

The Influence of Composition of the Dicyandiamide—Asymmetric Urea Complex Curing Catalyst System on the Thermal Effect of the Epoxy Diane Oligomer Polymerization Reaction

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Received June 26, 2014

Abstract—To decrease the curing temperature of epoxy compositions at the use of dicyandiamide (DCDA) as a latent hardener, a curing catalyst system including, in addition to DCDA, asymmetric urea has been studied. The dependencies of parameters of chemical transformations in catalyzed epoxy compositions, such as thermal effects and conversion, on the composition of the complex curing catalyst system have been established by the DSC and isothermal calorimetry techniques. It has been shown that the chosen optimal composition of the catalyst system allows curing the epoxy compositions in a two-stage regime at lower temperatures than in the case of the use of DCDA.

Keywords: curing catalysts, dicyandiamide, epoxy binders, latent curing systems, asymmetric ureas, thermal effects of reaction, polymeric composite materials

DOI: 10.1134/S1995421215030168

INTRODUCTION

Since the early 1950s, epoxide oligomers have been actively used in the aerospace, mechanical engineering, and civil industries (construction, radiotechnics, shipbuilding) as glues, coatings, and polymeric composite materials [1–9]. However, to obtain materials with optimal operational properties based on epoxy oligomers, it is necessary to choose the right composition of a curing system and the right curing regime. One of the most popular industrial latent hardeners for epoxide oligomer is dicyandiamide (DCDA), which allows one to synthesize one-component polymeric compositions able to keep their properties for a long time at the environment temperature. The main disadvantage of the DCDA hardener is a necessity of high temperature for curing of the epoxide matrix (170°C and higher), which is related to the latent character of this hardener due to its insolubility in the epoxide oligomer.

As seen from the literature data [10–14], there are two possible ways to solve the problem of decreasing the curing temperature based on activation of chemical interaction and improvement of compatibility between the epoxide oligomer and sparingly soluble DCDA. The first way is the use the accelerants (acetylacetonates of various metals and substituted urea

[15–17]), salts and complex compounds of tertiary amines [18], and imidazole derivatives [19–21]; the second way is chemical modification of DCDA.

In our earlier work [15], a mechanism of curing of the DCDA–epoxide oligomer system in the presence of asymmetric urea (Dyhard-UR500) accelerant was studied. The chemical compositions and structures of the catalyzed epoxy system in the uncured and cured states were established by the IR and NMR spectroscopy techniques. In continuation of this work, the dependences of parameters of chemical transformations of the epoxide composition have been established by calorimetric techniques that allow one to find the most balanced composition of the complex DCDA–Dyhard-UR500 curing catalyst system and the optimal temperature–time regime of curing.

MATERIALS AND METHODS

The components used in this work were as follows.

—Epoxy diane oligomer (*GOST* (State Standard) 10587–84) (ED-20, FKP Sverdlov Zavod) with a mass fraction of epoxide groups of 21.7% and mass fraction of hydroxyl groups of 1.3%.

—Dicyandiamide (DCDA) (Dyhard-UR100S, AlzChem AG) of 95% purity, micronized (>90% of the

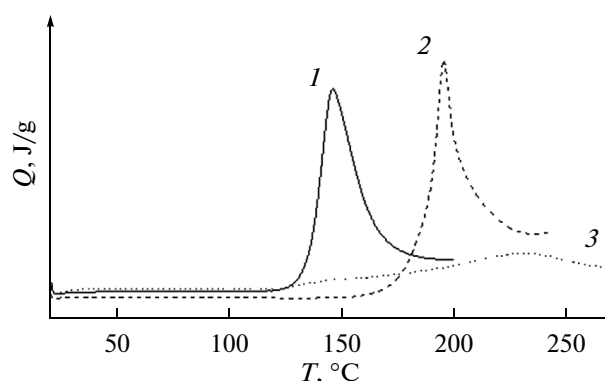


Fig. 1. Kinetic curves of the curing process of the ED-20 epoxy diene oligomer samples depending on the curing catalyst system. The composition of the catalyst system per 100 pbw of ED-20, pbw: (1) DCDA : Dyhard-UR500 = 6 : 0.5, (2) DCDA = 6, and (3) Dyhard-UR500 = 0.5. Heating rate is 5°C/min.

5- μ m fraction) and used without preliminary purification.

