Preparation of Polyurethane Sheets Using Surfboard Manufacturing Waste and Evaluation of Their Properties to Use in Brazil's Construction Industry

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Abstract: The aim objective of this study was to identify the potential of PU solid waste generation to produce and characterize a new product, namely, thermal-acoustic insulation sheets. Polyurethane sheets were prepared by incorporating different percentages (3 per cent, 5 per cent, 10 per cent, 15 per cent and 20 per cent) of the PU waste collected, with two particle sizes into the matrix. The intended use of these PU sheets was as thermal and acoustic insulation for the construction industry. The properties of the sheets were evaluated through scanning electron microscopy (SEM), mechanical compressive strength tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TA) and determination of the sound pressure level (SPL). The results showed that the properties of the sheets are influenced by the particle size and the percentage of PU incorporated. From the SEM analysis it was observed that the material was homogeneous for all samples and for both particle sizes. Regarding the mechanical properties, the compressive strength of the sheets decreased with the addition of PU, regardless of the particle size. The DSC analysis revealed a T_g at -15°C and crystalline melting at 71°C for all of the sheets produced. The TA results indicated a degradation onset temperature of 200°C. The greatest reduction in the SPL was observed with the incorporation of 15 per cent of waste, regardless of the particle size. In this new approach a lower quantity of monomers can be used to

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obtain sheets with similar properties to those of the material with no waste incorporation. The results demonstrates that the production of PU sheets with the incorporation of residues is viable for providing a cleaner production technology with significant environmental and economic advantages.

**Keywords:** Solid waste, surfboard, polyurethane, insulation sheets, construction industry

### 1. Introduction

According to Vilar (1999) [1] in 1849 Wurtz described the laboratory synthesis of a substance called urethane, a product obtained from the chemical reaction between an isocyanate group and another substance with a hydroxyl group. An example of this synthesis procedure can be observed in Scheme 1 [2].

**Scheme 1:** Reaction between isocyanate and a hydroxyl used to obtain urethane

\[
\begin{align*}
\text{Isocyanate} & + \text{Hydroxyl} & \rightarrow \text{Urethane} \\
R^1\text{-N} & \text{C} & \text{O} \\
& \text{H} & \text{OR}^2 \\
\end{align*}
\]

However, it was the German industrial chemist Otto Bayer (1902–1982) who suggested the commercial application for the compound urethane. Initially, the product was developed as a substitute for rubber at the beginning of the Second World War [3].

Polyurethanes (PU) are basically produced through a reaction involving the polycondensation of an isocyanate (di or polyfunctional) with a polyol (two or more hydroxyls) and other reagents, such as catalysts, surfactants, chain extenders and water. Their structure can be cellular (flexible, semi-rigid and rigid foams and microcellular elastomers) or solid (elastomers, coatings, sealants, adhesives, etc.). Polyurethane foams can be defined as a class of polymers where the gas dispersion during the polymerization process gives rise to the formation of bulbs or cells interlinked in a tridimensional structure. PU foams can be synthesized from the polycondensation reaction with two variables. The first involves the addition reaction between an isocyanate and a polyol compound responsible for the polyurethane group formation and this can be considered as the polyurethane chain propagation reaction [2, 4]. An example of this synthesis can be observed in Scheme 2.
Scheme 2: Reaction involved in polyurethane synthesis from diisocyanate and polyol

\[
\begin{align*}
\text{Diisocyanate} & \quad + \quad \text{Polyol} \quad \rightarrow \quad \text{Polyurethane} \\
\text{O} &= \text{C} \equiv \text{N} - \text{R}^1 \quad . \quad \text{N} \equiv \text{C} \equiv \text{O} \\
\text{HO-R}^2\text{OH} & \quad \rightarrow \quad \text{C} \equiv \text{N} - \text{R}^1 \quad . \quad \text{N} \equiv \text{C} - \text{OR}^3\text{O} - \\
\end{align*}
\]

The second reaction occurs between isocyanate and water where carbonic acid is formed as an intermediate compound, which is decomposed into amine and carbon dioxide. The chemical branching, crosslinking and hydrogen bonds resulting from the reaction process are responsible for rigid segments in the final product [4].

According to the American Chemistry Council (2014) [3], PU can be found in inks, resistant elastomers, rigid insulation, flexible foam in mattresses and car seats, and sports articles such as roller skate wheels, skis and surfboards. The PU is mainly used in construction as thermal and acoustic insulation, for example in the form of sandwich roofs, walls and fills spaces in concrete.

