the role of a plasticizing agent.

The polymers, obtained by curing the compositions with the participation of the cycloaliphatic epoxy oligomer of UP-612 grade and in the presence of modifying additives, are characterized by greater rigidity (Fig. 3, composition CC-P – cycloaliphatic composition-polymer, UP-612 grade oligomer not modified, CC-PM – cycloaliphatic composition – polymer, UP-612 grade oligomer modified by acrylic acid methyl ester). The presence of AM in the compositions causes a decrease in the glass transition temperature of the samples and an increase in highly elastic deformation (Fig. 3, compositions CC-P and CC-MP). The cured compositions with the participation of the diene epoxy oligomers and oligoamide of L-20 grade have a lower glass transition temperature than in the presence of PE-220 (Fig. 3, compositions DC-PM ((epoxydian (ED-20 grade oligomer) composition - with PE-220 grade oligomer modified by acrylic acid methyl ester)), DC-LM ((ED-20 grade oligomer) composition - with L-20 grade oligoamide (condensation product of linseed oil dimerized fatty acids)) modified by acrylic acid methyl ester).

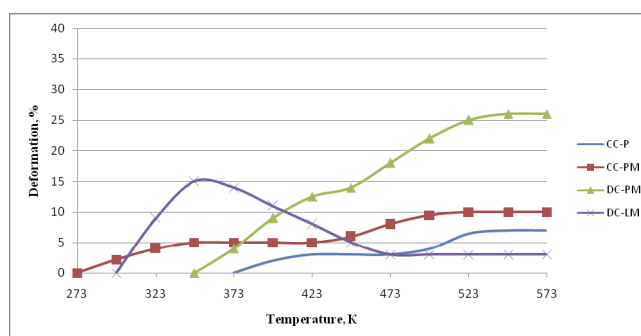


Fig. 3. Thermomechanical curves based on the compositions CC-P, CC-PM, DC-PM, DC-LM

For the polymers, based on compositions involving oligoamide L-20 (composition DC-LM), an additional cross linking of the polymer at the temperature increase is observed. On the thermomechanical curve this is indicated by a smooth decrease in highly elastic deformation.

The samples, obtained by structuring the composition based on ED-20 and UP-612, which is modified with MGP-9, are destroyed at 563–573 K and practically do not deform, what indicates the formation of rigid brittle structures.

Thus, the thermomechanical studies have shown, that during the radiation-chemical curing the epoxy compositions have the cross-linked structure and are characterized by a fairly high heat resistance (563–613 K). More rigid cross-linked polymers are formed at structuring the compositions, based on cycloaliphatic epoxy oligomers and the MGP-9 grade modifier, as compared to the compositions based on the aliphatic diene oligomer and unsaturated oligomer

PE-220. With inclusion of AM into the composition, the highly elastic deformation increases, the glass transition temperature decreases, and the heat resistance increases.

For the compositions containing the aliphatic DEG oligomer, as well as in the presence of L-20 grade oligoamide an increase in temperature causes intensification of the structuring process and a decrease in highly elastic deformation.

The behavior of the compositions cured under the impact of electrons, accelerated by the absorbed radiation dose of 120 kGy, and under exposure to high temperature and oxygen, as well as the polymers thermal stability were studied using DTA (differential thermal analysis) and TG (thermogravimetric) analysis [9,10].

The table presents the data on estimation of the thermal stability of compositions, which are cured by the absorbed radiation dose of 120 kGy and heat-treated at 393 K for 15 minutes.

Table

Thermal stability of polymers obtained when the compositions are irradiated by the absorbed radiation dose of 120 kGy and heat-treated at 393 K for 15 min

Composition	Temperature, K, at which the mass loss is, %					Temperature of maximum mass loss rate, K
	10	20	30	40	50	
DC-LMM	510	576	633	663	693	653
DC2-LMM	513	610	653	676	713	685
CC-LMM	553	590	616	653	700	615
DC-LMT	550	610	653	690	718	683

Modification of the compositions by oligoester acrylate of TGM-3 grade ((DC-LMT – epoxydian (ED-20 grade oligomer) composition – with L-20 grade oligoamide modified by acrylic acid methyl ester and tri-(oxyethyleneglicol)- α,ω -dimethacrylate)) promotes the formation of polymers with greater thermal stability than when they are modified by MGP-9 (DC-LMM composition – epoxydian ((ED-20 grade oligomer) composition – with L-20 grade oligoamide modified by acrylic acid methyl ester and α,ω -methacryl(bis-triethyleneglycol)phthalate)). The epoxy oligomers with lower molecular weight form polymers with higher thermal stability (DC2-LMM and DC-LMM).

