STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF BENZIMIDAZOLE DERIVATIVES

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Abstract:	Keyword
This article discusses the physicochemical properties of benzimidazole derivatives. Benzimidazole and the process of its use are listed. The biochemical composition and formation of benzimidazole are also being studied.	**benzimidazole, stabilizer, polymerization process, polyamides, polymers, molecular system, molecular bond, epoxy resin.**

INTRODUCTION

Research in the field of creating new effective high-molecular stabilizers is of undoubted theoretical and practical interest. This is primarily due to the fact that the introduction of small amounts of effective stabilizers can significantly increase the service life of polymer materials and products based on them. Such a task is especially relevant in connection with the widespread use of polymer materials in various branches of industry and national economy, especially the climate of our country and Central Asia, where polymers can be subjected to intense heat, light, moisture and other climatic factors.

Currently used industrial low molecular weight stabilizers are prone to migration, volatilization and solvent extraction. These disadvantages are eliminated or reduced when using oligomeric or high-molecular stabilizers. By polymerization of epichlorohydrin with nitrogen-containing heterocyclic compounds, we synthesized oligomeric compounds that have complexing properties to divalent metal ions and are effective stabilizers for PVC, polyamides and other polymers.

For liquid reaction systems, even externally homogeneous, a certain type of supramolecular organization is characteristic: aggregates of different types – molecular associates, clusters of nematic type, etc. [3]. Their presence and diversity affect the kinetic features of the polymer formation process [4]. In single–component systems, inhomogeneities are density fluctuations, in multicomponent systems - concentration fluctuations with different temporal and spatial parameters. Depending on the structure of the molecules, clusters can be more or less organized and have different lifetimes: from 10-5 to 102 s. The supramolecular structure (clusters) is formed due to strong dipole-dipole interactions, hydrogen or complementary group bonds, and Vandervaals forces between molecules. The interaction between complex molecules is carried out at the expense of all groups, taking into account their molecular and topological structure, as well as possible conformation.

Table 1 **Some popular epoxy resins**

Pitch	**A reagent that forms a resin by reaction with ECG**	M_n	**Epoxy number**	**Softening temperature,° C**
ЭД-5	бисфенол А	360–470	18–23	0
ЭД-6	–″-	480–600	13–18	10
ЭД-20	-″-	400	19–22	η=13–20 Па·с при 25
ЭТФ	Трифенол	-	19,5	40–65
ДЭГ-1	диэтиленгликоль	-	24	η=0,07 Па·с при 40
УП-610	*n*-аминофенол	-	28	184
ХТ-711	дихлордиаминодифенилметан	-	25	η=14 Па·с при 50
ЭА	Анилин	-	31,2	η=0,35 Па·с при 25
ЭН-6	наволачная смола	-	18	40

Epoxy oligomers (EOS) are no exception [1]. The methods of static light scattering [6,7], NMR with a pulsed magnetic field gradient [8, 19], X-ray diffraction analysis and IR spectroscopy investigated the structure formation in epoxidian oligomers with a molecular weight from 340 to 104 [2,10] and proved the presence of associates. It is established that in low molecular weight epoxides there is a temperature region in which two spinspin relaxation times are observed. One of them refers to the less mobile, and the other to the more mobile phase [4]. The content of the sedentary phase increases with a decrease in temperature, as well as with an increase in the molecular weight of EO. Estimates of the size of the associates give the following: ~34 nm for DGEB, 5-20 nm for ED-20 and 5-50 nm for ED-16 [5]. According to the work, low molecular weight EOS (ED-24, ED-22, ED-20 and ED-16) containing a large proportion of DHEB (up to 50%) crystallize during long-term storage: DHEB is released into the crystalline phase. All oligomers with a molecular weight greater than 1500 are solid amorphous glasses, the glass transition temperature of which slightly increases from 50 to 75 ° with an increase in molecular weight from 1.5 • 103 to 1 • 104. According to GPH data, the content of DHEB in these oligomers does not exceed 1-5%, and therefore its isolation into a separate crystalline phase seems unlikely. However, long-term isothermal exposure at 100-130 °From all epoxy oligomers, both low-molecular and high-molecular (E-23, E-05, polymer with Mn~8000) is accompanied by a process of structural reorganization leading to crystallization of oligomers and polymers.

