# Modification of Epoxy-Amine Polymers by Oligohexamethyleneghuanidines*

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*Methods of introducing a water-soluble biocide modifier, oligohexamethyleneguanidine hydrochloride, into epoxy-amine systems were studied. The obvious way is the introduction of the modifier in the waterborne epoxy-amine systems. However, this leads to cured systems with reduced mechanical properties. Introduction of oligohexamethyleneguanidine hydrochloride solutions in organic solvents into epoxy-amine systems allows obtaining a homogeneous system, but their application is limited by the presence of a volatile solvent. Finally, introduction of oligohexamethyleneguanidine hydrochloride solutions in a water-soluble amine curing agent into epoxy-amine systems has good prospects. It is shown that the analyzed modifier has good solubility in ethylenediamine, but poor solubility in oligooxypropylenediamine. It was found that the modifier is capable of interacting chemically with epoxy resins at 22°C to form an elastic insoluble material. In an epoxy-amine system with a more active hardener (ethylenediamine) oligohexamethyleneguanidine hydrochloride acts as a plastifier (flexibilizer). This significantly reduces the glass transition temperature of the matrix (from 53 to 37°C).*

***Keywords:*** *epoxy resin, diamine, oligohexamethyleneguanidine, solubility, curing, plastification.*

## INTRODUCTION

Modification of epoxy oligomers (EO) and compositions based on them is now the main method of directed improvement of their properties [1–3]. A huge amount of inorganic and organic substances including oligomers and polymers are used as EO modifiers. Particular interest is attracted by modifiers having fragments reactive with respect to EO and/or the hardener. This allows them to form chemical bonds with the polyepoxy matrix. As a result, the modifying effect considerably increases [4–6]. Oligohexamethyleneguanidines (OHMG) – biocidal substances with a favorable combination of antimicrobic, toxicological and physicochemical properties [7, 8] – can be new interesting modifiers of this kind. Introduction of such oligomers into epoxy compositions would allow improving considerably the resistance of the hardened structures to various microorganisms. Besides, fixing OHMG fragments in an epoxy grid would provide steady long-lasting effect. However, open-literature information on the epoxy materials modified by OHMG is extremely limited. Works [9, 10] are among the few sources. In this regard, studying the modification of epoxy systems with OHMG and creating new modified compositions based on them is of great scientific and practical interest. This work is devoted to this problem.

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## EXPERIMENTAL

The main objects of the study were as follows: 1) a diane EO – Epikote 828 (Hexion) – with $M_n$ = 376 and average functionality of the epoxy groups $f_{ep}$ =1.99 and 2) an aliphatic EO – oligooxypropylenetriol polyglycidyl ester Laproksid 703 (macromer) with $M_n$ =742 and $f_{ep}$ =2.43. The characteristics were determined by the NMR technique described in [11]. Oligohexamethyleneguanidine hydrochloride OGMG-Gkh (Pharma-Pokrov) with $M_n$ =951 and average quantity of branchings per molecule 0.47 eq/mol was chosen as a modifier. The characteristics were determined by the NMR technique described in [12]. Diamines of various nature: ethylenediamine with $M_{NH}$=15.0 (analytical grade, Aldrich) and oligooxypropylenediamine Jeffamine D-230 with $M_{NH}$ = 57.6 (Huntsman) were used as hardeners of modified EO. In addition, in some cases chemically pure water-soluble organic solvents were used: acetone, tetrahydrofuran, dimethyl sulfoxide, dimethylformamide and ethanol.

Solutions of the initial components in each other were prepared by mechanical stirring. In some cases it was intensified by means of ultrasonic treatment in Elma D-78224 Singen-Htw at a frequency of 35 kHz within 15 min. Solubility was estimated visually and by means of differential scanning calorimetry. The diane EO was preliminarily kept before use at 60 °C for 3 h in a vacuum oven to remove possible crystallites and then cooled to 22 °C.

Samples for hardening were mixtures of EO or their mixtures with the stoichiometric quantity of a diamine introduced taking into account the total content of epoxide groups in the presence of the modifier introduced variously. Hardening was carried out at 22 °C. The moment of mixing the hardener and EO was considered to be the time of the reaction beginning.

