

Hybrid epoxy-amine hydroxyurethane-grafted polymer

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Abstract: Cured hybrid epoxy-amine hydroxyurethane-grafted polymer by novel structure with lengthy epoxy-amine chains, pendulous hydroxyurethane units and a controlled number of cross-links was prepared. These hybrid polymers combine increased flexibility with well balanced physical-mechanical and physical-chemical properties of conventional epoxy-amine systems and may be used, for example, for manufacturing of synthetic/artificial leather and sport monolithic floorings.

Keywords: linear epoxy-amine chains, hybrid hydroxyurethane-grafted polymers, synthetic nonisocyanate leather.

1. INTRODUCTION

Preparing of polymers with a specific topological structure of polymerchains is a perspective way of creating materials with needed properties.

Conventional epoxy-amine formulations are used as precursors for three-dimensional cross-linked networks [1, 2]. Chemical formation of resin-hardener networks used in case of bifunctional epoxy resins and tetrafunctional aminehardeners and the structures of the obtained networks are shown in Fig. 1 [2, p. 721].

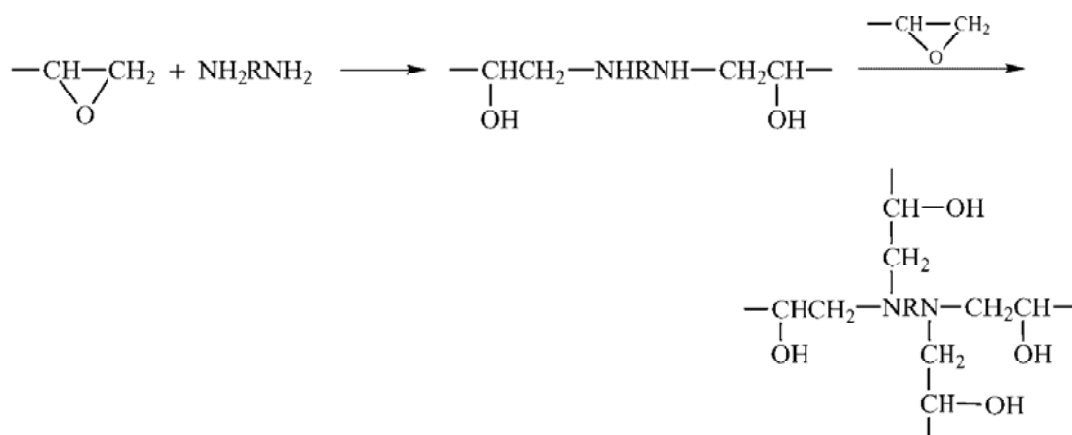


Fig. 1. Scheme of epoxy resin – amine interaction.

Structural Schemes of resin formation–hardener networks for epoxyaminethermoset polymers are shown in Fig. 2 [2, P. 749]:

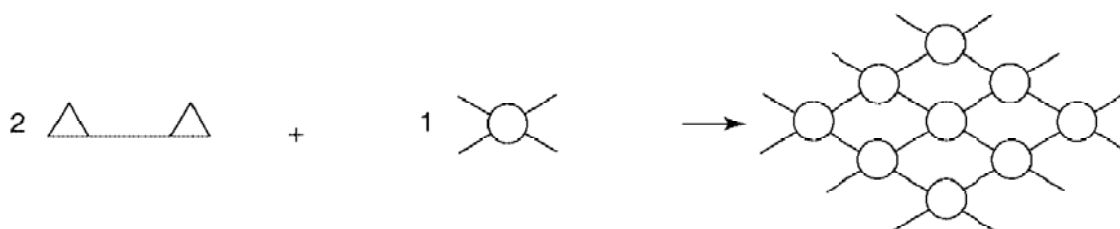


Fig. 2. Structural scheme of epoxyamine network.

Thermoplastic resins based on epoxy and amine monomers are also known in the art. For example, patent [3] discloses polymers based on diglycidyl ethers of polyhydric phenols and compounds such as alkanolamines and anilines having two amino hydrogen atoms per molecule. The process is carried out at extremely conditions: in a melt at a temperature of up to 250°C. or in a solution at a temperature of up to 200°C.

