

Synthesis of a New Mannich Polyether Polyol with Isocyanuric Structure

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The paper presents the synthesis and characterisation of a new Mannich polyether polyol with high nitrogen content and thermostable isocyanuric structure. The synthesis was performed by the alkoxylation in the absence of any catalyst of a Mannich base obtained by the reaction of cyanuric acid with a Mannich precursor reagent 1,3-oxazolidine. The Mannich polyol was characterised by ¹H NMR and ¹³C NMR, infrared spectroscopy and by the determination of some usual characteristics such as hydroxyl number, viscosity, amine equivalent, water content. The main application of this polyol is the production of "spray" rigid polyurethane foams with higher thermostability and inherent flame retardancy properties.

Keyword: 1,3-oxazolidine; isocyanuric Mannich polyether polyol; rigid polyurethanic foams.

Polyurethane industry received a large interest in the last years due to the multiple applications of polyurethanic foams, such as flexible or rigid foams, used in construction, transportation, furniture, carpets, appliances, packaging, coatings, adhesives, sealants, fonic and thermal isolation etc. [1,2,3]. Interest for reducing volatile organic compounds ("VOC") from the polyurethane foams, determine research for the synthesis of new reactive polyols for polyurethanes.

The cellular structure of rigid polyurethane foams is formed in a very short time (few seconds) by evaporation of the blowing agent due to the exothermal reaction between isocyanate groups and hydroxyl groups of the polyol, which needs some special characteristics of polyols [3,4].

The polyols for rigid polyurethane foams must have two important characteristics: a high functionality, such as 3-8 hydroxyl groups / molecule and a short chain derived from one hydroxyl group [3,5,6] to give a highly crosslinked rigid structure.

Mannich polyols represent a special group of aminic polyols for rigid polyurethane foams, with low equivalent weight, obtained by the alkoxylation of a Mannich base synthesized by aminomethylation of various acidic substrates C-H, O-H, P-H, N-H such as glucose derivatives [7], sorbitol, sucrose [8,12], phenols (phenol, paronylphenol, Bis-phenol, Bis-phenol A and other) [10,11,13,15], aniline, poliamine [14,15], mainly with propylene oxide (PO) or with a mixture of propyleneoxide with a small percentage of ethylene oxide (EO) [5,6,16]. Because of tertiary nitrogen atoms, Mannich polyether polyols are sufficiently reactive with isocyanates groups and can be used to prepare polyurethanes with reduced quantities of aminic catalysts or even none at all.

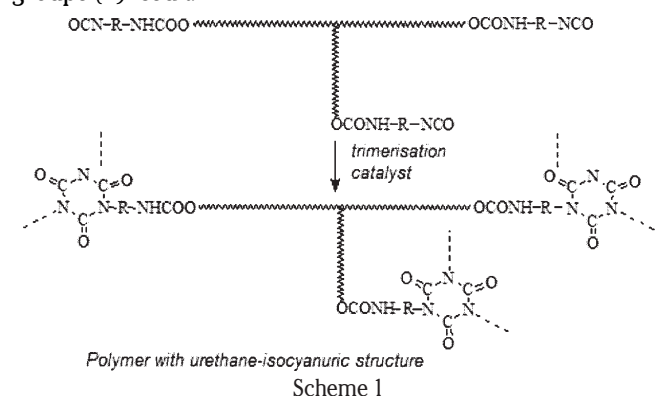
The presence of aromatic rings in the polyol structure improves all physico-mechanical properties of rigid polyurethane foams [4-6,16,23-25].

Mannich polyols from phenol, para-nonylphenol, formaldehyde, diethanolamine and propyleneoxide are produced by companies such as Dow Chemicals (Voranol^o), Hunstmann Corp. (Jeffol^o), SYNAIR Company

from USA, Synthesia in Spain, QUIMICA PUMEX in Mexico, S.C.OLTCHIM S.A.(Petol PM^o) in Romania [1,5,6,13].