The relaxation properties of the compositions cured by γ -radiation of Co⁶⁰ and accelerated electrons were determined by the dielectric method, which is one of the most sensitive methods for studying molecular relaxation used to determine the physical properties of polymers [11].

The research of the processes of the compositions dielectric relaxation depending on the molecular weight and nature of the epoxy oligomer (Fig. 4) showed, that in the molecules, containing the epoxy-oligomer of ED-22 grade (ED – epoxy diane oligomer), the dipole-segmental relaxation process is very weak. Even a slight decrease in the molecular weight of the oligomer, as compared to the ED-20 grade epoxydian oligomer, is accompanied by a shift of the maximum of dipole-segmental relaxation processes toward higher temperatures and indicates the formation of more rigid structures in the cured compositions. In the compositions, based on the cycloaliphatic oligomer, the maximum of the dipole-segmental relaxation processes is in the region of lower temperatures as compared to the polymers, based on the epoxydian oligomer.

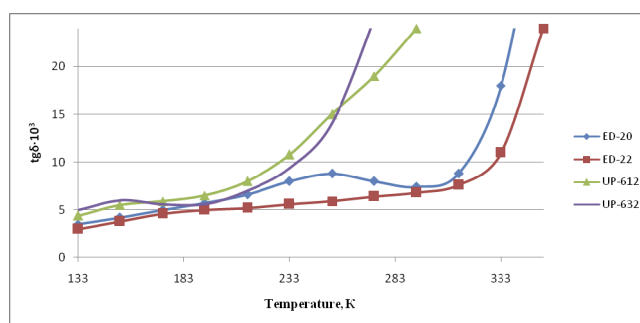


Fig.4. Temperature dependence of $\text{tg}\delta$ cured compositions based on ED-20, ED-22, UP-612, UP-632

On the whole, the dipole-segmental and dipole-radical relaxation processes in the cured compositions under study are observed in the temperature range of 223–283 K and 173–193 K, respectively.

In the compositions, containing the cycloaliphatic epoxy oligomer, in the process of radiation-chemical structuring the destruction processes also occur, resulting in an increase in the materials electrical conductivity at elevated temperatures, what leads to a distortion of the maximum position due to the segmental motion of macromolecules. However, according to the research data, it can be concluded, that the maximum dipole-segmental losses for these polymers are in the region of lower temperatures as compared to the cured compositions, containing Diane epoxy oligomers, what indicates the formation of a more micro-heterogeneous structure in the compositions, containing cycloaliphatic oligomers, and the structure imperfection of their spatial lattice.

The results of studying the influence of the nature of oligoesters with different length of the aliphatic chain and different content of aromatic nuclei on the relaxation properties during the radiation-chemical structuring (Fig. 5)

indicate, that the greatest plasticizing effect is observed when MDP-2, which has a greater amount of aliphatic and aromatic fragments in the molecule, as compared to other oligoester acrylates, is present in the compositions. The maximum dipole-segmental loss of the cured compositions with the participation of MDP-2 is shifted toward lower temperatures and makes 252K. The smallest plasticizing effect is made by MDP-1, which has a shorter aliphatic chain as compared to MGP-9, and a more compact molecule as compared to MDP-2. The maximum dipole-segmental loss in polymers with MDP-1 is shifted toward higher temperatures and makes 283K. MGP-9 and TGM-3 are in an intermediate position (the temperatures of the maxima of the dipole-segmental relaxation process are 254 K and 261 K, respectively).

