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HARDWARE DESIGN OF THE EPOXIDATION PROCESS OF NATURAL RUBBER WASTE

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Abstract. The objectives of this study were to examine the process of epoxidation scrap NR in a two-phase liquid-gas environment, the development of equipment design and energy-efficient method of performing this process. The presence of the epoxy groups in obtained ENR was confirmed by infrared spectroscopy. In addition to the qualitative analysis was conducted quantitative measurement of unsaturation rubbers and the concentration of epoxy groups in the ENR by titration methods. The loop reactor for recycling of scrap NR by epoxidation was designed. The reactor allows to work with viscous solutions of rubber and provides the necessary heating and mixing with the epoxidizing agent.

Keywords: Epoxidation, natural rubber scrap, reactor.

АППАРАТНОЕ ОФОРМЛЕНИЕ ПРОЦЕССА ЭПОКСИДИРОВАНИЯ ОТХОДОВ ПРОИЗВОДСТВА НАТУРАЛЬНОГО КАУЧУКА

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Аннотация. Цели данного исследования заключались в изучении процесса эпоксидирования скрапа НК в двухфазной среде жидкость-газ, обосновании конструкции оборудования и энергоэффективного способа проведения данного процесса. Наличие эпоксидных групп было подтверждено при помощи ИК-спектров полученных ЭНК. Помимо качественного анализа проводился количественные измерения непредельности каучуков и концентрации эпоксидных групп в ЭНК титрометрическими методами. Для проведения утилизации скрапа НК разработана конструкция циркуляционного реактора, который позволяет работать с вязкими растворами каучуков, обеспечивая нагрев и смешение с эпоксидирующим агентом.

Ключевые слова: Эпоксидирование, скрап натурального каучука, реактор.

Introduction. Currently, one of the types of the waste natural rubber (NR) production is a scrap. This scrap does not correspond to standards (ISO 2000:2008), and cannot be used in industrial production [1]. Chemical modification of scrap allows to create new kinds of synthetic rubbers having valuable physical chemical [2] and technological properties [3].

One of the most common ways to modify NR is epoxidation [4]. There are various ways of epoxidation NR (ENR) at the latex stage in a suspension containing significant amount of gel particles with peracetic acid [5], with glacial acetic acid and hydrogen peroxide *in situ*. This is a well known commercial method for producing ENR [4]. The epoxidation rate increases with increasing concentration of rubber.

In the paper [6] was proposed to use ENR as protective plating for metals, considering that the epoxy groups of the polymers can react with the hydrated metal surface to form strong chemical bonds [7].

Solutions of ENR obtained from scrap may be used for creating protective plantings with reduced consumption when they apply to the metal surfaces (Carbon Steel St3). In addition, a multi-purpose solution ENR may be used to protect equipment from corrosion during its conservation.

Based on the above, epoxidation is the promising method for scrap recycling and requires further studies.

Research objectives. The objective of this work was to develop and study of the epoxidation process of scrap NR for giving to it improved mechanical and technological properties. Possibility of carrying out the combined physical and chemical processes in one reaction chamber in the two-phase environment liquid-gas while reducing the total energy costs was studied.

Another objective of this study was to develop of energy-efficient ways to recycle scrap NR using low-tonnage equipment for carrying out the modification process. The main technical objective was to improve the design of the reactor for the purpose of implementation of the controlled process, while maintaining the required temperature of the reaction medium.

Materials and results of research. Research of epoxidation process was carried out using a low-molecular scrap NR (made in Vietnam) with viscosity average molecular weight of 300 thousand. Natural rubber was crushed and dissolved in xylene to a rubber concentration of 13 wt. %. As reagents for epoxidation mix of 3% aqueous solution of hydrogen peroxide and 65% aqueous solution of formic acid was used [8]. The number of components in the mixture was taken for the 5 mole% and 15 mole% epoxidation (with an excess of formic acid). Theoretical levels of epoxidized units were calculated according to the relation: $r_t = [H_2O_2]/[\text{Polyisoprene units}]$.

The mass composition of mixes is given in tab. 1.

