

Production of polyurethane foams based on sustainable components and study of the addition of PCMs in them

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Abstract – Polyurethane is the result of mixing two main components (Polyol and (poly)isocyaate), giving rise to an exothermic reaction and from which, by adjusting the formulations, it is possible to obtain several foams with unique properties. For this reason, these foams have numerous advantages over other materials, thus being able to have application in various areas, from the automotive market to civil construction, through the textile industry, electronic and cosmetic components.

Phase change materials are materials that have the ability to absorb/release large amounts of latent heat in a well-defined temperature range during their phase/state change process.

In order to meet the needs of technological and environmental development, this work obtained a foam where the two main components have a more sustainable base, adding phase change materials, with the objective of improving the thermal properties of foams, thus obtaining a product with better performance in terms of thermal insulation. The PCMs embedded in the foams were encapsulated and in the form of a concentrated dispersion.

During the work, several characterization techniques were used to study the properties of the foams produced. Among them, infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), measurement of thermal properties and densities, uniaxial compression assays, and scanning electron microscopy (SEM).

Initially it began by characterizing the Polyol derived from food oils. Polyisocyanate (Desmodur ECO N7300) was then characterized. Also following these actions, the thermal stability of the PCM was verified using a TGA analysis. After depending on the base formulation, changes were made to it, and the properties of foams obtained using the characterization techniques described above were analyzed.

The accomplishment of the work allowed us to conclude that a foam obtained from the two sustainable base components used in this work requires a lot of time to grow and cure, so it is necessary to replace part of the Polyol with a commercial Polyol (10%), thus finding a balance. On the other hand, it was also possible to conclude that the addition of PCM in the foam is beneficial for the desired properties, however the addition of 10% by weight was not found to be beneficial for it, being only necessary 5%.

Keywords: Sustainable Polyol, Sustainable Isocyanate, PCM, Thermal Properties, Thermal Insulation.

1 Introduction

Polyurethane is a polymer, which as the name implies, is formed by repeated units of urethane, and is often called PU. This material has numerous advantages over other materials and for this reason is a material that has application in various areas, from the automotive market to civil construction, through the textile industry, electronic components, and cosmetics. The large percentage of consumption of this polymer worldwide is in the form of foams. [1]

Recent studies show that global consumption of polyurethane foam will continue to grow through 2025, stating that the global market will grow from US\$37.8 billion (2020) to US\$54.3 billion (2025), with a higher consumption of rigid foam than flexible foam, given that the main application of this is in thermal insulation. On the other hand, the greatest consumption of flexible foams is in bedding and furniture. [2]

1.1 Polyurethane Chemistry

The main group of polyurethanes is called urethane. This is formed by the reaction of alcohols (group -OH), isocyanates (group -NCO) and other additives. Figure 1 shows the polyurethane structure.

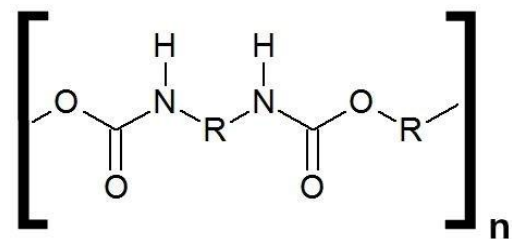


Figure 1. Polyurethane Structure [3]

NCO groups are highly reactive with active OH groups. This is due to the resonance structure presented by isocyanate, where the highest electronic density is concentrated in the oxygen atom. Figure 2 shows the resonance structure of isocyanate.

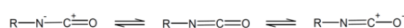


Figure 2. Isocyanate Resonance Structure [3]

During the production of polyurethane foams several reactions occur. However, the two main are the reaction between the polyol and isocyanate (forming the urethane bond) and between isocyanate and water (forming an amine and carbon dioxide). These reactions are present in figures 3 and 4, respectively.

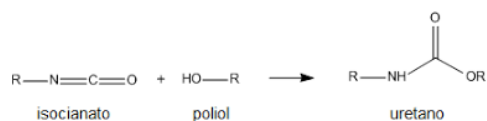


Figure 3. Reaction between polyol and isocyanate [3]

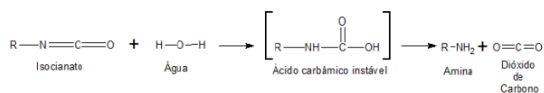


Figure 4. Reaction between isocyanate and water [3]

Primary and secondary alcohols react with isocyanate, producing urethanes. Its reactivity decreases as it moves to higher-order alcohol. Phenolic alcohols have a lower reactivity than the aliphatics, producing also fewer stable urethanes, so that the reaction can become reversible at temperatures below 100° C. Gaseous CO₂ produced in the reaction of water with isocyanate helps in the expansion of foam, that is, in the formation of its cellular structure. The other reaction product (Amine) can react with the isocyanate groups, giving rise to a disubstituted urea. This reaction is present in Figure 5.

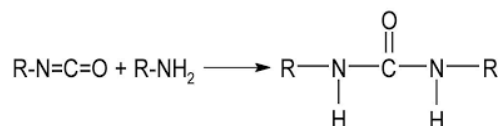


Figure 5. Reaction between isocyanate and amine [3]

During the foam reaction, isocyanate is always in excess, to ensure that all OH groups react. This makes it conducive to secondary reactions with active hydrogen atoms from some products of the main reactions, namely urea and urethane. These reactions may lead to biurets and allophanaths, and may be reversible at temperatures above 110° C, and whose products are supplementary sources of crosslinking. In figures 6 and 7, respectively, it is possible to visualize the schematic representation of these reactions.