Molecules with polar groups show the greatest tendency to associate formation: for example, according to diane associates, they consist of oligomer molecules of homologues with n>1 distributed in a DGEB medium; a complex structure of associates is proposed, with nuclei formed by hydrogen bonds between –OH and epoxigroups, and shells consist of diepoxide oligomers. J.C. Stevens and others [3] believe that the associative structure of diane EOS arises due to hydrogen bonds between epoxy and secondary OH groups, as well as from the forces of dispersion interaction.

Obviously, when heated, the associates are destroyed, and when a certain "threshold" temperature is reached, their complete disappearance occurs. According to the data, for the diane EO ED-20, this temperature is 90 ° C, and in oligomers with a larger molecular weight, the associates are preserved up to 120 ° C. According to V.G. Khozin's hierarchical model [7] thermally unstable secondary associates consist of a certain number of more thermally stable primary elements. When heated, secondary associates are destroyed to primary ones, the structural organization and the total number of which do not change. It is assumed that the number of molecules in secondary associates can reach tens of thousands for ED-20 and ED-26 oligomers, and a million in ED-8 and E-49 oligomers, in primary – about a hundred molecules for ED-20 and tens of thousands for ED-8 and E-49.

The associated structure of EO is affected by vibroacoustic, ultrasonic, thermal and mechanical treatment. The dependence of the size of the associates on the exposure time can be extreme: for example, during vibroacoustic processing, the effective size of the aggregates passes through the maximum, and with ultrasonic [8] and thermal [6] – through the minimum. At the same time, the dimensions and packing density of the associates change [2].

The flow of diane EO melts (Mn=376-3020) in a sufficiently wide range of velocities and shear stresses is Newtonian. The non–Newtonian behavior manifests itself only at shear stresses above 103 Pa, near the glass transition temperature, or, to a lesser extent, at shear rates above 1620 s-1. L.G. Nechitailo et al. believe that this may be due to the polydispersity of the EO or due to changes in the associated structure under mechanical influence under experimental conditions. Perhaps it is the latter phenomenon that can explain what X observed. Wang et al.: anomaly of the viscosity of pure DHEB in the range of shear rates 10-2-102 s–1.

In a number of works, the dependence of rheological anomalies on temperature has been found. For example, E.I. Vasilchenko et al. found that the viscosity of ED-20 at temperatures up to 50 ° C does not depend on the shear rate and decreases with the increase of the latter at higher temperatures. I.G. Gerasimov et al. [5] noted an increase in the viscosity coefficient of diane EOS during isothermal holding at temperatures up to 30 ° C for pure DGEB and up to 120 °C for ED-7.

Repeated attempts to describe the temperature dependence of viscosity by the Arrhenius equation end in failure. According to A. Ghijsels et al . The equation is applicable at

T>Tg+200 K; under these conditions, the activation energy of the viscous flow E is in the range of 20-200 kJ/mol. In the temperature range Tg<T<Tg+100 K, the viscosity dependence in the coordinates of the Arrhenius equation is usually nonlinear, and the apparent activation energy E varies with temperature and can be conditionally calculated only in a narrow temperature range. Thus, for the oligomer Epikote 1004 (Mn=1495), Eη varies from 400 kJ/mol at 60-70 °C to 100 kJ/mol at 125-175 °C, and for Epikote 1009 (Mn=3020) – from 230 kJ/mol at 100-130 °C to 109 kJ/mol at 160-190 °C.

