Development of polyurethane prepolymers for OCF

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Abstract

Recent changes in legislation have forced polyurethane (PU) one-component foam (OCF) producers to lower the amount of free monomeric isocyanate in their systems, to less than 1%. Also, it is required that the content of the commercial PU foams exhibits at least one year of shelf life and PU foams must be classified as B2 on the fire testing following DIN 4102-1: 1998-05, besides exhibiting a good physical quality.

The present work aims at developing a PU foam formulation which meets all of these specifications. The strategy was based on the synthesis and testing of toluene diisocyanate (TDI) based diluents (reactive and non-reactive), which, when incorporated into a base formulation, lead to the decrease of the free monomeric isocyanate content, improving the shelf-life, promoting the flame retardancy and maintaining the good physical properties of the foams.

The proposed objectives for this dissertation were successfully achieved, through formulations 806 and 792, which were prepared with non-reactive diluents (NCO=0%), PPNR-4 and PPNR-23, respectively. These diluents were obtained from 2,4'-TDI and flame retardants with OH functionality, namely a phosphorated polyether based diol and/or a brominated mono-alcohol.

A formulation without the addition of distilled components was also studied, which meets all the requirements except for the free monomeric content. This finding will contribute to the development of more viable formulations, in an economic point of view for the company.

Keywords: Prepolymer, Polyurethane, Foam, Rigid

1. Introduction

PU rigid foams play an important role in the insulation of buildings, allowing for a better energy efficiency and, therefore, economic competitiveness, however the PU OCF systems are used in the construction sector, either by professional and domestic users (DIY) in gap filling applications. There is, therefore, an increasing need for PU foams which comply with the current industry and safety standards, being safer and greener, both for the environment and human beings.

To obtain such characteristics, this work is centered in the introduction of a TDI based prepolymer/diluents, in the isocyanate component of the foam.

A PU OCF system consists of an aerosol can filled with PU prepolymers functionalized with NCO groups together with additives and propellant agents that will pressurize the can. The PU prepolymers are formed *in-situ* in the aerosol can upon its production, via reaction of a OH group from the polyol with the NCO groups, typically used in molar excess *versus* the amount of OH to ensure further curing with the moisture of the environment, when the content is sprayed out from the aerosol can.

The reaction between a primary or secondary alcohol and isocyanate produces urethane (1):

$$RNCO + R_1OH \rightarrow RNHCOOR_1 \qquad (1)$$

The reactivity of the primary alcohol is greater than a secondary alcohol in presence of isocyanate. The reaction is exothermic. [1]

The reaction between water from the environment and isocyanate produces CO_2 and amine (2):

$$RNCO + H_2O \longrightarrow RNH_2 + CO_2 \qquad (2)$$

The produced gas is important in the generation of the PU cellular structure. The water acts as a blowing agent in the foam. [2]

Excess of isocyanate might lead to the formation of secondary products, such as alophanates and biurets, through reaction with urethane groups. This is not desirable, because it results in a raise of viscosity inside the aerosol can.

The materials that compose a formulation inside the aerosol can are divided into 3 major components. Component A is a liquid polyol blend of polyol polyethers and polyesters. This component also includes additives such as catalyst, surfactants, flame retardants and others. Component B includes all the isocyanate based compounds, such as the prepolymers/diluents in this study. Finally, component C has the propellant agents, such as dimethylether (DME) and liquefied petroleum gas (LPG), allowing the mixture from the can to be sprayed. It is possible to tune the PU prepolymers/diluents and formulations in order to achieve the desired physical and chemical properties.

The main goal of this work is to obtain a foam with high physical quality, with less than 1%(m/m) total free monomer content (MDI+TDI), shelf-life of 12 months and a B2 classification in the fire test by the norm DIN 4102-1: 1998-05. This extended abstract reports on a work carried out to meet these challenging targets, which consists on the synthesis and testing of TDI based prepolymers/diluents in PU OCF systems.

2. Methods

The methods used in this work, are going to be explained in greater detail in the next subchapters.

2.1. Prepolymer/diluent production and aerosol can fabrication

After planning and calculating the quantities for the production of the prepolymers/diluents, the reagents are added into a 1000 mL ISO flask, having the precaution of adding first the monol, or polyol and then the isocyanate component. The weighing is done in a scale with 0.01 g of precision. The reagents are blended and heated at 80ºC and the %NCO evolution is monitored by frequent measurement.

