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BIO-BASED FOAM FOR THERMAL INSULATION. VALORISATION OF CNSL (CASHEW NUT SHELL LIQUID)

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Abstract

Everyone now knows that the building industry accounts for 43% of energy consumption and 25% of greenhouse gas emissions. It thus constitutes one of the key objectives in the pursuit of the "Factor 4" issues in 2050. The thermal insulation defects of buildings and mistreatment of airtightness problems are the main causes low energy performance of the built French park. The fight against energy waste therefore passes deals with the thermal insulation of heated buildings. The thermal insulation performances are firstly determined by their thermal conductivity and the physical quantity characterizing the behaviour of materials during the heat transfer by conduction. With an average thermal conductivity of 0.023 W/m.K, polyurethane foam remains very good for building insulation. The advantage of this material therefore results in a gain of living space. Indeed for a given heat resistance, the thickness of material required is lower than for the homologous. However, PU foams are generally expensive especially because of the presence of fossil compounds as well as adverse effects on the environment and health (discharge of volatile organic compounds VOCs). In 2007, the French chemical industry is committed to use by 2017, 15% of bio based raw materials and diversify its industrial resources used (agricultural resources, especially non-food processes, and lignocellulosic waste and co-products). However, only 8% of raw materials of the French chemical industry are renewable. Polyurethane foams are generally composed of two main compounds: Polyols, and isocyanate, the both from fossils resources. There is today part of a solution dealing with bio polyols from rape seed oils, but in most of case too much expensive for this industry. CNSL (Cashew Nut Shell Liquid) is a co-product of cashew nut exploitation. It is a kind of vegetal oil mainly composed of anacardic Acid and cardanol. This oil may be a very performant and low coast raw material ($ 300/ton) for polyol production to substitute fossil polyols in Polyurethane composition. CoDEM is today developing new bio based expanded foam with CNSL to reach a target thermal conductivity near 0,025 W/m.K This communication may explains the first part of our works substituting polyols and first results measured in our laboratory.

Keywords:

Polyurethane, Foam, insulation, CNSL, plant chemistry

1 INTRODUCTION & BIBLIOGRAPHY

The Green Chemistry initiative, since its inception in 1991, has evolved many active programs to make polyols from renewable resources like vegetable oils as the feed-stock for value-added fine chemicals and polyurethane polymers [BIERMANN 2000; JAN 2005; CLARK 1999; MECKING 2004 ; WARWELL 2001; BLANC 2000]. The utility of natural monomers and polymers, in-lieu of their structural diversity and complexity, to produce high value polymers after appropriate chemical modification methodologies has now been demonstrated [GALLEZOT 2007; METZGER 2006; CECILIA 2007; UYAMA 2003; TSUJIMOTO 2003; MAFFEZZOLI 2004; MUSANTE 2000; CAMPANELLA 2006]. Vegetable oil derivatives useful in the preparation of polyurethanes, epoxies, etc. have been reported [PETROVIC 2008; TAN 2010]. Nonedible vegetable oils such as the rubber seed oil[OKIEIMEN 2005; OKIEIMEN 2002] and cashew nut shell oil [SATHIYALEKSHMI 2004; SURESH 2005] have also been explored as sustainable feed-stock for some important commercial polymers. Mainly, these efforts could be attributed to the plentiful availability of these oils as a byproduct of the farm industry or to replace petrochemicals with environmentally friendly renewable resources and provide value addition to existing agricultural products to benefit agriculture and industry. Polyurethane chemistry is unique in terms of the versatile range of products that can be prepared using the same starting materials, namely, polyol and isocyanate, and the formulation can be tailored to make elastomers, adhesives, thermoplastics, or foams. Polyurethane foams constitute more than 60% of all polyurethane products. Rigid PU foams in the market are mainly prepared from sugar-based polyols and isocyanates. Foams based on PPO polyols are sensitive to hydrolysis and have moderate water absorption. Renewable resources as a source of polyols in the preparation of PU foam has also been widely studied [TAN 2011; VERONESE 2011; IONESCU 2012]. The preparation of rigid foams using soy-based polyol has recently been reported by Tan et al. [21]. Other vegetable oils like castor oil and rosin were also used to synthesize polyester polyols either alone or as a blend to prepare rigid PU foams [VERONESE 2011; IONESCU 2012].

