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Modification of Aliphatic Petroleum Resin by Peracetic Acid

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Abstract

This work demonstrates the possibility of obtaining modified aliphatic resin (PR_{C5}) by means of petroleum resin oxidation by peracetic acid. We have experimentally determined oxidation conditions that lead to producing resin with maximum epoxy and acid numbers. Ratio of «oxidative system: PR_{C5}» is 0.5:1, process duration is 2 hours. The modified resin structure is determined by IR and NMR spectroscopy.

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Keywords: modification; petroleum resin; C_5 fraction; liquid pyrolysis products; peracetic acid; epoxy groups

1. Introduction

Polymerization with formation of petroleum resin (PR) is one of the main methods of recycling of pyrolysis plants by-products. The content of unsaturated compounds in liquid pyrolysis products (by-products) is around 30-50 % [1-3]. PR is oligomeric hydrocarbon resin with various unsaturated bonds. They are often used as components of coatings and adhesive materials, as base for hot melt adhesives and to improve the properties of bitumen. Limited range and bad compatibility of PR with polar substances are caused by absence of functional groups in their structure. Therefore, certain problems during composite material production on the basis of PR can occur.

Currently, development and deployment of new resin types, especially modified, is one of the perspective

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directions of by-product utilization in petrochemical plants.

Resin modification (introduction of functional groups) can be carried out in two ways. The first way is mixing of liquid pyrolysis product fractions with various monomers, for example, vinylacetate, acrylonitrile, divinyl, acrylic and methacrylic acid or their esters[4-6]. The second way is the influence of various chemicals, such as maleic anhydride, α, β-unsaturated polybasic acids, fatty acid triglycerides (vegetable oils)[7-10] on petroleum resin or introduction of various additives such as surfactants, plasticizers, compatibilizing additives in PR [11,12].

The most widespread method of PR functionalization is oxidation. The introduction of polar functional groups in the resin polymeric chain is carried out using potassium permanganate, sodium hypochlorite or hydrogen peroxide. The oxidation in mild conditions leads to hydroxyl or epoxy groups forming in PR, whereas application of strong oxidants (for example, $KMnO_4$) will result in formation of carboxyl groups. Organic peroxyacids are widely used types of oxidant. Oxidation products are formed under their influence in mild conditions. Oxygen-containing petroleum resin production under the influence of peracetic acid is described in works[13,14]. It was established that the oxidant type and the petroleum resin structure have significant effect on the final result[15]. Oxidation of PR solutions allows obtaining products that are ready to use and require no further treatment.

Therefore, the goal of this work is to study the peracetic acid oxidation process of aliphatic petroleum resin obtained by polymerization of unsaturated C_5 fraction compounds derived from liquid pyrolysis products. The properties of modified resin formed in this process were also reviewed and assessed.

2. Experiment

2.1. Objects of research

As raw material for the modification process we are using petroleum resin (PR_{C5}) based on C_5 fraction of liquid pyrolysis products with boiling temperature of 30-70 °C. Polymerization of C_5 fraction unsaturated components is carried out in the following conditions: the catalyst system $TiCl_4$–$Al(C_2H_5)_2Cl$ with the equimolar ratio of components, $TiCl_4$ concentration – 2 %, temperature – 80 °C, pressure – 1,3 MPa, duration – 2 hours. At the end of the interaction the catalyst system $TiCl_4$–$Al(C_2H_5)_2Cl$ is deactivated by using 20% alkali solution NaOH.

Petroleum resin (PR_{C5}) modification is performed with the oxidizing system in 30% toluene solution using sulfuric acid as catalyst. The oxidative system consists of hydrogen peroxide and acetic acid with the equimolar ratio of components is dosed at 50-55 °C. After that, temperature increases to 70-75 °C and the process is carried out for 3 hours. After the interaction, multiple washing of the gained solution is performed with water to achieve neutral pH. The obtained modified resin (MPR_{C5}) is extracted from the organic layer by solvent removal.

2.2. Methods of research

Modified resin is investigated using standard methods. NMR spectra are recorded by using NMR Fourier spectrometer AVANCE AV-300 «Bruker» in $CDCl_3$. IR spectra are recorded using IR Fourier spectrometer FT-801 «Simex» using KBr glass.

3. Results and Discussion

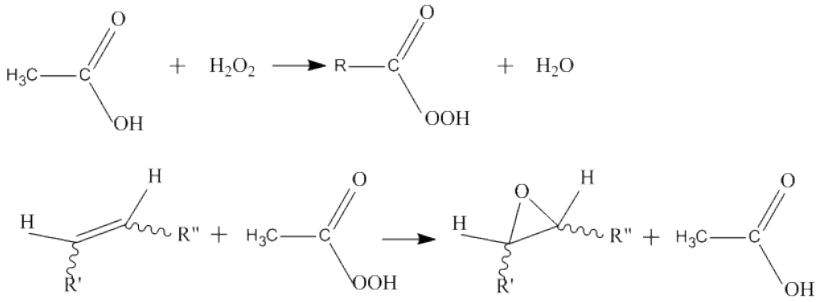
The ratio of oxidant and reagent is an important process parameter. The experiment is carried out to study the influence of oxidative system quantity on the property of the resulting resin (MPR_{C5}) at the following ratio of components «oxidative system : resin PR_{C5}»: 0.1:1; 0.25:1; 0.5:1; 0.75:1. Acid (AN, mg/g), bromine (BN, g/100 g) and epoxy (EN, %) numbers depending on the component ratio, process duration are presented in the Table 1.

