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Addition of calcium carbonate in the synthesis of flexible polyurethane foams

Adição de carbonato de cálcio na síntese de espumas flexíveis de poliuretano

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Within all their variability, foams constitute the largest segment in the polyurethane industry. Polyurethane is composed mainly of isocyanate (-N=C=O) and polyol (-OH) functional groups, presenting different characteristics by adding fillers. This polymer has a wide range of applications such as adhesives, coatings, varnishes, elastomers and foams. Aiming improvements in its thermal properties, calcium carbonate addition was investigated in proportions of 12.5%, 25% and 37.5% (w/w). This filler is widely used to change the properties of polymers, as it is easily found in nature and has a low cost. For the synthesis of polyurethane samples, isocyanate and polyol were reacted using "one shot" process. The obtained results demonstrated the change in the glass transition temperatures (T_g) of the material to higher values, which indicates a decrease in the mobility of the polymer chains. Also, an increase in decomposition temperature was observed via differential scanning calorimetry (DSC). With Fourier transform infrared spectroscopy (FTIR) analysis, it was possible to analyze that the material was successfully synthesized by the appearance of the characteristic bands of PU foams. Furthermore, with the addition of calcium carbonate, it was possible to identify the presence of two phases, which indicate that the material underwent changes in its crystallinity, identified through X-ray diffraction (XRD) analysis. Finally, it was possible to observe via optical microscopy (OM) analysis that the addition of filler significantly changed the morphology of the foams.
Keywords: foams, polyurethane, calcium carbonate.

Dentro de toda a sua variabilidade, as espumas constituem o maior segmento da indústria de poliuretanos. O poliuretano é composto principalmente pelos grupos funcionais isocianato (-N=C=O) e poliol (-OH), apresentando características diferenciadas pela adição de cargas. Este polímero possui uma ampla gama de aplicações como adesivos, revestimentos, vernizes, elastômeros e espumas. Visando melhorias em suas propriedades térmicas, investigou-se a adição de carbonato de cálcio nas proporções de 12,5%, 25% e 37,5% (m/m). Essa carga é muito utilizada para alterar as propriedades de polímeros, pois é facilmente encontrada na natureza e possui baixo custo. Para a síntese de amostras de poliuretano, o isocianato e o poliol foram reagidos usando o processo "one shot". Os resultados obtidos demonstraram a mudança nas temperaturas de transição vítrea (T_g) do material para valores mais elevados, o que indica uma diminuição na mobilidade das cadeias poliméricas. Além disso, foi observado um aumento na temperatura de decomposição via calorimetria diferencial de varredura (DSC). Com a análise de espectroscopia no infravermelho com transformada de Fourier (FTIR), foi possível analisar que o material foi sintetizado com sucesso pelo aparecimento das bandas características das espumas de PU. Além disso, com a adição de carbonato de cálcio, foi possível identificar a presença de duas fases, que indicam que o material sofreu alterações em sua cristalinidade, identificadas por meio de análise de difração de raios X (DRX). Por fim, foi possível observar através da análise de microscopia óptica (MO) que a adição de carga alterou significativamente a morfologia das espumas.
Palavras-chave: espumas, poliuretano, carbonato de cálcio.

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1. INTRODUCTION

The versatile chemistry of polyurethane (PU) allows for the production of various materials by using different reinforcements during synthesis [1]. PU foams belong to a significant class of cellular polymers that hold a prominent position in the global market. These foams have a wide range of applications, including mattresses, pillows, furniture, packaging, recreational items, footwear, as well as potential uses as biomaterials in implants, support for enzyme immobilization, and acoustic and thermal insulation in civil construction [2-6].

Industries engaged in the production of PU foams commonly employ additives to enhance and customize the material's characteristics, which results in increased dimensional stability and density [7, 8]. The incorporation of additives into polymeric materials can yield a composite biphasic material, enabling the transfer of some mechanical stress from the polymeric matrix to the dispersed filler phase, due to the filler's superior properties when compared to the pure polymer. Additionally, these additives have the capacity to enhance various material properties, including mechanical performance and thermal conductivity, leading to potential reductions in the overall material cost [9-11].

