Synthesis and properties of high temperature self-curing epoxy resin

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Abstract. A new bifunctional epoxy resin was synthesized by the reaction of replacing the hydrogen atom of amino groups from 4,4'-diaminodiphenylmethane and epichlorohydrin taken in a double excess in dichloroethane. In order to remove HCI formed during the synthesis, which can interact with the initial diamine, as well as with the oxirane rings of both epichlorohydrin and the synthesized product, an excess of potassium carbonate was introduced into the reaction mixture. The structure of the synthesized epoxy resin - 4,4’-methylenebis(N-(oxiran-2-ylmethyl) aniline) was characterized and proved by the methods of FTIR spectroscopy, nuclear magnetic resonance and elemental analysis. The kinetic parameters of the synthesized resin were characterized by differential scanning calorimetry. Using the Kissinger method, the activation energy of the self-curing reaction was calculated, the value of which was 1.139 kJ / mol. Such a low activation energy of epoxy resin allows to cure at low temperatures, but shortens the storage time. Two curing modes were studied: 1 mode - 10 hours at 150 °C, 2 step mode - 10 hours at 150 °C + 3 hours of postcuring at 180 °C.

1. Introduction

Epoxy-based materials are widely used as binders of composite materials, coating, adhesives due to their excellent mechanical, electrical properties, chemical resistance, and easy-to-cut [1,2,3]. Epoxy resins occupy almost 70 % of the whole thermosetting resin market. Technological progress leads to significant increase in requirements for construction material properties in a wide temperature range. Todays demands for compounds based on epoxy resins for integrated circuits require a glass transition temperature above 200 °C.

Primary and secondary di- and polyamines [4], polybasic acids [5] and their anhydrides [6], thiols [7] are traditionally used as hardeners for epoxy resins. At the same time, increasing the glass transition temperature of epoxy polymers is a challenging task. Many approaches to increasing the glass transition temperature of epoxy resins, as well as the moisture resistance of epoxy resins by modifying the structure of initial resins, that affects the properties of the final cured epoxy resins. In [8], the authors increase the glass transition temperature of epoxy polymers by including a naphthalene ring in the structure. Kaji and Dndo [9], Pan et al. [10], Wang et al. [11] and Castell et al. [12] synthesized a naphthalene-based epoxy resin containing naphthyl and phenyl structures. Xu et al. [13] and Ren and authors [14] synthesized epoxy resins with a naphthalene-cycloaliphatic group.
Two-component systems "epoxy resin - hardener" consist of microdefects, which give rise to heterogeneity due to incompatibility of components based on different solubility properties of epoxy resins and hardeners [15]. Therefore, in recent years, great interest has been attracted by epoxy resins capable of self-curing, thereby avoiding the above disadvantages and at the same time showing high values of the glass transition temperature.

The aim of this work was to synthesize the structure of a new heat-resistant self-curing epoxy resin. The cure characteristics and physical properties of the cured polymer were investigated using several analytical methods.

2. Materials and Methods

Glass transition temperature $T_g$ of epoxy resin was determined using differential scanning calorimeter METTLER TOLLEDO DSC 822e at scanning rate 5 °C/min.

$^1$H NMR spectra was recorded using Bruker Avance-Neo 400 spectrometer (operating at nominal proton frequency 400 MHz) in CDCl$_3$ using HMDS as an internal standard.

FTIR spectras were recorded using Bruker Vertex80V with 64 scans at 2 cm$^{-1}$ resolution.

2.1. Materials

In this study a commercially available 4,4'-diaminodiphenylmethane and epichlorohydrin (Acros Ltd.), magnesium sulfate, potassium carbonate, ethyl acetate, and dichloroethane (Vitakhim Ltd.) were used. Ethyl acetate and dichloroethane were additionally dried by distillation over phosphorus pentoxide. All chemicals used were reagent grade.

2.2. Methods

Glass transition temperature $T_g$ of epoxy resin was determined using differential scanning calorimeter METTLER TOLLEDO DSC 822e at scanning rate 5 °C/min.

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2.3. Synthesis

In a two-necked flask 5 g of 4,4'-methylenedianiline (1), 7.5 g of K$_2$CO$_3$ and 200 ml of dichloroethane were added and kept with constant stirring for 2 hours at room temperature. Then 4.7 ml of epichlorohydrin (2) was added and stirring was continued at 80 °C for 5 hours. After completion of the reaction, the mixture was cooled to room temperature. The solution was filtered to remove the inorganic residue. The solvent was distilled off on a rotary evaporator. The crude product was treated three times with ethyl acetate and distilled water and separated. MgSO$_4$ was added to the organic layer to remove the remaining water. The organic layer was filtered off, the solvent was evaporated (figure 1).

![Figure 1. Synthesis of 4,4'-methylenebis (N-(oxiran-2-ylmethyl) aniline).](image)

Compound 3 was a brown viscous substance, readily soluble in chloroform and alcohols, hardly soluble in acetone, and insoluble in alkanes and water.
3. Results

In the $^1$H NMR spectra of a solution of compound 3 in CDCl$_3$, in addition to the signals of the protons of the aromatic rings, CH and CH$_2$ groups, there is a singlet of two protons of the NH groups in position 4 of the aromatic fragment in the region (4.08 ppm).

