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Influence of electron irradiation on mechanical properties of epoxy polymers

The effect of different absorbed doses of electron irradiation with the energy of 12 MeV and heat treatment on the mechanical properties of ED-20 epoxy-dianic resin with hardener PEPA (11, 12 and 13 parts by weight per 100 parts by weight of epoxy resin) was investigated. Heat treatment of irradiated epoxy resin samples was performed in two modes: before or after electron irradiation. It is shown that the optimal choice of the content of hardener PEPA and using electron irradiation with the energy of 12 MeV in the integrated combination with heat treatment allow significantly improve the mechanical properties of epoxy-dianic resin. It was established that for the content of the hardener 12 parts by weight and absorbed doses of 10–20 kGy, the boundary of strength increases in 3 times, and additional heat treatment both before and after irradiation reduces this figure through the thermal destruction. Only for the content of hardener 11 and 13 parts by weight and these absorbed doses heat treatment of irradiated samples of epoxy resin leads to an increase in the boundary of strength. In doing so, the hardness increases regardless of the content of hardener for the absorbed doses greater than 50 kGy.

Key words: electron irradiation, heat treatment, epoxy-dianic resin, PEPA hardener, boundary of strength, hardness, mechanical properties, absorbed dose.

Introduction

Approximately 50 years have elapsed since the researchers first began to study the effect of ionizing radiation on polymeric materials and discovered, under its influence, the formation of additional chemical bonds and other beneficial effects in these materials [1]. The obtaining and application of composite materials, their radiation modification and stability have always been a pressing problem of science and technology [2–5]. Radiation-modified polymer materials are widely used in electronic, cable, electrochemical industries [4, 5]. The irradiation technologies used for the treatment of polymers contain a variety of techniques and sources of radiation. In particular, known methods of solidifying polymer-composite materials using magnetic fields and irradiation [6–9] are known. Today there is significant commercialization, which is aimed at treatment polymers by radiation. Important new products, obtaining which have become available due to radiation technologies, continue to enter the market, and interesting innovations in the application of radiation for high molecular weight materials are under research around the world.

Therefore, an important scientific and applied task of modern materials science is the search of methods of radiation treatment of polymeric materials to improve their physico-chemical and operating properties. In particular, establishing optimal conditions for electron irradiation and heat treatment will enhance the mechanical properties of epoxy polymers, which can be used for the creation of high quality structural and antifriction materials for mechanical engineering and instrumentation, which will have lower cost, lower weight, durability, increased resistance to aggressive environments. Obtaining such materials requires the study of the effect of various modes of electron irradiation and heat treatment on the mechanical properties of epoxy polymers, which is the main purpose of this work.