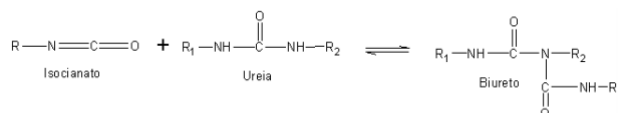


Figure 6. Reaction between isocyanate and urea [3]

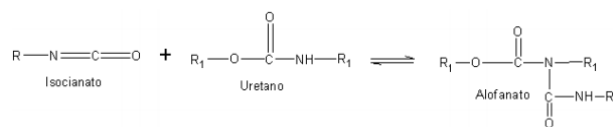


Figure 7. Reaction between isocyanate and urethane [3]

Another functional group that reacts with isocyanate is carboxylic acid, despite its reactivity with isocyanate being inferior to its reactivity with amines, alcohols, or water, thus forming an unstable anhydride, which in turn dissociates and gives rise to an amide and gaseous carbon dioxide. This reaction is present in Figure 8. [4]

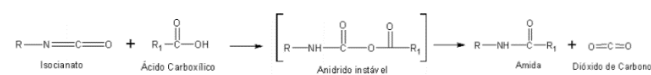


Figure 8. Reaction between isocyanate and carboxylic acid [3]

1.2 Foam production

There are four possible processes to use for foam production. In this work, the process used was the one-shot process. In this process, there is a component A, which contains the mixture of all reagents except isocyanate. And there is a B component, which contains isocyanate, or a mixture of them. Polyurethane results from mixing component A and component B. [3,4]

1.3 Raw materials

To produce polyurethane foams, it is necessary to use different raw materials. The most used raw materials are polyols, isocyanates, water, catalysts, surfactants, and expander agents. In addition to these, flame retardants, plasticizers, pigments, among others are also used.

1.3.1 Polyol

Polyols are alcohols with various OH groups. It is these functional groups that react with the NCO groups of isocyanates and form the urethane groups. For this reason, polyol is one of the most important products for the final characteristics of foam, and is also severely related to certain properties, such as flexibility, hardness, chemical resistance, and tensile strength. The OH value of the polyol and its functionality, i.e., the number of free OH groups, are of great importance, varying depending on the type of foam you want to obtain. For this reason, there are several types of polyols, the most used being polyol polyester and polyol polyether. In addition to these, the use of more sustainable base polyols has been increasingly recurrent, as is the case with polyols obtained from vegetable oils. [4]

1.3.2 Isocyanate

Along with polyols, isocyanates are fundamental for the formation of polyurethane foams. This raw material used can be aliphatic or aromatic. If it is aromatic, it gives greater rigidity. On the other hand, if it is aliphatic, it gives greater flexibility, so it is possible to adjust the foam to the desired application. The most

used isocyanates in the production of polyurethane foams are 2,4- and 2,6-TDI (Toluene Diisocyanate). 4,4-MDI (Diphenylmethane Diisocyanate) is another isocyanate possible to use. [4]

1.3.3 Water

Water is essential to provide active hydrogen to the reaction. When it reacts with isocyanate it releases carbon dioxide and polyurea molecules. The released carbon dioxide diffuses into the previously nucleated bubbles and promotes foam growth. [3]

1.3.4 Catalysts

In a simplified way, a catalyst is a compound that increases the speed of the reaction. There are two types of catalysts that can produce polyurethane foams. They are the gelling catalysts that promote the polymerization reaction and the filling catalysts, which promote the foam expansion reaction. Some examples of catalysts used are DABCO 33-LV and NIAX (filling catalysts) and DBTL (gelling catalyst). To form a good foam, it is necessary a balance between the two types of existing catalysts, because the use of too much gelling catalyst gives rise to a foam with the cells closed and shrunk. On the other hand, the use of excess filling catalyst gives rise to the collapse of the foam. [3]

1.3.5 Surfactants

Surfactants are very important in the production of polyurethane foams due to their multiple functions, such as mixing slightly miscible reagents, decreasing surface tension, controlling the size, and opening of cells, promoting the nucleation of bubbles during agitation, among others. The most important feature of these materials is the stabilization of cell walls, thus promoting foam stability during the curing process. The most used surfactants are silicone, with Silbyk 9001 being the most common example. [3]

1.3.6 Blowing Agents

The formation of polyurethane foams is directly related to the release of gas because it is through this mechanism that it is growing. Before the 1990s, the gases used as expanding agents were CFCs, however, due to the increasing degradation of the ozone layer they were no longer used and other gases, such as carbon dioxide and cyclopentane, began to be tested. There are two methods for gas formation:

In the case of chemical formation, the most widely used expander is water. Its function is to react with isocyanate in order to produce carbon dioxide, which will in turn promote the expansion of the foam, allowing to control the density of the foam. Thus, it is possible to affirm that the higher the water level in the formulation, the lower the foam density. In the case of physical formation, the main expanding agent is methylene chloride. This liquid has a low boiling point, and its main function is the reduction of the internal temperature of the foam, thus aiding the expansion. This material uses the temperature released during the

polymerization process to pass to the gaseous state and thus decrease the density of the foam. [3]

1.3.7 Flame Retardants

Polyurethane foams are highly flammable materials. For this reason, there are regulations requiring the use of flame retardants in order to control the combustion behavior of foams. The most used retardants in this type of foams are compounds based on nitrogen, phosphoric and halogenous phosphoretics. These can work on two different mechanisms, i.e., gaseous phase and condensed phase. In the condensed phase occurs the catalytic breakage of the polyurethane group, as well as dehydrogenation and dehydration reactions, forming a surface layer of coal that protects the foam. In the gas phase, retardants disrupt the combustion mechanism. [3]

1.3.8 Plasticizers

A plasticizer is a component that has as main function the reduction of the viscosity of the foam. Examples of plasticizers are used, dibutyl maleate, dioctyl phthaate, or diisobutyl adipate. [3]

2 **Experimental Part**

2.1 Technical description

The process of production of polyurethane foams based on sustainable reagents began by characterizing polyol, based on crude Glycerol and used food oils (Poliol_{OA}), developed in the framework of the master's thesis carried out by David Bastos in October 2019 at Instituto Superior Técnico. For this polyol, the value of hydroxyl groups (OH value) present in the molecule was measured, and a GPC analysis was performed in a view to obtain the distribution of molecular weights (\overline{M}_N e \overline{M}_W). The commercial polyisocyanato (Desmodur eco N 7300) was then characterized. It is an alifatic polyisocyanate, trimer of 1,5 – Pentamethylene – Diisocyalate (PDI), used as a hardener in polyurethane coating formulations. For this Isocyanate, a titration was performed to calculate the NCO index of the same.

