

# Investigation of the kinetics of heat treatment of epoxy polymers

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**Abstract.** The study examines the effect of the concentration of modifiers (BDI) on the annihilation characteristics of cured epoxy polymers using the positron annihilation method. The results show that both the concentration and size of microcavity defects decrease, which can be explained by the formation of densely sewn areas due to the production of additional bridges. The supramolecular structure of the formed epoxy polymer is discussed, with the identification of several distinct areas, including polymer globules formed by stacking chains of simple polyester macromolecules around polymerization centers, and the interglobular space consisting of the ends of macro chains and low molecular weight products. The end groups of polymerization-cured epoxy polymers, such as double bonds of the vinylidene type, hydroxyl and unreacted epoxy groups, create conditions for the splitting of BDI in the interglobular space. The study also demonstrates that at optimal concentrations of modifiers, there is a decrease in the radius and concentration of micropore defects, as well as a general decrease in the proportion of free volume. The curing processes of epoxy polymers and their heat treatment in the presence of modifiers are investigated, with BDI having a significant effect on the formation of the epoxy polymer structure.

## 1 Introduction

As is known [1-6], the use of amine derivatives as hardeners of epoxy resins has improved physical and mechanical properties. However, a number of valuable indicators can be achieved only with the use of isocyanate hardeners. Blocked diisocyanates (BDI) are a promising area in this area. The use of blocked diisocyanates makes it possible to reduce volatility and density, eliminate the toxicity of diisocyanates, and most importantly, prevent the interaction of isocyanate groups with the amine hardener of epoxy resin. This makes it possible to combine the curing of epoxy resins, i.e. BDI are capable of forming additional (when most of the epoxy groups are opened with the help of amine) crosslinking, according to hydroxyl and non-reacted epoxy groups at that time.

In the research works [3,7], it was shown that the gel formation process can occur at elevated temperatures (up to 90 °C), then an exothermal maximum of the order of 160-170 °

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C is observed. The metabolic decomposition of BDI takes place in the temperature range of 80-170 °C [8], i.e., temperature conditions are created for the "splitting" of BDI.

The authors of [8] proposed the mechanism of gelation in the epoxy resin-hardener reaction system. Considering that a number of reactions with the formation of various compounds are possible [9-10] and the features of the method used (high-resolution NMR), the following assumptions were made. If we arrange the BDI in descending order of their exchange decomposition temperatures, we get the following row of blocking agents: diethylamine > phenol > n-nitrosophenol >  $\epsilon$ -caprolactam > furfurylideneaminoethanol. Therefore, it is obvious that if the possibility of the exchange decomposition of BDI with the block agent diethylamine in the reaction system is discovered by the time of gelation, then the probability of the formation of similar processes with BDI lying in the row to the right will increase sharply.

Therefore, 2,4-toluene diisocyanate blocked by diethylamine was used in this work. This compound gives a fairly simple spectrum, which thereby facilitates the interpretation of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

## 2 Materials and methods

The object of the study is epoxidian oligomers, which have epoxy and hydroxyl groups in their composition. Secondary aromatic aminopiperidine was used to cure epoxidian oligomers.

To modify epoxidian oligomers, blocked diisocyanates (BDI) were used as modifiers, which are adducts of a mixture of 2,4- and 2,6 – toluenediisocyanate (in a ratio of 60:40) with the following blocking agents: diethyl amine, phenol, n-nirosophenol,  $\epsilon$ - caprolactam, furfurylidene-minoethanol.

$^1\text{H}$  NMR spectra were recorded on a C 60-HL spectrometer (Jeol, Japan). The operating frequency is 60 MHz. The peak areas were measured by an electronic integrator of the spectrometer with an accuracy of up to 2%.

The  $^{13}\text{C}$  NMR spectra were recorded on a WH-90 spectrometer (Bruker, Germany). The operating frequency is 90 MHz. The Fourier transform method was used using wide-field decoupling from spin-spin interaction, as well as the "incomplete decoupling from protons" mode. GMDS was used with internal ethanol, the chemical shift of which, relative to tetramethylsilane, was assumed by us to be 2.4 m.d.

A technique for measuring the lifetime of positrons. The essence of the method lies in the fact that simultaneously with the positron, the source also emits a gamma quantum. Annihilation photons are detected by two different detectors. The difference in the time of appearance of the signals from the two detectors determines the lifetime of the positrons.

Positrons are formed by the decay of two radioactive isotopes:  $^{22}\text{Na}$  and  $^{65}\text{Zn}$ . In this work, the positron stoker for experiments on measuring the lifetime was prepared by evaporating several drops of an aqueous solution of  $^{22}\text{NaCl}$  onto a thin (5-7 microns) aluminum foil (the source was covered with the same foil from above and strengthened in a mandrel). The size of the radioactive salt stain was 14-1.5 mm.

