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OPTIMIZATION OF THE PROCESS OF OBTAINING EPOXIDIZED NATURAL RUBBER FOR THE DEVELOPMENT OF NEW COMPOSITE MATERIALS ON ITS BASIS

Об'єктом дослідження є процес епоксидування скрапу натурального каучуку. Епоксидований натуральний каучук (ЕНК) має широкий діапазон застосування, наприклад, в покриттях бігових доріжок, шинах спеціального призначення, ремінних передачах, шлангах, взутті, клеях, герметиках, підлогових покриттях і інших галузях, де використовували тільки спеціальні синтетичні каучуки. Натуральний каучук (НК) модифікується реакцією епоксидування для досягнення більш високої маслостійкості, підвищеної адгезії, атмосферостійкості і демпфуючих характеристик матеріалів з його застосуванням. Перспективною є переробка вторинного, невідповідного стандартам, натурального каучуку (скрапу) як сировини для отримання ЕНК. Таким чином, вирішується завдання утилізації скрапу і повернення його в виробничий цикл. Для реалізації завдання епоксидування вторинного каучуку вивчалася можливість проведення суміщених фізико-хімічних процесів в двофазному середовищі вода-ксилол в одному реакційному просторі для зниження загальних енергетичних витрат. Використання суміщеного реакційно-роздільного процесу для епоксидування скрапу натурального каучуку дозволяє вирішити проблему накопичення і утилізації відходів каучукового виробництва найбільш ефективним способом. Вдалося отримати продукт з регульованим ступенем функціоналізації без значної кількості побічних продуктів. Для пошуку оптимального режиму проведення суміщеного реакційно-роздільного процесу епоксидування застосовувався метод планованого експерименту з отриманням рівняння регресії з його подальшим аналізом. Отримане рівняння регресії дозволило оптимізувати умови ведення процесу епоксидування НК з отриманням продуктів із заданими властивостями. В результаті реалізації планованого експерименту встановлено, що епоксидування при температурі 93 °С розведеного (10 % мас.) розчину натурального каучуку надоцтової кислоти, що утворюється «in situ», забезпечує більш високий ступінь епоксидування. Підібрано умови і співвідношення компонентів, при яких НК зберігає агрегативну стійкість в процесі епоксидування в середовищі вода-ксилол.

Ключові слова: *натуральний каучук, епоксидування, суміщений процес, реакційно-роздільний процес, утилізація скрапу.*

1. Introduction

Obtaining new composite materials based on epoxidized natural rubber (ENR) is a promising area of research [1, 2]. In industry, ENRs are synthesized by carrying out an epoxidation reaction of natural rubber in a suspension containing a significant amount of gel particles with peracetic acid formed in situ. The epoxidation reaction is a random process and, therefore, the addition of oxygen to double bonds occurs randomly, distributed along the polymer molecule. The rate of epoxidation increases with increasing rubber concentration [3].

ENR latexes are obtained by epoxidation of natural rubber (NR) at the latex stage in a suspension containing a significant amount of gel particles with peracetic acid [4] or using glacial acetic acid and hydrogen peroxide [5].

It is found that, using the technology of processing latex of nanocrystals, open-ring components increase with the reaction temperature and reaction time. It has been established that as the degree of epoxidation increases, the number of tetrahydrofuran rings increases [6].

The possibility of conducting combined physicochemical processes in a two-phase water-xylene medium in one reaction space with a decrease in the total energy costs was studied. A scheme of the process of epoxidation of scrap of NR with peracids in a water-xylene petroleum medium in a thermally insulated reactor was proposed [7].

Epoxidized natural rubber in the form of latex has good performance properties and has a wide range of applications. ENR-based latexes are potentially useful materials that have unique properties, such as: high resistance to oils and aging; have a high glass transition temperature. At a temperature of 20 °C, the relative permeability of air varies from NR, ENR 25, ENR 50, ENR 70, to the most permeable synthetic rubber [8].