Nevertheless, in the process of material selection for this specific application, it is imperative to consider various key factors. These considerations include the requirement for diminutive particles that can be readily dispersed within the polymer matrix, chemical purity to mitigate undesirable reactions, and abrasiveness, which has the potential to induce wear on mixing equipment and escalate expenses. Among the inorganic materials commonly employed as additives, notable options include calcium carbonate ($CaCO_3$), aluminum hydroxide ($Al(OH)_3$), silica (SiO_2), titanium dioxide (TiO_2), and talc ($Mg_3Si_4O_{10}(OH)_2$) [12].

$CaCO_3$ is a commonly employed substance in the polymer industry due to its cost-effectiveness and widespread availability in nature. Although it falls into the category of fillers, several studies have noted favorable enhancements in polymer properties when incorporating this filler. These enhancements encompass improved mechanical, thermal, and electrical properties, in addition to specialized applications such as flame retardancy [13-17].

The objective of this work is to analyze the thermal properties, using the differential scanning calorimetry (DSC) technique, of PU foam with the addition of $CaCO_3$ in different masses (12.5, 25 and 37.5% w\w), considering that most studies found in the literature use a variation of up to 30% by mass of $CaCO_3$ [18, 19]. Therefore, this work aims to investigate the final properties of the foam with significant amounts of filler in the polymer matrix. For this, the foams were characterized by X-ray diffraction (XRD) techniques to understand their crystalline structure, in addition to Fourier transform infrared spectroscopy (FTIR) and optical microscopy (OM) to investigate their chemical and morphological structure, respectively.

2. MATERIALS AND METHODS

2.1 Material synthesis

Commercial isocyanate and polyol were acquired from Redelease® (Brazil) and commercial calcium carbonate from Êxodo Científica®, all with analytical grade. To handle materials such as polyol and isocyanate, 20 mL syringes were used, and for storage, polypropylene (PP) pots with a capacity of 500 mL.

For the synthesis of PU samples, the isocyanate and polyol were reacted using the "one shot" process, with a mass ratio of 1:1. For the addition of $CaCO_3$, proportions of 12.5%, 25% and 37.5% (w/w) were used, and a control foam (0.0% $CaCO_3$ (w/w)) for comparison. The samples were prepared by inserting the polyol into the PP pot and $CaCO_3$ was added immediately afterwards. The polyol with $CaCO_3$ were homogenized for approximately 60 seconds at 300 RPM. Then, the isocyanate was added to the polyol mixture with $CaCO_3$ and homogenized again at the same speed for around 60 seconds and stopped when the foam expanded. The PU synthesis process takes place in two stages: the gelation reaction and the blowing reaction. The gelation reaction occurs through the reaction between urethane, isocyanate and alcohol to form foam, promoting the obtaining of a polymer using urethane monomer in the reaction [2].

The resulting compound reaches chemical equilibrium with the allophanate by reacting with the isocyanate. The other process is the blowing reaction, which occurs between the isocyanate and water, resulting in the production of carbon dioxide, which favors the expansion of the product, in addition to also forming an amine group, which reacts with an isocyanate group to create urea. dissubstituted. The disubstituted urea can then react with another isocyanate molecule to form a biuret-type compound. Finally, after this reaction process, the product will have the appearance of foam [2]. In Table 1, the mass values are presented for better visualization of the experimental procedure.

Table 1: Different masses of $CaCO_3$ added to the PU foam for sample synthesis.

Description	**Polyol mass (g)**	**Isocyanate mass (g)**	**Calcium carbonate mass (g)**
Control sample	10.090	10.205	0.000
Sample 1: PU + 12.5% $CaCO_3$	8.759	8.776	2.502
Sample 2: PU + 25% $CaCO_3$	7.500	7.503	5.008
Sample 3: PU + 37.5% $CaCO_3$	6.273	6.278	7.500

2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy analyzes were carried out on a Perkin Elmer spectrophotometer, model Spectrum 65, with ATR module, with a resolution of 64 scans, in the region of 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}. FTIR analysis was performed at the LCaMP Laboratory at FATEC Sorocaba.