Introduction of other thermostable rings such as: isocyanuric rings [9], imidic rings, oxazolidone rings, other aromatic triazinic rings [24-26] increases the thermostability and flame retardancy resistance of rigid polyurethane foams [2-6,26-30]. The presence of nitrogen, phosphorous and halogens such as chlorine atoms in the structure of foams also increase flame retardancy [2-6].

The best exemple is the production of urethane-isocyanuric foams made by the reaction of low functionality polyols with a large excess of isocyanates, in the presence of a catalyst for trimerization of isocyanate groups. Highly crosslinked polymers with urethane and isocyanuric groups (1) result.



This paper presents the synthesis of new Mannich polyether polyol with isocyanuric structure, the main difference between the urethane-isocyanuric foams and the rigid polyurethanic foams based on this new Mannich polyol, being that the isocyanuric rings are part of the polyol structure and they are not formed "in situ" by the trimerization of the isocyanates - $\text{N}=\text{C}=\text{O}$ groups. The paper present also the synthesis of a new Mannich polyether polyol by a new method, based on the use of a Mannich precursor reagent, a heterocyclic compound, such as 1,3-oxazolidine, resulted in absence of a catalyst, by the Mannich condensation reaction of an alkanolamine with aldehydes or ketones [6,14,16].

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Experimental part

Materials

diethanolamine (Fluka, > 98 %);
paraformaldehyde, (Degussa, 97-98%);
cyanuric acid (anhydrous, Fluka, 98.5%),
propyleneoxide (donated by S.C.Oltchim S.A-Romania;
99,2% were used as received.

Procedures

Synthesis of N-hydroxi-ethyl-1,3-oxazolidine and of the Mannich base was performed in a one litre four-neck round-bottom flask filter with stirrer, thermometer, dropping funnel and condenser.

Synthesis of N-substituted-1,3-oxazolidine (Mannich reagent precursor)

A mixture of N-hydroxi-ethyl-1,3-oxazolidine and water (10-13%) was obtained by the reaction (4) of 1 mol of diethanolamine (98%) with 1 mol of formaldehyde (as paraformaldehyde 97-98 %) at 55-65°C during 1-2 hours. The 1,3-oxazolidine was anhydridized by vacuum distillation, during 1-2 h at 15-20 mmHg and temperature of 80-95°C.

1,3-Oxazolidine is a low viscosity light yellow liquid, with the following characteristics: viscosity, at 25°C=25-35 cP; density=1,12"1,13 g/cm³; refractive index, at 25°C n_D =1,4765; boiling point, at 60 mmHg = 125-135°C.

Synthesis of Mannich base and of Mannich polyether polyol with isocyanuric structure

To 351g (3 mols) N-hydroxi-ethyl-1,3-oxazolidine with 1,5 % water content 129 g (1 mol) anhydrous cyanuric acid was added in portions at temperature between 45-50°C. The reaction is slightly exotherm. After the entire amount of cyanuric acid was added, temperature was increased to 110 – 120 °C and maintained for 1 h under stirring. The reaction (8) is practically quantitative (99, 2% yield) after 2 h.

The resulted product, i.e. the Mannich base with isocyanuric structure, is a viscous, braun-amber liquid, with a functionality equal to 6 (table 1).

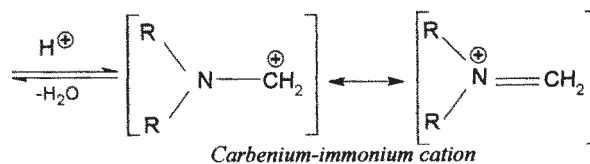
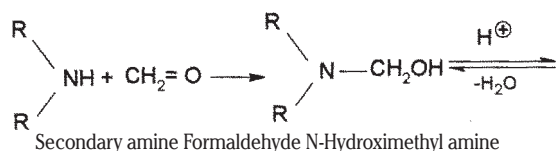
The Mannich polyether polyol was obtained from 1 mol Mannich base, which was propoxylated (9) with 6 mols PO in a stainless steel pressure reactor, in a self catalytic reaction, at 80-90 °C and 1-1,5 bars, under nitrogen atmosphere, during 2-3 h. After the addition of PO, the reaction mass is maintained 1 hour at 90-95°C for the consumption of the unreacted PO, then devolatilized by vacuum distillation.