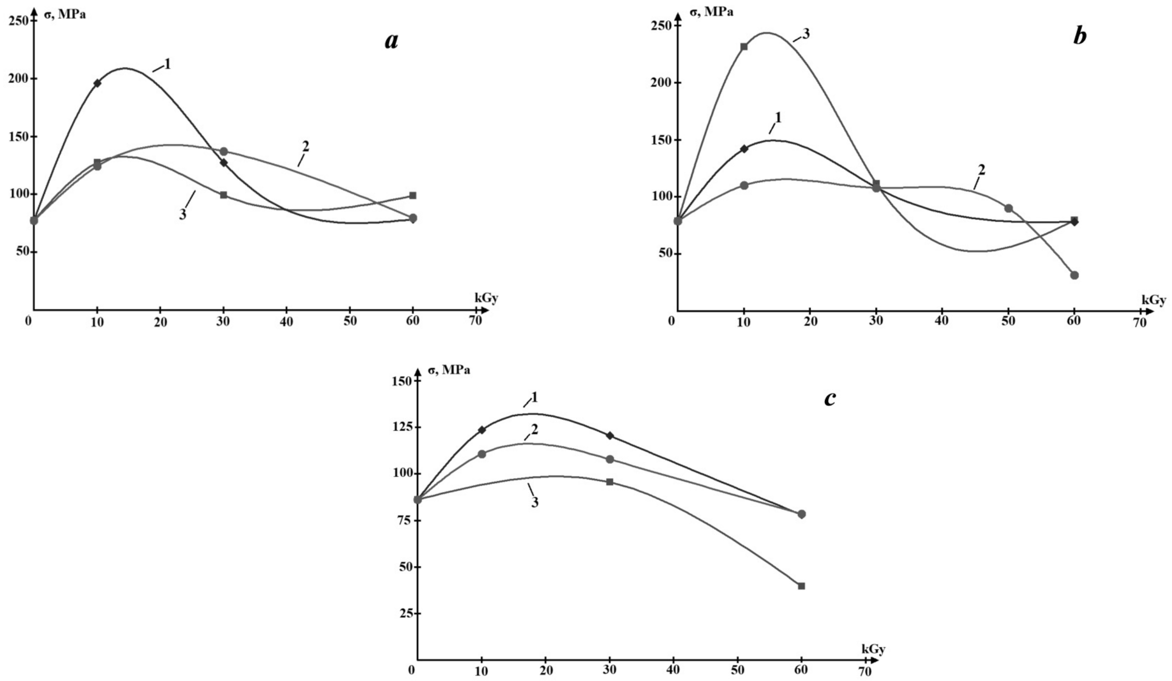
Experimental

The effect of irradiation with different doses of electrons with the energy of 12 MeV on the mechanical properties of ED-20 epoxy-dianic resin with hardener polyethylene polyamine (PEPA) (11, 12, 13 parts by weight per 100 parts by weight of epoxy resin) was investigated. The composition was poured into special forms, resulting in the samples of a cylindrical shape with a height h=1.5 cm and a diameter d=1 cm and parallelepiped shape samples measuring 1×1.5×1.5 cm for researching of the boundary of strength and hardness, respectively. Three methods of curing the epoxy polymer were used. The initial curing process in all three modes continued for 24 hours under normal conditions. The samples of the first group were irradiated with different electron doses. The samples of the second group after irradiation were further heat treated. The samples of the third group before irradiation were heat treated. The heat treatment was a stepwise drying process in a furnace at temperatures of 70… 130 °C for 6 hours. The samples of the epoxy resin were irradiated at the Institute of Electronic Physics on the microtron M-30 by the electron energy of 12 MeV and doses from 5 to 60 kGy. To ensure the stability of the room temperature of irradiation, which was recorded by a copper-constant differential thermocouple, the test samples were blown with nitrogen vapour. The compressive strength in conditions of normal separation was determined according to GOST 14759–69. The research was carried out on the UMM-5 breaking machine for the speed of movement of the lower traverse of 2 mm/min. In the studies of hardness, the samples were made in the form of a parallelogram with a smooth surface. In this case, a steel ball with a diameter of 5 mm was pressed into the surface of the tested material with an appropriate load for 60 seconds. The effort was chosen so that there remained a visible imprint whose diameter is smaller than the diameter of the ball. To determine the hardness, a table of the dependence of the hardness value on the diameter of the imprint, which was determined using a magnifying glass with a scale, was used.