—1,3-*bis*-(N,N-dimethylcarbamide)-4-methylbenzene (Dyhard-UR500, AlzChem AG) of 97–98% purity (>98% of the 8.5- to 9.5- μ m fraction).

—Phenyl glycidyl ether (PGE) (Ferak), prepurified by vacuum distillation.

The study of the parameters of chemical transformations of the epoxide composition and determination of enthalpies of the curing reactions of the catalyzed epoxy system were conducted in an MK DAK-1-1 Tian-Calvet isothermal microcalorimeter equipped with a system for automatic recording of heat flux.

The thermal analysis was carried out with a DSC822° Mettler Toledo differential scanning calorimeter. The studies were carried out in the temperature range of 25–200°C under a stream of nitrogen at the scanning speed of 5°C/min [22, 23]. The thermal effects of the reactions and their kinetic regularities were determined from the temperature dependences.

To perform calorimetric studies, catalyzed epoxy compositions were prepared in a specially designed glass reactor equipped with a water jacket for heating/cooling, a high-speed stirrer, and systems for dry argon feed and vacuum degassing, which allows one to quickly eliminate air bubbles and volatiles from the reaction mixture. Accurately weighed quantities of the ED-20 oligomer, DCDA hardener, and Dyhard-UR500 accelerant were carefully stirred and poured into the reactor. The composition was then heated until 70–80°C at constant stirring, held for 30 min, and vacuum degassed for 15 min until a residual vacuum of 1–2 mmHg was reached; then stirring was ceased and dry argon was fed into the reactor. The obtained composition was poured into an ampule.

RESULTS AND DISCUSSION

The choice of the composition of a DCDA–asymmetric urea (Dyhard-UR500) curing catalyst system that would allow one to carry out polymerization at temperatures of up to 140°C and obtain cured epoxide compositions with high heat-resistant properties was made experimentally in an extended range of component concentrations: 0.5 to 10 pbw of DCDA and 0.5 to 8 pbw of Dyhard-UR500 per 100 pbw of the ED-20 epoxy diene oligomer. The empirical approach was used mainly due to the extreme complexity of mechanism of curing the epoxide oligomer with such a complex curing catalyst system.

Based on a review of the literature and on previous experimental data [15], the following temperature regime of curing was chosen: prepolymerization of the composition at 100°C for 1 h to suppress the self-heating effect in the composition, i.e., to decrease the thermal effect of postcure reactions, and subsequent postcure at 140°C for 4 h.

In Fig. 1, the DSC curves of curing the compositions by the catalyst system having various component ratios are presented. The results in Fig. 1 prove that the curing reaction with DCDA in the presence of Dyhard-UR500 begins at a significantly lower temperature (curve 1) than one with pure DCDA (curve 2). This completely corresponds to the literature data [18]. The significant decrease of the heat release value and higher temperature of the maximum exothermic peak upon the reaction of ED-20 with Dyhard-UR500 (curve 3) can be due to the urea concentration in the reaction mixture being very low (0.5 pbw), and the DSC curve shows heat release related to the postreactions (attachment of secondary amine to epoxide groups, decomposition of the formed urethane groups, etc.). From the kinetic curves of the reaction of the epoxide composition polymerization, it is seen that there are almost no chemical reactions at a temperature lower than 100°C.

Studies on establishing the parameters of chemical transformations of the reaction of curing the composition 100 pbw ED-20 + 6 pbw DCDA + 0.5 pbw Dyhard-UR500 in the isothermal regime showed (Fig. 2) that, at 120°C, an essential part of the reaction runs during switching of the measuring regime of the microcalorimeter (time of heating the sample ampoule in the measuring cell until the preset temperature is 15 min), and at the increase of temperature up to 140°C the heat release curve shows only the “tails” of the completed curing reaction: the heat losses are up to 65–70% (33.5 kJ/mol instead of 92–104 kJ/mol). This does not allow one to establish the exact quantitative dependences of the heat release for the given temperature; thus, the kinetic curves of the curing processes at 140°C are not given here.