Patents [4, 5] disclose thermoplastic polyetheramines (TPEA) having aromatic ether/amine repeating units in their backbones and pendant hydroxyl moieties. Such polyetheramines are prepared by reacting diglycidyl ethers of dihydric aromatic compounds such as the diglycidyl ether of bisphenol-A (DGEBA), hydroquinone, or resorcinol with amines having no more than two amine hydrogen atoms per molecule, such as piperazine, monoethanolamine (MEA), and mono-amine functionalized poly(alkylene oxide). These polyetheramines are thermoplastic polymers and have an improved barrier to oxygen and a relatively high flexural strength and modulus. The disadvantage of these products is that they can be processed or melted at temperatures of 150 to 200°C. by using only special equipment, or solutions in high-boiling toxic solvents. A fragment of a TPEA polymer chain is shown below in Fig. 3 [2, P. 697].

It is known in the art to use hydroxyurethanes for improving some properties of thick cross-linked epoxy polymer networks. For example, patent [6] describes certain polyhydroxyurethane networks that are produced based on reactions between oligomers comprising terminal cyclocarbonate groups and oligomers comprising terminal primary amine groups.

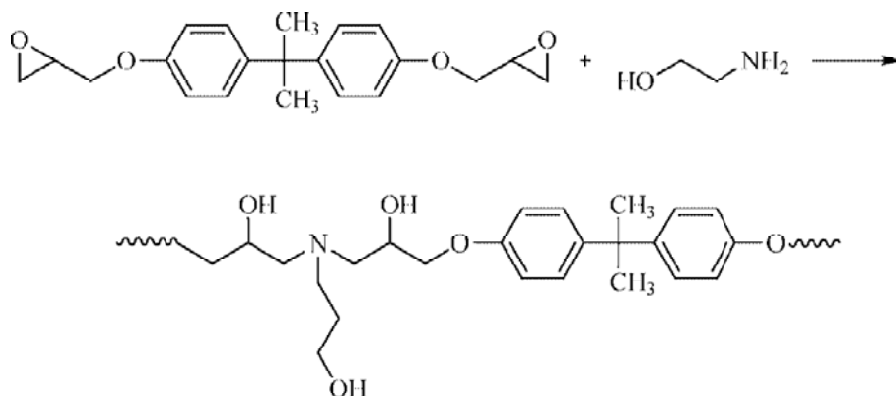


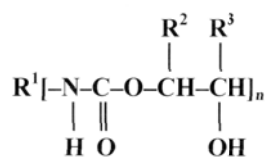
Fig. 3. Elementary unit of the TPEA polymer chain on the base of DGEBA and MEA.

Oligomers comprising terminal cyclocarbonate groups are the products of epoxyresins reacting with carbon dioxide in the presence of a catalyst, the conversion of epoxy groups into cyclocarbonate groups being 85 to 95%.

Pat. Application [7] discloses a liquid cross-linkable oligomer composition that contains a hydroxyurethane-amine adduct and a liquid-reacting oligomer. The hydroxyurethane-amine adduct is a product of an epoxy-amine adduct reacting with a compound having one or more terminal cyclocarbonate groups.

Patent [8] describes a method and an apparatus for synthesis of oligomeric cyclocarbonates and their use in making a star-shaped structure of the polymer network.

Patent [9] discloses three-dimensional epoxy-amine polymer networks modified by a hydroxyalkyl urethane, which is obtained as a result of a reaction between a primary amine (one equivalent of the primary amine groups) and a monocyclic carbonate (one equivalent of the cyclocarbonate groups). Such hydroxyalkyl urethane modifier is not bound chemically to the main polymer network and is represented by the following formula (1):



(1),



wherein R^1 is a residue of the primary amine, R^2 and R^3 are the same or different and are selected from the group consisting of H, alkyl, and hydroxyalkyl, and n satisfies the following condition: $n \geq 2$.