Cashew (Anacardium occidentale L.) nut shell (CNS) is a by- product of cashew production. It is a source of unsaturated long- chain phenols, such as anacardic acids, anacardols, cardols and their isomers. Both anacardic acids and cardols were reported to have antitumor [MELO CAVALCANTE 2005; KUBO 1993; KOZUBEK 2001], antimicrobial [KUBO 1993], urease inhibitory [KUBO 1999], lipoxy- genase activities [HA 2005] as well as uncoupling ability [TOYOMIZU 2000]. On the other hand, cardanols are widely used in coating and resin industry due to their outstanding resistance to softening action of mineral oil and high resistance to acids, alkalis, microbe, termite and insect. Anacardic acids are thermally labile and easily degraded to their corresponding cardanol by decarboxylation at high temperature [PHILIP 2008]. Several studies have been done on the extraction of phenols from CNS. According to Tyman et al. [TYMAN 1989], around 6.1 wt.% (based on dry weight of CNS) of cashew nut shell liquid (CNSL) was extracted by soaking CNS in light petroleum for a week and then subjecting the half-processed shell to soxhlet extraction at 40–60 °C for 12 h with light petroleum as the solvent. Due to the different uses of anacardic acids, anacardols and cardols, it is important to separate and purify these compounds in order to identify their properties for specific applications. Microanalysis of phenolic acids is an important aspect in the biochemistry of many natural products [YULIANA 2012]. Tyman et al. [TYMAN 1989] showed that the polarities of compounds detected in CNSL were similar. Therefore, purification of individual compound is difficult to achieve. To date, only anacardic acid isomer (15:0) and (15:3) are available in the purified form.

In the first part of our project, we have tried to prepare simple formulations with CNSL and other components in aim to make a low thermal conductivity material with the highest CNSL content as possible. We have also made a LCA (Life cycle analysis) to compare best formulation and to confirm the interest of having CNSL as a good raw material for expanded foams.

2 MATERIALS AND METHODES

2.1 Raw materials

1. CNSL:
   During this first step of the project we've worked with 2 different CNSL:
   - CNSL1: Artisanal prepared CNSL from Benin
   - CNSL2 : Industrial prepared CNSL from Ivory Coast. This second sample have been decarboxylated by a thermal treatment to reduce polymeric content and increase anacardic acid content.
2. Isocyanate
   Isocyanate reagent used in this project is a traditional and commercial product : diisocyanate de 4,4'-méthylènediphényle.
3. Other components

We have studied different way to expend formulated foams. So we both used Iso pentane as a chemical expansion agent and sodium bicarbonate as a thermal expansion agent.

In our first project step, we also tried to complete the mix with plant proteins by using "tubermine", a degraded protein from potatoes industry.

2.2 Thermal Conductivity

In this project we used a heat flow meter method to determine the thermal conductivity of formulated foams. The apparatus used is a lambdameter two flow meters with a single sample. The heat flow density is measured with two flowmeters placed against the test piece (the hot plate is located above the sample and the cold plate below).

Sample preparation and realization of measurements are performed according to EN 12667 standard.

At least three tests are carried out for each type of foam and the thermal conductivity was measured at 10 ° C with a temperature gradient of 20 ° C between the hot and cold plates.

2.3 Life cycle analysis

In this project we decided to compare in a first light orientation LCA, traditional PU foam made with fossil polyols and isocyanate, and our best formulation (F4 CNSL foam) with a lower thermal conductivity.

We use the software SimaPro V8 with the ecoinvent database v3. With this kind of materials, we have decided to use ILCD 2011 : the European calculation method which wins unanimous support in LCA world, especially with bio-resources.

3 FORMULATIONS & PROCESS

3.1 Without isocyanate

In a first approach we tried to prepare an expanded foam only made with plant resources and a thermal expansion reagent sodium bicarbonate. Next table (Tab. 1) presents tested formulations.

Tab. 1: Formulations without isocyanate

First step foam formulations			
Formulation	CNSL1 w%	Proteins w%	Bicarbonate w%
F1	50	48	2
F2	50	45	5
F3	48	42	10

The main difference between these formulations is bicarbonate content. Proteins and CNSL ratios have been adjusted.

To prepare these foams, we used the following process:

1. CNSL and protein mix to have a homogeneous "cream"

2. Bicarbonate addition

3. 80°C Thermal treatment during 30 minutes.