Table 1 - The composition of mixes for modification

Composition	The concentration of components in solution [wt. %]				
	NR	Xylene	Hydrogen peroxide	Formic acid	Water
No.1 (5 mol % epoxide content)	11,58	78,17	0,29	0,39	9,57
No. 2 (15 mol % epoxide content)	8,17	69,96	0,59	1,38	19,90

Qualitative analysis of the initial scrap NR and received ENR was carried out by IR spectroscopy of 40-50 microns films on a quartz glass in a wide range of wavelengths. The special attention was paid to absorption bands of epoxy, hydroxyl and carboxyl groups. For the quantitative analysis back titration was used, the content of epoxy groups were determined using the method [9], the change in the total unsaturation were determined using the iodine value method [10].

In order to ensure the necessary conditions for processing and modification was used a laboratory reactor for mass transfer.

The mixture of aqueous solutions of formic acid and hydrogen peroxide in low concentrations allows to obtain oxidizing agent - performic acid [11]. Low concentrations of the reagents increase the overall safety of the process, minimizes side reactions and eliminates the need for feeders and gradually adding substances.

The formation of acid in the aqueous solution of reagents proceeds with a faster rate than it`s consumed in the reaction. Evaporation of water results in intensive mixing of rubber solution and foam formation. Anticipated that the epoxidation reaction and other side reactions proceeded at the interface between the liquid and gas phases in the foam.

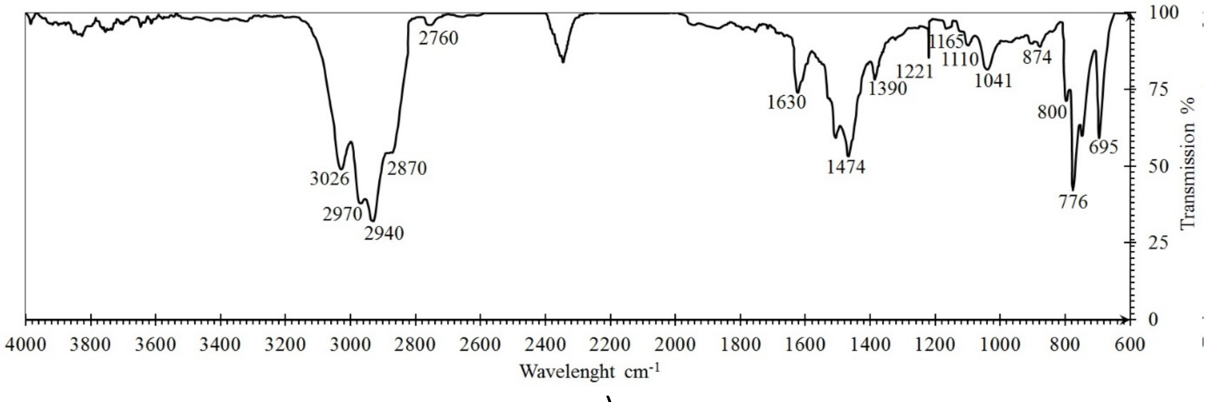
The time course of the process, excluding the heating and cooling was three hours. At the end of the process the solution changed its color to a yellowish white that indicates chemical reactions in the rubber solution; pH value for the first composition was 7, for the second - 6.4 due to an excess of formic acid.

Decrease of rubber unsaturation in first composition was 5.80 mol%. instead of theoretical 5.0 mol%, that indicates a relatively low extent of side reactions, such as of destruction, polymerization, ring-opening etc. For the second composition decrease of rubber unsaturation was 10.28 mol% instead of theoretical 15.0 mol%, that indicates incomplete epoxidation process. Thus, increasing the concentration of the reactants decreases the epoxy yield.