The second step of the process was the mixture of component A and B, in a single-step reaction.

After completing the first two stages, another third step was carried out, which consisted of adding different PCM percentages to the foam with better characteristics and properties. This material (PCM) is composed of microcapsules filled with phase-changing material, diluted in water (approximately 50%). Given the high percentage of water, it is necessary to evaporate it by about 70%, because an excess of water impairs the growth and properties of foam. In order to evaporate it, a TGA was previously performed to perceive the mass loss of the PCM as a function of temperature, thus knowing its degradation temperature and determining the heating limit point. Then, an analysis was performed under an optical microscope to confirm that the structure of the capsules involving the PCM was intact after heating. After verifying the possibility of water evaporation, the PCM was subjected to controlled heating at 100 °C, with constant

agitation. After losing 35% of the initial mass, the PCM would have only 30% of its initial water value, that is, the desired value.

After the production of the foams, several tests were carried out to characterize them, both at the physical, chemical, and mechanical levels. Characterization methods include FTIR, optical microscope, TGA, determination of apparent densities, ultrasonic, thermal conductivity, evaluation of cream times, foam growth and gel, compression assays, and SEM. Figure 9 shows a diagram of the work performed.

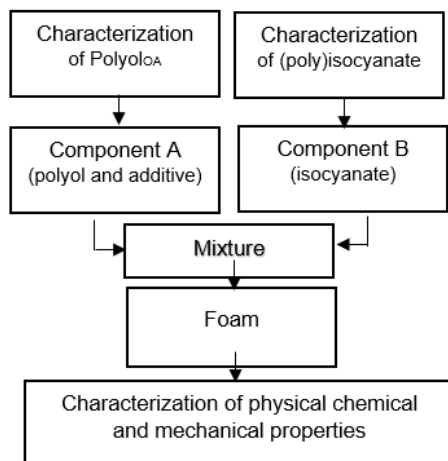


Figure 5. Diagram of the work performed

2.2 Foam Characterisation

Table 1. Formulation Base with Voranol

Components	Composition	Mass (g)
A	Polyol _{OA}	72,25
	Polyol Voranol 1010L	8,05
	H ₂ O	7,9
	DBTL	0,8
	DOP	19,35
	Silbyk-9001	1,6
	Dabco-33LV (diluted 1/10)	0,8
B	Isocyanate (Desmodur Eco)	134,7

Table 2. Formulation Base Without Voranol

Components	Composition	Mass (g)
A	Polyol _{OA}	80,3
	H ₂ O	7,9
	DBTL	0,8
	DOP	19,35
	Silbyk-9001	1,6
	Dabco-33LV (diluted 1/10)	0,8
B	Isocyanate (Desmodur Eco)	134,7

Table 3. Formulation Base with 10% PCM

Components	Composition	Mass (g)
A	Polyol _{OA}	72,25
	Polyol Voranol 1010L	8,05
	PCM	27,25
	H ₂ O	7,9
	DBTL	0,8
	DOP	19,35
	Silbyk-9001	1,6
Dabco-33LV (diluted 1/10)	0,8	
B	Isocyanate (Desmodur Eco)	134,7

Table 4. Formulation Base with 5% PCM

Components	Composition	Mass (g)
A	Polyol _{OA}	72,25
	Polyol Voranol 1010L	8,05
	PCM	15
	H ₂ O	7,9
	DBTL	0,8
	DOP	19,35
	Silbyk-9001	1,6
Dabco-33LV (diluted 1/10)	0,8	
B	Isocyanate (Desmodur Eco)	134,7

After the desired foams were obtained, the characterization of the foams started, to study the physical, chemical, and mechanical properties of the foams. For this it was necessary to resort to various methods and equipment:

2.2.1 Gel Permeation Chromatography (GPC) of Polyol_{OA}

This type of characterization allows determining the molecular weight of the desired sample. For this, samples with a high degree of dilution are required, so samples with 1 mg/ml concentration were prepared.

The first step of this technique is to run the solvent (Tetrahydrofuran - THF) through the column to stabilize the baseline of the chromatogram. After this step is completed, a small amount of sample is injected using a syringe.

2.2.2 Controlled evaporation of the PCM

As mentioned above, to be able to add higher percentages of PCM to the foam, it was necessary to evaporate 70% of the existing water. This evaporation process was carried out using a heating plate with thermocouple and constant agitation, which allowed a controlled heating in the 100 °C.

2.2.3 Optical microscope

This equipment was used to observe the original PCM microcapsules (dissolved in approximately 50% water), in order to perceive their behavior after heating in the order of 100 °C. This heating aimed at evaporation of the water present in the emulsion. Observations were performed under a microscope with magnifications of 40x and 100x.

2.2.4 Infrared Spectroscopy (FTIR)

The equipment intended for this type of characterization has two valences, they are the Accessory ATR and the MicroFTIR accessory. In this work both techniques were used.