Patent [10] describes an epoxy resin composition that comprises a cured reaction product of an epoxy base resin and a curing agent mixture. The curing agent mixture comprises a di-primary amine or polyamine and an aminohydroxyurethane (aminocarbamate) which is the reaction product of the amine and a cyclic carbonate and is represented by the formula (2):



where R^1 is a residue of the di-primary amine or polyamine that may consist of additional free amine hydrogen atoms, R^2 and R^3 are selected from the group consisting of H and alkyl, and at least one of R^2 and R^3 is hydrogen. The amine has a molecular weight of 60 to 400. Preferred carbonates are ethylene carbonate and propylene carbonate. A preferred curative comprises a mixture of amine and aminocarbamate used in a molar ratio of 1:1 to 2:1.

Thus, although the hardener comprises the aminohydroxyurethane, a pure amine is an indispensable main component of this hardener, and the final polymer has a thermoset cross-linked structure.

Thick cross-linked networks are also typical for epoxy-aminohydroxyurethane compositions described in U.S. patents [11].

A method of obtaining urethane-modified amines is presented by G. Rokicki and R. Łaziński [12]. Triethylenetetramine (TETA) was modified by different mono- and dicyclic carbonates at mole ratios TETA: carbonate from 1:1 to 4:1 and temperature 50-60° C. for 2-12 hours, thus aminohydroxyurethanes were obtained. The results of physical and mechanical investigations of an epoxy resin cross linked



with aminohydroxyurethanes show increase of strength features of the cured systems. However flexible materials were not obtained, and values of elongation at break were not more than 8 %.

A detailed review of polyhydroxyurethane networks and methods of preparation thereof are presented by O. Figovsky and L. Shapovalov [13] and by O. Figovsky, L. Shapovalov, A. Leykin, O. Birukova, R. Potashnikova [14].

A new polysiloxane-modified polyhydroxy polyurethane resin derived from a reaction between a 5-membered cyclic carbonate compound and an aminemodified polysiloxane compound are disclosed in US Patents [15]. The production process and resin compositions for thermal recording medium, imitation leather, thermoplastic polyolefin resin skin material, weather strip material, and weather strip also have been described. Such polymers have in their backbones only hydroxyurethane units but not epoxy-amine. A disadvantage of the disclosed method is an inconvenience in preparation of a polyhydroxy polyurethane resin, namely the long-time use (30 hours for first stage and 10 hours for second stage) of a toxic solvent (N-methylpyrrolidone) at 80-90°C. and subsequent separation of the product from the solvent. Another disadvantage is the use of toxic polyisocyanates for cross linking of resins.

Different variations of the aforementioned composition and method are also disclosed in these patent publications [15].

OBJECTS AND METHODS

The following commercially available raw materials were used:

– epoxy resins and glycidyl ethers: DER® 331 (standard diglycidyl ether of bisphenol A, EEW=187), D.E.N.® 431 (epoxy-novolac resin, EEW=175), Polypox® R11 (diglycidyl ether of cyclohexanedimethanol, EEW=175), Polypox® R14 (diglycidyl



ether of neopentyl glycol, EEW=155) all produced by Dow Chemical Company; epoxy resin ST-3000 (hydrogenated DGEBA, EEW=230) produced by KUKDO Chemical Co.; Heloxy® 48 (triglycidyl ether of trimethylol propane, EEW=145) produced by Momentive Specialty Chemicals Inc.;

– cyclic carbonate: Jeffsol® PC (propylene carbonate, CCEW=102) produced by Huntsman Corp.

– di-primary and polyfunctional amines: Vestamin® TMD [2,2,4(2,4,4)-trimethylhexamethylene diamine] produced by Evonik; Jeffamine® D400 (polyoxypropylene diamine, AEW=230, AHEW=115) and Jeffamine® T403 (polyoxypropylenetriamine, AEW=162, AHEW=81) both produced by Huntsman Corp.; PolyTHF®Amin 350 (polytetrahydrofuranamine, AEW=160.3 AHEW=88) produced by BASF; MXDA (meta-xylylenediamine, AEW=68; AHEW=34) produced by Mitsubishi Gas Chemical Comp.; D.E.H.® 20 (diethylenetriamine, AEW=51.5; AHEW=20.6) produced by Dow Chemical Company.