The activity of the source was 10-20 mk Ki and therefore no special protection against radioactive radiation was provided in the lifetime installation. The installation for measuring the BW spectra of the Institute of Electronics of the Academy of Sciences of the Republic of Uzbekistan was used in the work.

### 3 Results

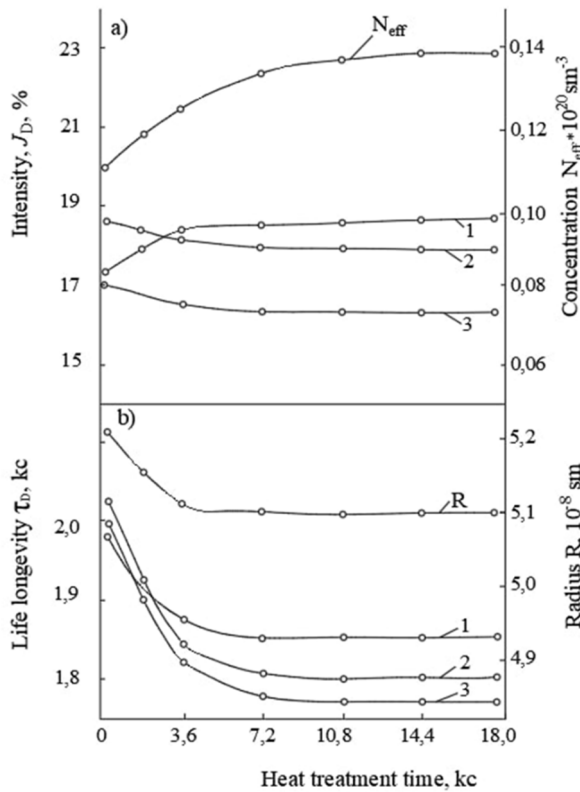
The kinetics of heat treatment of epoxy polymers cured with piperidine (curve 1) and modified BDI (BDI-2 (curve 2) and BDI-4 (curve 3) are shown; the concentration of modifiers 2 and 4 is 0.15 g/hydroxyequivalent), the results of which are shown in Figure 1.

A noticeable decrease in the value of  $\tau_D$ , (Fig.1, b) during heat treatment at a temperature of 443 K indicates a decrease in the size of micropores in crosslinked compositions, as a result of the transition of a linear polymer into a densely reticulated three-dimensional polymer.

The nature of the change in  $\tau_D$  for modified systems is similar (curves 2,3) to the unmodified system (curve 1). However, the relative change in the value of  $\tau_D$  for modified systems is greater. This indicates an even more significant reduction in the size of micropores, and the efficiency of modifier 4 (curve 3) is higher than modifier 2 (curve 2).

Changes  $J_D$  in the temperature during heat treatment are different for different systems (Figure 1, a).

In an unmodified composition,  $J_D$  increases slightly at the initial stage of heat treatment and does not change further (curve 1). A similar effect of increasing the concentration of microdefects was also obtained. It is associated with the formation of a rigid grid with a heterogeneous density structure.

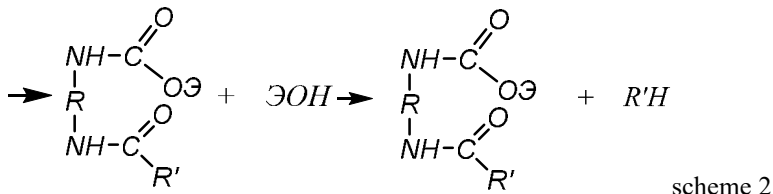
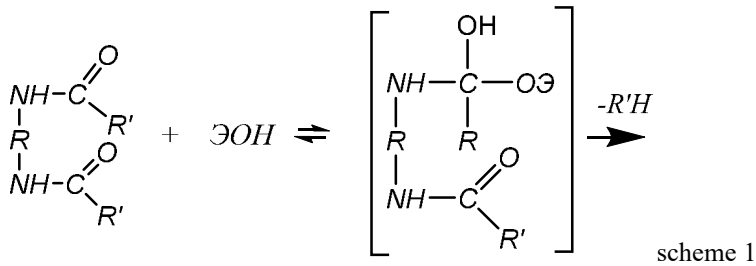


**Fig. 1.** Change in the intensity of JD (a) and lifetime  $\tau_D$  (b) of the long-lived component of the positron lifetime spectrum during heat treatment at 423 K of epoxy piperidine polymers containing modifiers, as well as the calculated parameters of microdefects R and  $N_{eff}$ : 1 - without modifier; 2 - with modifier 1 and 2 <0.18 g/hydroxyequivalent); 3 - 4 and 5 (0.45 g/hydroxyequivalent).

