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Epoxy–diane co-oligomer modified with benzamide

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Abstract

The epoxy-diane oligomer ranks second (the phenol-formaldehyde oligomer ranks first) among the oligomers by volume of production in the world.

It is known that the epoxy-diane oligomer is widely used as a binder in the preparation of many target composites. The reason for this is that its indicators can be adjusted during synthesis. On an industrial scale, it is produced under various brands (Ed-16, ED-20, ED-22, etc.) the produced oligomer has both positive sides and many disadvantages. The disadvantages include low temperature resistance and adhesive ability, some presence of free monomers in the system, and so on. In order to eliminate these indicators, the epoxy-diane oligomer was modified with organic compounds of various natures [1-3].

The modification process was carried out in an alkaline medium by the method of co-polycondensation. Modification during synthesis (chemical modification) is currently characterized by its relevance. It has become clear from the literature studies that the method of chemical modification is of more interest to researchers working in this field than physical modification. This is due to the fact that the performance indicators of composites based on epoxy-diane oligomer chemically modified by co-polycondensation are approximately 1.5-2.0 times higher than the corresponding indicators of composites based on epoxy–diane oligomer obtained by polycondensation [4-5].

Keywords: benzamide, modifier, modification, co-polycondensation, co-oligomer.

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1. Introduction

Epoxy–diane oligomer of various brands is widely used all over the world (in the USA, Europe, Japan, China, Korea, etc.), its production is growing rapidly from year to year. Russia alone produces more than 100 thousand tons of epoxy-diane oligomers of various brands per year.

Since the molecular mass of epoxy-diane oligomers differs from each other by the amount of epoxy groups in their composition, their aggregate state (solid, liquid and viscous fluid) also differs. The solid-state epoxy-diane oligomer is mainly used in the preparation of powdered colors.

In the research work, epoxy-diane oligomer was used as a modifier of a simple amide derivative of nitrogen-contain in organic compound-benzoic acid (benzamide).

Benzamide - $C_6H_5CONH_3$ mass of molecules 121 g/mol, melting temperature 115 ^{0}C, density 1341 kg/m^3, it is a compound of white color, powdered, partially soluble in water and well soluble in organic solvents.

The main raw materials for the production of epoxy–diane oligomer are epichlorohydrin and diphenylpropane. Sodium hydroxide was used as a catalyst. The adhesive ability, heat

resistance, solidification rate, molecular mass and saire indicators of epoxy–Diane oligomer modified by co-polycondensation method have been improved. Spectral analyses of soligomer IR, NMR, DMM, DT and TQ have been studied. For the purpose of comparison, the main indicators of both non-modified and modified epoxy–diane s-oligomer were studied in parallel [6-9].

From the results obtained, it was found that the modification by co-polycondensation method is a chemical modification. The most important indicator for the epoxy–diane oligomer is its high adhesive and heat–resistant ability. At the expense of the functional (amid) group of the modifier, the functionality of the oligomer increased, the connections in the macromolecule were strengthened, and as a result, the main indicators also improved.

2. Experiments

Considering that there agents used in the production of epoxy-diane oligomer are relatively cheap and environmentally friendly, the co-polycondensation reaction to increase its functionality was carried out as follows:

A calculated amount of 12 % aqueous sodium hydroxide solution is added to a 250–300 ml three-necked flask equipped with a stirrer, a reverse refrigerator, a drip funnel and a thermometer, then, gradually stirring, diphenylolpropane is added to it. After complete dissolution of diphenylolpropane, epichlorohydrin is added to the mixture in parts (in the calculated amount).

The reaction mass is heated in a water bath at a temperature of 70-75 ^{0}C for 45-50 minutes and reheated for 30 minutes with the addition of a 25% sodium hydroxide solution. It is mixed at 90-95 ^{0}C for 60 minutes with the gradual addition of benzamide to the reaction mass (up to ¼ diphenylolpropane).

The resulting functionalized polymer is washed to a neutral reaction and dried in a vacuum drying cabinet at 50-70 ^{0}C to a constant mass. The modified epoxy-diane co-oligomer is highly soluble in acetone, toluene, dioxane, tetrahydrofuran and dimethylformamide. Does not dissolve in water.