Results and discussion

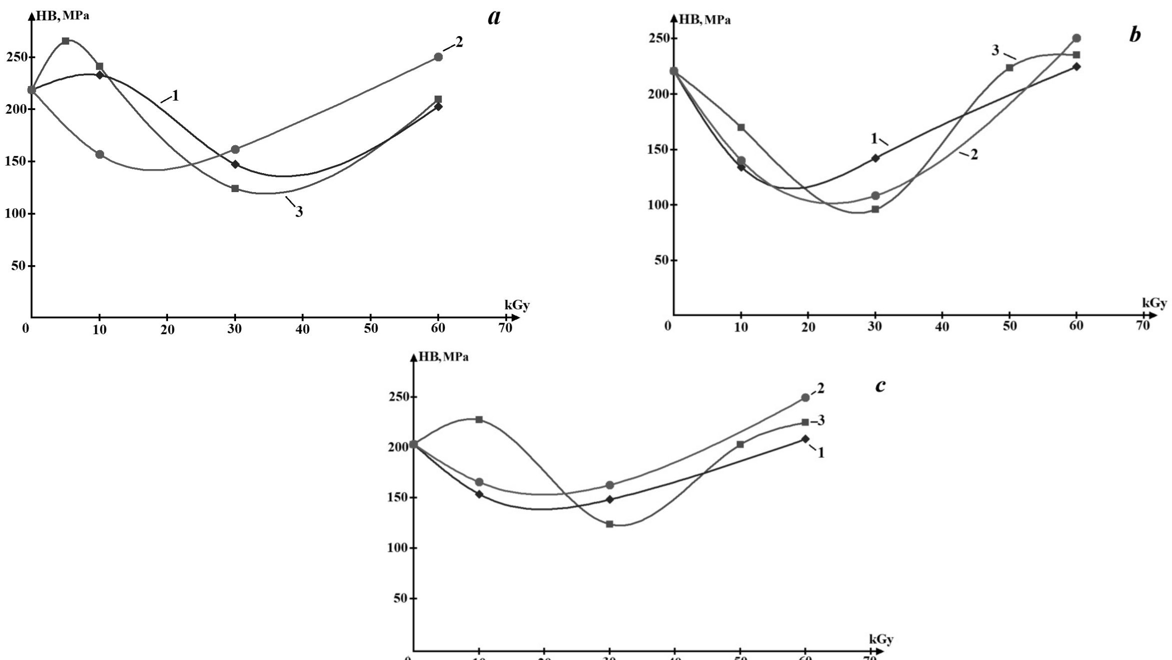
Figure 1 shows the dependencies of the boundary of strength for epoxy-dianic resin on the absorbed doses of electron irradiation. As can be seen from Figure 1, the strength of the epoxy polymer, which is obtained by different methods, increases for irradiation doses up to 10–20 kGy, and then monotonically decreases with increasing dose. In polymeric materials, the processes of excitation and ionization of polymer molecules take place under the action of irradiation resulting in the chemical bonds be torn in the polymer macromolecule and free radicals are forming [10]. The interaction of free radicals with the chains of polymer macromolecules leads to the formation of additional intermolecular bonds («cross-linking» of the polymer) and in process of their accumulation — spatial networks. The Young modulus and therefore strength and hardness for the polymer increase with increasing the number of such bonds. The destruction of intermolecular bonds under the action of irradiation leads to the destruction of the polymer matrix and, accordingly, to the reduction of the strength and hardness of the polymer. The probability of these two mechanisms of chemical transformations in polymers determines their physico-mechanical properties. As is known from the theory of material resistance [11], the critical mechanical stress of the material's destruction is directly proportional to Young's modulus. Therefore, such specific dependencies of the boundary of strength on the absorbed dose for samples of epoxy polymers are associated with changes in the value of the Young modulus under irradiation. Two processes are happening in polymers under the influence of electron irradiation: transverse «cross-linking» and destruction [10, 12]. The transverse «cross-linking» resulting in macromolecules of the polymer through creating transverse chemical bonds between linear macromolecules. The volatile products and macromolecules of less length are formed under the destruction of macromolecules. Also, the destruction of polymer molecules could be happening due to additional heat treatment. Besides, creating of microcracks, the size and depth of which depends on the irradiation dose are possible in the volume of polymers under the electron irradiation with the energy $E > 2$ MeV [13].

The maximum relative increase of the boundary of strength is equal to 3 (see Fig. 1 b) for the content of hardener 12 parts by weight at the electron irradiation without heat treatment. In this case, additional heat treatment, both before and after irradiation, reduces the strength due to thermal destruction. Only additional thermal treatment of irradiated epoxy polymers with the content of hardener of 11 and 13 parts by weight by the doses of 10–20 kGy leads to the increasing boundary of strength. According to the results of our previous work [14], the boundary of strength for epoxy-dianic resin with the content of hardener 12 parts by weight, which was irradiated by the electrons with an energy of 10 MeV and much greater doses (about 0.2 MGy), increases less than 2 times.



a — 11 parts by weight; *b* — 12 parts by weight; *c* — 13 parts by weight;
1 — samples of epoxy polymer, which initially were irradiated, followed by additional heat treatment;
2 — samples of epoxy polymer, which initially exposed the additional heat treatment before irradiation;
3 — the same irradiated samples without additional heat treatment

Figure. 1. The dependencies of the boundary of strength on the absorbed doses of electron irradiation for an epoxy-dianic resin with different content of PEPA hardener



a — 11 parts by weight; *b* — 12 parts by weight; *c* — 13 parts by weight;
1 — samples of epoxy polymer, which initially exposed the additional heat treatment before irradiation;
2 — samples of epoxy polymer, which initially were irradiated, followed by additional heat treatment;
3 — the same irradiated samples without additional heat treatment

Figure 2. The dependencies of the hardness on the absorbed doses of electron irradiation for an epoxy-dianic resin with different content of PEPA hardener

The maximum increase of the boundary of strength for an epoxy-dianic resin at doses of 10–20 kGy may be related to the dominant role of transverse intermolecular «cross-linking». Processes of radiation destruction and creating of microcracks, which lead to the reduction boundary of strength, are becoming effective for doses of more than 20 kGy. Also, the mass fraction of hardener in the epoxy resin significantly affects the magnitude of the boundary of strength of the obtained samples of epoxy polymer. Similar considerations can be made regarding the obtained results of hardness for irradiated samples of epoxy resin (Fig. 2).