The resulted Mannich polyether polyol with isocyanuric structure is a homogenous substance, viscous, braun-amber liquid, with a functionality equal to 6 and a short chain derived from one hydroxyl group of Mannich base, it was successfully used directly for the preparation of rigid polyurethanic foams without any supplementary purification (table 2).

Results and discussions

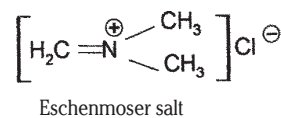
In the classical Mannich reaction, the reactive species are the carbenium - immonium cations, a very reactive intermediates which results from the addition reaction (2) of an aminic component (preferable secondary amine) to formaldehyde, which is the most used carbonylic component, followed by elimination of water (2) [6,18-20].

Addition-Elimination reactions



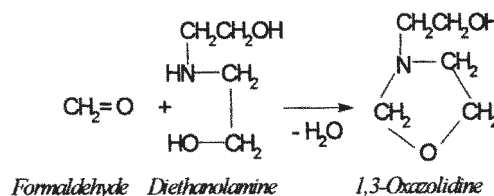
Scheme 2

A stable substance with the structure of the carbenium-immonium cation (3) the reactive intermediate of Mannich reaction, named "Eschenmoser salt" was obtained and may be used, to synthesize Mannich bases [18-20].



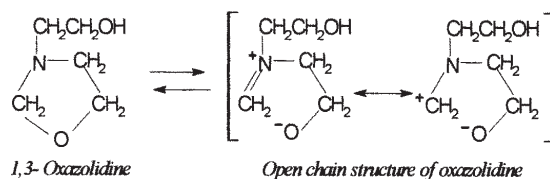
Scheme 3

A Mannich precursor reagent such as N-substituted 1,3-oxazolidine can be formed by the reaction of diethanolamine with formaldehyde (4).



Scheme 4

The high reactivity of oxazolidines is explained by the equilibrium (5) between the cyclic form and the open chain form, which has a similar structure with the immonium cation (2) (the reactive species in the classical Mannich reaction) [6,16,20,22].

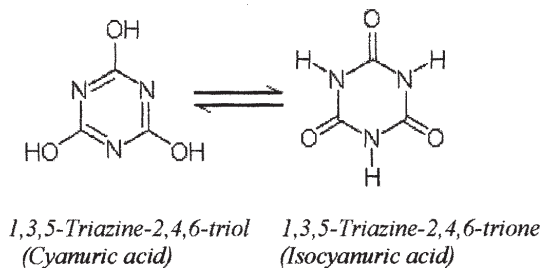


Scheme 5

1,3-Oxazolidine easily reacts with a large number of compounds, the same used as acidic substrates in the classic Mannich reactions such as phenols, aniline, ketones, amides, etc. [16] and has the advantage that it's a distillable compound and therefore after synthesis can be anhydridized by vacuum distillation. In this way can be obtained a Mannich base with the same structure as for classical Mannich reaction, which can be directly alkoxyated, avoiding Mannich base anhydridization by distillation when can result secondary condensation reactions that can lead to a higher intensity of colour and an increase of viscosity of Mannich base [28].

The cyanuric acid, the trimer of the cyanic acid (HOCN), has two mesomeric forms (6): cyanuric acid and isocyanuric acid. Infrared spectrum and other physical methods indicate that isocyanuric acid structure is the predominant structure. Substituted derivatives from both

isocyanuric acid and cyanuric acid such as: melamine, esters of isocyanuric acid (isocyanurates) and other are known [21,27].