Two degrees of epoxidation of 25 mol % (ENR-25) and 50 mol % (ENR-50) were studied for their potential use as commercial rubbers, and both are proposed as materials

for the development of composite materials. Excellent enhancement of ENR is achieved using siliceous fillers, which allows to obtain a given level of strength even in the absence of binding agents [9].

An industrial methodology and hardware design for the scrap processing (waste products of natural rubber production) are developed and proposed by the authors [10].

Therefore, it is relevant to obtain new epoxidation products based on natural rubber scrap with improved physicochemical and technological properties.

Thus, *the object of research* is the process of epoxidation of natural rubber scrap.

The aim of research is obtaining products with a controlled epoxidation degree.

2. Methods of research

To implement the planned experiment, it is necessary to consider in detail the reaction process that occurs during the epoxidation of natural rubber and select the influencing factors.

The epoxidation reaction proceeds in two stages: at the first stage, the formation of a strong oxidizing agent – peracetic acid, at the second stage, the peroxy acid reacts with double bonds of 1,4-cis-polyisoprene with the formation of an oxirane ring [11]:
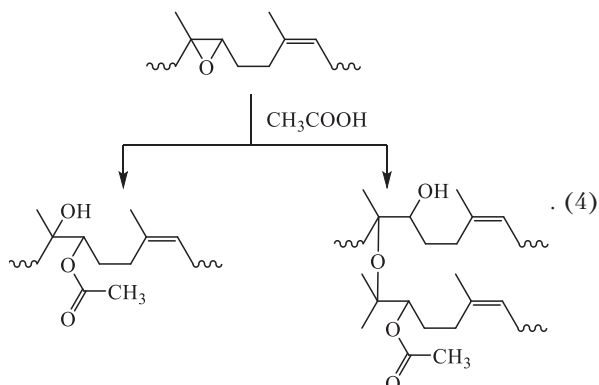
$$CH_3COOH + H_2O_2 \rightleftharpoons CH_3COOOH + H_2O, \quad (1)$$
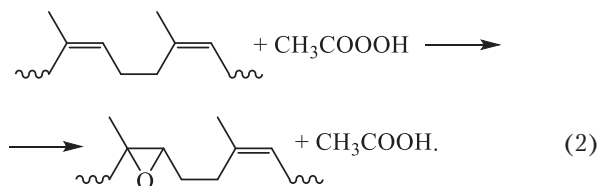
Epoxidized natural rubber in the solution is unstable, reactions can occur over time:

– hydration of the oxirane ring in the presence of water and acid:
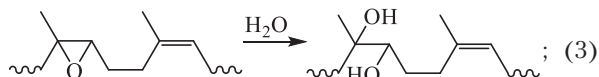
– opening of the epoxy ring with the formation of carboxyl groups or cross-linking [12]:

Taking into account the complex mechanism of organic reactions and the presence of a number of adverse reactions, the yield of the target product is a function of many variables (temperature, pressure, component concen-

trations, time, hydrodynamic conditions, physicochemical properties of solutions, etc.). To solve the problem, the experiment planning method was selected [13].

Based on previous studies [7, 11, 14], the following variation factors are identified:

– reaction temperature $t_{epox.}$, °C – X_1;
– reaction time $\tau_{epox.}$, – X_2;
– dosage of epoxidizing agent (EA) – hydrogen peroxide CH_2O_2, mol %. – X_3.

The epoxidation degreeper mole was taken as a state variable – Y.

This involves setting the planned experiment according to plan 23 into three factors and 8 experiments. The experiments are performed without randomization.

The epoxidation process is carried out in a batch reactor – a thermally insulated three-necked flask equipped with a thermometer, reflux condenser and heater. Let's use a 10 % by weight solution of natural rubber scrap in petroleum xylene, as well as aqueous solutions of 5 % by weight acetic acid and 35 % by weight hydrogen peroxide.