It is estimated that the Brazilian PU market has exceeded 350 thousand tons per year [3], and different market segments use this feedstock. Grijó (2011) considers that the production chain of the surfboard industry in Florianópolis generates 107 tons of PU solid waste per year [6]. The environmental aspects and the responsibility related to the industrial production of surfboards need to be given more attention, considering the promising economic perspective associated with the popularization of this sport in Brazil and the around world.

The code LER 170604 of the European list of residues applies to PU, because this is an insulation material classified as non-hazardous waste [7]. The US Environmental Protection Agency (2014) [8] classified PU waste as a non-hazardous solid and the American Chemistry Council (2014) [3] notes that PU is an inert solid which is reactive with water. According to the Brazilian technical standard NBR 10004 [9] and the Brazilian National Plan for Solid Residues (Plano Nacional de Resíduos Sólidos) [10] the residues originating from the manufacturing of surfboards are classified as Class IIA non-inert industrial waste.

The industrial surfboard production chain has positive effects, such as income and leisure, enabling a better quality of life for local inhabitants and tourists. On the other hand, there are negative impacts on the environment, mainly those associated with the residues, and PU is the principal solid waste generated. The exposure of humans to these chemicals can cause eye and respiratory tract irritation with symptoms including coryza, tearing, coughing, headache, dizziness, nausea and breathlessness. In the case of fire, HCN and its derivatives are chemical asphyxiating can be lethal, depending on the concentration in the environment and time of contact. The main extinction method is the use of water as cooling agent. Water
contaminated with combustion products must not be released into the soil, drainage channels, or other such disposal routes but instead it must be recovered, treated and properly discarded.

Barcelos et al. (2013) mapped the surfboard production micro-chain in Florianópolis, Santa Catarina State (SC), Brazil and described the surfboard production cycle. It was possible to verify opportunities during the production stages for improvement of the process through the reduction or reuse of solid residues, mainly PU. PU decomposes slowly in the environment, it is a combustible solid and it has a long useful life, thus, this waste can be reused, recycled or incinerated for energy recovery, based on national, regional and local technical standards [3, 11].

The concept of sustainability has been established in the scientific arena as a multi-disciplinary subject that guides the various research areas. It is based on three foundations: economic development, social development and environmental protection. Studies on the development of technologies which aggregate in their essence the concrete objectives of contributing to social-environmental advances are of great importance.

The Brundtland Report (WCED 1987) highlights that sustainable development is conceived as being that which is able to satisfy our needs without compromising the capacity of future generations to supply their own needs [5, 12, 13, 14, 15, 16].

In the production processes, the search to reduce energy and optimize the flow of materials, sub-products, final and other products, gives rise to sustainable practices, such as reverse logistic [17] and cleaner production processes [18, 19, 20].

Making waste into a product similar to the initial one or to another product results in saving energy and natural resources, and brings back to the production cycle elements which would otherwise be discarded [5, 16, 17, 19, 20, 21, 22, 23, 24]. When the generation of residues cannot be avoided, these should be recovered, reused or recycled in order to minimize their being disposed of in industrial or municipal landfills or even in the environment [19, 20, 25, 26, 27].

The recycling of materials has become a field which merits extensive research and the development and application of resources, since there is environmental and economic interest in avoiding the discarding of material in the environment. In this regard, for viable routes are being sought to achieve the reuse of materials, both in their original chemical formulation and after chemical transformation, and to find a market for their application. One feasible alternative for the recycling of thermoset polymers waste is the use of polyurethane residue as an aggregate for the resins of which it is comprised [28, 29].

In the international scenario, Brazil occupies a leading position with regard to recycling, holding fourth place in terms of the mechanical recycling of plastic [30]. Industrial waste recycling has been intensified in
recent decades with the development of several techniques able to reincorporate these residues into the composition of new materials [4, 19, 22, 26, 31, 32, 33, 34].

In this context, the aim of this study was to identify the potential of PU solid waste generation to produce and characterize a new product, namely, thermal-acoustic insulation sheets.

2. Materials and Methods

PU samples were collected in three surfboard production plants in Florianópolis (SC, Brazil) and in an experimental study PU sheets were produced with the incorporation of PU residues, for application as thermal and acoustic insulation in buildings.

2.1 Samples Characterization

PU is classified as a combustible solid with an ignition rate of between 271°C and 378°C, and its decomposition starts at 203°C [3, 11, 22, 35, 36], consistent with the findings reported herein.

When heated, PU can undergo non-flaming degradation (without burning). When polyurethanes undergo thermal degradation some toxic chemicals can be emitted, which can sometimes be seen as a smoke or vapors. This type of degradation is of great concern partly because of the lack of visible warning signals that chemicals are being released during this process [3, 22, 36, 37].