Currently, it is considered correct to describe the temperature dependence of the viscosity of amorphous bodies, including linear EOS, by the Williams-Landel-Ferry equation (VLF):

$$\ln a_T = -C_1 \frac{T - T_g}{T - T_g + C_2}, \qquad a_T = \frac{\tau(T)}{\tau(T_g)} \cong \frac{\eta(T)}{\eta(T_g)}$$

where C1 and C2 are constants, for most polymers equal, respectively, 17.44 and 51.6 [36]; τ(T) and τ(Tg), n(T) and N(Tg) are relaxation time and melt viscosity at temperature Tg<T<Tg+100K and glass transition temperature.

The ratio B/T0 characterizes the fragility of the system – the deviation of the temperature dependence lnη = f(1/T) from the Arrhenius linear dependence. The temperature dependence of the viscosity of EO ED-16, ED-8 and DGEB is straightened in the coordinates of the FFT equation at T0 = 230, 250 and 175K, respectively.

Constants C1 and C2 tend to increase with the molecular weight of the diane EO and do not correspond to the above universal values (Tables 1 and 2).

If the values of C1 depend on the measurement methods, then the constants of C2 practically coincide (Fig. 1), and $C_1 = k_1/C_1{}^{*} = k_2 C_1{}^{**}$.

$\lg\eta = -k_1 \lg\sigma = k_2 \lg\tau$, (3)

where n, σ and τ are viscosity, electrical conductivity and relaxation time. The exponents of the degree of ki depend on the molecular weight (M) of IT.

It is generally assumed that for any amorphous bodies n(Td)≈1012-1013 Pa•c. Naturally, EOS are no exception. However, T. Koike, using the ratio (3) between σ and σ and taking σ(Td) as the glass transition criterion, found that, depending on the molecular weight, EO, n(Td) varies from 1012 to 108 Pa•c, decreasing with ee falling as a consequence of the dependence k1(M).

Table 2

ЭO	M_n	M_w/M_n	T_g, °C	C_1	C_2
Epikote 828	388	1,06	–16	11,27	25,8
				12,92*	28,0*
Epikote 834	590	1,23	0	12,23	36,0
				12,29*	33,9*
Epikote 1001	1396	1,55	30	13,89	45,7
				10,99*	48,3*

		–		16,14**	48,9**
Epikote 1001F	1696	1,78	31	14,10	49,2
				12,24*	50,8*
Epikote 1002	1891	1,63	39	15,36	42,2
				11,05*	47,1*
		–		16,54**	48,8**
Epikote 1003	2078	–	45	15,71**	48,8**
Epikote 1002F	2111	1,79	42	14,13	50,7
				11,63*	51,3*
Epikote 1004	2640	1,72	54	14,99	50,0
				9,76*	54,6*
		–		15,46**	52,6**
Epikote 1005	2757	–	59	16,70**	52,6**
Epikote 1004F	3606	1.98	57	14.94	43.2
				9.71*	46.8*
Epikote 1007	3903	–	69	16.11**	52.9**
Epikote 1009	9454	–	82	15.48**	46.6**

The values of constants calculated from the temperature dependence of the electrical conductivity (*) and the time of dielectric relaxation (**) are given.

Table 2 shows the constants of the FFT equation for some Diane EOS. It follows from the presented data that the ratios T0 / Tg = 0.88 and V/T 0 = 1.57 = 0.15, that is, practically independent of the molecular weight (M).

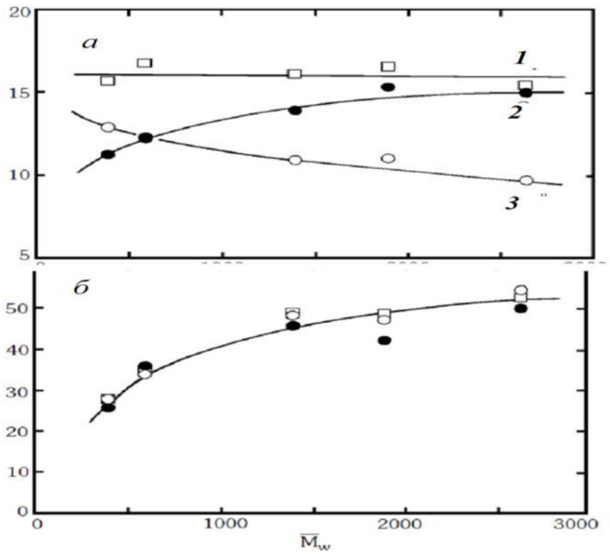

Fig. 1. Dependence of the constants of the VLF equation C 1 (a) and C 2 (b) on the molecular weight of the EO obtained from the dielectric (1), viscosity (2) and electrical conductivity (3)