FTIR-ATR

The FTIR, "Fourier-Transform Infrared Spectroscopy", is a characterization technique that allows obtaining the infrared spectrum of absorption of samples in the gaseous, liquid, or solid states. After obtaining the InfraRed record of the sample it is possible to form graphs, which allow detecting the presence of different functional groups in the sample.

Only one spectrum per sample was obtained, and these were obtained through 8 scans per sample, in a range of 4000 to 500 cm^{-1} and with a resolution of 4 cm^{-1} .

MicroFTIR

This accessory of the equipment allows to observe the number of cells per unit area, thus allowing to check if a foam is more open or closed.

2.2.5 SEM

To carry out this test, pieces of the center of the foam were cut and placed on squares with 2 cm of foam of conductive tape. Then, each sample was subjected to a coating with gold and palladium, to make it conductive, since the foam is a material that has no electrical conductivity.

In order to make possible a comparison between the different foams, a sample of each foam was observed, at two magnifications in each sample.

2.2.6 Thermogravimetric Analysis (TGA)

The equipment used to perform the thermogravimetric analysis has a precision scale inside the oven, where the crucibles are placed. The mechanism evaluates the mass variation of the sample with temperature over time, being possible to program the heating rate. This test can be carried out in inert gas or ambient air. The data are translated into a graph of the thermogravimetric curve that describes the mass loss (as a percentage) as a function of temperature or time.

In the characterization of the thermal behavior of the foam and the verification of its decomposition, a nitrogen atmosphere was used at an inlet flow rate of 200 ml/min. In the Base without Voranol, 8.311 mg was weighed, in the Base with Voranol 8.637 mg, in foam with 5% PCM 8.066 mg, and in foam with 10% PCM 7.316 mg, in aluminum pan, with heating of $5^{\circ}\text{C}/\text{min}$ between 30°C and 600°C .

2.2.7 Determination of apparent density

In the evaluation of the use of these foams for thermal insulation, it is important to characterize their apparent density, knowing that the less dense foams are more appropriate for this purpose.

In order to characterize the foams, they were cut, with the aid of a scalpel, a knife and a ruler in cubes with 2.5 cm of edge. For each foam sample, the test was performed for three cubes, the data were obtained through an analytical scale and the density equation.

In each sample, the mean values obtained in the three cubes were performed.

2.2.8 Helium Pycnometer

This characterization technique needs 5 measurements for each sample, with the result presenting the average of 5.

Before starting the measurements, a calibration was always performed to the V_a and V_c , with the small sphere, of 20 measurements, or until you find 3 measurements with a standard deviation of less than 0.005%. If 3 concordant measurements were not found, the average would be made with the last 3 measurements. V_a represents the volume added, that is, the volume of the calibration sphere and V_c represents the volume of the calibration cell.

2.2.9 Thermal properties

The equipment used for this characterization test was ISOMET 2114, with a needle probe, as it is more suitable for soft materials, such as Polyurethane foams. This method is called by heated wire method. A dynamic measurement method was used, as it reduces the measurement time compared to stationary measurement methods.

To perform these tests, the probe was inserted (in the range 0.015 - $0.05\text{ W}/(\text{m}\cdot\text{K})$) centered on the sample and a depth of approximately 5 cm. After inserting the probe into the foam, the F1 key of the equipment was pressed and the equipment in turn performs the measurements. After the measurements have been completed, the F4 key and the equipment showed the measurement results. Three tests were performed for each foam, except for 5% PCM foam, which performed 4 tests. Each foam was shaped like a cube with 10 cm of its sides.

In addition to thermal conductivity, it was possible to calculate thermal effusibility. This property was calculated from the properties obtained by the equipment.

2.2.10 Evaluation of cream, growth, and foam gel times

The evaluation of the moisture curing phenomenon is carried out by measuring cream time, growth time and gel time after the introduction of foam into the mold. For this characterization, only one sample measurement was performed, and a stopwatch was used.

The cream time begins after mixing the polyol with isocyanate and ends when the mixture begins to react, this has a creamy appearance due to the formation of small bubbles. The second measurement is the growth time, in which the foam expands and ends when it begins to stagnate. Finally, the gel time, where the foam forms a connection to any object that meets with it and ends the moment this adhesion ceases to occur.

2.2.11 Uniaxial compression tests

The equipment used in this assay allows the application of a force (N) to determine the behavior of the foam. The parameters for performing the assay are: Cubic sample, with 2.5 cm of edge, with an extension criterion of 12.5 mm. After the sample was

placed between the plates, the test was started at a compression speed of 10 mm/min. Once the 12.5 mm extension has been reached, force is stopped and about 5 minutes are needed for the foam to recover and stabilize, thus obtaining the deformation suffered by the foam (Final Force).

Thus, it is possible to calculate the Nominal Compression Stress using equation 1:

$$\sigma_n = \frac{F}{A} \quad (1)$$

Where F is the Final Force of the landing (N), and A the section area (cm²).

For each foam, the test was performed in six different samples, three of which were performed in the direction of foam growth, and the remaining three in the direction perpendicular to the direction of growth of the foam.

3 Results and Discussion

3.1 Characterization of Polyol_{OA}

Observing the Thf GPC graph, it is perceived that the peak of thf is located at 22 minutes, for this reason, in the Polyol_{OA} GPC we will have to remove this peak (Figure 10). In order to obtain a more accurate Mn and Mw value, only data until the 22nd minute were considered.

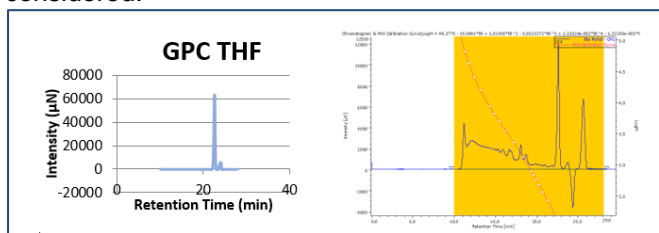


Figure 6. On the left is the THF GPC graph and on the right is the polyol GPC graph.

