



# Advanced biobased and rigid foams, based on urethane-modified isocyanurate from oxypropylated gambier tannin polyol



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## ABSTRACT

Rigid and biobased urethane-modified isocyanurate (PUIR) foams with an isocyanate/hydroxyl molar ratio equal to 3, were synthesized from glycerol-based and/or gambier tannin-based polyols, obtained by oxypropylation process. The content of each polyol was varied progressively and respectively from 0 to 100%. The synthesized PUIR foams were fully characterized and compared. Density, compressive modulus, thermal conductivity and closed-cell content were studied. Cell morphology was also observed by scanning electron microscopy. Furthermore, thermal stability and flammability were investigated to study the impact of the aromatic structure provided by the tannins. The results show that the tannin-based polyol favors some PUIR foams properties such as fire retardancy and high compressive strength behavior.

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## 1. Introduction

As general rigid polyurethane (PUR) foams, foams based on isocyanurates are more and more produced as commercial insulation materials e.g. for building or transportation applications. Polyisocyanurate (PIR) foams are based on a PIR network obtained by the trimerization of isocyanate groups into an isocyanurate ring at high temperature [1]. PIR foams are increasingly developed since they bring higher performances compared to conventional PUR foams, such as, higher fire resistance and thermal stability. However, PIR foams present some drawbacks such as low mechanical properties (very friable) due to their high crosslink density [2]. To increase the corresponding properties, many modifications were tested like adding amide, imide, oxalidone, carbodiimide or urethane linkages [2,3]. One of the best approach seems to be the elaboration of polyurethane-modified isocyanurate (PUIR) foams

*Abbreviations:*  $\lambda$ , thermal conductivity; DMCHA, *N,N*-dimethylcyclohexylamine; EHC, Effective Heat of Combustion; HOMO, homopolymers; HRR, Heat Release Rate;  $I_{OH}$ , Hydroxyl index; OPG, oxypropylated glycerol; OPT, tannin-based liquid polyol; PHRR, Peak of Heat Release Rate; PIR, polyisocyanurate; PMDI, 4,4'-Methylenebis(phenyl isocyanate); PO, propylene oxide; PPO, polypropylene oxide chains;  $P_r$ , residual weight percentage; PUIR, urethane-modified isocyanurate; PUR, polyurethane;  $t_{ig}$ , ignition time; SEC, Size Exclusion Chromatography; st.dev, standard deviation; THR, Total Heat Released value; TSR, Total Smoke Release.

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[4], since the introduction of urethane segments via polyol reaction with isocyanates decreases the foam fragility. Unfortunately, the corresponding thermal stability and fire resistance were deteriorated [5,6]. The selection of the right chemical architecture, mainly focused on the polyol, seems to be a key point to address these issues [5]. The accurate choice of the versatile and more and more often biobased macromolecules can lead to tailor-made foams with advanced properties.

Tannins were already described and used as polyols for PUR foams [7,8] with only open-cells structures. Tannins can be directly extracted from different plants. They present a complex chemical structure based on condensation products of flavonoid units, which form oligomers and macromolecular structure [9]. They are mainly classified in two major groups: the hydrolysable and the condensed tannins which represent more than 90% of the world commercial production. The reactivity of tannins is essentially due to the phenolic hydroxyl groups. Depending on their botanical source, tannin structures with regards to hydroxyl (OH) group content and molecular weight may differ considerably, affecting different properties, such as the solubility. Condensed tannin from gambier (GT) has been selected in the present study. This tannin has a lower degree of polymerization than other tannins as it is composed of approximately 50% monomeric catechin [10]. One of the main drawbacks for tannins as aromatic polyols is that they possess native hydroxyl groups which present a limited reactivity due to different factors such as steric hindrance or limited accessibility of

reactive groups. However, after chemical modifications of the native hydroxyl groups [7], the reaction with isocyanate can take place to synthesize PUR foams [7,8]. Among other chemical processes, oxypropylation is a promising approach to increase tannin reactivity [11]. Through an anionic ring-opening polymerization of propylene oxide (PO) in presence of catalyst at high temperature, polypropylene oxide chains (PPO) are grafted onto the tannin leading to a tannin-based liquid polyol (OPT). Reaction of OPT with isocyanates can produce PURs that can compete in many aspects with polyols derived from petrochemicals [12]. Thermal and oxidative stability of the PURs from OPT are better than those based on polyester polyol.

Tannin-based polyols seems to be interesting macropolyols for the elaboration of PUIR foams, since they are aromatic and biobased chemicals with particular structures. This study is then focused on (i) the use of OPT to develop new macromolecular architectures based on PUIR and on (ii) the analysis of the effects of the polyol structure on the final foam morphology, thermal properties and flammability. The effects of the tannin-based polyols aromatic structure on the properties, such as fire retardancy were compared with those of more conventional polyether polyol based on oxypropylated glycerol (OPG), which is also biobased. Different PUIR foams were prepared with a same proportion of polyols content, and a OPT content from 0 up to 100% of this polyols part.