Having prepared the prepolymers/diluents, the PU formulation is defined using a calculus sheet, named Foamcalc, proprietary of the company Greenseal Research, Ltd. The formulation is divided into 3 components. Component A (polyols and aditives), component B (isocyanates and prepolymers/diluents), and component C (blowing agents). After the components are chosen, the NCO/OH value is selected, as well as the gas percentage, the volume of the can and the number of cans to be made. [3] The software calculates the quantity for each compound belonging to the formulation.

The production of the can is started by weighing and inserting the component B in the can. After a proper homogenization of all the raw materials that are included in component A and that were weighted into a separate plastic container, this component is added to the can which is, afterwards, closed with an aerosol valve. The gases are added and the can is shaken vigorously for ca. 1 minute to homogenize the mixture. It is stored at room temperature for 24h, in order to proceed to the next step of testing and evaluating the foam. [3]

2.2. Characterization

The prepared cans are submitted to a series of tests, which include the spray and the evaluation of the foam properties at 5ºC and 23ºC to simulate different environmental conditions, the assessment of the flame resistance, the aging test and the determination of the free isocyanate monomer content.

2.2.1. Foam evaluation

The test and evaluation of the foams is divided into two parts. First the quick-tests and then the evaluation of the foams sprayed at 23ºC and 5ºC. The quick-test consists on measuring the output of the foam (froth) leaving the can. The can is stored for 4 hours in a refrigerator at 5ºC, after which it is sprayed for 10 seconds directly on a scale. The output value is calculated dividing the weight of the material that comes out of the can by 10 seconds. The minimum accepted output rate is 4.5 g/s for a 1000 mL can, or 3.5 g/s for a 395 mL can, such as the ones used in the present study.

Then, we proceed to spray the foam in a mold and on paper at 5ºC, and a day later the same procedure is done at 23ºC. [4]

Table 1 lists the properties evaluated in the quick-test. Reference [4] explains in greater detail all the procedures for these tests.

Table 1. Properties evaluated in the quick-test.

	23ºC	**5ºC**
Paper	Shaking rate; Froth outflow; Froth shrinkage; Crumbling at 1h, 2h e 24h	Output; Shaking rate; Froth outflow; Froth shrinkage; Crumbling at 1h, 2h e 24h
Mould	Shrinkage	Shrinkage

After the foam is properly cured, a day later after the foam was sprayed, samples of foam are cut to be evaluated in more detail. The properties are evaluated visually, from 5 (excellent) to -5 (bad). Table 2 lists all the properties evaluated. Reference [5] and [6], explain in greater detail how to visually evaluate the different physical aspects of the foams.

Table 2. Properties evaluated.

Properties	Glass bubbles
	Curing Shrinkage/Warping
	Cell Structure
	Voids & Pinholes
	Base holes
	Cell collapse
	Curing Streaks

2.2.2. Fire resistance test

The fire resistance test was done following the norm in Annex I/A 1.3 “B2 – Prufüng von PU Hartschäumen aus Einweg Druckbe-hältern; Brennkastenprufüng von PUR-Montageschaum nach DIN 4102-1: 1998-05”. Each sample is exposed to the flame for 15 seconds. If the flame height is lower than 15 cm, throughout the entire test of 15 seconds, the sample is classified as B2, otherwise it is B3. Figure 1 shows the certified chamber where the fire resistance test takes place.

Figure 1. Chamber for the fire resistance test.

2.2.3. Aging test

The accelerated aging test has the objective to determine the shelf-life of the formulation, which should be of 12 months at 23ºC. The cans produced are placed in a stove at 45ºC. A day at 45ºC corresponds to a week at 23ºC. All the cans of the formulation in study are placed in the stove with exception of the first can. The cans are removed from the oven after periods of time corresponding to 3, 4, 6 and 12 months. The output and the quality of the foams are measured at 5ºC and 23ºC.

2.2.4. Free monomer content analysis

The chromatographic analysis of the content of the cans allows to determine the free monomeric MDI and TDI content in the can. This analysis follows an optimized and validated HPLC-UV described in [7].