2.3 X-ray Diffraction (XRD)

X-ray diffractograms were obtained using a Shimadzu X-ray diffractometer (XRD-6100). Measurement conditions used were continuous scans at a voltage of 40.0 kV, current of 30.0 mA and scan range from 5 to 65 degrees, at 2 degrees per minute.

2.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were performed in a TA Instruments DSC 25. Analysis used a heating ramp of 10 °C/min, with a temperature range of 0 to 350° C and a nitrogen flow of 50 mL/min.

2.5 Optical Microscopy (OM)

To obtain images of the cross-sections of the foams, a Leica EZ4W optical microscope (OM) was used coupled to the computer.

3. RESULTS AND DISCUSSION

Figure 1 demonstrates the final appearance of the foams after the synthesis. As it is possible to verify, there has been a change in expansion, it can be noted that, when increasing the amount of load, the foams presented greater irregularities on their surfaces. PU foam is a hydrophilic material, and due to the poor adhesion of $CaCO_3$ in the PU foam matrix, it causes cellular collapse, and this collapse increases as the amount of $CaCO_3$ is added to the polymeric matrix. It can also lead to a delay in cell formation when opening the pores due to the blowing reaction. The inorganic charge can end up diffusing with the release of carbon dioxide, causing this abnormality in the morphology and texture of the foam. In other words, the size of the pores and cavities relatively shrink when the percentage of $CaCO_3$ is high [20].

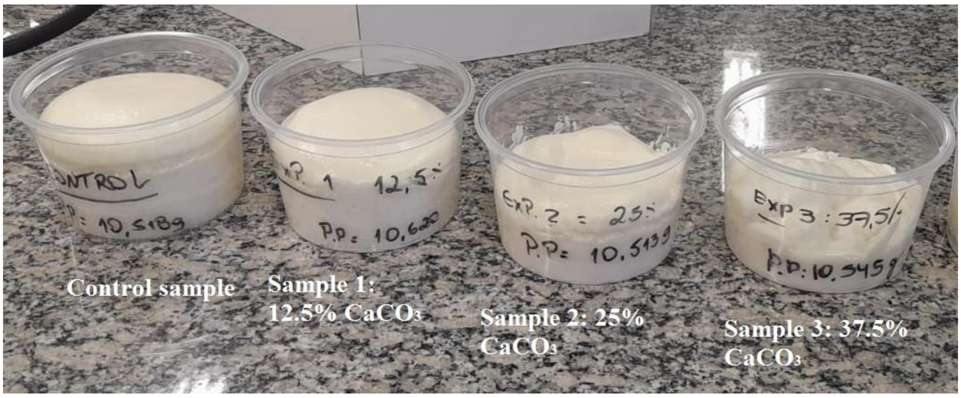

Figure 1: Samples of polyurethane foams with $CaCO_3$.

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

When observing the FTIR graph, Figure 2, it is evident that the PU formation reaction was successful, as indicated by the appearance of the primary reference bands. At 3350 cm^{-1}, there is stretching of the residual –OH groups from the polyol that did not participate in the urethane formation [21]. At 2930 cm^{-1} and 2850 cm^{-1}, there are stretching vibrations of the asymmetric and symmetric methylene groups, respectively. The presence of the carbonyl bond is notable at 1713 cm^{-1}. The band at 1594 cm^{-1} originates from the aromatic rings present in the isocyanate. Bending vibrations at 1511 cm^{-1}, arising from urethane, are observable, in addition to the stretching vibration of C-N (amide II) at 1412 cm^{-1}. The bending vibration of the C-H bond is evident at 1307 cm^{-1} in CH_3 groups. At 1084 cm^{-1}, there are stretching vibrations of the C-O-C bond, while the band at 2272 cm^{-1} is related to the isocyanate groups that remain from the reaction [22-24]. Finally, it is worth mentioning that the addition of calcium carbonate as a filler did not change the absorption spectrum, as expected [25].

