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The Effect of Curing Mode on the Parameters of Molecular Meshes of Epoxy and Polyester Copolymers †

Irina N. Vikhareva

Nanotechnology REC, South Ural State University, Lenin Prospect 76, 454080 Chelyabinsk, Russia; vikharevain@susu.ru; Tel.: +7-(351)-267-99-00

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Abstract: The establishment of the patterns of formation and structure of mesh polymers, as well as the methods of their controlled synthesis, makes it possible to rationally manage the technological processes of obtaining and processing materials based on them. This paper determines the possibility of directional variation in the parameters of the molecular grid of epoxy and polyester resin copolymers using a polyamide hardener. For this purpose, the influence of temperature regimes on the curing mixing technology of the original components was studied. The values of the Huggins constants were initially calculated. For this purpose, the swelling of copolymers in chloroform, xylene, dimethylformamide and acetone was studied. Taking into account the thermodynamic criteria, based on the results obtained, a solvent was selected that provides optimal swelling conditions for the synthesized copolymer. Experimental data describing the process of collecting copolymer samples were obtained. Using the Florey equation, the parameters of the structural grids of the developed polymer compositions were calculated.

Keywords: copolymer; crosslinking; epoxy resin; hardener; polyester; polyamine; swelling

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1. Introduction

Aliphatic polyesters are an attractive class of biologically based polymers [1]. However, the thermal and mechanical properties, as well as the service life of products based on them, polysebacates in particular, are unsatisfactory for certain applications [2]. The introduction of modifying resins as hardeners promotes the formation of mesh polymers [3]. Mesh polymers of various natures and crosslinking densities are widely used in modern composite materials [4–7]. The scope of application of the copolymers obtained depends on the degree of crosslinking of the components and the parameters of the molecular grids, which can be adjusted during the curing process and which determine their physical, mechanical and operational parameters [8]. This method is universal and makes it possible to obtain mesh polymers with any properties. Currently, methods of direct investigation of the structural characteristics of mesh polymers are actively developing. In this regard, it is relevant to study the regularities of the formation of polymer grids in the interaction of multifunctional compounds, as well as the means of their directed synthesis with a given structure and properties.

2. Materials and Methods

2.1. Materials

Polyester 24K is a specialized polycondensation product synthesized from ethylene glycol and glycerin, combined with sebacic acid. This resin exhibits a paraffin-like consistency, characterized by its gray to dark gray or brown coloration (Figure 1). The main characteristics of the PE resin: acid number, mg KOH per 1 g of polyester—8–18; mass fraction of hydroxyl groups, % —5.2–8.0.

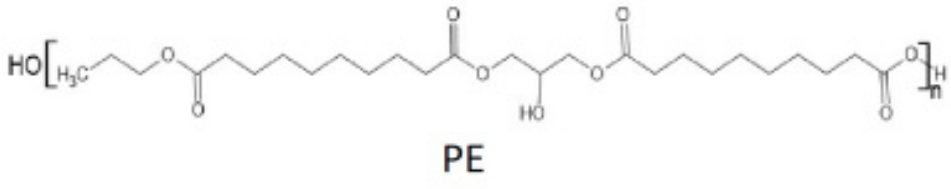


Figure 1. Polyester 24K [9].

Epoxyamine resin (EAR) is synthesized through the reaction of aniline with epichlorohydrin and is produced by Kurskkhimprom LLC in Kursk, Russia. This resin appears as a liquid that ranges in color from yellow-brown to dark red. Notable properties of EAR include a mass fraction of epoxy groups of at least 31.2% and a dynamic viscosity at 25 °C of no more than 0.35 Pa·s (Figure 2).

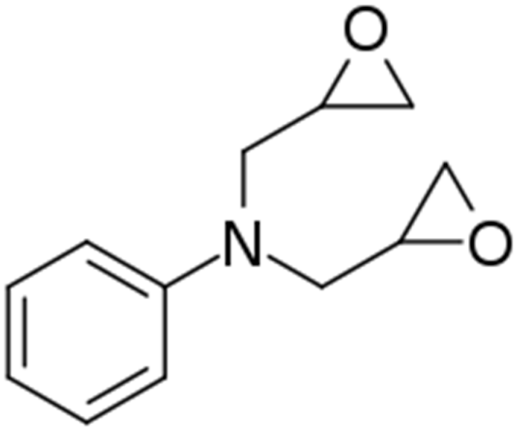


Figure 2. Epoxyamine resin (EAR) [9].