4,4'-methylenebis (N-(oxiran-2-ylmethyl) aniline) (3). The yield is 86%.

$^1$H NMR spectra, δ, ppm: 3.08-3.12 m (4H, CH$_2$), 3.21 m (4H, CH$_2$), 3.50 m (1H, CH), 3.57 m (1H, CH), 3.64-3.68 m (2H, CH$_2$), 4.06 s (2H, NH), 6.50 d (4H, CH$_{ar}$), 6.90 d (4H, CH$_{ar}$) (figure 2).

![Figure 2. $^1$H NMR spectra of 4,4'-methylenebis (N-(oxiran-2-ylmethyl) aniline).](image)

The completeness of the reaction (figure 1) was controlled using FTIR spectroscopy by monitoring the absorption band at 3450 cm$^{-1}$ (figure 3), that is attributed to the hydroxyl groups of epichlorohydrin. The absorption band at 3450 cm$^{-1}$ completely disappears during the synthesis.

![Figure 3. FTIR spectra of epoxy resin and epichlorohydrin.](image)

The quantitative content of free epoxy groups was determined using back titration method ISO 3001:1999. The experimental value - 27.6 % is close to theoretical value - 27.74 %.
Elemental analysis of the synthesized epoxy resin was carried out using Elementar Vario EL cube. Found, %: C 73.70; H 7.25; N 9.20. C_{19}H_{22}N_{2}O_{2}. Calculated, %: C 73.55; H 7.10; N 9.03.

4. Discussions
Two curing modes of synthesized epoxy resin were studied: 1 mode - 10 hours at 150 °C, 2 step mode - 10 hours at 150 °C + 3 hours of postcuring at 180 °C The completeness of the reaction was monitored using FTIR spectroscopy by the disappearance of the absorption band at 910 cm\(^{-1}\) [16]. A schematic diagram of the curing reaction of the synthesized resin is shown in figure 4.

![Figure 4. Curing reaction of epoxy resin.](image)

Figure 4. Curing reaction of epoxy resin.

Figure 5 shows the DSC cure curves of the synthesized resin. The parameters of the kinetics were calculated using the Kissinger model [17, 18]. According to the Kissinger model, the activation energy can be calculated using the peak reaction temperatures at different heating rates. The relationship can be expressed by the following equation:

\[
\ln \left( \frac{q}{T_m} \right) = \frac{E_a}{R T_m} - \ln \left( \frac{A R}{E_a} \right)
\]

where \( T_m \) – maximum temperature of reaction, K; \( A \) – pre-exponential factor; \( q \) – constant heating rate, °C/min; \( E_a \) – activation energy, J/mol; \( R \) – universal gas constant 8.314 J/(mol*K).

![Figure 5. DSC curves of curing reaction of epoxy resin at different heating rates.](image)
**Table 1.** Calculated kinetic parameters of synthesized epoxy resin.

| Heating rate. °C/min | Temperature of reaction peak. ºC |
|----------------------|----------------------------------|
| 2.5                  | 152                              |
| 5.0                  | 167                              |
| 10.0                 | 185                              |

The activation energy was calculated using the dependence diagram of $\ln(q/T_m^2)$ from $1000/T_m$ (figure 6), where $T_m$- peak temperature on DSC curve, K; $q$ – heating rate, K/min.

$$E_a = -1.181 \times 8.314 \text{ J/mol}*K \times 1000K = 9.820 \text{ kJ/mol.}$$ (2)

The calculated activation energy was 9.82 kJ/mol.

Figure 7 shows the DSC curve of the cured resin using mode 1. The glass transition temperature of self-cured synthesized epoxy resin at scanning rate 5 °C/min is higher than 200 °C.

Figure 8 shows the DSC curve for the second curing mode of epoxy resin. The glass transition temperature of the synthesized resin after self-curing is in the range of 210-215 °C.
Figure 8. DSC curve of cured epoxy resin using mode 2.

5. Conclusions
Using 4,4-diaminodiphenylmethane and epichlorohydrin taken in a double excess in dichloroethane, a bifunctional epoxy resin was synthesized by the reaction of replacing the hydrogen atom of amino groups. The structure of the synthesized epoxy resin - 4,4'-methylenbis (N-(oxiran-2-yl-methyl) aniline) was characterized and proved by the methods of FTIR spectroscopy, NMR spectroscopy and elemental analysis. Using the Kissinger method, the activation energy of the self-curing reaction was calculated, the value of which was 1.139 kJ/mol. Two curing modes of epoxy resin were studied: mode 1 - 10 hours at 150 °C, mode 2 - 10 hours at 150 °C + 3 hours of postcuring at 180 °C. An epoxy resin was synthesized from 4,4-diaminodiphenylmethane and epichlorohydrin.

The activation energy of this resin was calculated based on DSC results. The high glass transition temperature and low activation energy of synthesized epoxy resin provide opportunity for use as a matrix of modern composite materials.

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