Using the Excel obtained by the GPC program and equations 2 and 3, it was possible to determine the values of M_n and M_w , respectively:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (2)$$

$$M_w = \frac{\sum N_i \times M_i^2}{\sum N_i \times M_i} \quad (3)$$

Thus, $M_n = 10861,7$ e $M_w = 37149,7$.

In addition to the GPC, a titration was also performed at the same Polyol to calculate VOH. Three measurements were performed, where the mean value obtained was 60 mg KOH/g Polyol.

By the conventional formula, for a commercial-based polyol, the functionality would be given by equation 4:

$$f = \frac{VOH \times M_w}{56100} = \frac{60 \times 37149,7}{56100} = 40 \quad (4)$$

This is an absurd value, since M_w obtained by GPC was calculated using polystyrene standards. For this reason, for calculations of the Polyol ratio, a functionality value equal to 2 was used. [4]

3.2 Isocyanate characterization

For this reagent, a titration was also performed in order to calculate the %NCO, so the value obtained was equal to the value provided by the manufacturer (21.9%).

3.3 PCM Characterization

A TGA was first performed to analyse the behavior of the PCM. The graph obtained is shown in Figure 11. The continuous line represents the TG signal, and the dashed line represents the DTG signal.

As can be seen, there is an initial loss of mass up to 100 °C, which corresponds to the water present in the PCM. The next peak of mass loss is around 250°C. After this temperature is visible that the TGA signal reaches close to -100%, indicating that the entire mass of the sample was lost, thus observing that at this temperature the degradation of the material occurred.

After this analysis, samples of original PCM, PCM heated to controlled temperature were taken, and the same were observed under optical microscope.

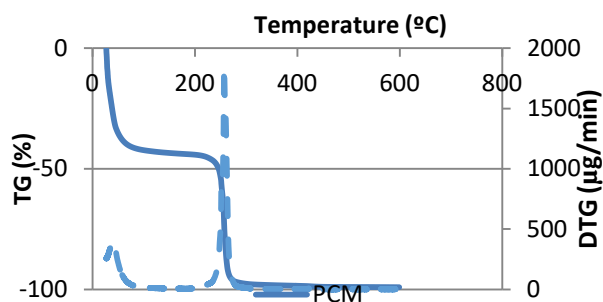


Figure 7. Graph of the PCM behavior

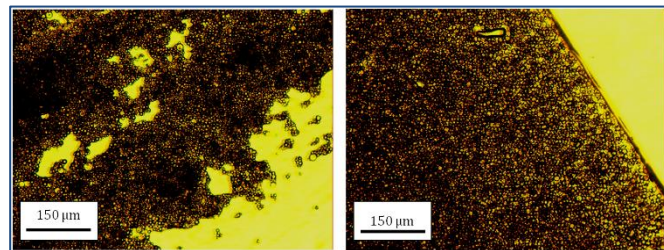


Figure 8. Images obtained with an optical microscope

In these images (figure 12), obtained with a magnification of 100x it is possible to verify the comparison between the original PCM (on the left) with the PCM heated to controlled temperature, with the objective of evaporating excess water (right). Through these images it can be affirmed that it is possible to remove the water, by controlled heating, without harming the content of phase-changing material, since the microcapsules remain intact.

3.4 Foams Characterization

3.4.1 FTIR

This technique is commonly used, because from the analysis of the FTIR graphics of the foam, it is possible, through the bands, to identify the main functional groups that constitute the same. Figure 13 shows an FTIR chart compiling the curves obtained for each type of foam under study.

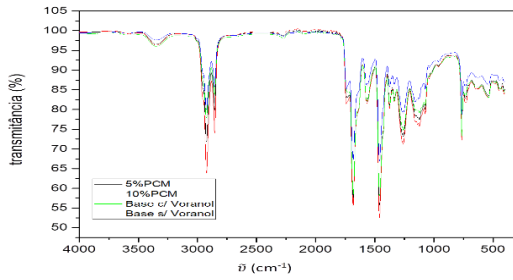


Figure 9. Graph of FTIR

At 3357cm^{-1} it is possible to recognize a band, corresponding to the group OH. This band may be directly connected to the OH groups of the polyol, which have not reacted, or may be corresponding to N-H connections of the urethane. The bands between 2924 and 2856cm^{-1} correspond to the elongation of the C-H connections. When adding PCMs to the foam, these are the peaks where the greatest difference is noticed and this can be explained through the nature of the PCMs, that is, if they are alifatic, they have more CH and CH_2 groups, thus increasing these peaks. At 1742cm^{-1} it is possible to observe a band. This band can correspond to the presence of C=O connections of the urethane in the foam, while the band present at 1682cm^{-1} can be related to the presence of C=O connections of urea. At 1684cm^{-1} it is possible to observe a band, corresponding to the C=C connections. At 1460cm^{-1} there is another main band, corresponding to the bending of the C-H connections. Between 1258 and 1074cm^{-1} is where the greatest disparity of voranol foams for foams without Voranol is noted. These bands correspond to the elongation of the C-O and C-N connections, which can be explained by the addition of Voranol, which in turn increases the number of C-O connections, and by the increase of the urea formed (visible at the peak at 1682cm^{-1}), which in turn increases the number of C-N connections. On the other hand, it can also be concluded that the addition of Voranol in the formulation will promote the formation of urethane, leading to a possible percentage of unreacted isocyanate, now has reacted completely. It is also possible to observe a peak at 764cm^{-1} , corresponding to bending in the C-H connections. [6,7,8]