The hardener, known as PAH, is derived from the interaction of polymerized fatty acids from vegetable oils and polyethylene polyamines, also sourced from Kurskkhimprom LLC. This hardener is characterized as a homogeneous, transparent, viscous liquid that varies in color from yellow to dark brown. Its primary specifications include an amine number between 90 and 120 mg HCl/g and an amine number ranging from 139 to 185 mg KOH/g (Figure 3).

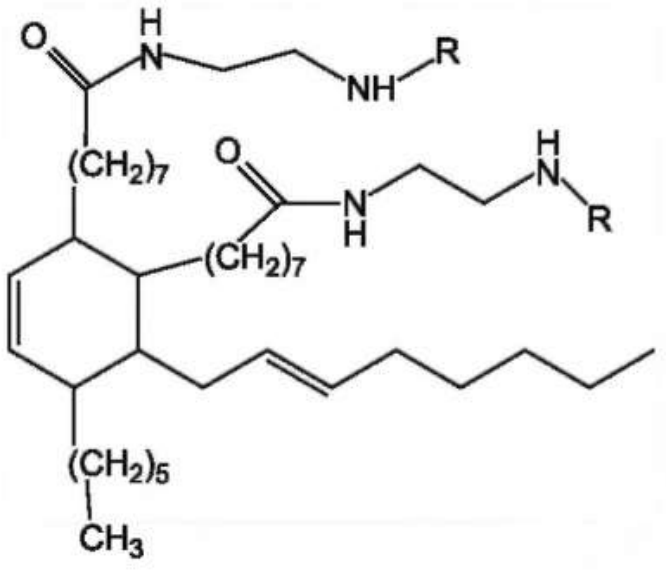


Figure 3. The hardener (PAH) [9].

2.2. Method of Obtaining Samples

Samples of copolymers were synthesized by blending polyester with epoxyamine resin and a hardener in specific ratios. The resulting compositions were then poured into silicone molds and cured under predetermined conditions.

2.3. Methods of the Analysis of the Samples

Density was determined by hydrostatic weighing on a balance with a measurement error of 0.0001 g (ASTM D 792).

The degree of polymer curing was determined by the extraction of films in acetone for 24 h. The sample weight was 1 g. The sample was weighed to an accuracy of 0.001 g and placed in a solvent. After 24 h, the polymer film was weighed again with the same accuracy. The sample was then dried in a vacuum oven for 24 h. The degree of curing was calculated based on the data obtained using the Formula (1):

$$S\ (\%) = (m - m_1)/m \cdot 100 \quad (1)$$

where m_1 is the mass of the dried sample, g, and m is the mass of the sample, g.

The swelling of the samples was carried out in an appropriate solvent for 24 h, under constant stirring. The samples were then carefully removed from the solvent, the excess solvent was removed with a lint-free material and weighed, fixing the result. Further, the samples were dried under vacuum to a constant weight. The degree of swelling was calculated using the Formula (2):

$$Ds\ (\%) = \frac{m_2 - m_1}{m_1} * 100 \quad (2)$$

where m_1 is the mass of the dried sample, g, and m_2 is the mass of the swollen sample, g.

3. Results and Discussion

Based on preliminary experiments, the ratios of components for obtaining polymer samples were established: EAR:PE:PAH = 3:2:4. The designations of the samples and their curing modes are presented in Table 1.

Table 1. Designations of samples and their curing modes.

Sample	Curing Modes
1	22 °C/56 h
2	22 °C/24 h, 60 °C/1 h, 80 °C/1 h
3	22 °C/24 h, 80 °C/1 h, 100 °C/1 h, 120 °C/1 h
4	60 °C/1 h, 80 °C/1 h, 120 °C/1 h
5	22 °C/24 h, 80 °C/1 h, 120 °C/3 h

The resulting plates were plastic polymers approximately 3 mm thick.

The occurrence of the reaction between the components of the mixture and the production of the polymer is confirmed by IR spectra.

To calculate the structural parameters of the grid of the obtained copolymers, it is necessary to know the density of the samples. The results obtained are shown in Table 2.