Table 1. Properties of modified resin

Property	Process duration, h	Ratio of components « oxidative system : resin PR_{C5}»			
		0.1 : 1	0.25 : 1	0.5 : 1	0.75 : 1
AN, mg/g	0.0	0.7	0.7	0.7	0.7
	0.5	1.6	1.9	2.2	2.0

	1.0	1.8	2.4	3.3	3.1
	1.5	2.2	2.4	6.0	5.9
	2.0	2.4	3.3	6.1	6.0
	2.5	2.4	3.5	6.2	6.2
	3.0	2.4	3.7	6.2	6.3
BN, g/100 g	0.0	27.2	27.2	27.2	27.2
	0.5	22.0	18.2	16.4	16.9
	1.0	20.8	17.6	16.2	15.3
	1.5	19.3	16.4	15.2	14.8
	2.0	17.7	15.2	14.8	14.3
	2.5	17.6	15.0	14.2	13.8
	3.0	17.5	14.8	13.7	13.3
EN, %	0.0	0.0	0.0	0.0	0.0
	0.5	0.8	1.5	2.5	2.4
	1.0	1.2	3.3	6.2	4.7
	1.5	1.6	4.8	7.9	8.7
	2.0	1.8	4.8	8.9	8.8
	2.5	1.9	4.9	8.9	8.9
	3.0	2.2	5.0	8.9	8.9

The data shows that the amount of the used oxidizing agent and the oxidation duration can affect the properties of modified resin. Simultaneously with oxidation (increase of the acid number) epoxidation process happens at double bonds (epoxy number increases and bromine number decreases). This fact is explained by the oxidation in Prilezhaev method[16]:



Practically no changes are noticed in the properties of the resin 2 hours after the start reaction. Reduction of the bromine numbers proves that the process is carried out with the double bonds participation. The maximum epoxy number achieved when the components ratio of oxidative system and PR_{C5} is (0.5-0.75) : 1.

To prove the resultant modification the following groups of protons with different chemical shift (ppm) are allocated in the ^{1}H-NMR spectra: A – aromatic, B – olefin, D – methine, E – methylene, F – methyl protons, C – methine protons in the α-position to oxygen of the epoxy group and E' – methylene protons in the α-position to the double bond. The ^{1}H-NMR spectra analysis (Table 2) of the obtained resin showed that normalized integrated intensity (NII) of B and E' protons decreased and NII of C protons increased as the amount of oxidative system increased. These facts also confirm participation of double bonds in the process.

The availability of aromatic proton signals in the spectra is explained by presence of solvent remains in PR_{C5}.

Table 2. Normalized integrated intensity of modified resin protons

Proton type	Ratio of components «oxidative system : resin PR_{C5}»				
(ppm)	0 : 1	0.1 : 1	0.25 : 1	0.5 : 1	0.75 : 1
A (6.5-7.8)	1.2	1.3	1.0	1.3	1.1
B (4.5-6.5)	10.7	8.9	8.8	8.1	8.2
C (2.5-4.5)	7.5	10.4	12.1	10.9	13.3
E' (1.9-2.5)	20.3	20.3	18.4	17.5	16.4
D (1.4-1.9)	21.1	17.2	18.0	16.2	15.2
E (1.1-1.9)	11.1	14.5	15.3	17.2	18.7
F (0.1-1.1)	28.1	27.4	26.5	28.8	27.1
	100.0	100.0	100.0	100.0	100.0

In the IR spectra of modified resin MPR_{C5} there are absorption bands of hydroxyl (3400-3440 cm^{-1}), carbonyl (1715-1730 cm^{-1}) groups and oxygen-containing ring (1240-1250, 1045-1075 cm^{-1}), that are not present in case of PR_{C5} resin. For example, see Fig. 1. Also in the IR spectra of modified resin there is a decrease of absorption band intensity of the valence and deformation vibrations –C=C–H (3040-3045, 960-970 cm^{-1}).

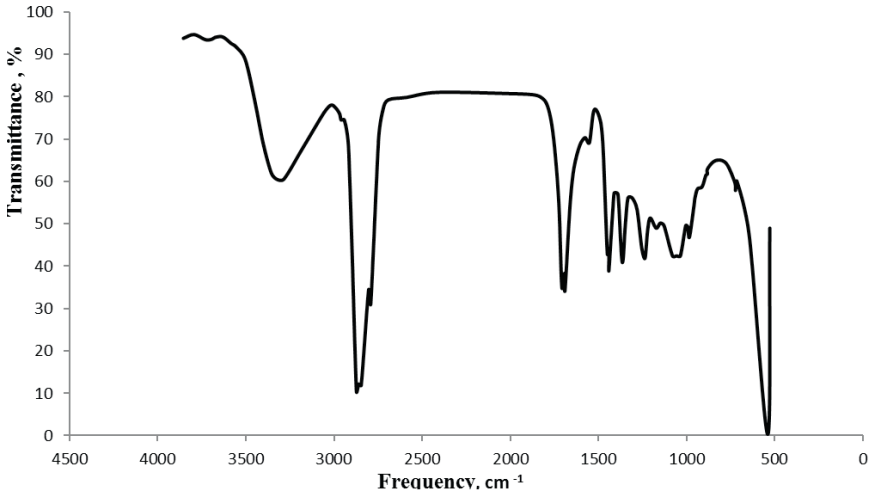


Fig. 1. IR spectra of modified resin MPR_{C5} (the components ratio of oxidative system and PR_{C5} is 0.5 : 1)

4. Conclusions

The study demonstrates the possibility of modified resin (MPR_{C5}) production by means of interaction between highly unsaturated aliphatic petroleum resin PR_{C5} and peracetic acid prepared in situ.

The maximum values of acid and epoxy numbers were received in the following conditions: the ratio «oxidative system : resin PR_{C5}» – 0.5 : 1, duration – 2 hours.

Modified resin MPR_{C5} dissolve in chlorinated hydrocarbons, set under the heating and have molecular weight between 570 and 690.

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