

# Epoxidized dinaphthol application as the basis for binder with advanced carbonation level to reducing their flammability

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**Abstract.** The possibility of using polymers based on epoxyphenolic binders to obtain fiberglass with an intense level of carbonization has been investigated. The correlation between the pyrolytic transformations intensity and the fire hazard indicators of polymers is shown. It is established that the conditions for the intensive passage of pyrolytic reactions are facilitated by the presence in the matrix system of conjugated aromatic (naphthalene) radicals. The C/H ratio in the carbonized layer is confirmed by the data of IR spectroscopy both at the preparation stage and after exposure to characteristic temperatures.

## Introduction

Currently, the use of polymeric materials in the industry has become widespread. However, based on the fiberglass products use conditions, they are increasingly tightened requirements for their performance parameters.

As raw materials (ingredients) for fiberglass receipt binders often use epoxy resin [1]. Advantages of these resins are expressed in sufficient manufacturability upon their receipt, high rates of adhesion, thermal and heat resistance, resistance to corrosive environments [2].

Among other requirements for the polymer composites characteristics is the reduction of the combustibility of polymers used in all industries and construction.

In turn, combustibility – is a complex characteristic of a material's ability to resist the effects of combustion. It includes the following values (fire hazard indicators):

- 1) combustion or self-ignition temperature;
- 2) burn-up rate and flame propagation velocity across the surface;
- 3) parameters characterizing the conditions under which a self-sustaining combustion process is possible, such as atmosphere composition (oxygen index) or temperature (temperature index) [2].

To obtain materials with specified properties, it is necessary to scrutiny the destruction process mechanism, as well as the epoxies carbonization, the structure and properties of the carbonized products formed. This formulation of the problem causes the possibility of obtaining materials with low flammability without flame retardants and fillers use.

## Analysis of recent research and publications

A considerable amount of work is devoted to the study of these issues using modern research methods.

Thus, in [3], a fire-resistant polymer composition and a laminate based on it were proposed. However, the paper does not pay attention to the mechanism of material combustibility reducing. Another work [4] is dedicated to the use of a "fire-resistant" epoxy composition. However, it uses phosphorus-containing components as fillers that reduce flammability. The epoxy composition,

presented in [5], has not been investigated by the authors at the stage of thermal destruction.

Thus, in [6, 7], the relation of the oxygen index (one of the indices of polymers flammability) to the amount of carbon residue in the thermodestruction of both unfilled polymers and polymers using fire-retardant additive and fillers is shown.

