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Nanocomposites with polyurethane polymer matrix/ particulate material

Nanocompósitos com matriz polimérica de poliuretano/material particulado

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ABSTRACT

The environment is currently considered one of the main concerns of the industrial sector and society. In the particular case of the oil industry, one of the biggest environmental catastrophes that can happen are large oil spills, where to reduce or minimize the environmental damage caused, various cleaning methods are used. Thus, nanocomposites aim to change the mechanical, physical and chemical properties of polymer matrices. The main focus of modifying Polyurethanes has been directed to materials science, the objective of which is to obtain particulate materials, allowing surfaces to be differentiated, reducing surface energy and increasing interlayer spacing for polymer intercalation. This particulate material, produced and modified, interspersed with the Polymer, allows us to absorb crude oil, as it is hydrophobic and, consequently, organophilic. The factors that define the degree of sorption of organic compounds are: hydrophobicity, porosity, molecular structure and volume, and the volume of the surface area of the sorbent material. Therefore, the sorbent must be wettable by the hydrophobic compound and non-wettable or slightly wettable by water. Sorbent materials must have characteristics such as a large surface area, high porosity, good oleophilic character, as well as good oil retention capacity and ease of application. Polyurethane presents several of these characteristics, making it an interesting sorbent for the oil sector. The present work studies the obtaining of these nanocomposites, using a particulate material to combat leaks or spills of hydrocarbons.

Keywords: Leaks, Nanocomposites, Polyurethane, Hydrophobic.

INTRODUCTION

Oil exploration is an activity that can cause serious damage to the environment, both in normally operating facilities, and will be the cause of accidents and failures, causing environmental impacts on physical, biotic and socioeconomic environments (DOS SANTOS, 2012). Accidents occurring in the extraction, transportation or storage of oil are constant concerns for all countries, therefore, several strategies have been developed to minimize accidents and are arranged in three broad categories: mechanical coatings, chemical treatment agents and burning in situ. Pollution is almost always related to exploration activities, mainly

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associated with oil spills and changes to coastal and terrestrial ecosystems. The most common containment method is the use of barriers with polymeric sorbent materials, with high mechanical and physical-chemical resistance characteristics. In addition, covers (skimmers) or manual removal, and even dispersing agents, can be used.

With this alarming situation of disasters and focused on sustainability, several studies were developed on the adsorption properties of some particulate materials in oil that have adsorbing power and can be used as molecular sieves, as bleaching and clarifying agents for vegetable and mineral oils. , as catalytic supports, as filtration agents, as adsorbents for oils in water, among others.

In context, the properties of the polyurethane polymer can be adjusted through two strategies, one of which involves modifying its three basic building blocks: the polyether or polyester, the diisocyanate, and the chain extender, and the other is the introduction of components inorganic substances in the polyurethane matrix (AYRES; ORÉFICE, 2007). The efficiency of these particulate materials in modifying the properties of this polymer is mainly determined by the degree of dispersion in the polymer matrix.

In this, we sought to develop a process in the material, introducing it into the polymer matrix, which, according to Menezes et al. (2008), much research has been carried out to develop a new class of materials, clay-polymer nanocomposites.

In this way, it was understood that by interspersing Polyurethane in the lamellas of this hydrophobic material, produced and modified, there is the possibility of containing hydrocarbon leaks with the absorption of oil, however, without altering or even reducing its density, a matter of great environmental demand. . Tanobe apud Bara (2011) tested flexible polyurethane foams with different densities as petroleum and marine diesel sorbents with artificial seawater. The tests were carried out in a static and dynamic system where good oil sorption results per gram of sorbent were verified.

Taking into account the research problem that would be the effective intercalation of the particulate with the polymer, aimed at the adsorption of hydrocarbons (with the objective of 97% to 100% of oil removed), and mainly not modifying or reducing the density of the final product.

OBJECTIVE

In this article, the main objective was the development of nanocomposites with a polyurethane polymer matrix interspersed with particulate material.

The focus of the project is the sorption of oil from the effective intercalation of the polymer with the produced and modified material, which we will describe in the next chapter. The main expected results are the containment of hydrocarbon leaks and their reuse.

Specific objectives

- Describe in detail the treatment of particulate matter for its effective hydrophobization, mentioning its characteristics, preparation methodologies, intercalation compounds and characterization techniques;
- Raise the possibility of intercalating polymeric nanocomposites in particulate material, without altering or reducing the density of the final product (ρ sea water 1.025g/ml and ρ fresh water 1.000g/ml);
- Analyze the framing of the properties of polymeric nanocomposites in the produced and modified material , in relation to the formation of foams for sorption of oil leaks;
- Propose the reuse of spilled hydrocarbons by reversing the synthesis of polyurethane acquired using biodegradable castor oil.