Scheme 6

Cyanuric acid has 3 acidic hydroxyl groups but it is difficult to directly alkoxyate in order to obtain a Mannich polyol with isocyanuric structure because of two reasons:

a) the very low solubility of cyanuric acid in organic solvents. In water it has a low solubility of 0,125% at room temperature and 4% at the boiling point of water [5,21]. It is slightly soluble in alcohol, but this solvent complicate the synthesis of polyether.

Water is a bad solvent because it generates diols (polyalkylene glycols) during the alkoxylation reaction, which decreases in an unacceptable manner the functionality of the resulted polyols [5,6,29].

b) the presence of the majority tautomeric isocyanuric form, practically impossible to be alkoxyated due to the urea structure [5,29].

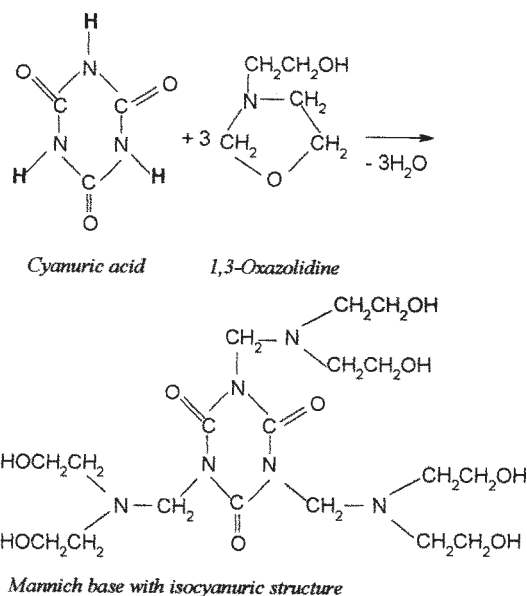
To obtain new isocyanuric Mannich polyether polyol, the Mannich base with isocyanuric stabilized structure, has been first obtained by a very simple and easy process, i.e. by the Mannich reaction of the cyanuric acid with a Mannich reagent precursor, the N-substituted 1,3-oxazolidine.

The synthesis of new isocyanuric Mannich polyether polyolw has the following steps:

1. synthesis of anhydrous 1,3-oxazolidine ;
2. synthesis of the Mannich base with isocyanuric stabilized structure;
3. alkoxylation of the Mannich base.

The synthesis of the Mannich base (7) with a stabilized isocyanuric structure, is based on the reaction of 3 mols of 1,3-oxazolidine with one mol of cyanuric acid in the isocyanuric form. It is well known that all the compounds with amidic or ureic structure has active hydrogens and reacts as acidic substrates in Mannich reactions [6,9,16,17].

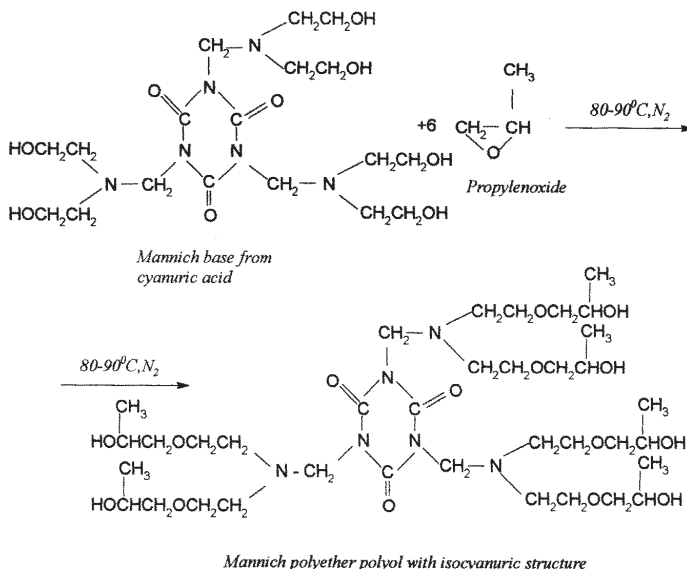
Finally, the Mannich polyether polyols (table 2) are obtained by the alkoxylation of the Mannich base with isocyanuric structure (1 mol) (8) with propyleneoxide (5 or 6 mols) in the absence of any catalysts.