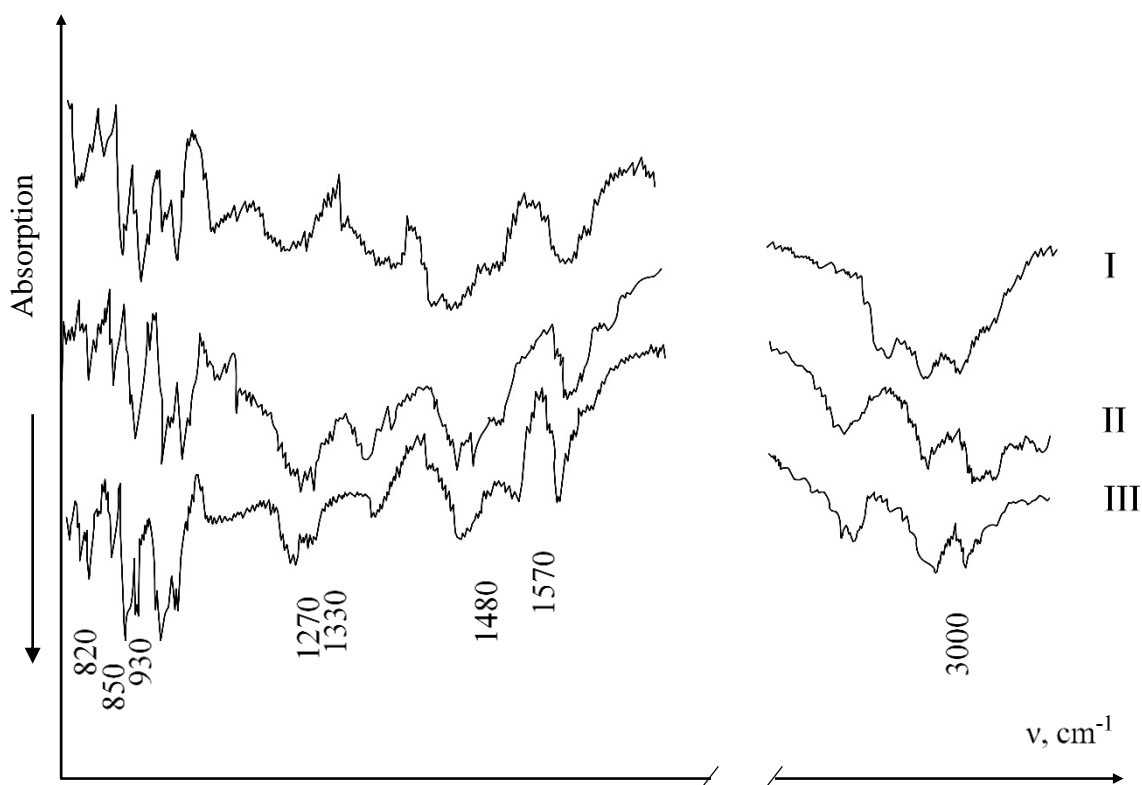
However, a number of issues are still unclear. First of all, this relates to the correlation of the original polymer grid structure with the structure and properties of the carbonized product, as well as the dependence of the flammability indices of fiberglass on the intensity of their carbonation. For example, in [8] it was shown that the structure of coke (porosity and permeability), the rate of carbon-producing, as well as some flammability rates depend on the carbon and hydrogen atoms ratio in the binding molecule.

## Main Part

In this connection, it was necessary to consider the carbonization process of crosslinked polyepoxides formed during the stage of its thermal and thermal-oxidative breakdown.

As object of research on the basis of their degree of combustibility and percent of carbon residue under linear heating [9] were used: bromine-containing oligomer; 4, 4'-diglycidyl ether - 1, 1'-dinaphthol; 2, 2'-diglycidyl ether - 1, 1'- dinaphthol; 4, 4' - diglycidyl ether - 1, 1'- dinaphtholmethyl.

Elemental analysis was used to establish the gross formula, determine the relationships and quantitative composition of the obtained substances. The infrared spectrum (Fig. 1) contain absorption bands in the area of  $930$ ,  $1330$ , and  $3000\text{ cm}^{-1}$ , which are characteristic of epoxy cycle oscillations; in the area of  $820$ - $850\text{ cm}^{-1}$  for 1, 2 and 1, 4 disubstituted naphthalene; in the area of  $1480$  and  $1570\text{ cm}^{-1}$  – for skeletal oscillations of naphthalene rings; in the area of  $1240\text{ cm}^{-1}$  – for ester bonds.



**Fig. 1. IR spectra of: 4, 4'-diglycidyl ether - 1, 1'- dinaphthol (I); 2, 2'-diglycidyl ether - 1, 1'- dinaphthol (II); 4, 4' - diglycidyl ether - 1, 1'- dinaphtholmethyl (III)**

To obtain a mesh structure polyepoxy, the interaction of epoxidized dinaphthols with novolac

phenol-formaldehyde resin brand “CΦ-010” (teardrop temperature according to Ubbelode ~ 120 °C). For this purpose, previously prepared spirit-acetone mixture of epoxidized dinaphthol and phenolic resin at a ratio of reactive reagents 100:60.

Some quantitative indicators of elemental analysis of the presented binders are shown in Table 1. As can be seen from the presented data, the ratio of hydrogen to carbon in the polymers is quite high.