It has been used a chromatographic system of high resolution, Perkin-Elmer 4000 Series, with a UV-Vis detector, equipped with a quaternary pump. The column used was a Spherisorb ODS2, with porosity of 5μm, 4.6x50 mm brand Waters.

3. Results and discussion

It should be noted that a proprietary base formulation belonging to Greenseal Research Ltd. has been used in this work. The effect of the addition of selected new prepolymers/diluents was studied in detail, to achieve a formulation complying with the requirements for commercial PU OCF systems.

3.1. Prepolymers/diluents

A series of prepolymers and diluents were prepared and studied. We will include in this chapter only the most relevant ones. The prepolymers and diluents listed in Table 3, were the ones selected because of their good foamability, when sprayed from an aerosol can filled with prepolymer and gas.

Table 3. Best prepolymers/diluents selected.(confidencial)

A reactive prepolymer (PPR) is a prepolymer which still has NCO groups present, which are able to react, promoting the achievement of a cured, rigid foam, without outflow issues. Usually the %NCO in these prepolymers is higher than 1. A (non-reactive) diluent (PPNR) presents a %NCO value near zero. The ratio mentioned in Table 3, refers to the NCO/OH ratio. For example a ratio of one, means that we have one NCO group for one OH group.

A series of formulations were prepared with these prepolymers/diluents. The most representative ones are referred in the next section. We will divide the results in two types of formulations: formulations based on distilled processes and formulations based on non-distilled processes.

3.2. Formulations based on distilled processes

Table 4 lists the formulations tested in this sub-chapter, and the corresponding prepolymers or diluents used for each one.

Table 4. Formulations with distilled components.

Formulation	Prepolymer
750	PPR-24
789	PPNR-26
792	PPNR-23
806	PPNR-4

Formulation 750 contains a reactive prepoylmer (PPR-24) of 2,4'-TDI with reactive flame retardant (mono-alcohol) and posteriorly diluted with TEP. Formulation 789 uses a diluent similar to PPR-24, but non-reactive (PPNR-26). Formulation 792 uses a diluent similar to PPNR-26, but not diluted with TEP. Moreover, the content of 2-ethyl hexanol (mono-alcohol) was increased, which despite being flammable, promotes the decrease of viscosity, increase of output and free monomer content reduction. Finally, formulation 806 contains a non-reactive (%NCO=0) diluent, obtained from a two-step reaction, of 2,4'-TDI with a phosphorated polyether based diol and a brominated monol.

We first start by analyzing the output of the formulations (Table 5 and Figure 2). Formulation 750 exhibits a decrease in the output, over the time of the aging test. At 6 months the output is at 1.7 g/s, which is less than the minimum allowed of 3.5 g/s. This means that the formulation has a shelf-life of less than

6 months. As the aging progresses the viscosity of the prepolymer in the can increases, leading to a lower output. Formulation 789 has also a shelf-life of less than 6 months. We can see a decrease on the output until 6 months of aging, but after that it starts to increase reaching a value of 6.8 g/s for 12 months. Formulation 792 presents an output over 3.5 g/s during the course of the aging process, having therefore a shelf-life of 12 months. Formulation 806 presents a shelf-life of 12 months, going in line with the objectives proposed by this work.

Table 5. Output for the formulation with distilled components.

Formulation	750	789	792	806
Month	**Output (g/s)**	**Output (g/s)**	**Output (g/s)**	**Output (g/s)**
0	7.5	5.3	8.3	4.0
3	4.3	3.0	7.6	4.5
4	4.3	4.2	8.8	3.7
6	1.7	1.8	9.7	3.5
12	-	6.8	6.7	4.0

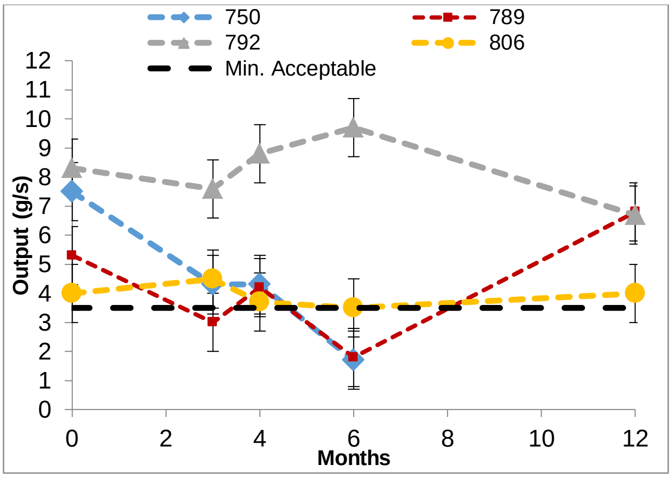

Figure 2. Output for the formulations with distilled components.