Due to the risk of reaction to fire (flaming) associated with PU, the installation of panels must strictly adhere to the relevant regulations. The chemical decomposition of PU during combustion can produce smoke, droplets and inflamed particles. The smoke is composed mainly of carbon oxides, that is, carbon dioxide (CO₂) and carbon monoxide (CO), which are physical and chemical asphyxiating gases, respectively, and also particulate carbon (soot). The proportion of carbon oxide formed is dependent on the environment, and the more limited the oxygen the higher the amount of carbon monoxide (CO) and soot formed will be. In the presence of flames or temperatures higher than 800°C, the formation of hydrocyanic acid (HCN) and other compounds containing nitrogen occurs [3, 11, 37, 38].

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2004 [42]; ABNT NBR ISO 15366-2 2006 [43]; ABNT NBR ISO 31000 2009 [44]. In this regard the physicochemical properties of PU are important.

2.2 Material and Preparation of PU/PU Residues Sheets

The reagents formulated polyether polyol and polymeric isocyanate were acquired from the company Arinos and the PU residues were donated by SRS LTDA. All reagents were used as they were received and safety recommendations were adhered to [45].

The crude residue originating from the post-production process of the surfboard machining was classified by sieving through a size 9 mesh (granulometric classification), and this material was used to produce the sheets. The residue was mixed with the monomers (formulated polyether polyol and polymeric isocyanate) for 0.5min and then poured into an aluminum mold with dimensions of 0.39m x 0.24m x 0.025m. Samples of PU/PU residue sheets were prepared with different quantities of residue (3 per cent, 5 per cent, 10 per cent, 15 per cent and 20 per cent by weight), the total mass of each sheet being 147g.

2.3 Scanning Electron Microscopy Analysis

Micrographs of PU sheets fractured in liquid nitrogen were obtained by scanning electron microscopy (SEM) using a JEOL microscope (model JSM 6060), operating at 10kV.

2.4 Thermal Characterization

Differential scanning calorimetry (DSC) was carried out with a Q2000 calorimeter (TA Instruments, Universal). The sample temperature varied from -50 to 150°C with a heating/cooling rate of 10°Cmin-1 and under nitrogen atmosphere.

Thermogravimetric (TGA) analysis was performed in a Q500 analyzer (TA Instruments), calibrated with palladium, using a nitrogen flow of 100mLmin-1, a heating rate of 20°Cmin-1 and an environmental temperature of up to 900°C.

2.5 Characterization of Mechanical Properties

In order to perform the tensile tests, specimens were cut from the PU sheets and prepared in shape of parallelepipeds (dimensions 0.25m x 0.25m x 0.50m). Mechanical tests were carried out by compression in a Universal testing machine with an EMIC, model DL 30000, load cell of 5kN, according to the standard ASTM D 638 – 14 (2014) [46]. The specimens were submitted to pressure increases until plastic deformation of the material occurred at environmental temperature.
2.6 Measure of the Sound Pressure Level

To determine the sound pressure level (SPL), a Minippa, model MSL 1351C, sound level meter was placed inside acoustic anechoic chambers, which were prepared from PU residues.

3. Results and Discussion

3.1 Preparation of PU/PU Residue Sheets

The PU waste was classified by sieving into two particle sizes: 9 mesh and the crude residue. Different quantities of waste (3 per cent, 5 per cent, 10 per cent, 15 per cent and 20 per cent by weight) were incorporated into the PU matrix, with a total mass of 147g per sheet, and thus similar products with decreasing quantities of monomers were produced.

Fig. 1 show the residues used to produce the sheets and two of the sheets obtained. The residue with a particle size of 9 mesh can be seen in Fig. 1a end crude residue (Fig. 1b). Fig. 1c shows the PU sheet with no residue added and Fig. 1d the PU sheet with 5 per cent of crude residue added. The visual appearance of the sheets was similar, regardless of the residue used.

![Fig. 1](image)

Fig. 1 (1a) PU residue with a particle size of 9 mesh, (1b) crude residue, (1c) PU sheet with no residue and (1d) PU sheet with 5 per cent of crude residue added
Sheets of PU/PU residues were obtained with dimensions of 0.24m x 0.025m x 0.39m and they had a light yellow color. The sheets were easy to cut regardless of the percentage of residue incorporated, allowing samples with different dimensions to be obtained.

The use of the residue to produce this product can reduce the volume of waste disposed of in industrial or municipal landfills. The global reuse of these residues will thus reduce their negative impact on the environment.