4. Drying at 50°C to constant mass. Unmolding and surfacing to have a conform 30cm x 30cm x 5cm sample for thermal conductivity analysis.

3.2 With Isocyanate

If the protein and CNSL foams expanded with bicarbonate was a first interesting approach, we decided to have a more traditional PU formulation substituting only polyols by CNSL. Next tab presents formulations with isocyanate.

Tab. 2. Formulations with isocyanate

Formulation	CNSL2 w%	Polyols w%	Isocyanate w%
F4	50	0	50
F5	35	15	50
F6	25	25	50
Control	0	50	50

In this step, we also used an isopentane expanding agent to increase the natural expansion due to isocyanate and polyol reaction. Polyols and CNSL are mixed followed by addition of isocyanate and isopentane with a cream time near 45s. Then we mold the preparation at 37°C during 20 minutes. The 30cm x 30cm x 5cm is then unmolding and surfacing.

4 RESULTS & DISCUSSION

4.1 Appearance and density

The 3 first formulations lead to solid and porous materials but not light enough and at the first sight we knew that we had an open and too much bigger porosity. Tab. 3 presents bulk density of the first 3 formulations.

Tab.3 Bulk density of without isocyanate formulations

Formulation	Bulk density (kg/m^{-3})	variations (kg/m^{-3})
F1	450	25
F2	300	8
F3	265	14

Average size of porosity on the F2 formulation is around 4 to 6 mm as shown on figure 1.

This first way to obtain solid foams works but does not lead to very light materials. In the second way, with isocyanate, we made the bulk density decrease to 60 kg.m^{-3} with smaller porosity as shown in tab 4 and figure 2.

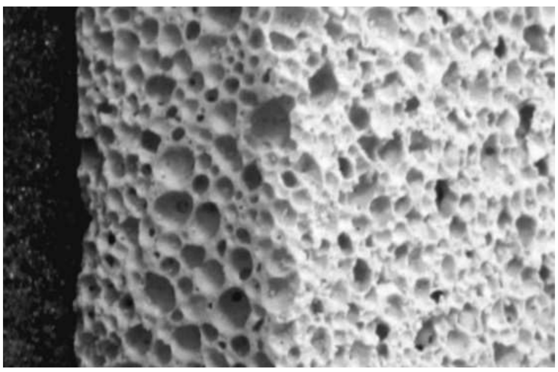

Fig. 1: Picture of the F2 expanded foam

Tab 4. Bulk density of F4 to F6

Formulation	Bulk density (kg/m^{-3})	variations (kg/m^{-3})
F4	105	3
F5	88	4
F6	63	2
Control	52	3

With an average porosity size near 0.5 to 1mm, the second formulation series seems to be better to obtain a lightweight foam but not enough homogenous and we can observe in lower part of material a bigger porosity.

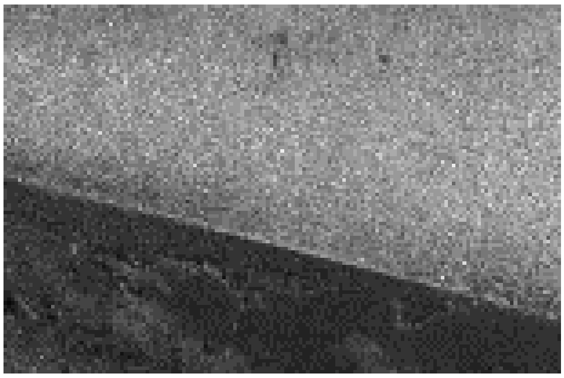

Fig. 2: Picture of the F5 Formulation

4.2 Thermal Conductivity

To confirm our first analysis, every sample have been tested in 3 thermal conductivity measurements according to the EN 12667 standard. The results are presented in the next table.

As it is shown in the previous table, and according to their higher bulk density, foams without isocyanate lead to higher thermal conductivity but not too bad for such a density. The F2 formulation is quite interesting to develop mechanical resistant materials for window thermal bridge treatment.

The natural reaction of Isocyanate with polyol and CO_2 extraction lead to very interesting formulations with CNSL. Of course at this step of our project, CNSL has not been modified to optimize the reaction. Nonetheless the substitution of petro based polyols lead to very good thermal performances.