Comparison of curves 1 and 1' (Fig. 2) shows the similarity of the chemical processes conducted at the temperatures of 100 and 120°C: close values of

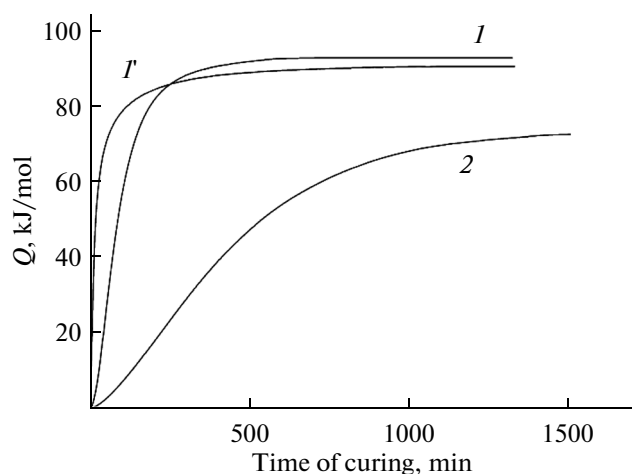


Fig. 2. Kinetic curves of the heat release of the isothermal curing process of the polymeric compositions based on the (1, 1') ED-20 and (2) PGE at (1, 2) 100 and (1') 120°C. Composition, pbw: (1, 1') ED-20 : DCDA : Dyhard-UR500 = 100 : 6 : 0.5; (2) PGE : DCDA : Dyhard-UR500 = 100 : 6 : 0.5.

the total thermal effects of curing and the slowdown of the reaction at high conversion degrees. The kinetic curve of the interaction of PGE with the complex catalyst system (see Fig. 2, curve 2) fundamentally differs from the curing curves of ED-20, which may be related to the change of the stoichiometric ratio of epoxide groups to the used curing system.

The influence of the DCDA and Dyhard-UR500 concentrations on the ED-20 curing kinetics is illustrated by the dependencies in Figs. 3–7. The increase of the DCDA concentration (Figs. 4 and 5a) allows one to slightly increase the heat release peak temperature in the DSC curve of the curing process and total heat of the reaction. Thus, it can be supposed that the curing rate in the presence of 6 pbw of DCDA at a constant temperature is lower than that of the experimental compositions with lower concentrations of the curing agent, but the heat release is higher (95.04 kJ/mol). However, the total heat of the curing reaction determined using the isothermal microcalorimetry (see Fig. 4) is almost the same in all the cases, lying in the range of 84.82–95.04 kJ/mol. An insignificant decrease in the heat of the curing process for the DCDA concentration of 4 pbw may be caused by a high reaction rate at the initial stage and, thus, by loss when switching the fixed regime of the calorimeter.

The increase of the Dyhard-UR500 concentration (Figs. 5b and 6) significantly decreases the heat release peak temperature in the DSC curing curve and increases the total heat of the reaction determined by the DSC and the microcalorimetry techniques (Fig. 7).

All this proves that there is a significant activating/catalyzing effect of asymmetric urea and the change of the curing mechanism: the increase of

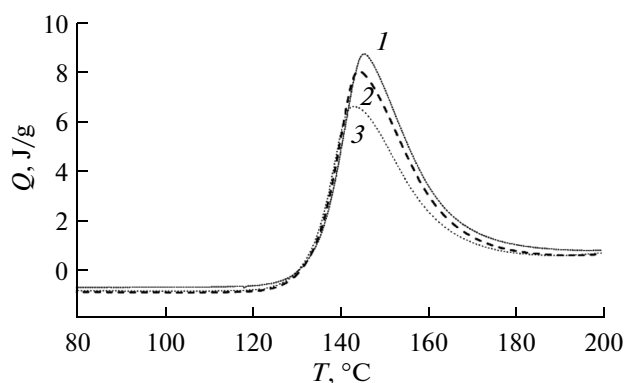


Fig. 3. Heat release curves at curing the epoxy compositions depending on the DCDA concentration in the curing catalyst system composition, pbw: (1) 6, (2) 5, and (3) 4. The Dyhard-UR500 concentration in all the compositions is 0.5 pbw per 100 pbw of ED-20. Scanning regime at heating rate of 5°C/min.