THEORETICAL FRAMEWORK

PARTICULATE MATERIAL

The need for continuous improvement in oil spill response instruments is essential, in the legal and technical-scientific dimensions. In Brazil, among the laws that oblige companies to be prepared for accidents are CONAMA Resolution nº. 293/01 (CANTAGALLO; MILANELLI; BRITO, 2007 apud BRASIL, 2001), Law no. 9,966/00 (known as the “oil law”, of April 28, 2000) and Decree no. 4,871/03, of November 6, 2003 (CANTAGALLO; MILANELLI; BRITO, 2007 apud BRASIL, 2000- 2003). In this context, the Environmental Sensitivity to Oil Spills Letters (SAO letters), defined by the federal government, are included, which are an integral part of the Individual Emergency Plans and Area Plans and constitute a fundamental element for guiding response actions. to oil leaks, as they help to outline, in advance, the containment, removal and cleaning strategies recommended for each environment (CANTAGALLO; MILANELLI ; BRITO, 2007 apud BRASIL, 2004).

The particulate material used in this research has unique properties, where it was produced and modified in the laboratory, in sufficient quantities for the tests carried out. With hydrophobic characteristics and adherent to oil, it led to proposals regarding hydrocarbon absorption, flame retardancy and dimensional stability at low loading levels, typically 1-5% by mass (AYRES; ORÉFICE, 2007).

POLYMERIC NANOCOMPOSITES

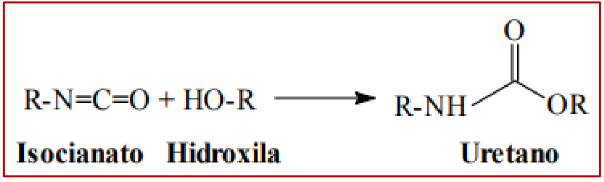
nanocomposites are hybrid materials in which inorganic substances of nanometric dimensions are dispersed in a polymeric matrix. One of the most promising systems is the hybrid based on organic polymers and inorganic clay minerals made up of layered silicates. Layered polymer/silicate nanocomposites are similar to conventional polymer composites in that they use fillers to improve properties not available in unfilled polymers. However, nanocomposites have unique properties when compared to polymers, as they present high mechanical, thermal, barrier properties, flame retardancy and dimensional stability at low loading levels, typically 1-5% by mass (AYRES; ORÉFICE, 2007).

The factors that define the degree of sorption of organic compounds are: hydrophobicity, porosity, molecular structure and volume, and the volume of the surface area of the sorbent material. These factors effectively influence when choosing or determining which materials to use to absorb crude oil (petroleum) or its derivatives. Therefore, the sorbent must be wettable by the hydrophobic compound and not wettable or slightly wettable by water. Sorbent materials must have characteristics such as a large surface area, high porosity, good oleophilic character, as well as good oil retention capacity and ease of application. Polyurethane presents several of these characteristics and is therefore an interesting sorbent for the oil sector. Porous organic polymers are widely used in modern sorption technologies (SILVA JÚNIOR; MULINARI; AYRES; ORÉFICE, 2007).

POLYURETHANES

In 1849, Wurtz published the laboratory synthesis of a substance he called urethane (or urethane), which was the product of the chemical reaction between an isocyanate group and another substance with the hydroxyl group, seen in Figure 1 (VILAR apud CANGEMI; SANTOS; CLARO NETO, 2009).

Figure 1. Synthesis of the Isocyanate group with Hydroxyl group resulting in Urethane