The study of the kinetics of the epoxidation process [11] allows the following limitations to be formed for factors:

– temperature – $89 < X_1 < 93$ °C;
– reaction time without taking into account the heating time – $0.5 < X_2 < 1.5$ hours;
– the amount of hydrogen peroxide – $20 < X_3 < 40$ mol. %.

The temperature variation range is adopted on the basis of data on the maximum reaction rate with the minimum degree of occurrence of adverse reactions [11]. Based on certain restrictions, an experiment planning matrix is formed (Table 1).

Table 1

The matrix of the planned experiment

Name		X_1	X_2	X_3
Zero level, X_{io}		91	1	30
Interval of variation, ΔX_i		2	0.5	10
Upper level, X_{iu}		93	1.5	40
Lower level, X_{il}		89	0.5	20
Units		°C	h	mol %
Experiment	State variable Y, mol. %	Plan		
		X_1	X_2	X_3
1	26.86	1	1	1
2	24.71	−1	1	1
3	17.84	1	-1	1
4	15.72	−1	−1	1
5	11.92	1	1	−1
6	10.85	−1	1	−1
7	6.24	1	−1	−1
8	6.05	−1	−1	−1

After isolation from the reaction mass, the technical product of epoxidation of nanocrystals is analyzed for the residual content of double bonds (iodine number) according to the Ganus method [15]. The percentage of epoxy oxygen in the epoxidized product (epoxy number) is determined by reverse titration of excess HCl [16].

3. Research results and discussion

Based on the data obtained, it is calculated:
– conversion (C) EA: ratio of the iodine number of the epoxidation product to the iodine number of the starting rubber (Table 2);
– epoxidation degree (ED): the ratio of the proportion of EA that went into the formation of epoxy groups to the initial amount of EA (Table 3);
– conversion degree (CD): the ratio of the EA proportion that went into the practical formation of epoxy groups to its theoretical amount (Table 3).

As a result of the implementation of the planning matrix (Table 1), the linear regression equation is obtained:

$$Y = 15.024 + 0.691 \cdot X_1 + 3.561 \cdot X_2 + 6.259 \cdot X_3. \qquad (5)$$

As follows from equation (5), the third factor, the concentration of hydrogen peroxide, has the greatest influence on the yield of the finished product. The following factors for the degree of influence are: temperature and time of the epoxidation process.

To create composite materials and industrial applications, the products of experiments 1 and 2 (ENK-25) are recommended, for the preparation of which the degree of conversion of the epoxy agent exceeds 60 %.

Qualitative analysis of the products was carried out using infrared spectroscopy (IR spectroscopy) on a Specord 75 IR spectrophotometer (Germany) of films with a thickness of 40–50 μm of the original scrap of natural rubber and the obtained epoxidized rubbers on silica glass in a wide wavelength range. Particular attention is paid to the absorption bands of epoxy, hydroxyl, and carboxyl groups (Fig. 1).

Table 2

Determination of the conversion degree of the epoxy agent (C) by the practical iodine number (I_P)

No.	Initial rubber	Planned experiment							
		1	2	3	4	5	6	7	8
I_P, g per 100 t of rubber	149.97	99.92	103.93	116.73	120.68	127.76	129.75	138.34	138.70
K, %	–	66.63	69.30	77.84	80.47	85.19	86.52	92.25	92.49

Table 3

Determination of the conversion degree of the epoxy agent (CD) with the ratio of its practical (ΔX_P) to the theoretical (ΔX_T) amount that went into the epoxidation of natural rubber