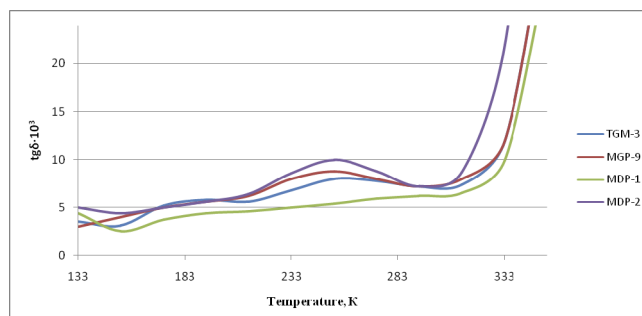


Fig. 5. Temperature dependence of the $tg\delta$ cured compositions based on TGM-3, MGP-9, MDP-1, and MDP-2

On the basis of the results of the research on the thermophysical and relaxation properties of radiation-curable epoxy composites, subject to the molecular characteristics and quantitative composition of the systems, the optimal compositions were chosen, allowing to obtain protective coatings on various metal surfaces (copper, aluminum, steel) with high adhesive strength (grade 1 by the method of lattice notches), bending strength = 1 mm, impact strength = 5 J, hardness = 0.900 rel. units, high chemical resistance, good dielectric properties ($\rho_v = 5,3 \cdot 10^{13}$ Ohm·m; $tg \delta$ at 1 kHz = 0.01 – 0.035; $\epsilon = 2.0 – 6.0$). The highest hardness and glittering effect of the materials are provided by cycloaliphatic oligomer UP-612 and modifier MGP-9.

CONCLUSIONS

Thus, the processes of radiation-chemical structuring of modified epoxy acrylic compositions, subject to the nature of epoxy oligomers and modifiers, were investigated. The thermophysical and relaxation properties of cross-linked polymers, obtained under exposure to γ -radiation of Co^{60} and electrons, accelerated by the absorbed radiation dose of 50–150 kGy, were studied. The influence of the chemical nature of epoxy oligomers and unsaturated modifiers on the processes of structure formation and molecular mobility of polymers was established.

It was determined, that when modifying epoxy oligomers with acrylic acid, methyl acrylic acid ester, MGP-9 or TGM-3 oligoester acrylates, the structuring of compositions, based on the DEG-1 aliphatic epoxy oligomer and UP-612 cycloaliphatic oligomer, was more efficient than with the compositions based on unsaturated ETO grade oligomers such as 2-ethylhexylepoxytallate oligomer and epoxidian oligomers of ED-20 and ED-22 grades. It was established, that the modifier oligoamide of L-20 grade, containing primary and secondary amino groups, increased the radiation sensitivity of the compositions, based on epoxidian and cycloaliphatic oligomers, and reduced the inhibitory effect of atmospheric oxygen.

As a result of the research, the optimal composition and the main technological parameters were determined, what made it possible to obtain materials with high physical and mechanical properties and adhesive strength to various metals. The application of the developed materials under industrial conditions will make it possible to organize a continuous high-speed radiation-chemical process for deposition of polymer coatings on metals, which provides improved working conditions, lower energy consumption as compared to the thermo-chemical process of the coating production, and will increase the corrosion resistance of metals.

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ДОСЛІДЖЕННЯ РАДІАЦІЙНО-ХІМІЧНОГО СТРУКТУРУВАННЯ КОМПОЗИЦІЙ НА ОСНОВІ ЕПОКСИДНИХ ОЛІГОМЕРІВ