DSC thermograms were obtained with the use of a DSC Q-100 differential scanning calorimeter (TA Instruments, USA) in the range from –85 to 200 °C in an argon atmosphere at a rate of 10 deg / min. The experimental data were interpreted with the use of TA Universal Analysis 2000 software package (V4.5A).

## RESULTS AND DISCUSSION

It is known that oligo- and polyhexamethyleneguanidines (all the more their salts, for example, hydrochlorides) are hydrophilic substances [7]. For this reason they are well compatible with water-based polymeric compositions and aqueous dispersions of oligo- and polymers. However, there are considerable difficulties when mixing OHMG with hydrophobic substances including EO. Thus, mixing OGMG-Gkh with Epikote 828, Laproksid 703 or their binary mixture 1 : 1 (mass) during 2 h at 20–140 °C, *inter alia,* in the conditions of ultrasonic processing (at a frequency of 35 kHz within 15 min) did not lead to noticeable dissolution of OHMG: the solute content in EO was less than 0.1% mass.

We studied three approaches to homogeneous introduction of OGMG-Gkh into epoxyamine compositions:

- dissolution of OHMG in water followed by introduction of this solution into water-based epoxy-amine adducts capable of being hardened;
- dissolution of OHMG in a hydrophilic organic solvent followed by introduction of this solution into EO, their mixtures or non-hardened epoxyamine systems;
- dissolution of OHMG in an amine hardener followed by combination with EO or their mixtures.

*Combination of OHMG aqueous solutions with water-based epoxyamine adducts*. As noted above, one of obvious ways of introducing OHMG into epoxyamine systems is using water-based epoxy-amine systems. Such systems can be aqueous dispersions of EO offered in the market in combination with water-based amine hardeners not breaking the stability of dispersions, as well as usual EO in combination with emulsifying polyamines acting not only as EO hardeners, but also as surfactants for it. Such hardeners, as a rule, have nonionic polar fragments (for example, oxypropylene ones) in their composition. This holds out a hope that adducts of oligooxypropylenediamine and EO can be components of the mentioned hardeners.

It is known due to the previously conducted studies [13, 14] that jellification in Epikote 828 – Jeffamine D-230 system occurs at a transformation degree of epoxy groups ~ 40%. Therefore, according to [15], Epikote 828 – Jeffamine D-230 adducts can be considered not to be meshy at amine excess more than 0.6 mol/mol of the mixture. However, even such adducts are rather viscous at room temperature (1.5–7.0 Pa·s at 22 °C) and hardly soluble in water (in spite of the fact that the amine itself dissolves well in it). This impedes OGMG-Gkh introduction into the epoxyamine system by this method. Besides, note that water-based systems, as a rule, have lower mechanical characteristics and higher shrinkage as compared to water-soluble ones [16, 17]. This makes the studied approach less attractive for further development.

*Dissolution of OHMG in hydrophilic organic solvents*. An easier and traditional method for introducing a hardly compatible modifier into a polymeric matrix is preliminary dissolution of the former in a low-molecular solvent. We studied OGMG-Gkh solubility in a number of water-soluble organic solvents (see the table). It was found that it is best dissolved in dimethylsulfoxide and ethanol. Note that a 10% alcohol solution of OGMG-Gkh is well compatible with Epikote 828. Besides, keeping this system during 7 days at 22 °C gives a solid elastic mass with a glass transition temperature of 11.5 °C (according to DSC at $w^+$ =10 K/min). This indicates a chemical interaction of OHMG with EO. Most likely, it is first of all the reaction of the epoxy groups of EO with the amino groups of hexamethylenediamine terminal fragments of OHMG.

OGMG-Gkh solubility in organic solvents at 22 °C

| Solvent | Solubility, g/ml |
|---|---|
| Acetone | not soluble |
| Dimethylformamide | not soluble |
| Tetrahydrofuran | 0.0066 |
| Dimethylsulfoxide | 0.0696 |
| Ethanol | 0.1049 |

Thus, this method of introducing OHMG into the epoxyamine system is promising, although its considerable shortcoming is the use of a volatile organic solvent. The latter circumstance can complicate the use of epoxyamine systems modified by OHMG as "green" (ecologically advantageous) materials, as well as to provoke increased shrinkage due to solvent evaporation.