Abbreviations used:

- 1) EEW - epoxy equivalent weight;
- 2) AEW - primary amine equivalent weight;
- 3) AHEW - amine hydrogen equivalent weight;
- 4) CCEW - cyclic carbonate equivalent weight;
- 5) f – functionality of the components.

Reactions between cyclic carbonate and primary amine groups were monitored by Nicolet 380 FT-IR spectrometer according to cyclic carbonate $\nu_{C=O}$ band at 1800 cm^{-1} . Dynamic viscosity was determined on Brookfield VN-II+ viscometer.

Pot life of compositions was determined according to ASTM D1084 as the time during which the viscosity is doubled.



The polymerized samples were tested with regard to the following mechanical and chemical properties: tensile strength and ultimate elongation were performed on unit Lloyd LR 50K according to ASTM D638M at a speed of 50 mm/min; hardness (Shore D) was determined on durometer CV (SHD0002, Bowers) according to ASTM D2240; weight gain at immersion in water (24 h @ 25° C.) was determined in accordance with ASTM D570; weight gain at immersion in 20% H₂SO₄ (24 h @ 25° C.) was determined in accordance with ASTM D543.

RESULTS AND DISCUSSION

Synthesis of hydroxyurethane-amines

Hydroxyurethane-amines (intermediate products) of the formula (2) with the number of free amine hydrogen atoms equal to 2 were synthesized from PC and different amines in a 500 ml glass reactor equipped with a stirrer and a heater (Table 1).

Table 1. Description of the intermediate hydroxyurethane-amines

Name of product	Amine	AEW/CCEW ratio	AHEW of product	f	Viscosity (25° C.), Pa·s
HUMA-1	TMD	2 : 1	130	2	9.15
HUMA-2	MXDA	2 : 1	119	2	1.48
HUMA-3	D-400	2 : 1	281	2	0.45
HUMA-4	PTHFA	2 : 1	226	2	0.7
HUPA-1	T-403	3 : 1	147	4	3.74
HUPA-2	DETA	2 : 1	68.3	3	6.7

Synthesis of the hybrid epoxy-amine hydroxyurethane-grafted polymers

The hybrid epoxy-amine hydroxyurethane-grafted polymer of a novel structure is obtained by curing a liquid oligomer composition which consists of diglycidyl ether



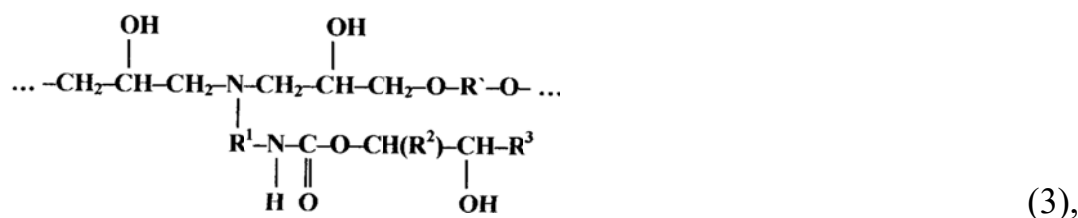
and aminohydroxyurethane of structural formula (2) with the number of free amine hydrogen atoms equal to 2, wherein the diglycidyl ether and aminohydroxyurethane are at stoichiometric ratio of glycidyl groups and free amine hydrogen atoms.

Curing of the grafted polymers (Table 2) were performed at RT for 7 days.