In addition to the α-relaxation transition (glass transition), a Tll transition for liquid resins was registered in the diane oligomers, and for solid ED-24, the melting peak of the resin, Tm, located between Tg and Tll, was observed. At the same time Tl/Tg = 1,2 [4]. The existence of the Tl transition has been repeatedly confirmed and is associated with a complex morphological (associative) structure of the EO, at T>Tll the liquid becomes structureless [5].

Table 3 ***Constants of the FFT equation for a series of Diane EO***

ЭО	M_n	T_g**, K**	$A\cdot 10^3$**, Па·с**	***B*****, K**	T_0**, K**
Epikote 828	376	258	1,2	339	231
Epikote1001	491	303	0,75	393	273
Epikote 1004	885	323	2,2	467	282
Epikote 1007	1932	343	6,2	471	303
Epikote 1009	2913	352	18	539	310

EO is characterized by low-temperature β-relaxation. One group of researchers attributes β-relaxation to the movement of the diphenylpropane unit, others to the movement of hydroxyester groups, while later researchers indicate that the processes of secondary relaxation are associated with the movement of fragments of diphenylolpropane, together diphenylolpropane and hydroxyester fragments, trans–isomerization of methylene groups and rotation of phenylene fragments, that is, that the β-peak is a combination of movements of both these blocks. According to this interpretation, the low-temperature side (from -110 to -80 °C) of the β-peak arises from the π-reversals of phenylene groups in diphenylpropane, and the high-temperature side is caused by the movement of hydroxyester groups (from -70 to -55 °C). J.-F. Shi and co. it has been shown that these movements differ in speed by about an order of magnitude, and the process of pi-reversal is faster. Both have similar relaxation time distributions given by a stretched exponential function:

$$\phi(t) = \exp[-(t/\tau_p)^{\alpha}] .$$

The indicator a, equal to 0.6 – 0.7, controls the width of the distribution, and the characteristic time tp is the time scale of the affected activation energy for the π–reversal of 50 kJ/mol, and for the trans-isomerization of 57 kJ/mol. These two movements do not seem to exhaust all the processes contributing to the □-peak. In the works of V.A. Berstein and co-authors, based on careful experimental studies, it was concluded that α- and β-processes are associated with the movement of the same kinetic units. However, the α-process is due to the cooperative movement associated with the environment of this unit, and the β-process is due to its non–cooperative movement. In other words, when a segment is in a dense environment of neighbors, α-relaxation occurs, and β–relaxation occurs in a loose environment. The theory of glass transition developed by V.G. Rostiashvili and co-authors leads to the same conclusion.

As stated by R. Casalini et al., in DHEB systems, β-relaxation is attributed to a molecular group including hydroxyl, which in EPON828 makes an insignificant contribution, being present in only one of ten molecules. They confirm the existence of two processes: structural relaxation, or α, and one secondary process, which in this system is called γ-relaxation. The first process is described by the FFT equation with parameters: $A=(1,2\pm0,3)\cdot10^{-12}$ с, $B=(3,1\pm0,1)\cdot T_0$, $T_0=234,2\pm0,6$ К.

The second obeys the Arrhenius law: $A=(7,0\pm2,7)\cdot10^{-14}$ с, $E=5,7\pm0,2$ ккал/мол.

The use of various types of hardeners makes it possible to obtain epoxy composites with a wide range of various physico-mechanical and physico-chemical properties – from elastic to rigid, with high strength, without losing their strength characteristics under prolonged exposure to elevated temperatures (up to 200 ° C and above).

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