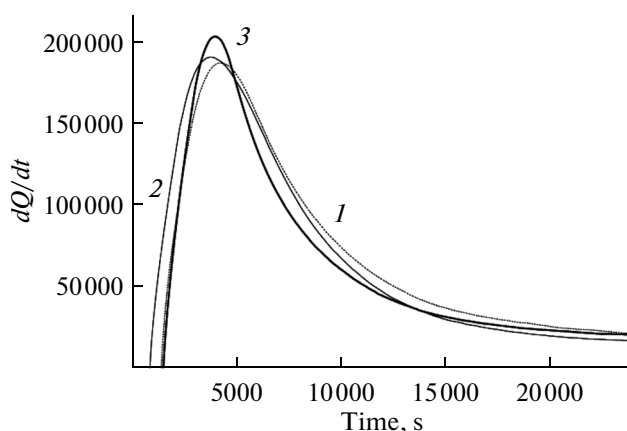


Fig. 4. Kinetic curves of the curing process of the epoxy compositions depending on the DCDA concentration in the curing catalyst system composition, pbw: (1) 6, (2) 5, and (3) 4. The Dyhard-UR500 concentration in all the compositions is 0.5 pbw per 100 pbw of ED-20. Isothermal microcalorimetry at 100°C.

Dyhard-UR500 concentration in the catalyst system contributes to the greater heat release (see Fig. 5b). The reactions of epoxide cycle homopolymerization prevail while DCDA scarcely participates in curing reaction. At a small Dyhard-UR500 concentration, the heat of the reaction is close to the heat of interaction of epoxide ring with amino group, and in this case DCDA makes the main contribution into the direction of the reaction and into structure of the formed polymer.

To study the kinetics of curing processes at high temperatures, the DSC technique with isothermal heating of the sample at reaching a definite temperature (120 and 140°C) was used (Figs. 8 and 9).

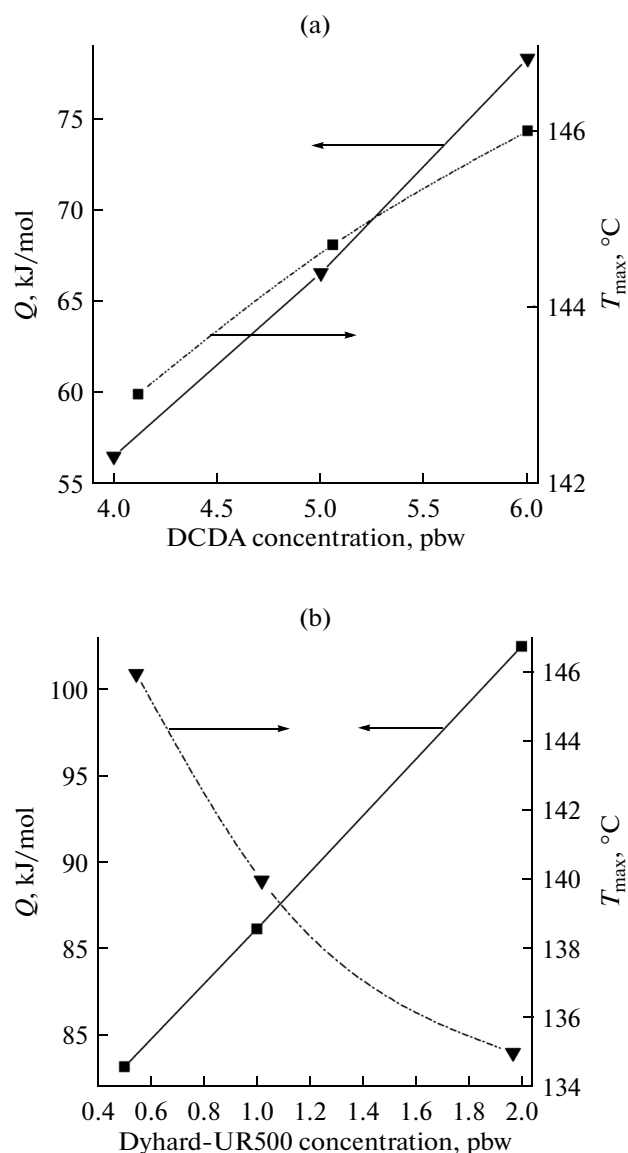


Fig. 5. Dependency of heat release and heat release peak temperature in DSC curves of the curing process of the composition based on the ED-20 oligomer on the composition of the DCDA–Dyhard-UR500 curing catalyst system: (a) the concentration of Dyhard-UR500 = 0.5 pbw; (b) the concentration of DCDA = 6 pbw. Heating rate is 5°C/min.