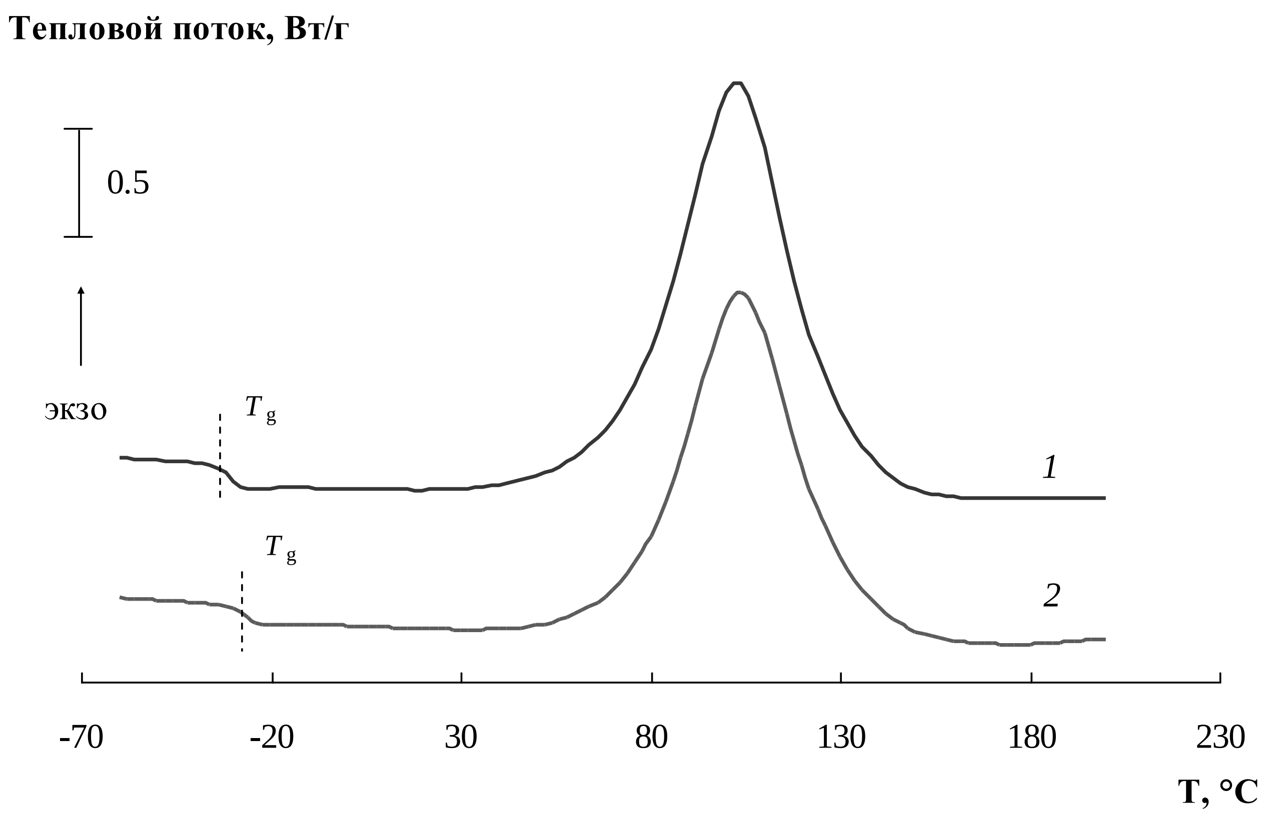


**Figure 1.** DSC thermograms of Epikote 828 – ethylene diamine epoxyamine system initially not hardened and not modified *(1)* and modified *(2)* with 5% of OGMG-Gkh

[Тепловой поток, Вт/г means Heat flow, W/g; экзо means exo]

DSC thermograms of completely hardened systems (Figure 2) are also characterized by a single limit glass transition point (determined by thermograms obtained by repeated scanning of non-hardened samples): 53 °C for the unmodified epoxyamine system and 37 °C for the system modified by OGMG-Gkh. (For comparison: glass transition temperature of initial OGMG-Gkh is 65 °C). This indicates that OGMG-Gkh is not separated as an individual phase upon hardening. Thus, it acts as a plasticiser or flexibilizer of the epoxyamine matrix.