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Досліджено процеси радіаційно-хімічного структурування модифікованих епоксикарбонатових композицій в залежності від природи епоксидних олігомерів і модифікаторів. У якості епоксидних олігомерів були обрані епоксидіанові олігомери марок ЕД-20, ЕД-22; у якості циклоаліфатичних олігомерів були обрані 3,4-епоксигексагідробензаль-3,4-епокси 1,1-біс-(гідроксиметил)-ціклогексан, марки УП-612, а також 3,4-епоксиціклогексилметил-3,3-епоксициклогексанкарбоксилат, марки УП-632; і дігліциділовий ефір діетиленгліколю ДЕГ був обраний в якості аліфатичного олігомера. Для модифікації епоксидних олігомерів використовували: ненасичені акрилові мономери, такі як акрилова кислота та складний ефір метілакрилової кислоти; ароматичні і аліфатичні олігоєфірні акрилати, такі як α , ω -метакрил (біс-діетиленгліколь) фталат (марки MDP-1), α , ω -метакриліди (діетиленглікольфталат) (марки MDP-2), α , ω -метакрил (біс-триетиленгліколь) фталат (марки MGP-9), три- (оксіетиленгліколь) - α , ω -диметакрилат (марка TGM-3); продукт конденсації димеризованих жирних кислот лляної олії і поліетиленполіамін, такого як олігоамід марки L-20; продукт конденсації рицинолевої кислоти, касторової олії і малеїнового ангідриду, такого як ненасичений полієфір РЕ-220. Вивчено теплофізичні і релаксаційні властивості сітчастих полімерів, отриманих під дією γ -випромінювання Co^{60} і електронів, прискорених поглиненою дозою випромінювання 50-150 кГр при струмі в пучку 2-4 мА і енергії електронів 240-300 кеВ. Відстань від випускного вікна прискорювача до опромінюваної поверхні зразків становила 63-80 мм. Теплофізичні властивості затверділих полімерів оцінювали за допомогою термомеханічних досліджень на термомеханографі при підйомі температури 1°/хв і тиску 0,54 МПа в інтервалі температур 293-673К, а також методом диференціального термічного і термогравіметричного аналізів на дериватографі системи Л. Паулік, Р. Паулік, Л. Ердеї в інтервалі температур 293-973 К зі швидкістю підйому 7°/хв. Релаксаційні властивості і молекулярну рухливість сітчастих полімерів вивчали діелектричним методом. Визначення тангенса кута діелектричних втрат здійснювали в температурному інтервалі 143-393К при частоті 1 кГц цифровим автоматичним мостом змінного струму Р-589. Вимірювання температури досліджуваного зразка проводили за допомогою потенціометра від термометричного мідь-константан, яка перебувала у вимірювальному відсіку разом із досліджуванним зразком. Охолодження зразків здійснювали шляхом розміщення відсіку в посудину з рідким азотом. В результаті досліджень встановлено вплив хімічної природи епоксидних олігомерів і ненасичених модифікаторів на процеси формування структури і молекулярну рухливість полімерів, отриманих в умовах радіаційно-хімічного затвердіння. Визначено, що при модифікації епоксидних олігомерів акриловою кислотою, метиловим ефіром акрилової кислоти, олігоєфіракрилатом МГФ-9 або ТГМ-3 структурування композицій на основі аліфатичного епоксидолігомера ДЕГ-1 і циклоаліфатичного олігомера УП-612 здійснюється більш ефективно у порівнянні з композиціями на основі ненасиченого олігомеру ОЕТ і епоксидіанових олігомерів ЕД-20 і ЕД-22. Встановлено, що модифікатор олігоамід Л-20, що містить первинні і вторинні аміногрупи, підвищує радіаційну чутливість композицій на основі епоксидіанових і циклоаліфатичних олігомерів і зменшує інгібуючу дію кисню повітря. Визначено оптимальний склад композицій та основні технологічні параметри, що дозволяють отримувати матеріали з високими фізико-механічними властивостями і адгезійною міцністю до різних металів. Застосування розроблених матеріалів у промислових умовах дозволить організувати безперервний високошвидкісний радіаційно-хімічний процес отримання полімерних покриттів на металах з поліпшеними умовами праці, меншими енерговитратами в порівнянні з термохімічним процесом отримання покриттів, і забезпечить підвищення корозійної стійкості металів.

КЛЮЧОВІ СЛОВА: радіаційно-хімічне структурування, іонізуюче випромінювання, диференційно-термічний аналіз, макромолекула, епоксидний олігомер

ИССЛЕДОВАНИЕ РАДИАЦИОННО-ХИМИЧЕСКОГО СТРУКТУРИРОВАНИЯ КОМПОЗИЦИЙ НА ОСНОВЕ ЭПОКСИДНЫХ ОЛИГОМЕРОВ

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Исследованы процессы радиационно-химического структурирования модифицированных эпоксикарбонатовых композиций в зависимости от природы эпоксидных олигомеров и модификаторов. В качестве эпоксидных олигомеров были выбраны эпоксидиановые олигомеры марок ЭД-20, ЭД-22; в качестве циклоаліфатических олигомеров были выбраны