3.4.2 MicroFTIR

The technique was performed and several images of each type of foam under study were obtained. Figure 14 shows the most representative image of each foam. Through these images it is possible to conclude that by adding Voranol to the foam, the cells become larger and more open, with regular size, without much difference between them. Comparing 5% PCM foam with Voranol Base foam, it is verified that the former has smaller cells than the second, as well as greater irregularity in the different cell sizes. When compared to 5% PCM foam with 10% PCM foam, it is noted that 5% PCM foam has a more organized structure, with a greater number of cells per unit area and with a mixture between open and closed cells. It is possible to observe then that the addition of PCM makes the foam cells more closed. [6]

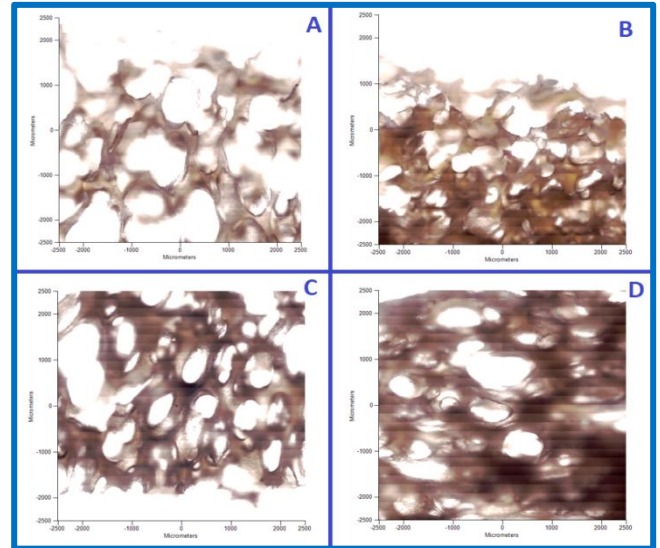


Figure 10. Image A- Base with Voranol; Image B- Base Without Voranol; Image C- Base 5% PCM; Image D- Base 10% PCM

3.4.3 SEM

The results of observations using SEM are shown in Figure 15. Figure 15.A shows that Polyurethane Foam Base without Voranol has a mostly smooth and flat surface structure. The cross-section area of the cell wall shows a homogeneous and compact material. Figure 15.B shows some changes by adding Voranol, namely cell walls with flaws in its surface, although it continues to have a smooth appearance. The cross-section area of the wall does not reveal changes from the previous one. The foam present in Figure 15.C has more uneven walls, with the presence of pores and circular deposits. This presence of pores on the walls and cutting of the section is due to the addition of PCM. In this same figure it is possible to observe some spheres of this material. Figure 15.D shows an increase in the number of pores (caused by the greater presence of PCM) also shows the increasingly oval cells. The size of the pores on the walls and section of the foam walls 5% PCM and 10% PCM vary between $20 - 60 \mu\text{m}$, while the spheres and circular deposits due to PCM are between $15 - 30 \mu\text{m}$. According to the PCM manufacturer, the microcapsules have a diameter of between $1 - 15 \mu\text{m}$. [5]

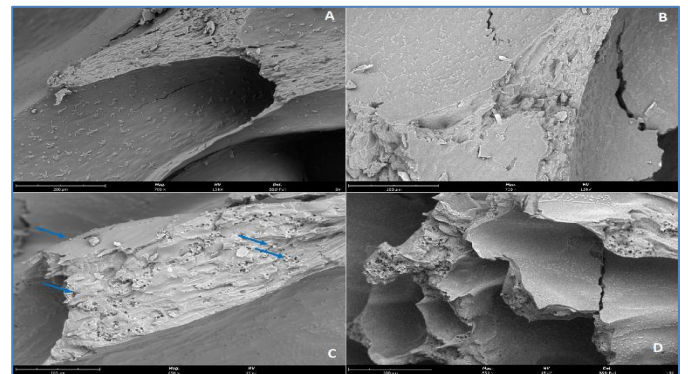


Figure 11. SEM images A- Base Without Voranol; B- Base with Voranol; C- Base 5% PCM; D- Base 10% PCM

3.4.4 TGA

With a thermogravimetric analysis it is possible to analyze the thermal behavior of the foams and thus evaluate their thermal stability. Figure 16 shows the graph with the TG curves of the foams represented. The results obtained using the graphs with the curves TG, DTG and heat flux graphs are present in table 5, represented below.

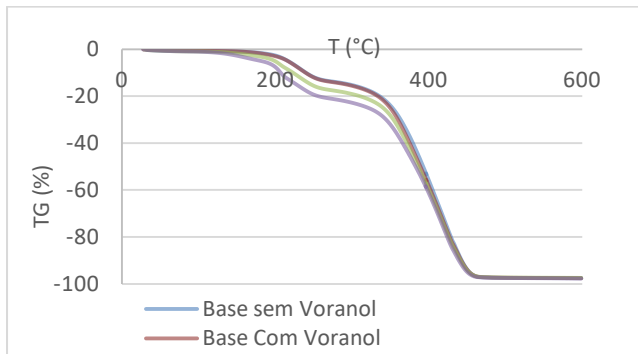


Figure 12. Graph TG

Table 5. Thermogravimetric Analysis

Foam	T _{patamar} (°C)	Δm (%)	T _{max} (°C)	ΔH degradation (mJ/mg)
Base Without Voranol	175 - 275	12,4	235	----
	305 - 475	81,6	425	110
		Total: 94,0		
Base With Voranol	180 - 275	12,3	235	----
	305 - 475	81,2	376; 425	69
		Total: 93,5		
5% PCM	183 - 215	5,2	205	----
	215 - 275	9	235	----
	305 - 475	77,6	373; 421	212
		Total: 91,8		
10% PCM	135 - 180	3,2	165	----
	180 - 220	8,6	205	----
	220 - 275	7,7	235	----
	310 - 475	73,7	369; 425	143
		Total: 93,2		

In both bases (without PCM) it is only possible to verify the existence of a T_{max} at the first peak (approximately 235°C). However, in base foams with PCM it is possible to check two maximums currently, appearing one T_{max} at 205°C and another at 235°C. This difference is due to the presence of PCM in foams. These initial levels are due to the evaporation of interstitial water by degradation of polyurethane, since, due to urethane bonds, these are generally considered thermally intermediate.