### 3.2 Scanning Electronic Microscopy Analysis

A similar morphology was observed for all sheets, as verified by scanning electronic microscopy (SEM). For the sheet prepared with 15 per cent crude PU, the images obtained can be observed in Fig. 2. Surfaces fractured cryogenically show the homogeneous stage due to the high degree of interfacial adhesion and wettability of the PU residue and the polymeric matrix. It was also verified that pores and canals are present throughout the sample, which is typical of expanded polymer systems. It can be observed in the photomicrographs in Fig. 2, with magnifications of 25 (A), 100 (B), 400 (C) and 800 (D) times, that the cells are of the closed type, that is, they are not necessarily interlinked and they do not communicate with the external environment [32, 33]. This behavior was observed for all sheets prepared.

![SEM images of PU residue sheets](image-url)
For all of the sheets prepared with 9-mesh and crude PU residues good adhesion was observed, independently of the percentage 3 per cent, 5 per cent, 10 per cent, 15 per cent and 20 per cent of PU residue incorporated. As expected, there was no chemical incompatibility due to the similar nature of the polymer and residue (urethane). The sheets are miscible because they present only one stage, that is, the polymers are well mixed and there is no segregation of the components. A polymeric matrix with closed cells is particularly important for materials to be used as thermal insulation, because the conductivity in the pores occurs through radiation and the greater the porosity the lower the thermal conductivity will be.

3.3 Thermal Characterization

The differential scanning calorimetry (DSC) results were similar for all of the PU sheets, regardless of the percentage of residue incorporated or the particle size. Fig. 3 shows the thermogram obtained for the PU sheet with 5 per cent of crude residue.

![DSC thermogram of sheet with 5 per cent of crude PU](image)

**Fig. 3** Differential scanning calorimetry thermogram of sheet with 5 per cent of crude PU, heating curve (1) and cooling curve (2)

The curve for the first heating and cooling cycle applied to the PU sheet sample with 5 per cent of crude residue can be observed in Fig. 3. On the heating curve (1 in Fig. 3) the T_g of the material was observed at -15°C, confirmed by the second curve for the heating/cooling cycle, and also there was an endothermic event at around 71°C, which corresponds to the fusion of the crystalline phase present in the polyurethane domains.
and an enthalpy of fusion of 66.51 J/g. On the cooling curve (2 in Fig. 3) no crystallization was observed and for the second run the endothermic event was not observed. Due to the chemical compatibility between the matrix and the residue, the observation of a T_g was expected for these samples, verifying the miscibility between matrix and residue.

Thermogravimetric analysis was performed to evaluate the thermal stability of the sheets.

Fig. 4. shows the TGA thermogram for the sheet with the incorporation of 5 per cent crude PU residue, and the behavior was similar for all the samples studied.

![TGA Thermogram of sheets with 5 per cent of crude PU](image)

The PU residue presented a main region of mass loss at between 216-473°C, while the PU sheets with PU residues incorporated exhibited four ranges of thermal degradation (Fig. 4). The first mass loss occurred when the temperature reached 95°C, which corresponds to a loss mass of 2 per cent. This was attributed to the release of water molecules absorbed in the material. The second and main range of degradation corresponds to 70 per cent of mass loss and occurred between 200°C and 430°C. This is associated with the main urethane failure mechanism, that is, the breaking of the polyol-isocyanate link formed during the polymerization, that is, the breaking of the N-O link of urethane (R_1-NH-CO2-R_2) in the main chain. This stage was attributed to the loss of the mechanical properties of the material. The material obtained in this study can replace commercial PU sheets for use as thermal insulation under conditions in which the
temperature is lower than 200°C, since it was verified that at this temperature the thermal degradation of the material begins, as previously established by Bayler and Hirschler [11].

At 430°C the third thermal degradation range begins, which corresponds to a mass loss of around 5 per cent. The end the material thermal degradation was observed at 538°C.

On analyzing Fig. 4 it can be verified that the sheets prepared with PU residue presented good thermal stability at environmental temperature and can be used to provide thermal insulation in buildings. Thus this material is stable within the temperature range to which it will be submitted when used as thermal insulation in buildings, that is, environmental temperature.

The behavior of the PU sheets prepared was similar to that of the commercial sheets and thus they show potential for use as thermal insulation, for example in sandwich configurations in walls and roofs.

The temperature at which thermal decomposition starts can vary according to the heating process, the presence of air and the polyurethane composition. However, thermal degradation process can start at temperatures lower than the ignition rate, where the action of heat or elevated temperature on the material provokes loss of physical, mechanical and other properties [11, 35, 37].