3,4-эпоксигексагидробензаль-3,4-эпокси 1,1-бис-(гидроксиметил)-циклогексан, марки УП-612, а также 3,4-эпоксициклогексилметил-3,3-эпоксициклогексанкарбоксилат, марки УП-632; и диглицидиловый эфир диэтиленгликоля ДЭГ был выбран в качестве алифатического олигомера. Для модификации эпоксидных олигомеров использовали: ненасыщенные акриловые мономеры, такие как акриловая кислота и сложный эфир метилакриловой кислоты; ароматические и алифатические олигоэфирные акрилаты, такие как α , ω -метакрил (бис-диэтиленгликоль) фталат (марки MDP-1), α , ω -метакрилди (диэтиленгликольфталат) (марки MDP-2), α , ω -метакрил (бис-триэтиленгликоль) фталат (марки MGP-9), три- (оксидиэтиленгликоль) - α , ω -диметакрилат (марка TGM-3); продукт конденсации димеризованных жирных кислот льняного масла и полиэтиленполиамина, такого как олигоамид марки L-20; продукт конденсации рицинолевой кислоты, касторового масла и малеинового ангидрида, такого как ненасыщенный полиэфир PE-220. Изучены теплофизические и релаксационные свойства сетчатых полимеров, полученных под действием γ -излучения Co^{60} и ускоренных электронов поглощенной дозой излучения 50-150 кГр при токе в пучке 2-4 мА и энергии электронов 240-300 кэВ. Расстояние от выпускного окна ускорителя до облучаемой поверхности образцов составляло 63-80 мм. Теплофизические свойства отвержденных полимеров оценивали с помощью термомеханических исследований на термомеханографе при подъеме температуры 1 °/мин и давлении 0,54 МПа в интервале температур 293-673К, а также методом дифференциального термического и термогравиметрического анализов на дериватографе системы Л. Паулик, Р. Паулик, Л. Эрдеи в интервале температур 293-973 К со скоростью подъема 7 °/мин. Релаксационные свойства и молекулярную подвижность сетчатых полимеров изучали диэлектрическим методом. Определение тангенса угла диэлектрических потерь осуществляли в температурном интервале 143-393К при частоте 1 кГц цифровым автоматическим мостом переменного тока Р-589. Измерение температуры исследуемого образца проводили с помощью потенциометра от термодпары медь-константан, которая находилась в измерительной ячейке вместе с исследуемым образцом. Охлаждение образцов осуществляли путем помещения ячейки в сосуд с жидким азотом. В результате исследований установлено влияние химической природы эпоксидных олигомеров и ненасыщенных модификаторов на процессы формирования структуры и молекулярную подвижность полимеров, полученных в условиях радиационно-химического отверждения. Определено, что при модификации эпоксидных олигомеров акриловой кислотой, метиловым эфиром акриловой кислоты, олигоэфиракрилатами МГФ-9 или ТГМ-3 структурирование композиций на основе алифатического эпоксиолигомера ДЭГ-1 и циклоалифатического олигомера УП-612 осуществляется более эффективно по сравнению с композициями на основе ненасыщенного олигомера ОЭТ и эпоксидиановых олигомеров ЭД-20 и ЭД-22. Установлено, что модификатор олигоамид L-20, содержащий первичные и вторичные аминогруппы, повышает радиационную чувствительность композиций на основе эпоксидиановых и циклоалифатических олигомеров и уменьшает ингибирующее действие кислорода воздуха. Определен оптимальный состав композиций и основные технологические параметры, позволяющие получать материалы с высокими физико-механическими свойствами и адгезионной прочностью к различным металлам. Применение разработанных материалов в промышленных условиях позволит организовать непрерывный высокоскоростной радиационно-химический процесс получения полимерных покрытий на металлах с улучшенными условиями труда, меньшими энергозатратами по сравнению с термхимическим процессом получения покрытий и обеспечит повышение коррозионной стойкости металлов.

КЛЮЧЕВЫЕ СЛОВА: радиационно-химическое структурирование, ионизирующее излучение, дифференциально-термический анализ, макромолекула, эпоксидный олигомер