On the other hand, there is a level common to all foams, in the same temperature range, which is the most significant level, with mass losses greater than 74% for all cases. This level corresponds to the temperature interval in which the decomposition of the polyurethane structure occurs.

There are two levels of mass loss common to the 4 foams. The first level (175 – 275 °C) is due to the decomposition of polyurethane in its predecessors, namely the urethane bond and polyol polyester, as well as the formation of combustible gases from the decomposition of the urethane connection. The second level (305 - 475 °C) is due to the degradation of more reticulated sections of the material, with the formation of more combustible gases, leaving only a charred waste. [9]

Through the graphs it was also possible to obtain the degradation enthalpy of each foam, which are present in the table above. By the values given through the TGA software for heat flow, it is possible to notice that the addition of 5% PCM makes the foam degradation process more energetic when compared to the bases. [5,10]

3.4.5 Densities

Through the methods mentioned above it was possible to calculate the apparent density, density of the material that makes up the foam and the porosity of the foam. The results obtained are present in table 6. The density values for a commercial foam were obtained in the scope of Raquel de Jesus da Graça Lopes's dissertation (2020). [11]

Table 6. Density Analysis

Foams	Apparent Density (g/cm ³)	Material Density (g/cm ³)	Porosity (%)
Base Without Voranol	0,28	1,33	80
Base with Voranol	0,25	1,45	85,3
5 % PCM	0,29	1,34	81,5
10 % PCM	0,28	1,22	84,3
Comercial Foam	0,10	---	---

As for the apparent density, it should be noted that regardless of the additions made, the results were not significantly affected. As for the density of the foam constituent material, there is an increase with the addition of Voranol and a decrease with the addition of PCM. In the base foam, the replacement of 10% of Polyol_{OA} by a commercial polyol, caused this foam to form more bonds (increasing the density of the foam constituent material), and consequently lead to better foam growth (decreasing the apparent density of the foam).

On the other hand, the PCMs added to the foam may be interfering with the formation of the urethane bonds, thus decreasing the density of the foam constituent material. In addition, as the foam is not so reactive, it will not grow so much, so its apparent density also tends to increase. In relation to porosity, and with analysis of the images obtained by MicroFTIR and SEM, it is verified that the increase in porosity with the addition of Voranol is due to the fact that this addition originates a foam with larger and more open cells. The decrease in porosity with the addition of 5%

PCM follows the same logic, since it can be observed that the addition of PCM in the foam originates a greater number of cells per unit area, however it originates more organized cells and with a mixture of open and closed cells. For 10% PCM again increases porosity. According to the SEM, this can be explained by the greater number of visible pores, both on the walls and in the section of cutting the walls, caused by the presence of a greater amount of PCM.

If we compare the apparent density of a commercial foam with the apparent densities of the foams obtained, we observe that the density of the commercial foam is about 1/3, however the density of the foam obtained is close to the density of the cork. If we analyze the commercial components, all are made in a very systematic way, with completely known reagents, thus obtaining linear polymer chains, with ease of being controlled. The same is not true for the bio-based components, which despite the will and interest, it is not yet possible to carry out these components with the same control, thus compromising the product obtained. Despite this difference, the obtained product remains fully capable of performing the desired task.

3.4.6 Thermal Properties

Through the thermal conductivity tests it was possible to obtain the results presented in table 7. The values represented for a commercial foam were obtained in the scope of Raquel de Jesus da Graça Lopes's dissertation (2020). [11]

Table 7. Thermal Properties Analysis

Properties	Cp (J/kg.K)	λ (W/m.K)	α (m ² /s)	$(W.s^{0.5}m^{-2}K^{-1})$
Base Without Voranol	1190	0,052	1,6E-07	131
Base With Voranol	1080	0,057	2,1E-07	124
5% PCM	1205	0,056	1,6E-07	140
10% PCM	992	0,055	2,0E-07	123
Comercial Foam	1500	0,045	3,1E-07	80

Thermal diffusivity considers the amount of energy that is absorbed during the heating of the foam, giving more information during the transient state than just the thermal conductivity. A material with better thermal insulation should have a lower thermal diffusivity. This property is distinct from thermal effusivity, since diffusivity is related to the speed in achieving thermal equilibrium, while effusivity shows the material's ability to absorb heat. That is, the diffusivity indicates the penetration of thermal energy in the material and the effusivity indicates the thermal exchange to the surface of the same. [13]

A material with higher effusiveness can heat/cool faster than a material with a lower effusiveness.

Typical values of thermal effusivity of thermal insulation are between 1-400 $Ws^{1/2}m^{-2}K^{-1}$.