Based on the presented dependences, the following conclusions can be drawn:

—the curing reaction at elevated temperatures first takes place very quickly, which can cause significant self-heating of the reaction mass in large samples; and

—the reaction slows down at the second stage, and even after 200 min at 140°C there is a slight and exponentially decreasing heat release, which probably corresponds to the target curing reactions slowed

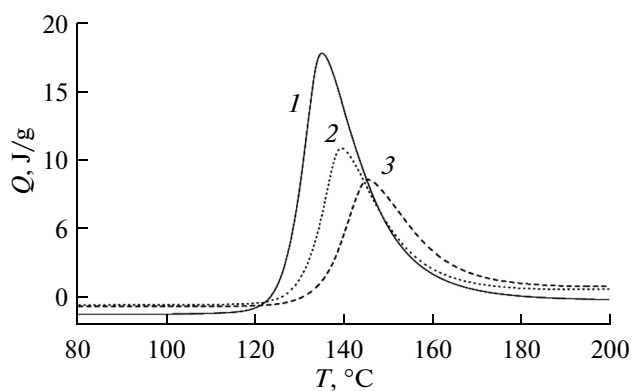


Fig. 6. Heat release curves upon curing of epoxy compositions depending on the Dyhard-UR500 concentration in the curing catalyst system composition, pbw: (1) 2, (2) 1, and (3) 0.5. The DCDA concentration in all the compositions is 6 pbw. Scanning regime at the heating rate of 5°C/min.

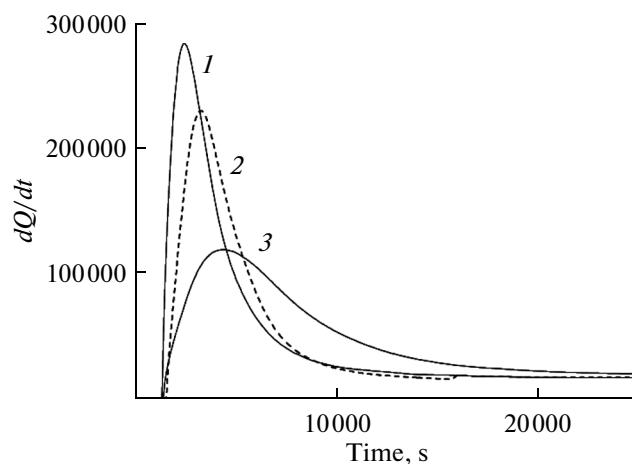


Fig. 7. Kinetic curves of the curing process of the epoxy compositions depending on the Dyhard-UR500 concentration in the curing catalyst system composition, pbw: (1) 2, (2) 1, and (3) 0.5. The DCDA concentration in all the compositions is 6 pbw. Isothermal microcalorimetry at 100°C.

down due to diffusion obstacles or thermal degradation reactions.

Based on the obtained results, the following curing regime of 1 h at 100°C + 4 h at 140°C is considered optimal. The study of the curing processes of the polymeric composition based on ED-20 + DCDA + Dyhard-UR500 should be continued. The use of other additives of asymmetric urea similar to Dyhard-UR500 will probably allow the DCDA activation temperature to be decreased, which will subsequently con-