**Table 1. Some physical and chemical properties of epoxidized dinaphthol**

Oligomer	Elemental analysis		
	C	H	O*
4, 4'-diglycidyl ether - 1, 1'- dinaphthol (I) (C <sub>26</sub> H <sub>22</sub> O <sub>4</sub> )	76,97	4,94	18,09
	78,39	5,53	16,08
2, 2'-diglycidyl ether - 1, 1'- dinaphthol (II) (C <sub>26</sub> H <sub>22</sub> O <sub>4</sub> )	75,87	4,82	19,31
	78,39	5,53	16,08
4, 4'-diglycidyl ether - 1, 1'- dinaphtholmethyl (III) (C <sub>27</sub> H <sub>24</sub> O <sub>4</sub> )	77,04	4,98	17,98
	78,64	5,83	15,53

Note. \* - found by subtraction.

Based on the principles of polymeric materials combustibility reducing, namely, the ratio of C/H bonds, as well as the rate and percentage of coking, thermogravimetric analysis of the obtained polymeric binders and industrial analogue was performed (Table 2).

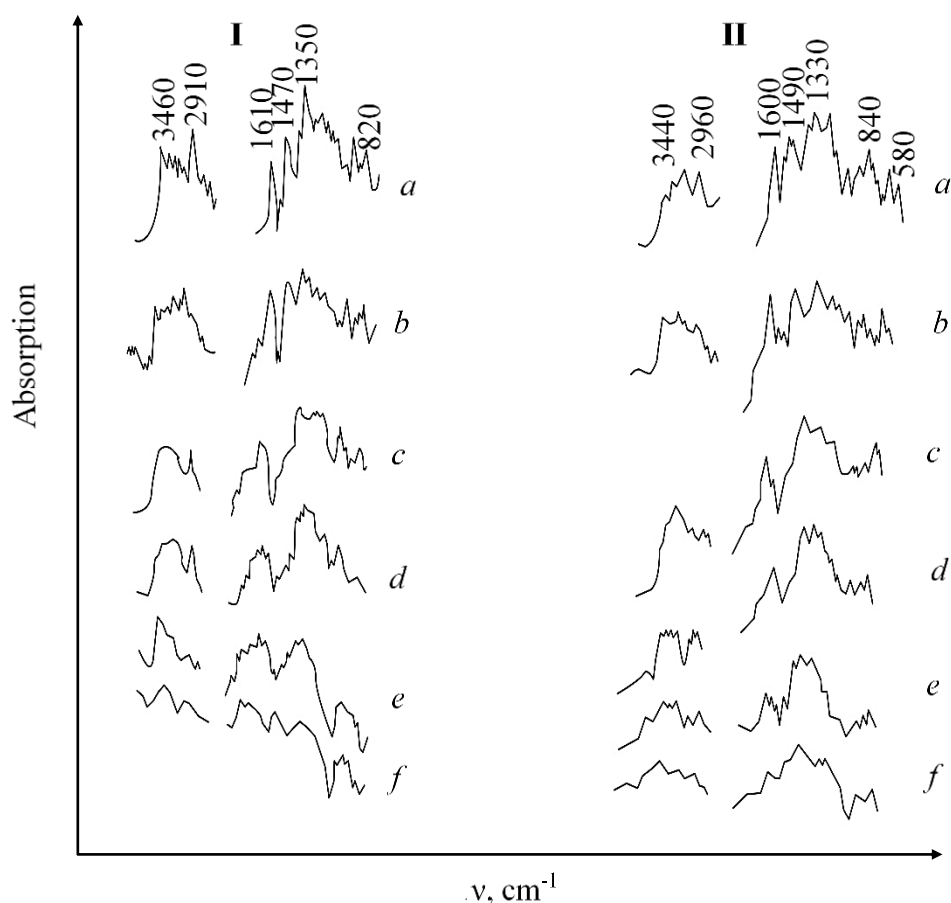
**Table 2. Characteristics of the polyepoxy destruction process**

Polyepoxy	The area of the maximum destruction speed, °C	Amount of carbon residue, %
4, 4'-diglycidyl ether - 1, 1'- dinaphthol	270-590	22
Bromine-containing epoxy system	280-680	19
2, 2'-diglycidyl ether - 1, 1'- dinaphthol	320-700	14
4, 4'-diglycidyl ether - 1, 1'- dinaphtholmethyl	330-720	12

The analysis of table data shows based binder 4, 4'-diglycidyl ether - 1, 1'- dinaphthol has a lower content of volatile components in the destruction, as well as a large percentage of the output of carbon residue, making it the most perspective for use in fiberglass systems among proposed binders.