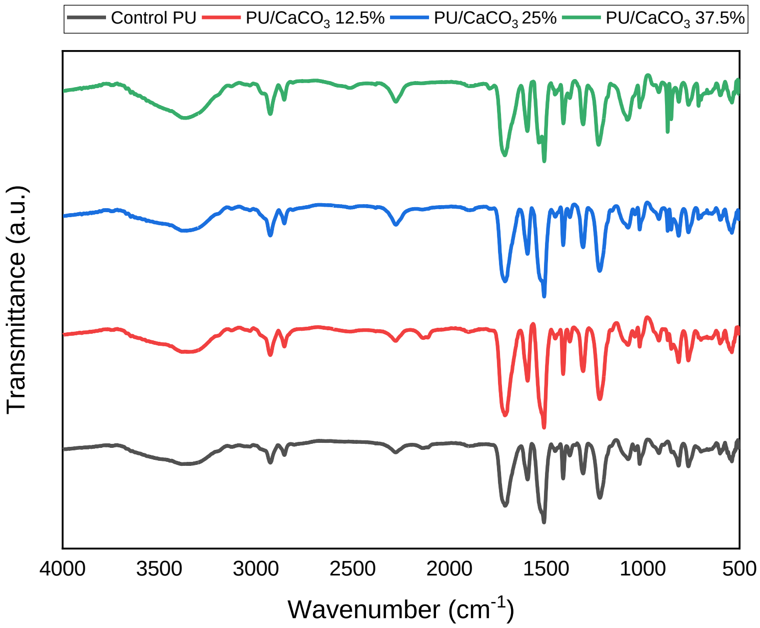

Figure 2: FTIR spectrum of polyurethane foams with $CaCO_3$.

3.1 X-ray diffraction (XRD)

XRD diffractograms of $CaCO_3$-loaded PU foams can be seen in Figure 3.

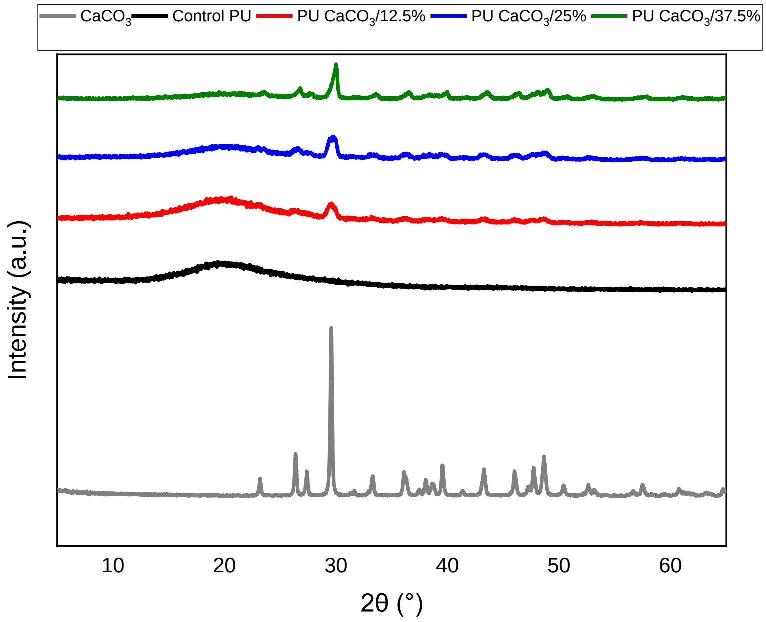

Figure 3: Diffractogram of PU foams with $CaCO_3$.

It is possible to infer that this PU foam is an amorphous material, as observed in many studies in the literature [26-28], on the other hand, $CaCO_3$ is a crystalline material. After adding the charges, the appearance of a crystalline peak in the 2θ region equal to 30° was detected. Therefore, it can be stated that there was the formation of a composite material, due to the presence of two distinct phases, an amorphous phase caused by the PU foam and a crystalline phase, which refers to $CaCO_3$. All samples of PU foams with $CaCO_3$ can be categorized as flexible, as the bands shown in the diffractogram refer to the flexible foam type, as demonstrated by Trovati et al. 2010. Therefore, a high proportion of polyol results in a lower amount of crosslinking in the urethane, making the foam less rigid and less crystalline, which classifies it as flexible [29-31].