Table 2. The density values of the film samples.

Sample	The Density Values, g/cm^3
1	1.21
2	1.30
3	1.22
4	1.34
5	1.10

The degree of curing of the samples is determined by the amount of sol fraction (Table 3). Based on this indicator, other parameters of the molecular grid of the obtained copolymers were calculated: j—the degree of crosslinking, the average number of crosslinking links per molecule; V_a—share of active circuits; α—branching factor; and γ—crosslinking density.

Table 3. The main indicators of copolymers.

Sample	S, %	j, %	Va, %	A	γ
1	21.78	3.78	60.66	0.264	1.46
2	27.54	3.04	52.05	0.249	1.25
3	20.69	3.96	62.37	0.269	1.51
4	22.56	3.66	59.47	0.263	1.43
5	15.99	5.00	70.01	0.287	1.79

The amount of sol fraction in the crosslinked polymer decreases with increasing processing temperature. The highest degree of curing was shown by sample 5. The curing mode of this sample at maximum temperature was the longest of all the samples presented. The sample (1) without heating was also characterized by the high value of the crosslinked polymer, which confirms the reaction between the components of the mixture during a long holding time; that is, post-curing occurs. The absence of the cold curing stage of the sample (4) and the acceleration of the reaction upon heating immediately after mixing reduced the degree of reacting components. In the case of sample (2), the lowest gel fraction was observed.

An important confirmation of the formation of a spatial grid in a copolymer is swelling in a solvent, and the swelling coefficient shows the frequency of the polymer grid formed [10].

To determine the structural parameters of the polymer crosslinking, the swelling of copolymer samples was studied. Initially, a solvent was selected based on the Huggins constant calculated according to Formula (3), which is a measure of the thermodynamic affinity of the polymer and the solvent. For this purpose, the following solvents were used: chloroform, xylene, dimethylformamide, and acetone (Table 4). A sample of copolymer 3, characterized by the lowest value of the sol fraction, was used as the object of the study.

$$\chi = 0.37 + 0.52\ Vp \quad (3)$$

where Vp is the volume fraction of the polymer in the swollen sample.

Table 4. Calculated values of the Huggins constant.

Sample	X			
	Chloroform	Xylene	Dimethylformamide	Acetone
3	0.839	0.721	0.882	0.737

The best solvent for determining the structural parameters of the polymer crosslinking is the solvent with the lowest value of the Huggins constant. In this case, xylene. Accordingly, further experiments were carried out using xylene. According to the experimental data obtained, the following indicators are calculated: Ds—degree of swelling; M_c—the molecular weight of the chain segment enclosed between the nodes; N_c—the number of circuits between nodes per unit volume; and n_c—the number of moles of chains enclosed between nodes (Table 5).

Table 5. Calculated characteristics of copolymers.

Sample	Ds, %	M_c, g/mol	$N_c \times 10^{23}$, 1/cm^3	n_c, mol/cm^3
1	44.44	74.26	0.0980	0.016
2	43.09	67.67	0.1156	0.019
3	52.84	76.09	0.0965	0.016
4	67.98	79.69	0.1012	0.017
5	46.92	77.01	0.0860	0.014

The calculated parameters confirm that the values of the degree of swelling are consistent with the obtained values of the molecular weight of the chain segment connected between the nodes. That is, the swelling coefficient is directly dependent on this value.

4. Conclusions

As a result of the modification of the epoxyamine resin with polyester based on sebacic acid using an amide hardener, a highly cross-linked copolymer was obtained. The amount of gel fraction and, accordingly, the degree of curing of the resulting product increases with an increase in the temperature regime of the curing process. However, in order to achieve the maximum degree of curing, it is necessary to carry out cold curing at the initial stage of the formation of the crosslinked polymer. Otherwise, it is likely that, with an increase in temperature, the supramolecular cohesion will be disrupted and the interaction of prepolymer molecules will fluctuate, which leads to a decrease in the amount of gel fraction. Experimentally found degrees of the swelling of copolymers confirm that the heating of the prepolymer mixture immediately after mixing accelerates the crosslinking processes and bonds are formed along all possible interaction centers. Accordingly, relaxation processes do not have time to go through in the system, and fluctuations contribute to a low degree of curing.

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