However, a distinctive feature of the dependencies the hardness of the epoxy resin is their increasing at irradiation doses greater than 30 kGy, and the additional heat treatment of the irradiated samples by such electron doses leads to an increase of the hardness. In this case, the formation of microcracks can make a secondary contribution to reducing the material hardness than the boundary of strength.

Conclusions

Conducted studies of the influence of heat treatment and high-energy electron irradiation on the mechanical properties of epoxy-dianic resin made it possible to establish the optimum technological conditions for obtaining this epoxy polymer with elevated values of the boundary of strength and hardness. Peculiarities of the formation of the structure and mechanical properties of epoxy resin under the action of electron irradiation and heat treatment are determined by the different relative contribution of the mechanisms of cross-linking, radiation destruction and the formation of microcracks. The obtained results can find their practical use in nuclear power, instrument making, mechanical and aircraft engineering for the creation of lighter, cheaper coatings and structural materials based on epoxy resin.

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Ю.А. Удовицкая, С.В. Лунёв, В.Т. Маслюк, И.Г. Мегела

Эпоксиполимерлердің механикалық қасиеттеріне электронды сәулеленудің әсері

ПЭПА қатайтқышы бар (11, 12 және 13 мас. с. бөліктері 100 мас.с. бөлікке эпоксидті шайыр) ЭД-20 маркалы эпоксидті-диан шайырының механикалық қасиеттеріне 12 МэВ энергиясы бар электронды сәулеленудің және термиялық өңдеудің әртүрлі жұтылған дозаларының әсері зерттелген. Эпоксидті шайырдың сәулеленген үлгілерінің термиялық өңдеуі екі режимде жүргізілді: сәулеленуден бұрын немесе электрондармен сәулеленуден кейін. ПЭПА қатайтқышының құрамын оңтайлы таңдауы және 12 МэВ энергиясы бар электронды сәулеленуді термиялық өңдеумен кешенді түрде қолдану эпоксидті-диан шайырының механикалық қасиеттерін едәуір жақсартатыны көрсетілген. Қатайтқыш құрамы 12 мас. с. және 10–20 кГр жұтылған дозалар үшін беріктік шегі 3 есе артатыны, ал қосымша термиялық өңдеу кезінде, сәулеленуге дейін және одан кейін, термиялық деструкцияға байланысты көрсеткішті төмендететіні анықталған. Эпоксидті шайырдың сәулеленген үлгілерінің термиялық өңдеуі 10–20 кГр жұтылған дозаларда тек 11 және 13 мас. с. қатайтқыш құрамы үшін олардың беріктік шегінің өсуіне әкеледі. Сонымен бірге қаттылық 50 кГр аса үлкен мөлшерде жұтылған дозаларда қатайтқыштың құрамына қарамастан артады.

Кілт сөздер: электронды сәулелену, термиялық өңдеу, эпоксидті шайыр, қатайтқыш, беріктік шегі, қаттылық, механикалық қасиеттер, жұтылған доза.

Ю.А. Удовицкая, С.В. Лунёв, В.Т. Маслюк, И.Г. Мегела

Влияние электронного облучения на механические свойства эпоксиполимеров

Исследовано влияние различных поглощенных доз электронного облучения с энергией 12 МэВ и термообработки на механические свойства эпоксидно-диановой смолы марки ЭД-20 с отвердителем ПЭПА (11, 12 и 13 мас. ч. на 100 масс. ч. эпоксидной смолы). Термообработка облученных образцов эпоксидной смолы проводилась в двух режимах: до и после облучения электронами. Показано, что оптимальный выбор содержания отвердителя ПЭПА и использование электронного облучения с энергией 12 МэВ в комплексном сочетании с термообработкой позволяют значительно улучшить механические свойства эпоксидно-диановой смолы. Было установлено, что для содержания отвердителя 12 мас. ч. и поглощенных доз 10–20 кГр предел прочности возрастает в 3 раза, а дополнительная термообработка, как до, так и после облучения, снижает данный показатель за счет термической деструкции. Термическая обработка облученных образцов эпоксидной смолы приводит к росту их предела прочности только для содержания отвердителя 11 и 13 мас. ч. при поглощенных дозах 10–20 кГр. При этом твердость возрастает, независимо от содержания отвердителя при поглощенных дозах, больших за 50 кГр.

Ключевые слова: электронное облучение, термообработка, эпоксидная смола, отвердитель, граница прочности, твердость, механические свойства, поглощенная доза.

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