3. Results and discussion

The number of epoxy groups in the co-oligomer was determined by an analytical method, the softening temperature was determined by aUbbelohde thermometer, and the density of the powdered co-oligomer was determined by a pycnometer (Table 1).

#	Indicators	Unmodified epoxy – diane oligomer	Modified epoxy – diane co – oligomer
1	Number of epoxy groups, %	20	14.6
2	Molecular weight	430	589
3	Softening temperature, ^{0}C	78	85
4	Density, kg/m^3	1250	1310
5	Adhesive strength, MPa	22	28
6	Solidification rate, %, at 150 ^{0}C for 5 hours	94	98
7	Heat resistance, ^{0}C	150	165

Table 1. Basic physico-chemical and physico-mechanical parameters of unmodified epoxy-diane oligomer and modified epoxy-diane co-oligomer

It is known from Table 1 that the main indicators of the modified epoxy-diane oligomer are higher than those of the unmodified oligomer. However, the number of epoxy groups in

the modified epoxy-diane co-oligomer decreased. This is due to the fact that the modification process is a chemical modification, that is, the epoxy groups react with the amide groups present in benzamide, which leads to a decrease in the number of epoxy groups.

The IR spectral analysis of the synthesized new ingredient, the co-oligomer, is shown in Figure 1.

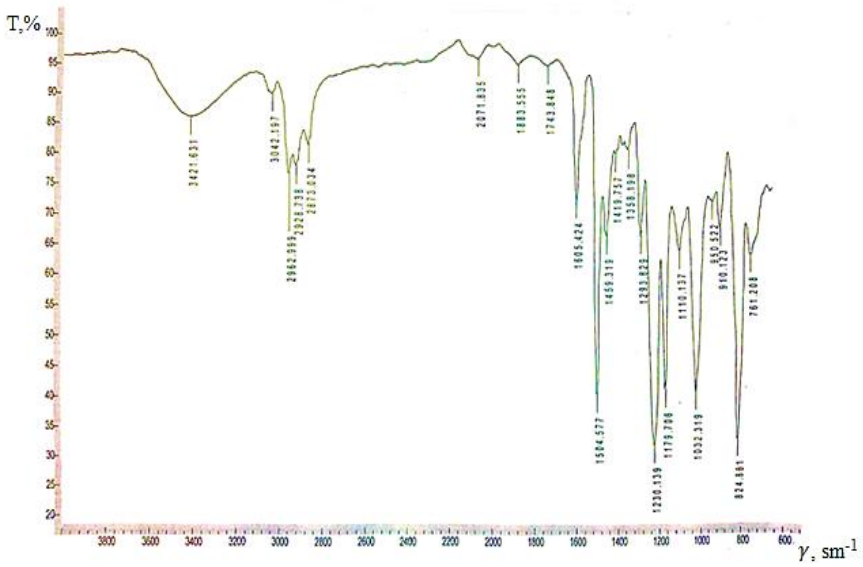

Figure 1. IR spectrum of the modified epoxy-diane oligomer

Analysis of IRS of epoxy-diane co-oligomer modified with benzamide revealed that, 3421.631– 3042.197 sm^{-1} swallowing strips > NH və – OH the valence vibration of their communications, 2962.999–2873.034 sm^{-1} accordingly, the deformation vibration of the CH group, 1605.424 – 1504.577 $sm^{-1}$with benzene ring C=O və > NH deformation vibration, 1459.319 – 1358.198 sm^{-1} > CH_2 and CH valence vibration of communication, 1293.829 – 1236.139 sm^{-1} – OH the deformation vibration of the group, 1179.706 –1110.137 sm^{-1} CH valence vibration, 1032.31–9910.52 sm^{-1} the CH deformation vibration in the asymmetric benzene ring and 824.881–761.208 sm^{-1} it has been confirmed that there is deformation vibration of the epoxide group.

In the NMR spectrum (Figure 2), which is specific to the co-oligomer $\delta = 6{,}811 - -7{,}190\ m.\delta.$ aromatic ring, $\delta = 3{,}330 - 3{,}696\ m.\delta.$ while in range> NH the presence of the group is confirmed. As well as, $\delta = 2{,}060 - 2{,}096\ m.\delta.$ the group – CH_3 (which is typical of the acetone group in acetone - deuterium) has been confirmed.