Table 2. Description of the grafted polymers

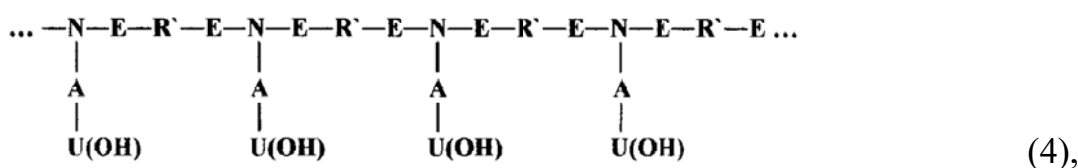
Example No.	Intermediate hydroxyurethane-amine	Epoxy resin	Cross-linking agents	
			amine	epoxy
1	HUMA-1	R11	-	-
2	HUMA-2	R14	-	-
3	HUMA-3	DER 331	-	-
4	HUMA-4	ST-3000	-	-
5	HUMA-1	DER 331	HUPA-1	H48
6	HUMA-2	R11	HUPA-2	DEN 431

A presumed structure of the main backbone of the novel epoxy-amine hydroxyurethane-grafted polymers can be presented by the following formula (3):



where R' is a residue of a diglycidyl ether (epoxy resin); R¹ is a residue of the di-primary amine; R² and R³ are residues of monocyclic carbonate and are selected from the group consisting of H, alkyl C₁-C₂, hydroxymethyl, and at least one of R² and R³ is hydrogen.

The schematic structural formula of the novel polymers according to examples 1-4 is the following:





where $\begin{matrix} E \\ | \\ E-R-E \end{matrix}$ is a residue of the polyfunctional epoxy resin, other designations being the same as above. Polyamines with a number of free amine hydrogen atoms more than 2 also were used for cross-linking.

The results of the tests of the hybrid epoxy-amine hydroxyurethane-grafted polymers are summarized in Table 3 given below.

Table 3. Properties of compositions (examples 1-6).

Measured Characteristics	Example No.					
	1	2	3	4	5	6
Pot life, min	60	40	60	50	25	30
Hardness, Shore D	15	20	35	20	44	60
Tensile strength, MPa	1.1	0.9	3.0	2.4	12	10
Elongation at break, %	147	130	275	183	72	73
Weight gain at immersion in water (24 h @ 25° C.), %	1.1	1.8	0.3	0.3	0.2	0.1
Weight gain at immersion in 10% NaOH(24 h @ 25° C.), %	1.1	1.4	0.6	0.5	0.3	0.1

Testing of Synthetic Leather

The coating formulations for imitation leathers, which contained the components described in Examples 1 to 3, were separately applied onto paper sheets and cured by drying to form on the paper substrate films of incompletely cured polymer coating having a thickness of 25 μm. The coated products were cut into separated pieces, applied onto a fabric substrates (see Table 3) and bonded to the substrates under pressure developed by a load. After bonding to the fabric and solidification of the coating, the paper substrates were peeled off. As a result, samples A, B, and C of the synthetic leather shown in Table 4 were obtained.

Tensile properties of the samples were determined according to ASTM D638.



Cold crack resistance was measured according to CFFA-6 (STANDARDTEST METHODS. CHEMICAL COATED FABRICS AND FILM. Chemical Fabrics & Film Association, Inc. Cleveland, 2011).

Table 4. Main Properties of Synthetic Leather

Sample	Fabric type	Tensile Strength, MPa	Elongation, %	Cold crack resistance, °C.
A	non-woven synthetic soft	70	45	-20
B	non-woven synthetic hard thin	76	33	-20
C	thin synthetic knitwear	24	155	-20

The hybrid epoxy-amine hydroxyurethane-grafted polymer No. 1 was used as in Sample A, the hybrid epoxy-amine hydroxyurethane-grafted polymer No. 2 was used as in Sample B, the hybrid epoxy-amine hydroxyurethane-grafted polymer No. 3 was used as in Sample C.

CONCLUSION

A method of synthesis of novel polymers with lengthy epoxy-amine chains, pendulous hydroxyurethane units and a controlled number of cross-links was proposed. Cured hybrid epoxy-amine hydroxyurethane-grafted polymer with presumably linear structure was prepared.

Testings of hybrid polymers demonstrate increased flexibility with well balanced physical-mechanical and physical-chemical properties of conventional epoxy-amine systems. These materials may be used, for example, for manufacturing of synthetic/artificial leather and sport monolithic floorings.



On the subject of hybrid epoxy-amine hydroxyurethane-grafted polymer US patent application was filed [16].

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