The free monomeric MDI and TDI content of the formulations in study is presented in Table 6. All these formulations are found to be within the limit of 1% of free monomeric content.

Table 6. Content of free monomeric MDI/TDI in the formulations with distilled components.

Formulation	%MDI	%TDI
750	0.46	0.11
789	0.29	0.13
792	0.51	0.20
806	0.74	0.23

The results for the fire resistance test are shown in Table 7. All formulations in this study obtained a classification of B2 in the fire resistance test. Formulations 750 and 789 exhibit an excellent flame retardancy because they contain a reactive flame retardant (mono-alcohol), which is very effective for such property. Formulation 792 contains the reactive flame retardant (mono-alcohol), but also contains a higher amount of 2-ethyl hexanol, which degrades the flame retardancy performance. Overall, it is not so effective in this property, but is still classified as B2.

Table 7. Results of the fire resistance test (DIN-4102), for the formulations with distilled components.

Formulation	750	789	792	806
Flame height (cm)	6	5	12	11
	6	5	12	12
	5	5	13	10
	6	5	13	-
	7	6	12	-
	6	-	-	-
Average of the flame height (cm)	6	5	12	11

The radar graphs allow for a more visual view of the quality of the foams (Figure 3, Figure 4, Figure 5 and Figure 6). Formulations 750 and 789 show some quality issues, in what regards base holes and shrinkage at 23ºC. The main responsible for such issue is the presence of TEP in the prepolymer. We might revert these effects by lowering the NCO/OH ratio, and increasing the catalysts amount in the formulation. Using a higher amount of catalyst, the pressure developed in the foam increases, eliminating the base holes and shrinkage. [5] The shaking rate at

5ºC is quite low, especially for formulation 789. At lower temperatures the shaking rate is worse. The only difference between the two formulations is the reactiveness of the diluent. The overall quality of formulation 792 is good. There are some minor problems as base holes in mold and on paper. The formulation 806 presents an excellent foam quality, having high grades in almost every evaluated characteristic.

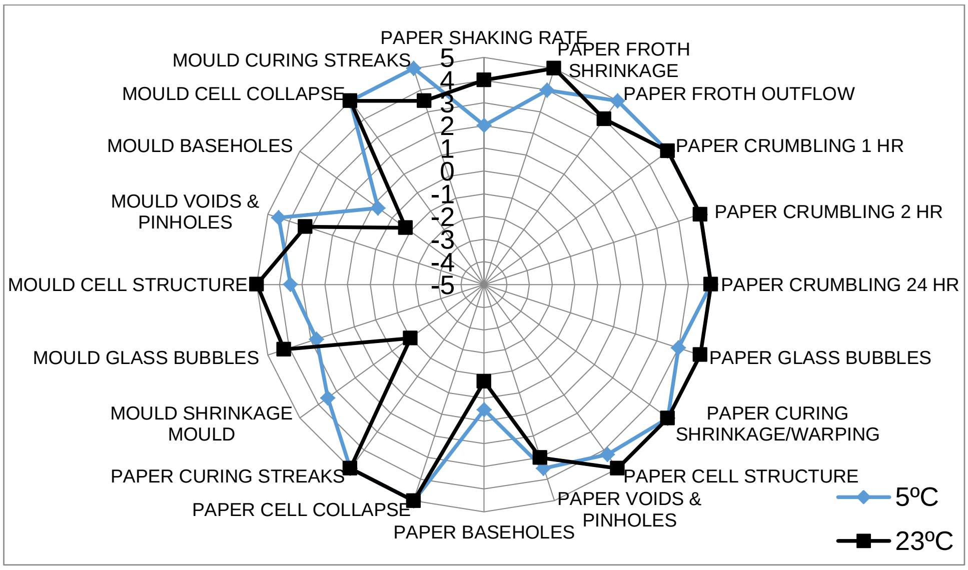

Figure 3. Radar graph for formulation 750.

