The study of interaction between rubber seed oil and epoxy resin

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Abstract. Plant oils are regarded as relatively cheap renewable and sustainable raw materials that could be efficiently used for manufacturing of glues, coatings, flooring and other materials. Among the plant oils, rubber seed oil (RSO) is of particular interest as it contains the large amount of free fatty acids. Development of new innovative cost-effective technologies for processing renewable agricultural products of plant origin is of acute practical importance as they are considered as advanced sustainable raw materials for manufacturing the products of “green” chemistry. According to the literature review, free fatty acids could enhance performance of polymer composite materials, in particular, on the base of epoxy polymers. Having applied the methods of infrared spectroscopy and titrimetry, the authors identified the absence of chemical interaction between epoxy resin and rubber seed oil at room temperature. Having used the data of differential scanning calorimetry, it was stated that epoxy resins react with rubber seed oil at elevated temperatures.

1. Introduction

Plant oils are seen as green, relatively cheap renewable raw materials that could be successfully applied in manufacturing glues, coatings, flooring and other materials [1]. Chemical composition of plant oils ensures their involvement in various chemical transformations [2]. Regardless the predominance of products based on petroleum in the last years, plant or vegetable oils are being used widely in both edible and non-edible applications, such as surface coatings, in particular paints, rubber and plastic processing and many others. These diverse fields of applications have resulted in increase in the demand for plant oils.

At the same time, development of new innovative cost-effective technologies for processing renewable agricultural products of plant origin is of acute practical importance as they are considered as advanced sustainable raw materials for manufacturing the products of “green” chemistry.

Among plant oils, rubber seed oil (RSO) containing the large amount of free fatty acids is of particular interest [3]. The results of the previous studies have shown that free fatty acids [4, 5] could positively affect the properties of polymer composite materials, in particular, those on the base of epoxy polymers. However, the research letters are lacking the data related to possible chemical interaction between rubber seed oil with epoxy groups. Oil content in the rubber seed is found as 49% by mechanical press with periodic addition of solvent. RSO is obtained in high yield as an agricultural by-product of Hevea cultivated for its latex primarily and is traditionally used as a planting material. Nevertheless, the previous researches have shown it to be a rich source of oil that could be compared in its quality with dry oils generally used in surface coatings.
Due to this, studying the conditions of interaction between epoxy resins with rubber seed oil is of utmost academic interest.

2. Materials and methods

Epoxy polymers have been obtained on the base of epoxy diane resin ED-20 (All-Union Standard GOST 10587-84) and aminophenol hardener APh-2 (Technical Conditions 2492-052-00205423-2004). As a modifier, there was used the liquid part of rubber seed oil, extracted from the seeds of *Hevea brasiliensis* that vegetates the Southern territories of Vietnam (province Vung Tau) (TCVN 5374:2008). *Hevea brasiliensis* seed was found to be rich in oil with an average optimum yield of 40.02% (w/w).

The modifier has been obtained by compaction method at the pressure of 25-30 MPa and the temperature ranging 160–180°C followed by centrifugation [6] and compaction. The properties of rubber seed oils are presented in the table 1. As the model free fatty acid, there was used oleic acid (All-Union GOST 7580-91).

Oleic acid, also known as oleate, relates to the class of organic compounds – long-chain fatty acids. Those are fatty acids with an aliphatic tail containing 13 and 21 atoms of carbon. Oleate exists as a liquid and is regarded as practically insoluble in water and relatively neutral. Oleic acid can be found in a number of food items, this makes it a potential biomarker. Oleic acid is considered a potentially toxic compound.

| Properties                        | Rubber seed oil |
|-----------------------------------|----------------|
| Density, g/cm³                    | 0.923          |
| Iodine absorption number, g I₂/100 g | 131.4          |
| The content of free fatty acids, % wt. | 28.2%          |
| Acid index, mg KOH/g              | 56.1           |
| Iodometric scale color, mg I₂/100 cm³ | 300            |

Infrared spectrum has been taken by means of IK Fourier-transform spectrometer “InfraLUM FT-08” in the range 500–4000 cm⁻¹. This instrument is operated by means SpectraLUM software run under Windows environment and provides simple control enabling even unskilled personnel to master the instrument operation easily. The major functions include peak identification, derivative quantification, quantitative calibration creation, etc. Library search module allows plugging spectra libraries and creating own user’s libraries.

Acid-base titration has been carried out in compliance with the All-Union Standard GOST 25794.1-83. This method of quantitative analysis is commonly used for determining the concentration of a base of an acid by neutralizing it with a standard solution of acid or base when the concentration is known. For monitoring the acid-base reaction, a pH indicator is used.

In order to record heat effects accompanying chemical interaction of the components, there has been used differential scanning calorimeter DSC 1 STAR System produced by Mettler Toledo (USA), the heating rate of specimens accounted for 10°C/min. The DSC utilizes an innovative patented DSC sensor with 120 thermocouples which guarantees unmatched sensitivity. The signal-to-noise ratio, an important instrument parameter, is determined by the number of thermocouples and their specific arrangement. The tests have been implemented in air.