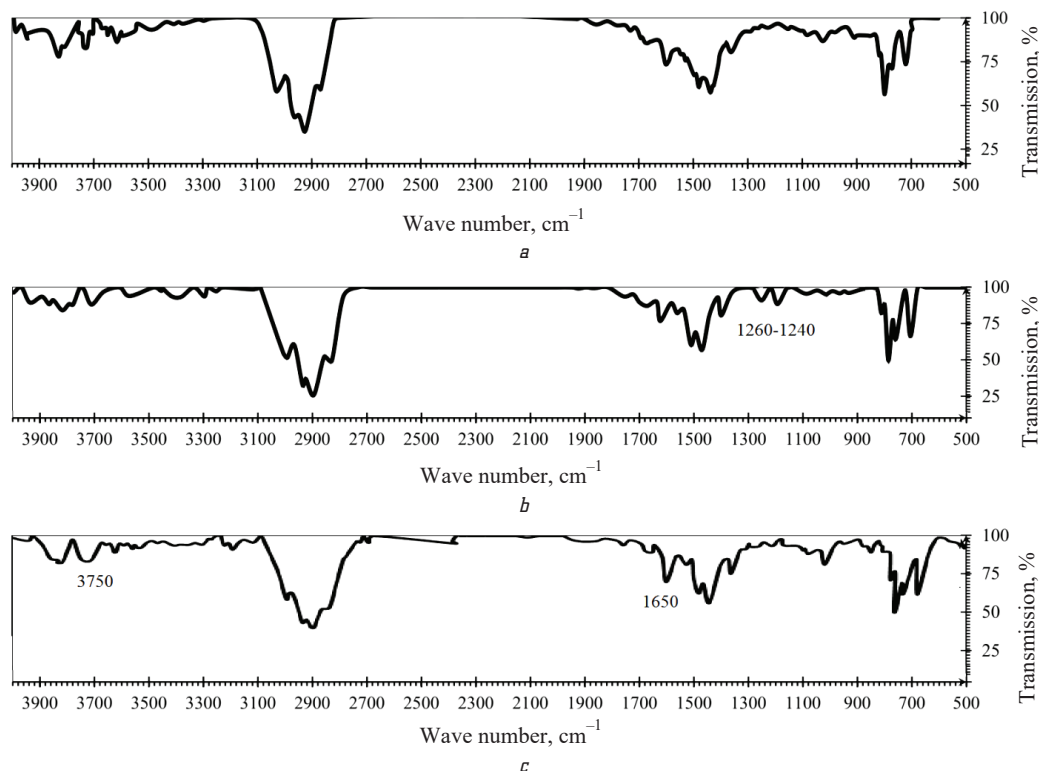| No.	Planned experiment							
	1	2	3	4	5	6	7	8
ΔX_P, % mol	26.86	24.71	17.84	15.72	11.92	10.85	6.24	6.05
ΔX_T, % mol	40.00	40.00	40.00	40.00	20.00	20.00	20.00	20.00
CD, %	67.15	61.78	44.60	39.30	59.60	54.25	31.20	30.25

Fig. 1. Characteristic infrared spectra: a – source material – scrap of natural rubber; b – epoxidized NR (experiment 2); c – epoxidized NR (experiment 6)

The presence of epoxy groups at the maximum degree of epoxidation is confirmed by the presence of absorption bands in the range of $1260-1240$ cm^{-1} in the IR spectra of the products (Fig. 1, *b*) corresponding to stretching vibrations of the epoxy ring [17, 18]. This mode of production of ENR is characteristic at a temperature of 93 °C and a maximum concentration of EA – 40.0 mol. %

The presence of absorption bands of hydroxyl groups at 3750 cm^{-1} and intense at 1650 cm^{-1} confirms the passage of the reaction of the opening of the epoxy cycle (4). Therefore, with an insignificant epoxidation degree (less than 11.0 % mol), the concentration ratio of the epoxy group/acetic acid increases, which leads to its opening by reaction (4).

4. Conclusions

The regression equation obtained in the work allows optimizing the conditions for conducting the process of epoxidation of nanocrystals and obtaining products with desired properties. Synthesized epoxidized rubber can be used in the development of new composite materials, including as a protective coating of metals [19, 20].

Thus, it is found that epoxidation at a temperature of 93 °C of a diluted (10 % wt. %) solution of natural rubber with peracetic acid formed «in situ» provides a higher epoxidation degree. The conditions and ratios of the components are selected under which NR retains aggregative stability during epoxidation in a water-xylene medium.

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