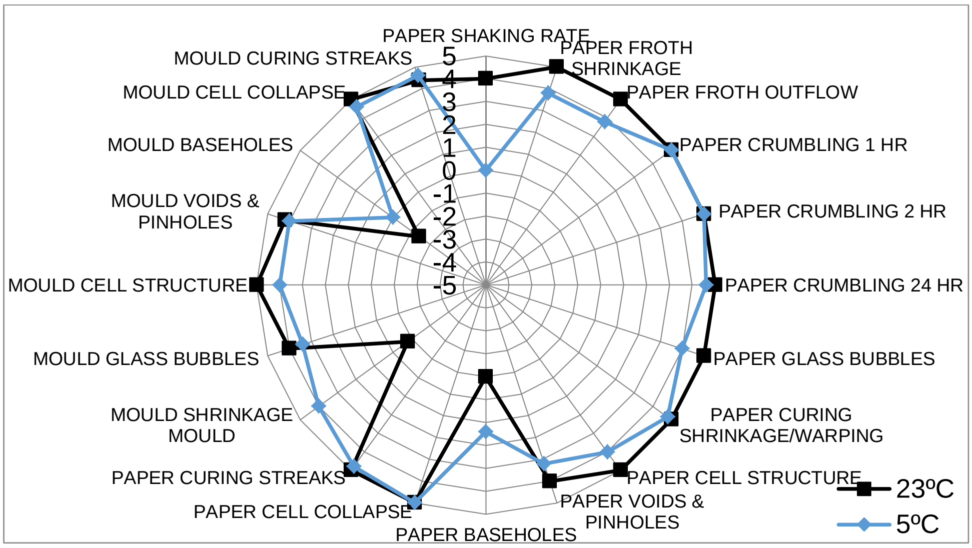

Figure 4. Radar graph for formulation 789.

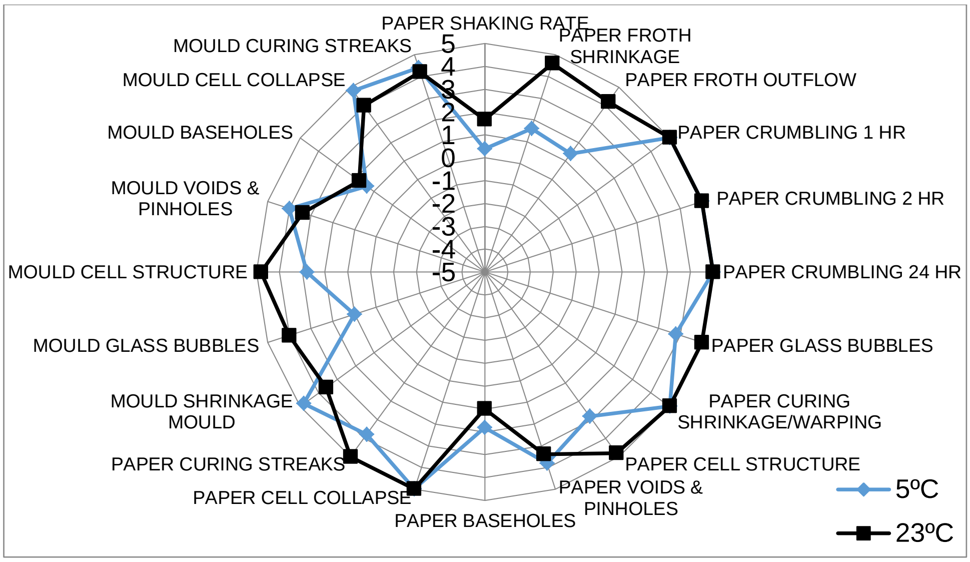

Figure 5. Radar graph for formulation 792.