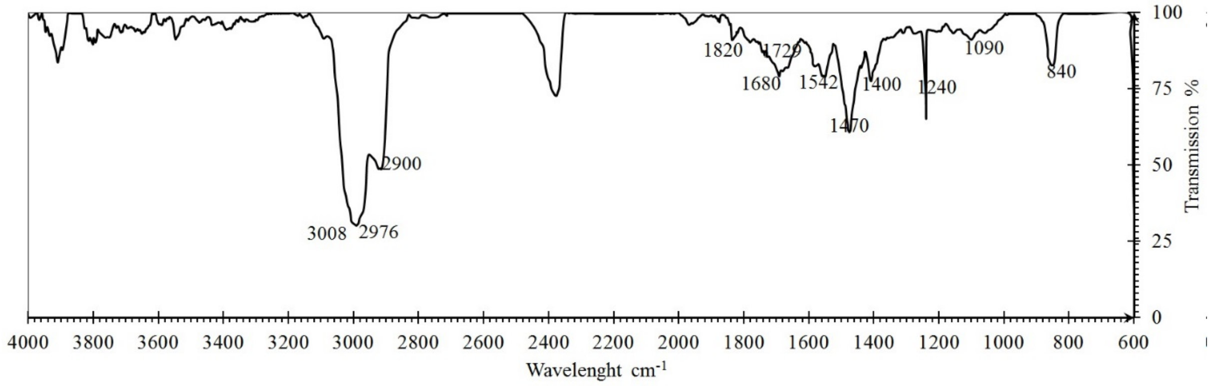
IR spectrum of scrap, which was used in research is shown in (Fig. 1a), the IR spectra of the products with theoretical epoxy yield equal to 5 mol% and 15 mol% are shown in (Fig. 1b-c), respectively.

During the epoxidation IR spectroscopy was used to follow the changing of chemical composition of the obtained product. Disappearance of the absorption bands in the 1680-1620 cm^{-1} corresponds to the stretching vibrations of the double bonds C=C [12] in the 1,4-cis polyisoprene backbone of scrap indicates decrease in unsaturation [13]. A peak at 1729 cm^{-1} corresponds to the stretching vibrations of the acidic carbonyl groups of the ketone or aldehyde type in the first composition [12]. In addition, the presence of peaks at 1542 cm^{-1} and 1400 cm^{-1} corresponds to the symmetric and asymmetric stretching vibrations of the acidic terminal groups [14]. This indicates the break of the polymer chain and the occurrence of side reactions with formic acid during epoxidation. Absorption peaks in the range of 950-840 cm^{-1} corresponds to the stretching vibrations of the epoxy ring [2]. The presence of the peak at 921 cm^{-1} indicates the presence of the epoxy groups in the second composition. Small peak at 1650 cm^{-1} corresponds to deformation vibrations of OH groups, that indicates ring-opening of the epoxy groups with the accession of hydrogen [13] in the second composition. Partial hydration of the epoxy groups, catalyzed by an excess of the formic acid in aqueous solution, occurs in the presence of water [15].

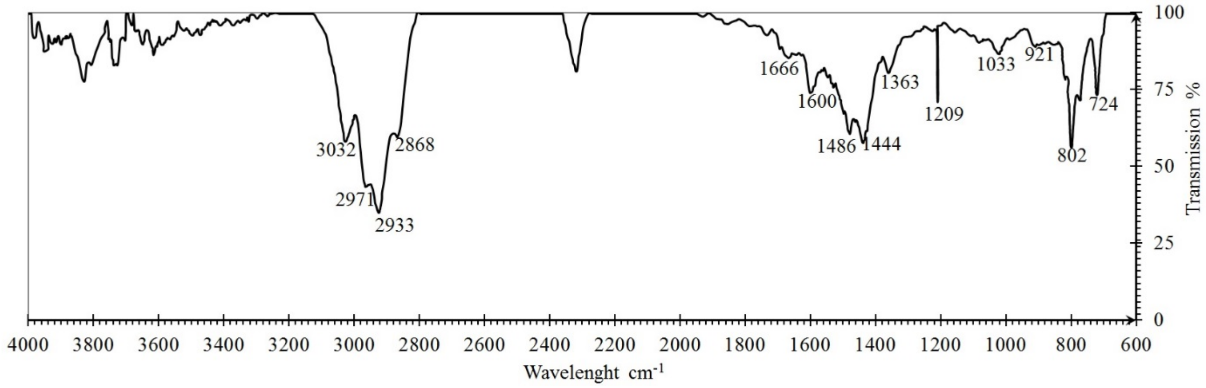
The scheme of combined reactive separation process epoxidation of natural rubber scrap in water-xylene medium was proposed [16].



a)



b)



c)

Figure 1 - IR spectra of:

a) –scrap NR;

b) - sample with the calculated epoxy yield about 5 mol%;

c) - sample with the calculated epoxy yield about 15 mol%.