3.2 Differential Scanning Calorimetry (DSC)

In this study, DSC was used to determine the glass transition temperature (T_g) of unfilled PU foams and with different masses of $CaCO_3$ fillers. It is noted that there was an increase in T_g with the addition of $CaCO_3$ in relation to the pure PU sample, as shown in Table 2 and Figure 4. This observation is different from that reported by other studies in the literature, which indicate that the addition of $CaCO_3$ does not significantly alter T_g. Therefore, a large amount of load may have affected the PU foam structure during the synthesis reaction [32-35].

Table 2: T_g temperatures and initial decomposition temperature for PU foams samples with $CaCO_3$ addition.

Sample	**T_g (°C)**	**$T_{initial}$(°C)**
Control PU	159.9	288.2
PU + 12.5% $CaCO_3$	224.6	314.7

PU + 25% $CaCO_3$	192.5	321.3
PU + 37.5% $CaCO_3$	197.7	275.5

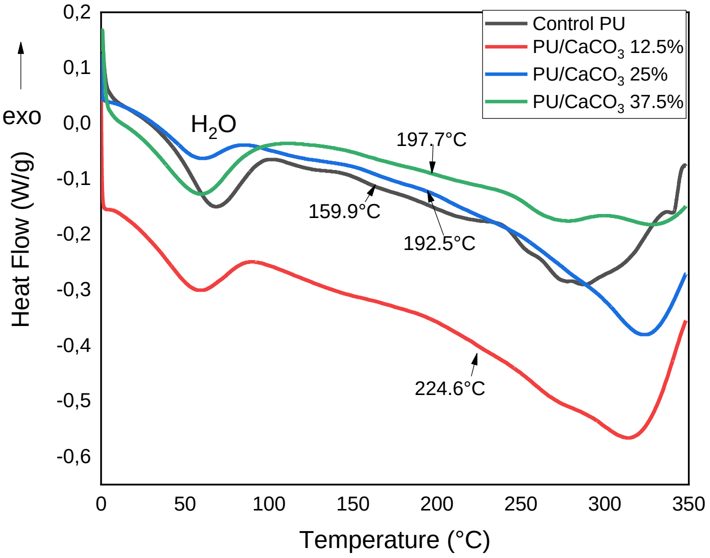

Figure 4: DSC curves of polyurethane samples with calcium carbonate.

This increase in the T_g of the pure PU foam in relation to the PU foam composed of 12.5% (w/w) of $CaCO_3$ indicates that the load hinders the mobility of the PU polymer chains. On the other hand, the decrease in T_g shows greater mobility of the PU chains. This considerable increase may be linked to the lower mobility of the PU chains, as well as the high thermal resistance characteristic of the filler, acting as a heat protectant in the PU structure. Peaks around 70 ºC, for pure PU sample, and 59 °C for the others, is related to the humidity in the foams. In relation to the initial decomposition temperature ($T_{initial}$), there is an increase in composite foams when compared to pure PU, but with 37.5% (w/w) $CaCO_3$ the temperature is once again close to that of pure PU, indicating greater mobility of the PU chains. As it is an amorphous material, it is possible to analyze the glass transition T_g, and the temperature at which decomposition begins [33-35].

3.3 Optical microscopy (OM)

In Figure 5, morphologies of the foams are shown: Pure PU foam (a), PU foam with 12.5% $CaCO_3$ (b), PU foam with 25% $CaCO_3$ (c) and PU foam with 37.5% $CaCO_3$ (d), respectively. It can be observed that the pure foam (a) presented a well-defined morphological structure, of the polyhedral type, which has well-distributed cells with a regular size. In the PU sample with 12.5% $CaCO_3$ (b), a significant change in its structure is noted, which now shows cells with smaller sizes, whilst presenting irregularities in terms of their distribution. This phenomenon may have occurred due to the high amount of filler used, which could end up causing damage to the polymeric matrix [36, 37].

PU sample with 25% $CaCO_3$ (c) demonstrated a smaller cell size than the previous sample, as well as a greater presence of damage to the foam morphology, such as the presence of tears. In this way, the increase in load strongly influenced the nucleation effect of the foam cell wall, whose structure presented greater irregularities [38, 39].