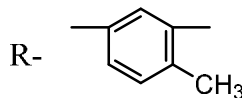
During the heat treatment of epoxy polymers modified with BDI, the value of  $\tau_D$  not only did not increase, but, on the contrary, decreases slightly with the time of heat treatment (curves 2 and 3). A greater increase was obtained in the case of using modifier 4 (curve 3), given the nature of the change in curve 2, it can be assumed that only when a higher temperature is reached, BDI-2 begins to manifest itself, i.e. blocked diisocyanates with a high temperature of exchange decomposition (commensurate with the temperature of heat treatment) have a modifying effect on epoxy polymers only during heat treatment.

A noticeable change in the values of  $\tau_D$  and  $J_D$  for modified systems shows that when a certain temperature is reached, modifiers have a very significant effect on the formation of an epoxy polymer. As a result of such an impact, a structure with a lower concentration (change in the value of  $J_D$ ) and the size (change in the value of  $J_D$ ) of micro-cavities-defects is formed. Modifiers with a lower temperature of exchange decomposition are more active according to the positron annihilation method.

As already noted in the supramolecular structure of the resulting epoxy polymer, given the accepted structure of the amorphous polymer, several areas can be distinguished. Polymer globules formed by a lattice around polymerization centers of chains of macromolecules of a simple polyether type. And the interglobular space consists of the ends of macro chains and low molecular weight products. The terminal groups of polymerized cured epoxy polymers include vinylidene-type double bonds, hydroxyl and unreacted epoxy groups. Thus, conditions for the splitting of BDI are created in the interglobular space. And when a certain temperature is reached, the process of transesterification occurs according to scheme 1 and 2.



Where:



$R'$ - block agent.

$EOH$  is an epoxy polymer (or tertiary amine) containing a hydroxyl group.

At the same time, as shown by the conducted studies using positron diagnostics, there is a decrease in both the concentration and the size of the micro cavities of defects. This can be explained by the formation of tightly stitched areas by obtaining additional bridges.

However, for BDI and formed with the help of blocking agents diethylamine or phenol, the probability of formation of such bridges is low. Apparently, therefore, the change in the annihilation characteristics of  $\tau_D$  and  $J_D$  is insignificant and is in the region of low concentrations.

**Table 1.** Dependence of the radius  $R$ , the concentration of  $N_{\text{eff}}$  micropores, and the free volume  $f_{\text{cb}}$  on the type and concentration of blocked diisocyanate in an epoxy piperidine polymer.

Conditional Designation-calculation of the modifier	Concentration the differential Modifier concentration, g/hydrocequivalent mic	Radius $R=10^{-8}$ , $\text{cm}^{-3}$	Concentration micropores $N_{\text{eff}}=10^{+29}$ , $\text{cm}^{-3}$	Value Free volume value $f_{\text{cb}}$ , %
Without modifier		3.868	1.006	2.42
1	0.15	3.851	0.981	2.35
	optimal (0.15)	3.851	0.981	2.35
	0.6	4.012	1.043	2.82
2	0.15	3.851	0.972	2.32
	optimal (0.15)	3.851	0.972	2.32
	0.6	3.953	1.028	2.66
3	0.15	3.837	0.972	2.30
	optimal (0.3)	3.841	0.968	2.29
	0.6	3.878	1.012	2.47
4	0.15	3.840	0.959	2.27
	optimal (0.3)	3.837	0.955	2.26
	0.6	3.845	0.970	2.31
5	0.15	3.821	0.952	2.22
	optimal (0.3)	3.795	0.946	2.16
	0.6	3.846	0.968	2.30

As can be seen from Table 1, when modifying for some concentrations of epoxy piperidine polymers of BDI, the radius of  $R_0$  and the concentration of  $N_{\text{eff}}$  micropore defects decrease. Accordingly, there is a decrease in the proportion of free volume  $f_{\text{cb}}$  of the epoxy polymer.

## 4 Conclusion

The effect of the concentration of modifiers (BDI) on the annihilation characteristics of approved epoxy polymers was studied by the method of positron annihilation. It is shown that at optimal concentrations of modifiers, there is a decrease in the radius and concentration of micropores, as well as a general decrease in the proportion of free volume. The curing processes of epoxy polymers and their heat treatment in the presence of modifiers are investigated. It was found that BDI with a low exchange decomposition temperature have a significant effect on the formation of the epoxy polymer structure already at the curing stage, while BDI with a high exchange decomposition temperature only during heat treatment.

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