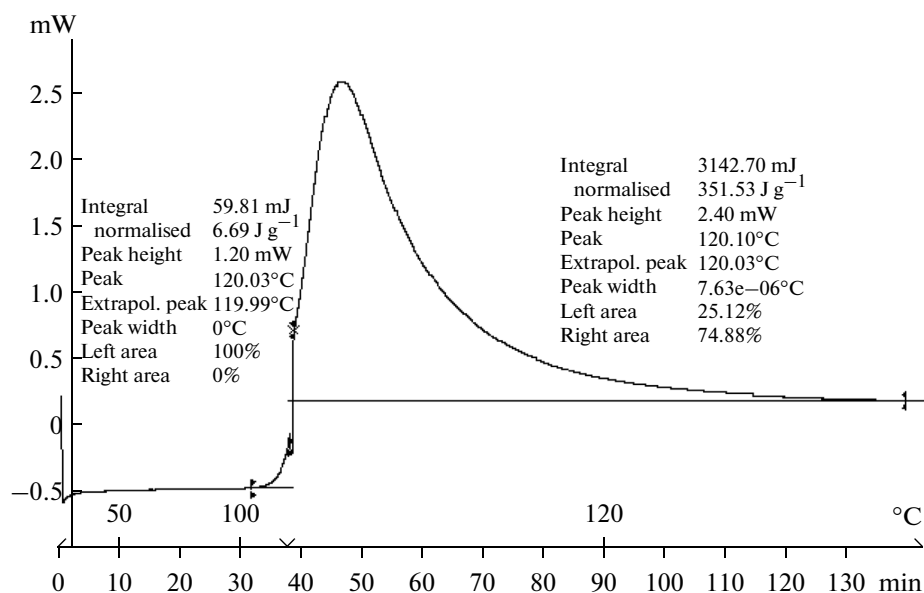


Fig. 8. Kinetic curve of the heat release upon curing of epoxy compositions by the curing catalyst system at heating in the scanning regime (5°C/min) up to 120°C and subsequent maintenance in the isothermal regime. The component ratio in the composition is ED-20 : DCDA : Dyhard-UR500 = 100 : 6 : 0.5 pbw. Total heat release is >81.22 kJ/mol.

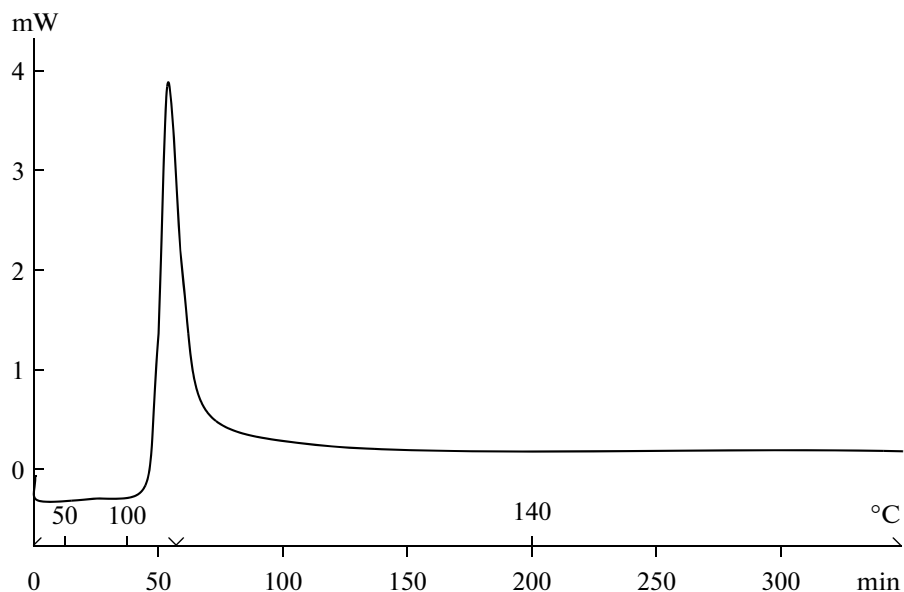


Fig. 9. Kinetic curve of the heat release upon curing of epoxy compositions by the curing catalyst system at heating in the scanning regime (5°C/min) up to 140°C and subsequent maintenance in the isothermal regime. The component ratio in the composition is ED-20 : DCDA : Dyhard-UR500 = 100 : 6 : 0.5 pbw. Total heat release is 106.34 kJ/mol.

tribute to better compatibility of reagents and to the formation of polymers with the improved strength and thermochemical properties.

CONCLUSIONS

Hence, a study of influence of a complex curing catalyst system composition on the parameters and

mechanisms of chemical transformation in an epoxide composition was carried out using the calorimetric analysis techniques. It was shown by differential scanning calorimetry that the introduction of asymmetric urea (Dyhard UR-500) into the epoxide composition allows to decrease the curing temperature until 140°C. It was established that the optimal ratio between the epoxy diene oligomer and the catalyst curing system is

ED-20 : DCDA : Dyhard-UR500 = 100 : 6 : 0.5 pbw. The chosen curing regime includes two-stage heating of the catalyzed epoxy system to suppress the self-heating effect of the composition: 1 h at 100°C + 4 h at 140°C. It is noteworthy that the chosen catalyzed epoxy systems, due to the presence of latent catalysts, can be used for the development of hi-tech one-component epoxide binders characterized by a long shelf life (no less than 4 months).

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Translated by E. Petrova