It is possible to observe that the effusivity is higher for the foam with 5% PCM. This property decreases from Voranol-free Base to Voranol Base, increases to foam with 5% PCM, and decreases back into foam with 10% PCM. The increased effusiveness of the foam with 5% PCM allows it to absorb (and dissipate) more easily the heat to the surface, without increasing its temperature. Its lower thermal diffusivity allows the material not to reach temperature peaks, taking longer to achieve a thermal balance, but allowing to maintain its physical and chemical integrity. The overall result shows that the addition of Voranol increases the thermal conductivity of foams, which you would expect since this compound has a value between 0.140 – 0.151 W/mK. Base foams with Voranol and 10% PCM have lower calorific capacity, which can be accounted for by convection heat losses through pore walls. As it was possible to verify by MicroFTIR and SEM, the Base foam with Voranol has larger and more open cells and the 10% PCM foam has a greater number of pores, thus justifying this fact. On the other hand, this determines that they have greater thermal diffusivity, but less effusiveness. The presence of PCMs in 5% PCM foam may explain the higher value of calorific capacity since these materials will help in maintaining latent heat in the foam.

If we compare the foams obtained with a commercial foam, we can conclude that the commercial foam has lower thermal conductivity and effusivity, so its surface has less capacity to absorb/ release heat, despite its superior thermal diffusivity, which represents better capacity to reach thermal equilibrium. Thus, 5% PCM foam will be faster to absorb air heat (air thermal effusivity = 0.0006 $Ws^{1/2}m^{-2}K^{-1}$) but slower to adapt to the environment to which it is exposed, when compared to a commercial foam, since it takes longer to reach thermal equilibrium. [14,15]

3.4.7 Cream, growth and gel times

The times of cream (Cream Time), growth (Rise Time) and gel (Gel Time) of the foam were calculated for each type of foam under study. Every 5 minutes, the growth of the same was verified and the value was recorded. When checking the completion of each step, its time has been recorded, and the results are expressed in Table 8.

Table 8. Time of conclusion analysis

Times	Base Without Voranol	Base With Voranol	5% PCM	10% PCM
Cream Time	5 minutes	5 minutes	10 minutes	15 minutes
Rise Time	1 hour and 45 minutes	1 hour and 25 minutes	1 hour and 25 minutes	1 hour and 30 minutes
Gel Time	50 minutes	45 minutes	35 minutes	35 minutes
Total	2 hours and 40 minutes	2 hours and 15 minutes	2 hours and 10 minutes	2 hours and 20 minutes

It is noted that the replacement of only 10% by weight of Polyol_{OA} by Voranol in foam significantly decreases its growth time. It was also observed that the addition of PCM slows cream time, however, decreases gel time, so it is possible to obtain a foam at the same time as one without PCM. [16]

3.4.8 Uniaxial compression tests

For each foam, the test was performed in six different samples, three of which were performed in the direction of foam growth, and the remaining three in the direction perpendicular to the direction of growth of the foam.

For each assay it was possible to obtain two graphs, one being a stress/time graph and another extension/time graph. The second is the same for all foams since the test execution conditions are the same for all cases. Thus, a Stress/Time graph was performed for each test. After observing each chart, it was possible to obtain a single chart for each type of foam, with the average of the values of the remaining graphs. These graphs are attached, as are the two tables with the main results extracted from them. The Nominal Compression Stress values, calculated for each foam, in the different directions are expressed in table 9.

Table 9. Nominal Compression Stress Values

<i>Nominal Compression Stress (MPa)</i>		
	Foam Growth Sense	Prependicular Direction to the Foam Growth
Base Without Voranol	0,13	0,12
Base with Voranol	0,10	0,19
5 % PCM	0,12	0,17
10 % PCM	0,13	0,13

Analyzing the data obtained, it can be observed, as expected, that the addition of PCMs to the foam worsens its mechanical properties, thus decreasing its Nominal Compression Stress. In the direction of the direction of growth of the foam, there is no significant difference in any of the foams, highlighting only a small difference in the base foam with Voranol. In the direction perpendicular to the direction of growth of the foam there is an improvement of the mechanical properties with the addition of Voranol, which is once again due to the improvement of the bonds, resulting from the better formation of the urethane, followed by the expected decline of resistance, due to the increase of the phase change materials, which make the structure more fragile. [15]

4 Conclusions and Future Work

Through the analysis of FTIR spectroscopy, it was possible to observe that both Polyol and isocyanate reacted in totality, since the presence of the bands corresponding to these raw materials was not verified in the foam. Regarding the analysis of MicroFTIR and SEM, it is possible to verify that the addition of Voranol to the foam originates larger and more open cells, with regular size and no great difference between them. On the other hand, it is also possible to observe that the addition of PCM to the foam originates more closed cells, the presence of great number of pores, as well as circular deposits in uneven walls.

From the thermogravimetric analysis, it was possible to verify that the beginning of the decomposition of the polyurethane structure for the foams mentioned is higher than 305°C, with mass losses greater than 74%.

As for thermal properties, it was found that the addition of Voranol is disadvantages, since it decreased the heat capacity and increased the thermal conductivity, however, when adding PCM to the foam, this variation was reversed, thus noting an improvement of thermal properties due to the addition of these materials.

With this work, it was possible to conclude that among the foams obtained, the one that best suits the desired application is the 5% PCM foam. This foam presented a density comparable to the density of cork and it is the foam that takes less formation time. This foam also presented better mechanical strength results and a calorific capacity closer to the values for commercial foam, despite the higher thermal conductivity. On the other hand, for 10% PCM foam there were no improvements in properties, so it was concluded not to be advantageous for this application, making it an exaggerated percentage. In addition to the conclusions drawn, it can also be said that this particular foam is a very promising material both because it is more sustainable and because it can compete with the commercial foams on the market, in the sense that the addition of PCM can overcome the thermal properties of the now existing foams.

A possible future work could be to repeat the tests with the same amounts of PCM, but using different base formulations, or test other type of PCMs, such as PCMs by coating. It would also be possible to test PCMs with different transition temperatures simultaneously, with the aim of covering a wider range of temperatures. It would also be important to carry out steam absorption tests and continue the mechanical testing of the foams.

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