Scheme 7

Because of the high content of tertiary nitrogen atoms of the Mannich base, which have catalytic properties, the propyleneoxide addition to highly reactive primary hydroxyl groups, can be made at low temperature 80-90°C in a self-catalytic reaction [5,27,29,30].

The infrared spectrum of oxazolidine shows a strong absorption at 1650 cm^{-1} (-CH=N- imine group), proving the existence of the mentioned equilibrium between cyclic structure and open chain structure having $\text{CH}_2=\text{N}$ - bond (fig. 1) [20,22,23].



Scheme 8

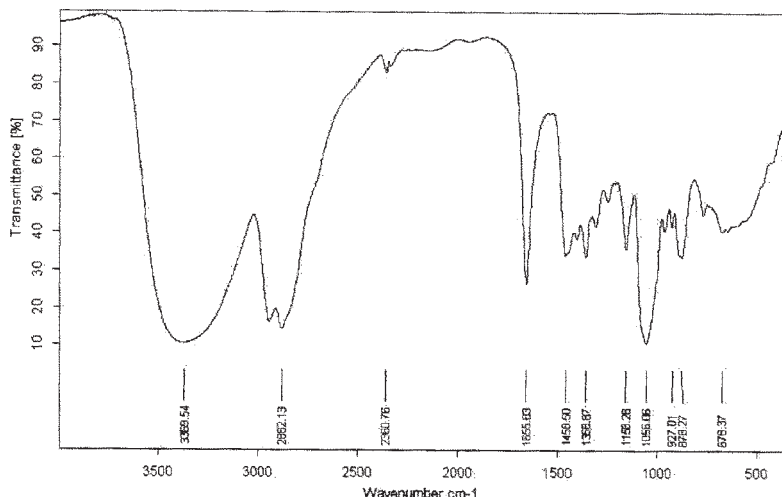


Fig. 1. Infrared spectrum of N-hydroxy-ethyl-1,3-oxazolidine

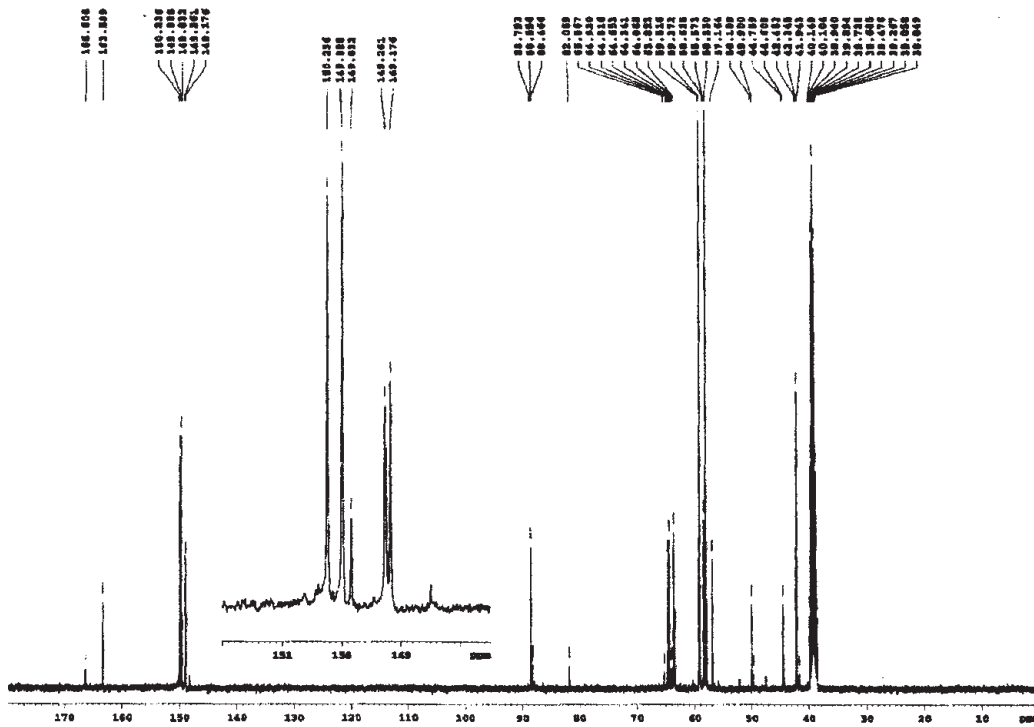


Fig. 2. ¹³C RMN(100 Mhz) Spectrum of Mannich base cyanuric acid

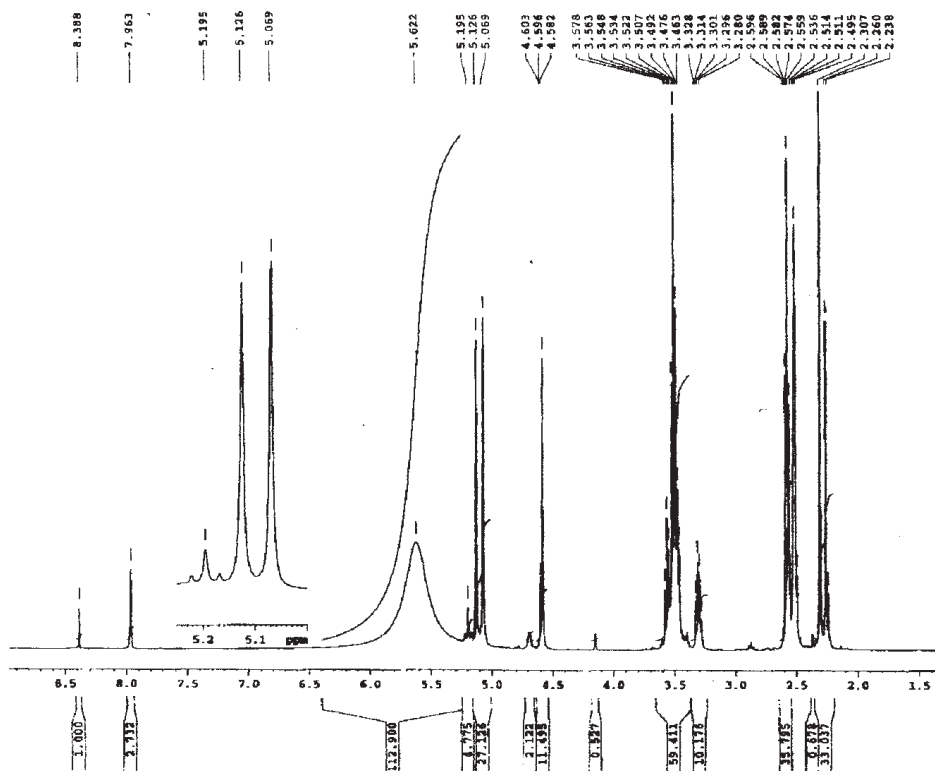
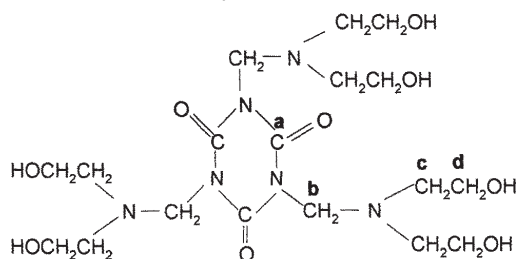


Fig. 3. ¹H RMN(400 Mhz) Spectrum of Mannich base cyanuric acid

The ¹³C RMN (100 MHz) spectrum of Mannich base from cyanuric acid shows peaks at 150 ppm for C₁ from isocyanuric ring (C=O), at 58 ppm for C₂ from -CH₂-CH₂-OH and at 40 ppm for C_d from -CH₂-CH₂-OH (fig. 2).