Tab. 5: expanded foams thermal conductivity

Formulation	Thermal Conductivity (mW/m.K)	variations (mW/m.K)
F1	62.7	2.5
F2	48.1	2.3
F3	56.0	2.6
F4	34.4	1.6
F5	32.8	1.7
F6	28.1	1.5
Control	25.6	0.8

4.3 LCA Analysis

At this step of the project it was interesting to compare the F4 and the Control formulation in LCA to be sure of the good sense of our work. This was done by comparing a functional unit of one square meter insulation with a thermal resistance of 5. All the extraction and process steps have been considered till the out of a factory in Picardie. Polyols and isocyanate are produced near Paris. CNSL is produced in Ivory Coast and for this project it has been sent to CoDEM by plane.

We have done only a simple orientation LCA based on ILCD 2011 Method with 6 main indicators. Results are shown in figure 3.

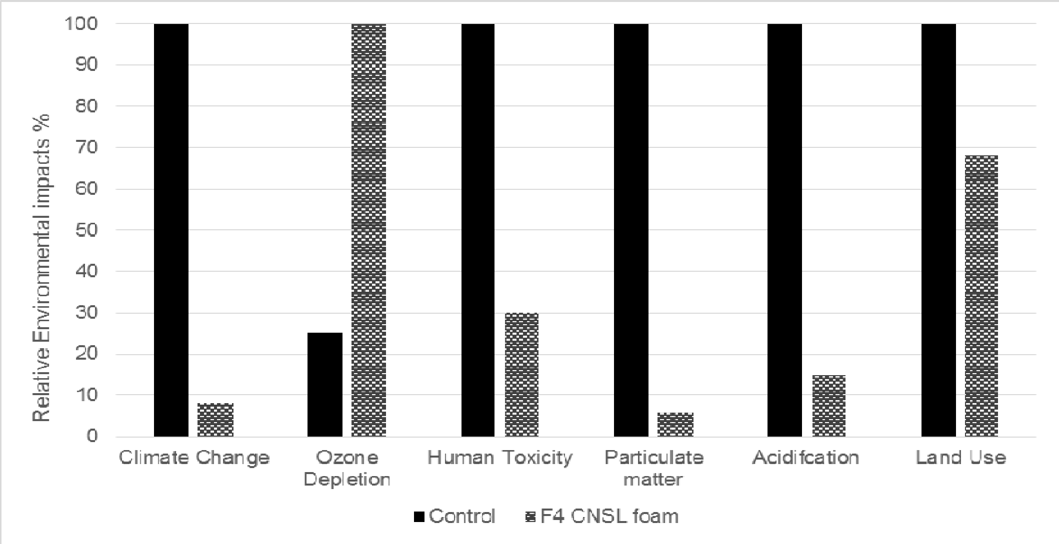

Fig. 3: Orientation LCA results

Reading this figure, our F4 formulation lead to a very eco-friendly solution compared to classical Polyol/Isocyanate formulation. The only bad result is obtained with the Ozone depletion indicator. This can be explained by the transportation from Ivory Coast. In an industrial valorization, transportation by boat for CNSL will be favoured. All other indicators show an important amelioration of environmental impact by using CNSL to produce a thermal insulation R=5. A first step by reducing the use of petro based polyol more than optimizing isocyanate content could lead to a very interesting compromise.

4.4 Discussion

This project started in 2012 and we have today very interesting thermal performances and a good reduction of environmental impacts. Until now, we did not modify the whole composition (use of industrial isocyanate). Now we know that we can adapt adjuvant and other reagents to have a better control of expansion. A PhD thesis supported by French ANRT recently started to understand all the mechanisms implied in the reaction. Process and reaction optimization by modifying CNSL to lead to a 0.025 W/m.K foam with low LCA impact, and of course low cost is one of the targets. CNSL is today 2 or 4 times cheaper than petro based polyols.

5 CONCLUSIONS & PERSPECTIVES

These first results show that we can use CNSL to produce expanded foam for thermal insulation but substitution of isocyanate is not possible for instance to lead to very low thermal conductivity. However, a 100% bio based solution may be interesting for some particular applications to reduce thermal bridges under windows for example and to replace high density in polyurethane. We also work on a chemical synthesis to have a very low thermal conductivity foam without isocyanate, but that way will be developed in the last part of our research project.

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