## 2. Experimental

### 2.1. Materials

Tannin polyols were obtained from the oxypropylation of gambier tannin (*Uncaria gambir*) obtained from Silva Chimica (Gambier CM, St. Michele Mondovi, Italy). The corresponding synthesis conditions were fully described in a previous work [11]. OPT polyols used in this study corresponding to a weight ratio between tannin and propylene oxide of 20/80 (20% of biobased content). Potassium hydroxide (KOH) is used as a catalyst at 5 wt%. During the oxypropylation reaction, some homopolymers (HOMO) of poly(propylene) oxide were produced. The synthesized tannin-based polyols were introduced into foam formulations, without any type of purification *i.e.*, with HOMO and KOH residues, since these latter can be involved in the foam formation. Commercial polyether polyol based on oxypropylated glycerol (OPG) was kindly supplied by CECA (Adiansol GO360).

The isocyanate was polymeric 4,4'-Methylenebis(phenyl isocyanate) (PMDI) from BorsodChem (Ongronat 2500). The chemical blowing agent (Sulfo 50P) is composed of water and surfactants. It was supplied by Laguerre Chimie. Silicone (Tegostab B84501 from Evonik). Two specific catalysts were used: *N,N*-dimethylcyclohexylamine (DMCHA from BorsodChem) and potassium octoate (Niix catalyst K-Zero300 from Momentive) as a PUR and PIR catalyst, respectively. Isopentane from Inventec was used as physical blowing agent. All these chemicals were used as received without further purification.

### 2.2. Foam synthesis

Several foams were prepared with different ratios of each polyols. The OPG is progressively replaced by OPT in the different formulations, with a corresponding polyol functionality and structures evolution. Each PUIR is labeled as follow % OPT/% OPG (% wt/wt). The different PUIR are: 0/100, 25/75, 50/50, 75/25 and 100/0.

Generally, isocyanate/hydroxyl molar ratio (NCO/OH) is used for PURs synthesis. For this study, a NCO/OH molar ratio of 3 was used for PUIR foam formulations. Table 1 presents the details concerning

**Table 1**  
PUIR foams formulation.

Component	pbw
OPT	0–100
OPG	100–0
PMDI	230–255
Sulfo 50P	2.1–2.2
B84501	2.9–3.1
DMCHA	0.5
KZéro-3000	2.6–2.8
Isopentane	19.6–21.1

the basic formulation. The amount of isocyanate was calculated and based on total reactive hydroxyl groups *i.e.*, with both polyols (OPT and OPG) and Sulfo 50P which acts as a blowing agent. With the exception of the relative polyols ratio and the corresponding isocyanate content whose proportions were adjusted to maintain a constant NCO/OH molar ratio, all other components were kept constant.

The procedure to synthesize PUIR foams is composed of several successive steps. First, the polyols are stirred together during 10 s. Then, the water blowing agent, surfactant, catalysts and physical blowing agent are successively added and stirred 10 s, to homogenize the mixture. Afterwards, the pre-weighted isocyanate is quickly added to the mixture and the reactive mixture is stirred during 10 s. The foams rise freely and are kept overnight at room temperature for curing before demolding. To perform the different tests, several foams are elaborated for each formulation.

### 2.3. Characterization techniques

Hydroxyl index ( $I_{OH}$ ) is a key parameter in the characterization of polyols. This value represents the amount of KOH, in milligrams, equivalent to the OH content of 1 g of polyol.  $I_{OH}$  was determined by the standard esterification method using phthalic anhydride [13]. Polyol (2 g) and the phthalation reagent (20 mL) were heated at 115 °C for 45 min, cooled to room temperature. Pyridine (30 mL) was then added, later water was also introduced (30 mL). The solution was then titrated with a 1.0 M sodium hydroxide (NaOH) solution. The phthalation reagent was a 1.0 M solution of phthalic anhydride in pyridine. Hydroxyl index ( $I_{OH}$ ) in mg of KOH·g<sup>-1</sup> was determined according to Eq. (1):

$$I_{OH} = \frac{(V_{blank} - V_S) \times C \times 56.1}{W_S} \quad (1)$$

$V_{blank}$  (mL) and  $V_S$  (mL) are the volumes of NaOH solution required for blank and polyol sample titrations, respectively.  $C$  (mol·L<sup>-1</sup>) is the NaOH solution concentration and  $W_S$  (g) is the polyol weight.

Quantitative <sup>1</sup>H NMR was used to estimate the degree of polymerization of PO onto tannin [14]. A standard solution of PFB in DMSO-*d*<sub>6</sub> was prepared by weighting 33 mg of PFB diluted in 0.40 mL of DMSO-*d*<sub>6</sub>. 20 mg of OPT were dissolved into 800 μL. An aliquot of the standard solution (0.10 mL) was added. The solution was then transferred into a 5 mm NMR tube. The relaxation delay was set to 10 s with 32 scans.

Quantitative <sup>31</sup>P NMR spectra were acquired using a Bruker 400 MHz equipped with a "Quad probe" dedicated to <sup>31</sup>P, <sup>13</sup>C, <sup>19</sup>F and <sup>1</sup>H NMR acquisition. A relaxation delay of 10 s was used, and the number of scans was 512. Samples were prepared according to previous procedures [15]. A solvent mixture of anhydrous pyridine and CDCl<sub>3</sub> (1.6:1, v/v) was first prepared. It was further used for the preparation of the relaxation reagent (Chromium (III) acetylacetonate, 5 mg·mL<sup>-1</sup>) and the internal standard solutions (Cholesterol,

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