Mannich base from cyanuric acid
Scheme 9

The ¹H RMN (400 MHz) spectrum Mannich base from cyanuric acid (fig. 3) in deuterated dimethylsulfoxide shows:

- singlets at 4,5 -5,1 ppm which are assigned to protons from methylene groups CH₂ grafted to the nitrogen of triazine ring (position b);
- triplets at 3,4 – 3,5 ppm are assigned to protons from methylene groups CH₂ bonded on hydroxilic group (position d);
- triplets at 2,55 ppm (next to solvent signal) can be assigned to protons from methylene groups CH₂ bonded to tertiary nitrogen of aminomethylated groups (position c).

Table 1
CHARACTERISTICS OF MANNICH BASE FROM CYANURIC ACID AND 1,3-OXAZOLIDINE

Exp. No.	Functionality of Mannich base	Hydroxyl number in mg KOH / g.	Amine equivalent in %	Viscosity at 25 °C in CP	Water in %
1.	6	681,8	0,23	30714	0,19
2.	6	671,8	0,25	25318	0,19
3.	6	665,4	0,31	28287	0,30
4.	6	635,2	0,32	26045	0,35
5.	6	642,5	0,37	26723	0,29

Table 2
CHARACTERISTICS OF MANNICH POLYETHER POLYOL WITH ISOCYANURIC STRUCTURE

Exp. No.	Functionality of polyol	Mole ratio ¹ of reactants in moles	Hydroxyl number in mg KOH/g	Amine equivalent in %	Viscosity at 25°C in cP	Water in %
1.	6	1 : 5	570,9	0,20	2893,6	0,20
2.	6	1 : 6	577,5	0,21	2343,6	0,20
3.	6	1 : 6,5	440,1	0,29	1719,0	0,41
4.	6	1 : 6,5	490,8	0,28	1903,5	0,39
5.	6	1 : 6,5	498,2	0,27	1895,3	0,43

1. Mole ratio = [Mannich base]: [PO]

The Mannich base from cyanuric acid and 1,3-oxazolidine in molar ratio =1:3 has a high viscosity and hydroxyl number.

We obtained a Mannich polyether polyol with a viscosity of about 2000 cP or less, and a hydroxyl number in the range of 400-600 mg KOH/g and the content of tertiary nitrogen between 0,2-0,4% amine equivalent(table 2).

Conclusions

We conclude that a new Mannich polyether polyol with isocyanuric structure was obtained by the reaction of anhydrous cyanuric acid with a Mannich reagent precursor such as 1,3-oxazolidine in 1:3 molar ratio, followed by the propoxylation of the resulted Mannich base, in the absence of any catalyst at low alkoxylation temperature 80-90°C.

After alkoxylation, hydroxyl index and viscosity decrease up to a convenient value to use the Mannich polyether polyol for rigid foams. The isocyanuric rings percentage content of polyol depend on the numbers of moles of reactants used and can vary between 6-7%.

The resulted Mannich polyols due to the high aminic tertiary nitrogens content have a high reactivity in the foaming process, with catalytic effect in the reaction of hydroxyl groups with isocyanates.

The synthesized Mannich polyols can be used for the production of rigid polyurethane foams without any purification step and are recommended to be used for "spray" rigid polyurethane foam formulations.

Due to the presence of the isocyanuric ring, the rigid polyurethane foams obtained with this Mannich polyols have higher physico-mechanical properties, thermostability and flame resistance as compared to rigid polyurethane foams based on classical aliphatic polyether polyols.

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