However, unlike the linear degradation, polymer degradation indexes in conditions close to the fire dynamics will certainly be different. In this regard, IR spectra disrupted binding in these conditions (Fig. 2) were conducted.

Analysis of the infrared spectra of polymer binders, heat-treated at characteristic temperatures led to the conclusion that the heat treatment of 600 °C is accompanied by increased aromaticity polymer structure (Fig. 2). To establish the degree of carbonization ratio of proposed binding examined the relative change in the optical density of the absorption bands 1600 (1610) and 820 (840) cm<sup>-1</sup>, responsible, respectively, for valence aromatic rings oscillations and deformation oscillations of monosubstituted benzene rings.



**Fig. 2. IR spectra of polymeric binders during carbonization (based binder 4, 4'-diglycidyl ether - I, 1'- dinaphthol – I; bromine-containing based binder - II): a – 20 °C (initial material) b – 200 °C c – 300 °C, d – 400 °C, e – 500 °C, f – 600 °C**

According to the degree of change of this ratio with temperature increasing, the proportion of conjugated structures in the composite on the basis of epoxidized dinaphthol is much higher than that of the industrial analogue, indicating a more intensive carbonization of these polymers.

In addition, a comparative analysis of the experimental data showed that the material based on 4, 4'-diglycidyl ether - 1, 1'- dinaphthol was more thermostable from the obtained polymers in inert conditions [10]. The latter is largely explained by the improved combination of physical and chemical contacts that are realized at the topological level of the polymer mesh. At the same time, in the bromine-containing epoxy system, the crosslinking density is higher, which has a negative effect on the formation of a complex of thermophysical characteristics.

To confirm the effect of carbonization intensity on the flammability of polymeric materials and to determine general trends, tests were conducted to determine the characteristic temperatures by standard test methods (Table 3).

**Table 3. Combustion and ignition temperatures of polymer composites**

The basis for polymer binder of FRP	Combustion temperature, °C [11]	FRP ignition temperature, °C
4, 4'-diglycidyl ether - 1, 1'- dinaphthol	515	820-870
Mixed system: epoksydian oligomer “ЕД-20” + bromine-containing oligomer	475	790-840

The combustion and ignition temperatures of polymers (both block and film-forming samples) show a significant advantage (7.7% difference in the combustion temperature) of the naphthalene

binders over the known industrial counterparts used in fiberglass systems with reduced flammability.

A possible explanation for the increase in ignition temperature of the proposed binder is described by the combination of endothermic and exothermic homogeneous processes in the condensed phase (polymeric binder) and chemical transformations in the gas phase. At the same time, the decisive moment for achieving the combustion is to establish the critical rate of the gas-phase reaction in the gas layer adjacent to the surface of the solid sample. That is, the presence of a sufficient layer of carbon residue simply blocks the diffusion of volatile polymer destruction products to the reaction zone, thereby increasing the combustion temperature of the material.

The rate of formation of combustible products and their diffusion into the environment capacity is essential for the implementation of gas-phase combustion. The polymer material is ignited at a critical rate of release of flammable pyrolysis gases. The development of a self-accelerating flare reaction is accompanied by a change in the sign of the temperature gradient in the gas phase near the surface. The moment of ignition corresponds to the condition of equality of heat emission due to the gas-phase reaction of local heat losses.

## Conclusions

On the example of four types of epoxy binders shows the effect of the intensity of coking on the characteristic combustion temperatures of polymer composites. In the process of heating the crosslinked polymers in the presence of condensed fragments, it is formed a qualitatively new structure, that prevents the heating of the undeveloped lower layers and impedes the diffusion of volatile products into the combustion zone.

It seems to us that the formation of dense, carbonized destruction products in an oxidizing environment for 4, 4'-diglycidyl ether - 1, 1'-dinaphthol allows us to reduce a number of fire hazard indicators of fiberglass based on it.

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