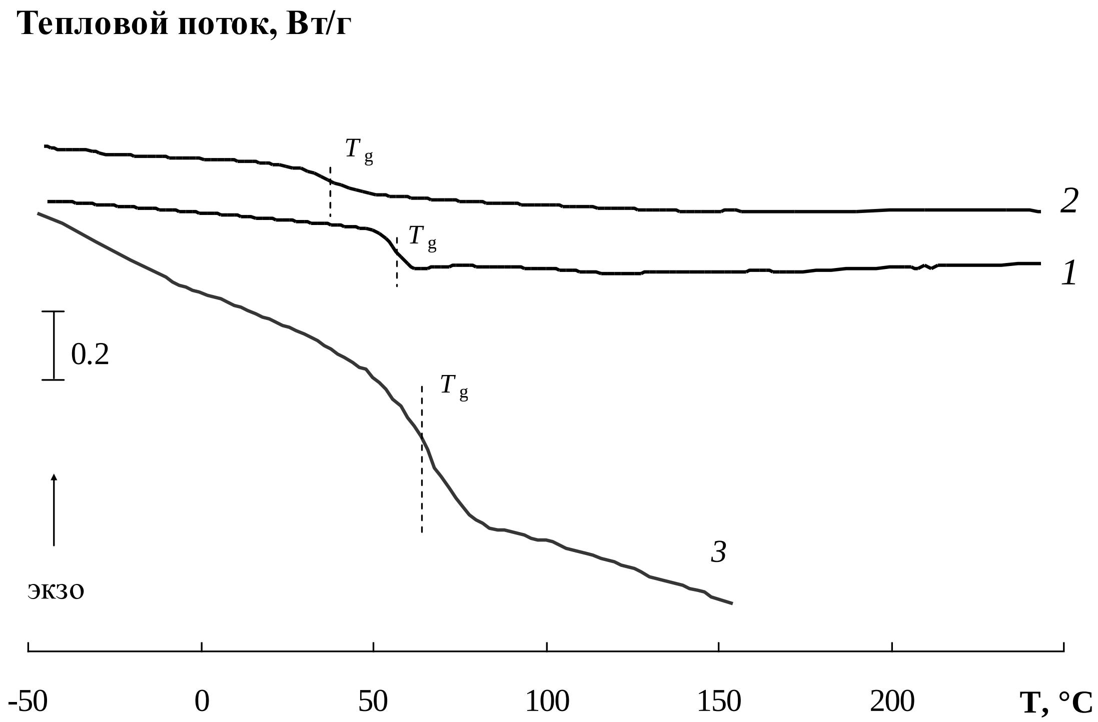


**Figure 2.** DSC thermograms of Epikote 828 – ethylene diamine epoxyamine system completely hardened and not modified *(1)* and modified *(2)* with 5% of OGMG-Gkh, as well as of initial OGMG-Gkh *(3)*

[Тепловой поток, Вт/г means Heat flow, W/g; экзо means exo]

Note that hardening diane EOs with a low molecular weight (such as Epikote 828) by low-chain diamines (in this case, ethylene diamine) results in rather rigid and fragile products [15]. From this point of view, modifying them with OHMG, in addition to giving them biocidal properties, will potentially improve also their mechanical properties. The main problem in this case is product expansion and search for other hydrophilic EO hardeners capable of dissolving OHMG.

## Conclusions

Methods of introducing a water-soluble biocidal modifier – oligohexamethyleneguanidine hydrochloride – into epoxyamine systems were studied. It was shown that this modifier is capable of interacting chemically with EO in a homogeneous system even at 22 °C. As a result, an elastic insoluble material is formed. In an epoxyamine system containing in addition a more active hardener, OHMG acts as a plasticizer or a flexibilizer considerably reducing the matrix glass transition temperature (from 53 to 37 °C).

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