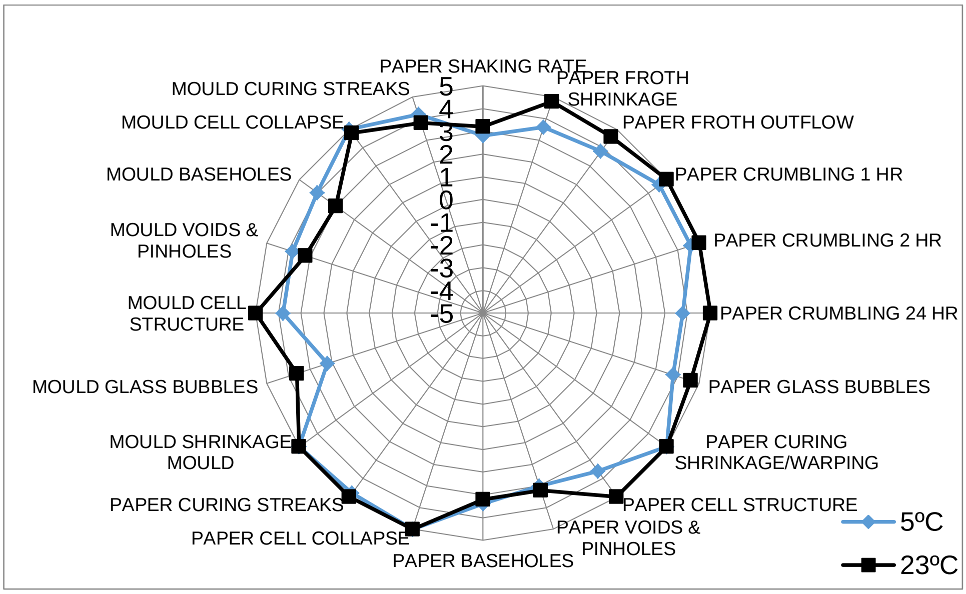

Figure 6. Radar graph for formulation 806.

Table 8 summarizes the main results for all the formulations studied in this sub-chapter. Formulations 792 and 806 are the ones with comply with all the requirements.

Table 8. Overall view of formulations study with distilled components.

Formulation	Prepolymer/Diluent	Average Output (g/s)		Fire resistance test (Average of the flame height)	%fmMDI and %fmTDI	Quality
		0 months	12 months			
750	PPR-24	7.5	<1	B2 (6 cm)	0.57	Shrinkage and base holes
789	PPNR-26	5.3	6.8*	B2 (5 cm)	0.42	Shrinkage and base holes
792	PPNR-23	8.3	6.7	B2 (12 cm)	0.71	Acceptable
806	PPNR-4	4.0	4.0	B2 (11 cm)	0.97	Good quality

*Note that the shelf-life at 6 months was below 3.5 g/s.

3.3. Formulations based on non-distilled processes.

In this sub-chapter we report on a base formulation free of any distilled component, to which a newly developed prepolymer, PPR-13 is added (Table 9). This approach consists of a simpler and more economic synthesis process, being relevant in an economic and commercial point of view, for the company because this does not possess a distillation unit.

Table 9. Formulation without distilled components.

Formulation	Prepolymer
869	PPR-13

We start by analyzing the output of the formulation. Table 10 and Figure 7 show that the formulation has a shelf-life of 12 months, since the output is above 3.5 g/s over the 52 days of accelerated aging test.

Table 10. Output for the formulation without distilled components.

Formulation	869
Month	**Output (g/s)**
0	7.5
3	6.7
6	7.0
12	3.7

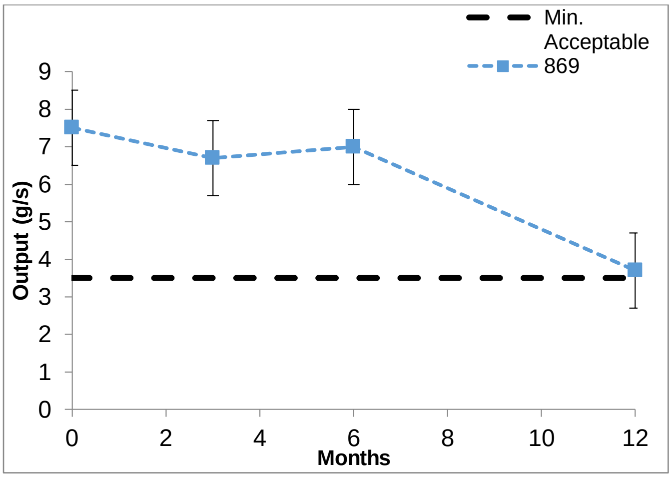

Figure 7. Output for the formulations without distilled components.

However, the free monomeric content of the formulation (Table 11) is superior to the 1% minimum required.

Table 11. Content of MDI/TDI in the formulation without distilled components.