3. Results and discussions

In the results of the previous research, there is a generally accepted statement that oxygen-acids could interact with epoxy resin under the following scheme [4, 5]:

![Diagram](image-url)
In the course of the present research work, the probability of interaction between epoxy diane resin ED-20 and rubber seed oil have been studied at room temperature. The choice of the temperature mode is preconditioned by the fact that hardening of epoxy resin by aminophenol APh-2 occurs without heat intake. Oleic acid has been used as the model compound, free fatty acid.

In order to control the process, the method of titriometry and infrared spectroscopy have been applied to the specimens. The tests have been carried out immediately after components mixing followed by the next test done 1 hour after the mixing.

The selection of the given time interval is generated by the fact that gel time for compounds does not exceed one hour.

| Compounds | Acid index, mg KOH/g |
|-----------|---------------------|
| Epoxy diane resin ED-20        | 2.3                 |
| Rubber seed oil                  | 56.1                |
| Oleic acid                       | 192.1               |
| ED-20 + 10 % wt. of rubber seed oil (straight after mixing) | 6.9/7.1 |
| ED-20 + 10 % wt. of rubber seed oil (after one hour exposure at room temperature) | 7.0/7.1 |
| ED-20 + 10 % wt. of oleic acid (straight after mixing) | 19.3/19.4 |
| ED-20 + 10 % wt. of oleic acid (after one hour exposure at room temperature) | 19.5/19.4 |

Note: Experimental values of acid index are presented in the numerator; the estimated values are given in the denominator.

The results of findings have shown that there is no visible difference in the values of the acid index of the binary mixture of epoxy diane resin ED-20 and rubber seed oil immediately after mixing and after one hour of exposure at room temperature (table 2).

The experimental and calculated values (obtained on the principle of additivity) of the acid index of binary mixtures coincide with each other. This fact provides clear evidence that there is no chemical interaction between epoxy diane resin ED-20 and acid groups of rubber seed oil at room temperature.

The lack of the changes of intensity of absorption bands in the infrared spectrums of epoxy groups (in the range of 915÷930 cm⁻¹) and hydroxyl groups (ranging 3200÷3500 cm⁻¹) of the mixture ED-20 and rubber seed oil, after one hour of exposure, provides the plausible evidence of the absence of chemical reactions between these components at room temperatures (fig.1).

The similar result has been obtained when titrating the binary mixture of epoxy diane resin ED-20 and oleic acid (table 1).

The data obtained by means of infrared spectroscopic analysis also demonstrate zero chemical interaction of rubber seed oil with the hardener aminophenol APh-2 without heat intake.

In order to identify the possible interaction of carboxyl groups of free fatty acids, being a constituent part of rubber seed oil, with epoxy diane resin ED-20 at the elevated temperatures, the method of differential scanning calorimetry has been applied.
Figure 1. Infrared spectrum of the overlap of the mixtures: epoxy diane resin ED-20 and rubber seed oil (10:1) immediately after components mixing and exposure at room temperature for one hour.

Figure 2. Infrared spectrums of overlap of the mixtures: aminophenol APh-2-Rubber seed oil (3:1) immediately after the components mixing and exposure at room temperature for one hour.
The results of the investigation demonstrated on the figure 3 prove the presence of chemical interaction between epoxy resin and rubber seed oil. This reaction initiates at the temperature of 188°C and is exoenergic one, i.e. the reaction accompanied by the evolution of energy. The results and findings are exhibited in the table 2 and figure 3 below.

Along with that, its heat effect is significantly lower than of the compositions containing the hardener [7-8].

Homopolymerization of epoxy diane resin ED-20 occurs at the temperatures exceeding its interaction with rubber seed oil. Thus, the thermal effect of this reaction is slightly lower. The findings are presented in the table 3 and figure 3 below.

**Figure 3.** Differential scanning calorimetry curves of 1- epoxy diane resin ED-20 and rubber seed oil taken in the ratio 10:1 immediately after mixing

**Table 3.** Thermodynamic characteristics of the thermal transformations peaks of epoxy resin and its mixture with rubber seed oil

| Parameter          | Composition’s compound | At the initial moment |
|--------------------|------------------------|----------------------|
|                    | Epoxy diane resin ED-20| ED-20+Rubber seed oil|
| ΔH, J/g            | 5                      | 7                    |
| T₀, °C             | 259                    | 188                  |
| T_m, °C            | 290                    | 193                  |
| T_k, °C            | 204                    |                      |
| Peak height, mWt   | -2.5                   |                      |
| ΔT, °C             | 16                     |                      |
4. Conclusions

Among the plant oils, rubber seed oil (RSO) is of particular interest as it contains the large amount of free fatty acids. According to the literature review, free fatty acids could enhance performance of polymer composite materials, in particular, on the base of epoxy polymers.

By the methods of titrimetry and infrared spectroscopy it was stated that both rubber seed oil and oleic acid do not enter into chemical interaction with epoxy resin at room temperature. At the same time, the results of differential scanning calorimetry have shown that rubber seed oil reacts with epoxy diane resin ED-20 at elevated temperatures [9, 10, 11]. The thermodynamic parameters of the obtained epoxidation indicate that an increase in the process temperature would increase the rate of epoxide formation and useful to scale up the production of epoxidised rubber seed oils [12].

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