Finally, PU sample with 37.5% $CaCO_3$ (d) presented the previously highlighted characteristics in a more expressive way, in which it is possible to observe practically the total loss of the morphological regularity of the foam. Therefore, high amounts of charge end up significantly affecting and damaging the PU cells. Consequently, decreased mechanical properties may occur [28].

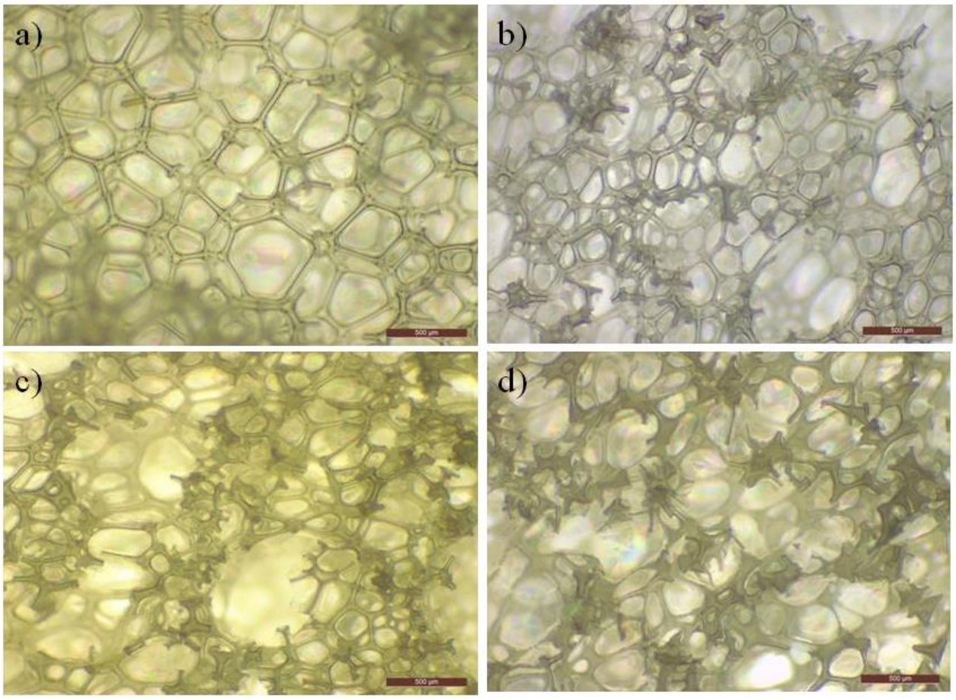

Figure 5: Optical microscopy of the cross-section of PU foams: (a) pure PU, (b) PU/$CaCO_3$ 12.5%, (c) PU/$CaCO_3$ 25%, (d) PU/$CaCO_3$ 37.5%.

4. CONCLUSION

The addition of $CaCO_3$ in the synthesis of polyurethane foams promoted an improvement in the thermal properties of the polymer. With DSC it was possible to observe the increase in T_g with the addition of $CaCO_3$. Furthermore, there was an increase in the temperature at which decomposition ($T_{initial}$) began for samples with 12.5 and 25% (w/w) of $CaCO_3$. The FTIR spectra show no interaction between the $CaCO_3$ particles and the PU chains, since there was no change in the spectrum of pure PU when compared to the spectra of PU loaded with $CaCO_3$. Through the XRD characterization technique, it was possible to observe that the obtained PU is amorphous and the $CaCO_3$ has a crystalline structure. Thus, after adding the filler, it was noted that a composite material was obtained. With OM analysis, it was possible to observe that the addition of $CaCO_3$ significantly changed the morphology of the foams, where it is possible to observe irregularities in the formation of the polymeric matrix with the addition of high amounts of filler, which can lead to consequent loss of mechanic properties of the material. High levels of $CaCO_3$ can lead to a reduction in several properties of the material, since this load can end up agglomerating in the morphology of the foam.

However, it is important to highlight that there are still opportunities for future research, such as exploring particle sizes and incorporation methods; mechanical strength, hardness and compression in order to further characterize the properties of the composite.

5. ACKNOWLEDGMENTS

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