KINETIC REGULARITIES OF THE REACTION OF OLIGO-4-AMINOPHENOL WITH EPOXY RESINS

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Epoxy resins in the overwhelming majority acquire technically important properties only as a result of their transformation into a network polymer, i.e. when interacting with hardeners. In turn, the chemical nature and structure of both the resin and hardener molecules during curing are one of the determining factors affecting the network structure of the obtained compositions, which has a primary effect on the technological properties of the initial compositions. In this regard, we have studied the kinetic regularities of the reaction of oligo-4-aminophenol (OAPh) with epoxy resins.

OAPh obtained by aminophenol oligomerization in the presence of H_2O_2 ($\overline{M}_w = 820$ and $\overline{M}_n = 540$, the content of hydroxyl groups is 15.1 %), epoxy resin ED-20 and nitrogen-containing epoxy resin (NER) were used. The content of epoxy groups of this resin was 12.5 %. To obtain a homogeneous mixture in the reaction of OAPh with epoxy resins, excesses of the latter were used. A solution of triethanolamine (TEA) in butanol was used as a catalyst.

The study of the kinetic regularities of the copolymerization of OAPh with these resins was carried out in their mixture in the absence of solvents.

It has been established that the most favorable temperature range for studying the kinetics of these reactions is 373–393 K, i.e. at such temperatures it is convenient to monitor the progress of the process. The calculated values of some kinetic parameters are given in Table 1.

Table 1. Kinetic parameters of the reaction of OAPh with ED-20 (1–3) and nitrogen-containing epoxy resin (4–6). $[TEA]_0 = 0.18$ mol/l

№	[Epoxy groups]$_0$, mol/l	$[-OH]_0$, mol/l	T, K	$W_0 \cdot 10^3$, mol·l^{-1}·min^{-1}	$k \cdot 10^4$, l·mol^{-1}·min^{-1}	E, kJ/mol
1	5.6	1.2	373	4.84	7.2	
2	5.6	1.2	383	8.06	12	74.5
3	5.6	1.2	393	14.1	21	
4	5.2	1.1	373	5.1	8.9	
5	5.2	1.1	383	9.7	17	71.2
6	5.2	1.1	393	14.3	25	

It was found that these reactions, starting from 373 K, proceed at a noticeable rate and, with an increase in temperature to 393 K, intensify ~3.7 and ~3.5 times, respectively, for NER and ED-20. Table 1 shows that the rate constants of these reactions are quite high, and the activation energies are 71.2 kJ/mol for the NER reaction and 74.5 kJ/mol for the ED-20 reaction.

At the same time, NER in the reaction with OAPh exhibits a higher reactivity than ED-20, which is apparently due to the presence of more electronegative fragments and elements in the composition of NER, compared to ED-20. In addition, due to the participation of a more mobile ester fragment in the composition of the NER, its macromolecules become more flexible and mobile. It should be noted that the oxirane ring opening scheme of both AES and ED-20 during the interaction of OAPh is identical to that in the reaction of OAPh with epichlorohydrin in the presence of (TEA).

Thus, the study of the kinetic regularities of OAPh copolymerization with epoxy resins showed that AES in the reaction with OAPh exhibits a higher reactivity.