The use of PU sheets for thermal insulation can improve significantly the energetic efficiency of buildings, reducing the amount of energy spent on heating and cooling the building, and they can also contribute to obtaining lighter structures, while adhering to the American Chemistry Council (2014) [3] and with the Brazilian technical standards ABNT NBR 15366-2 (2006) [43], ABNT NBR 15575-1 [47] and 15575-6 (2013) [48].

3.4 Mechanical Properties

Compressive tests were performed to evaluate the strength of the interface between the expanded PU and the PU residues and the results are shown in Fig. 5. In general, the compressive strength values for the sheets decreased with the addition of PU residues, independently of the particle size. The maximum compressive strength for the pure PU was higher than the values obtained for the sheets prepared with the residue, as can be observed in Fig. 5.
The decrease in the mechanical compressive strength with an increase in the residue content observed for the sheets can be attributed to the residue encapsulation, and the interactions of the chains are predominantly of the secondary type, despite no discontinuities being observed in polymeric matrix analyzed by SEM. The materials prepared with crude residue presented lower maximum compressive values when compared to the material confectioned with 9 mesh residues.

The sheets have no structural function, the use is to application of thermal and sound insulation.

### 3.5 Sound Pressure Level

The average sound pressure levels (SPLs) for the PU sheets measured inside the acoustic anechoic chambers are reported in Table 1. The average SPL value obtained outside the acoustic anechoic chambers was 92dBA.

<table>
<thead>
<tr>
<th>Composition PU residue (per cent)</th>
<th>SPL (dBA) 9 mesh size</th>
<th>SPL (dBA) Crude material</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>86.9</td>
<td>86.9</td>
</tr>
<tr>
<td>3</td>
<td>86.7</td>
<td>86.3</td>
</tr>
<tr>
<td>5</td>
<td>82.6</td>
<td>82.2</td>
</tr>
<tr>
<td>10</td>
<td>77.8</td>
<td>77.4</td>
</tr>
<tr>
<td>15</td>
<td>72.5</td>
<td>72.2</td>
</tr>
<tr>
<td>20</td>
<td>76.6</td>
<td>75.2</td>
</tr>
</tbody>
</table>
The sound pressure level results for all the samples (for both particle sizes) showed a decrease as the percentage of residue increased. It was observed that the samples produced with material of a larger particle size (crude residue) presented better results, that is, a greater reduction occurred. The greatest sound pressure level reduction was observed with 15 per cent of residue. This, it is clear that the PU sheets with residue incorporated can be applied to achieve a sound pressure level reduction and thus they can be used for acoustic insulation in buildings as an alternative to satisfy the Brazilian technical standard NBR [47].

4. Conclusion

This study started with the identification of PU solid waste from the surfboards productive stages. A methodology for PU plaques confection using PU residues was established decreasing the dependence on the monomers for production.

In the PU matrix, PU residue was successfully incorporated in different proportions (3%, 5%, 10%, 15% and 20%) in two granulometry (9 Mesh and crude). The incorporation of residue to the product can reduce the volume of waste taken to the industry or municipal landfills. The global use of smaller amount of residues will reduce the negative impact on the environment.

Before the application in focus, an evaluation of the material morphology was carried out and related to the studies of tensile strength, reduction of the sound pressure level and temperature of degradation of plaques.

By Scanning electronic microscopy characterization is possible observe that plaques obtained presented adhesion between the residue and the polymeric matrix. However, a decrease on the mechanical strength occurs for all the percentages of residues incorporated, but the values of mechanical strength are according with the application needs suggested for the material confectioned.

In the differential scanning calorimetry analysis, a crystalline fusion of polymer was observed with the temperature around 71°C for all the plaques confectioned. By the thermal analysis, PU mixtures presented four stages in their degradation. The degradation of material is triggered from 200 °C; in other words, the material is stable for the temperature variation that will be submitted, in this case, the environmental temperature as thermal insulation in buildings. The termal decomposition of 70% of the material occurs in temperatures few superior than 400 °C, for example, in case of fire. All the plaques confectioned presented decrease of sound pressure level. The properties studied presented appropriate results for application in building systems in order to use the material as thermal and sound insulation plaques in building systems, attending to the NBR 15575-1 (2013).
The use of less monomer for polyurethane production can imply in the cost reduction and environmental and economic benefits for manufacturers and the community. A successfully application of eco-materials involves a most cleaning production process and probable will become one of the strategic choices for polymer enterprises to increase their competitiveness.

Both from the economic and environmental viewpoint, PU residues incorporation was a successful alternative for feasibility of use of residues generated by enterprises. The material prepared had the aim to be used as thermo-acoustic insulation plaques in building systems.

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