chemistry proceedings

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Proceeding Paper

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

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† Presented at the 28th International Electronic Conference on Synthetic Organic Chemistry (ECSOC 2024), 15–30 November 2024; Available online: https://sciforum.net/event/ecsoc-28.

Abstract: The establishment of patterns of formation and structure of mesh polymers, as well as methods of their controlled synthesis, make it possible to rationally manage the technological processes of obtaining and processing materials based on them. The paper determines the possibility of directional variation of the parameters of the molecular grid of epoxy and polyester resin copolymers using a polyamide hardener. For this purpose, the influence of temperature regimes of curing, mixing technology of the original components has been studied. The values of the Huggins constants were initially calculated. For this purpose, the swelling of copolymers in chloroform, xylene, dimethyformamide 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 have been obtained. Using the Florey equation, the parameters of the structural grids of the developed polymer compositions are calculated.

Keywords: copolymer; cross-linking; epoxy resin; hardener; polyester; polyamine; swelling

Citation: Vikhareva, I.N. The Effect of Curing Modes on the Parameters of Molecular Meshes of Epoxy and Polyester Copolymers. *Chem. Proc.* **2024**, *6*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2024

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, in particular, and polysebacates, are unsatisfactory for certain applications [2]. The introduction of modifying resins as hardeners promotes the formation of mesh polymers [3]. Mesh polymers of various nature 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 way is universal and allows 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 ways of their directed synthesis with a given structure and properties.

2. Materials and Methods

2.1. Materials

Polyester 24K, a polycondensation product of ethylene glycol and glycerin with sebacic acid, was purchased from SPE Abika, Moscow, Russia. Polyester 24K is a paraffin-like mass from gray to dark gray or brown in color. The initial components for the production of 24K polyester are shown in 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.

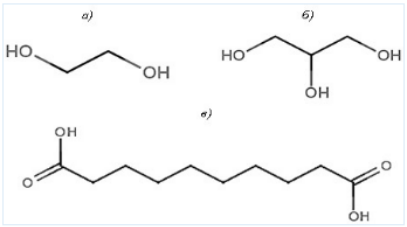

Figure 1. The initial components for the production of 24K polyester: a—ethylene glycol; b—glycerin; c—sebacic acid.

Epoxyamine resin (EAR, Figure 2), a product of the reaction of aniline with epichlorohydrin, is produced by Kurskkhimprom LLC, Kursk, Russia. The resin is a liquid from yellow-brown to dark red in color. Properties of EA resin: Mass fraction of epoxy groups, %, not less—31.2; Dynamic viscosity at 25 °C, Pa · s, no more—0.35.

The hardener (PAH, Figure 3), a product of the interaction of polymerized fatty acids vegetable oils and polyethylene polyamines, was purchased from Kurskkhimprom LLC, Kursk, Russia. The hardener is a homogeneous transparent viscous liquid from yellow to dark brown color. The main characteristics of the hardener: Amine number, mg HC1/g—90–120; Amine number, mg KOH/g—139–185.

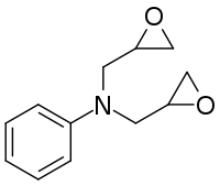

Figure 2. Epoxyamine resin (EAR).

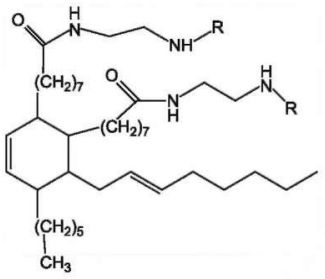

Figure 3. The hardener (PAH).

2.2. Method of Obtaining Samples

Samples of copolymers were obtained by mixing the components: polyester and epoxyamine resin and a hardener in certain proportions. The compositions were poured into silicone molds and kept according to the selected conditions. Film curing modes are described below.

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 curing of the polymer was determined by extracting the films for 24 h in acetone. The mass of the sample was 1 g. The sample was weighed to the nearest 0.001 g and placed in a solvent. After 24 h, a sample of the polymer film was weighed with an

accuracy of 0.001 g. Then the sample was dried in a vacuum oven for 24 h. The degree of curing was calculated using the Formula (1):

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

where m_1—mass of dried sample, g; m—mass of sample, g.

The swelling of the samples was carried out in an appropriate solvent for 24 h, constantly 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):

$$Ds\ (\%) = \frac{m2 - m1}{m1} * 100 \quad (2)$$

where m_1—mass of dried sample, g; m_2—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 the 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 the 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 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; γ—crosslinking density.

Table 3. The main indicators of copolymers.

Sample	S, %	j, %	Va, %	α	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 is the longest of all the samples presented. The sample (1) without heating is also characterized by a 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 is 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 [9].

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, 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—the volume fraction of the polymer in the swollen sample.

Table 4. Calculated values of the Huggins constant.

Sample	χ			
	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; 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	Nc ▪ 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 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 curing. However, in order to achieve the maximum degree of curing, it is necessary to carry out cold curing at the initial stage of formation of the crosslinked polymer. Otherwise, it is likely that with an increase in temperature, the supramolecular cohesion is disrupted and the interaction of prepolymer molecules is fluctuating, which leads to a decrease in the amount of gel fraction. Experimentally found degrees of swelling of copolymers confirm that 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.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement:

Conflicts of Interest: The author declare no conflicts of interest.

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