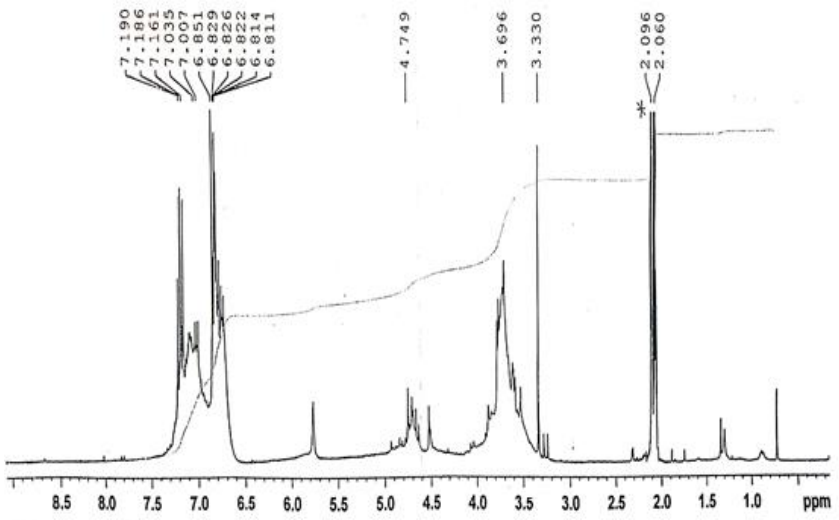

Figure 2. NMR spectrum of modified epoxy-diane oligomer

DMM (the distribution of the mass of molecules) was determined by the liquid chromotographic method ("Kovo firm"). The DMM of both the non-modified epoxy-diane oligomer and the modified epoxy-diane co-oligomer have been studied.

It was found that the molecular mass of epoxy-diane co-oligomer modified by co-polycondensation is higher than the molecular mass of epoxy-diane oligomer not modified. So, in the non-modified epoxy-diane oligomer $\overline{M_w} = 290$; $\overline{M_n} = 260$; $\frac{\overline{M_w}}{\overline{M_n}} = 1.115$ in the benzamide-modified co-oligomer $\overline{M_w} = 520$; $\overline{M_n} = 430$; $\frac{\overline{M_w}}{\overline{M_n}} = 1{,}209$ and $\sum \frac{\overline{M_w}}{\overline{M_n}} = 2.32$.

DT and TQ analysis of epoxy-diane co-oligomer modified with benzamide was carried out and the main indicators are given in Table 2.

The process of thermal destruction took place in three stages and water was obtained in the first stage, low-molecular compounds with new composition in the second stage, and dehydrogenation process and coke was obtained in the third stage.

No.	Indicators	Unit of measure	Quantity
1	Mass loss in the first phase $(\Delta m_1)_t$	%	6.38
2	Mass loss in the second phase (Δm_2)	%	15.89
3	Mass loss in the third stage (Δm_3)	%	45.6
4	Initial temperature of destruction	^{0}C	123.6
5	Half – life temperature	^{0}C	428.5
6	Coke number	%	28.9

Table 2. Results of the process of destruction of modified co-oligomer

4. Conclusion

The epoxy-diane oligomer was first modified with benzamide in an alkaline medium and studied its basic physicochemical and physico-mechanical parameters. It was found that modification of the epoxy-diane oligomer by co-polycondensation with benzamide is a chemical modification, and the functionality of the resulting co-oligomer increased due to amide groups. As a result, the main indicators have also increased, only the number of epoxy groups has decreased. This confirms that the process is a chemical modification. According to the results of the physico-chemical analysis of the IR, NMR, DT and TG spectra carried out at the same time, it became known that the factor influencing the main parameters of the co-oligomer synthesized by the method of co-polycondensation is the production of a higher molecular weight compound by reaction with benzamide-containing amide groups. The newly synthesized co-oligomer is recommended to be used as a binder in the production of composites for various purposes.

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