Formulation	%MDI	%TDI
869	1.97	0.13

The results for the fire resistance test are shown in Table 12. Formulation 869 successfully obtained a classification of B2 in the fire resistance test.

Table 12. Results of the fire resistance test, for the formulations with distilled components.

Formulation	869
Flame height (cm)	10
	13
	12
	11
	10
	10
Average of the flame height (cm)	11

The quality of the foam produced by the formulation 869 is shown in Figure 8. As we can see the foam presents good physical qualities, having all the parameters evaluated with high grades. The only aspect to notice is some base holes on paper at 23ºC, but nothing too significant.

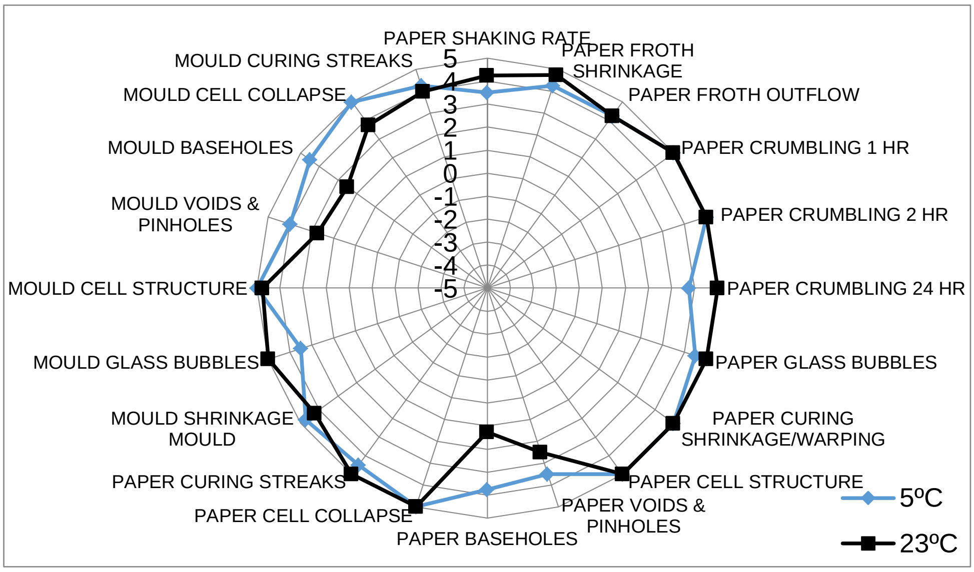

Figure 8. Radar graph for formulation 869.

Table 13 summarizes all the main aspect of this formulation.

Table 13. Summary for formulation 869.

Formulation	**Prepolymer**	**Average Output (g/s)**		**Fire resistance test (Average of the flame height)**	**%fmMDI and %fmTDI**	**Quality**
		0 months	**12 months**			
869	PPR-13	7.5	3.7	B2 (11 cm)	2.1	Good quality

4. Conclusions

The objectives outlined at this work were successfully achieved.

It was possible to conclude that the incorporation in formulations of prepolymers and diluents derived from 2,4'-TDI and a new mono-alcohol with flame retardant proprieties, provides an excellent flame retardancy capability and a quite low free monomer content. Nevertheless, when diluted with triethyl phosphate (PPR-24 and PPNR-26) they result in shelf-life issues and foam quality issues, namely shrinkage and baseholes. In this sense, the best compromise was found using this prepolymer/diluent, for a good flame retardancy and low free monomer content effect, together with 2-ethylhexanol in the polyol blend which, besides reducing the free monomeric content also promotes a dilution effect, avoiding the use of TEP as a solvent (formulation 792 with PPNR-23).

Formulation 806, with PPNR-4, goes in line with all the objectives. The foam produced presents an excellent foam quality. In terms of output this formulation presents a steady output through the aging, exhibiting a shelf-life of 12 months. It has a B2 classification in the fire resistance test and the free monomeric MDI and TDI is below the limit of 1%.

In order to study an economically more viable approach for the company, i.e., without the use of distilled components in the base formulation, we have developed formulation 869. The formulation successfully fulfills all the requirements, except the free monomeric content, which is quite above 1%. This finding will contribute to the development of more viable formulations, in an economic point of view and a strong effort will be placed in order to lower the free monomeric content to below 1%, and 0.1% or a longer term.

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