The authors suggested use of reactors with circulation for carrying out the epoxidation of scrap. The proposed reactor for epoxidation of scrap NR schematically shown in Fig. 2. The reactor consists of: an U-shaped vertical vessel with input section 1 and output section 2; overflow pipe 3; a three-tiered stirrer 4 mounted on a shaft 5 and disposed in the input section 1 between the grid plates 6, 7 mounted above and below the stirrer; a reaction chamber 8; flanged fittings 9,10,12; a shaft hole 11 with end face mechanical seal; a heat exchanger 13 mounted under the flange cover 15 by use of vertical rods 14, also vertical rods are used to supply heat medium to the heat exchanger; drop eliminators 16, 17 mounted on rods and shaft; flanged fittings 18,19 for removal of the vapor phase and for emptying the reactor when it is stopped.

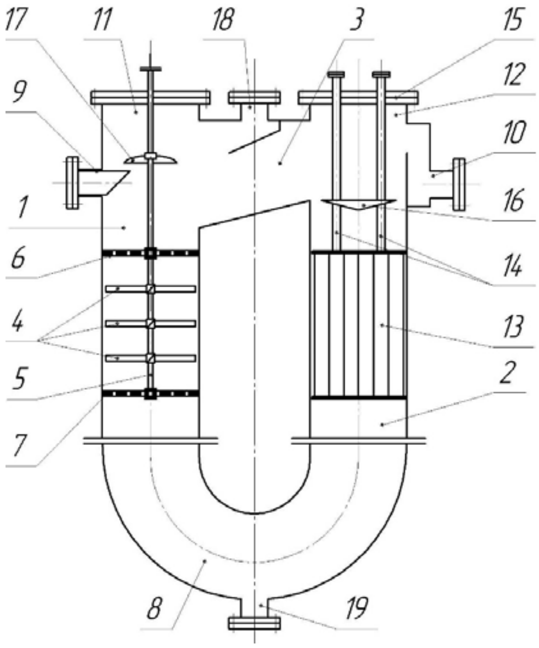


Figure 2 - Reactor

The reactor design provides for the convenience of assembly and dismantling due to sectional packet structure [17]. In addition, such a reactor design provides: hydrodynamic conditions necessary for working with a viscous reaction mixture, the absence of a stagnant zones; high degree of emulsification, which significantly intensifies the epoxidation.

Conclusions. It was found that the use of the epoxidation for modification of scrap NR allows to solve problem of the safe recycling of waste rubber production in the most efficient way. As a result of this research, ENR with regulated epoxy yield and without a significant amount of side reactions was obtained.

The proposed method for the epoxidation NR in the U-shaped reactor allows to carry out the controlled reaction with high conversion rate of scrap NR to ENR due to the possibility of regulating the temperature in the reaction zone of the reactor.

Since the epoxidation reaction proceeds in the kinetic range [18], it is necessary to analyze the diffusion processes of the reagents transfer from the liquid and gas phases to the solvent in order to find the optimal hydrodynamic conditions for the process.

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УДК 666.198

ПЕРСПЕКТИВА ИСПОЛЬЗОВАНИЯ ЭНЕРГИИ ПЛАЗМЫ ПРИ ПРОИЗВОДСТВЕ МИКРОСФЕР НА ОСНОВЕ АЛЮМОСИЛИКАТНЫХ ОТХОДОВ

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Аннотация. Работе показана возможность использования золошлаковых отходов при производстве микросфер плазменным методом. Описаны физико-химические процессы плавления золошлаковых отходов с учетом реального химического состава и посредством перерасчета на трехкомпонентную систему.

Ключевые слова: микросферы, электроплазменный стенд, физико-химические процессы, утилизация отходов.

VISTA ENERGY PLASMA PRODUCTION BASED MICROSPHERES ALUMINOSILICATE WASTE

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Abstract. The work shows the possibility of using slag waste in the production of microspheres plasma method. We describe the physical and chemical processes of melting slag waste, taking into account the real chemical composition and by recalculation on the three-component system.