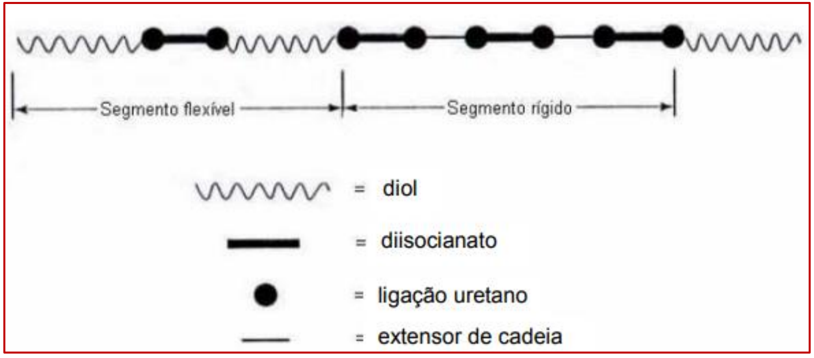


However, this discovery only had commercial application in the 20th century, after Otto Bayer developed the first polyurethane polymers in Germany in the 1940s. In the 1950s, the exact formula for making various PU foams was discovered: flexible for mattresses and padded or rigid materials for technical applications. In the 1960s, the use of chlorofluorocarbons (CFC) as an expanding agent for rigid foams resulted in the widespread use of this material in thermal insulation. In the 1970s, semi-rigid foams coated with thermoplastic materials definitively entered the automobile industry. In the 1980s, there was an increase in the commercial importance of PUs due to the use of injection and reaction molding – RIM (CANGEMI; SANTOS; CLARO NETO, 2009).

Through Vilar apud Cangemi , Santos and Claro Neto (2009), in 1990 onwards, due to concern for the environment, industries renounced CFCs as a propellant, considered harmful to the stratospheric ozone layer. New propellants that do not harm the environment have begun to be tested, such as carbon dioxide (CO_2) or cyclopentane, and another advance in PU production is the constant flammability of the material, which is currently remedied, meeting all standards of fire safety, which have become increasingly strict (EMSLEY apud CANGEMI; SANTOS; CLARO NETO, 2009).

The polyurethane chain consists of an alternating sequence of rigid and flexible segments, thus, the characteristics of a resin depend directly on the nature of the isocyanate and polyol used in the synthesis, and can be prepared for specific applications by varying parameters such as: content of NCO/OH, type of isocyanate, chemical structure, molar mass and functionality of the polyol, shown in Figure 2 (VERONESE, 2009).

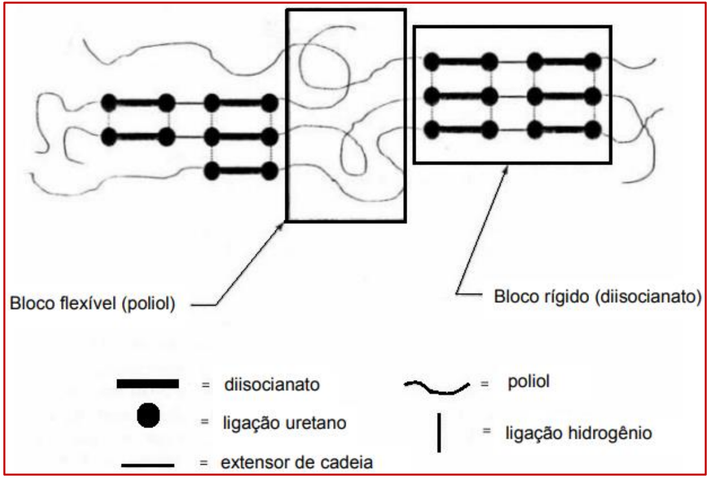
Figure 2. Structure of the Polyurethane chain.



Source: Veronese, 2009.

In the PU chain, the flexible segments are related to the polyol, with their flexibility being greater the greater the molar mass of the polyol, while the rigid segments are related to the isocyanate, with this graphical representation of the microdomains in Figure 3. Thus, the content of flexible and rigid segments directly influences the physical, mechanical and adhesive properties of the material. The rigid segments provide properties such as hardness, mechanical resistance and tenacity to the product, while the flexible segments contribute to the stretching of the material (CANGEMI; SANTOS; CLARO NETO, 2009; VERONESE, 2009; PEREIRA et al., 2004).

Figure 3. Graphical representation of the microdomains of the PU chain.

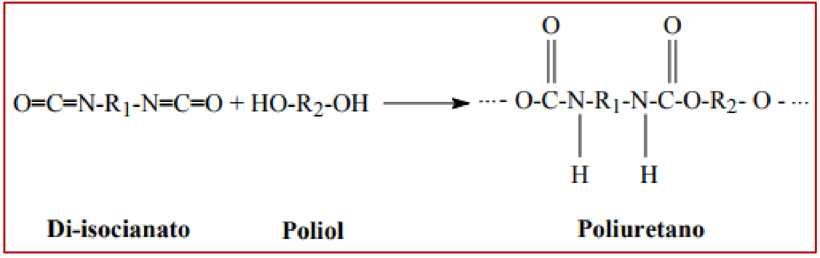


Source: Veronese, 2009.

Synthesis of polyurethane foam

The polymerization of urethanes occurs when a compound with two or more isocyanates reacts with a polyol, that is, a polyfunctional alcohol , below Figure 4 (CANGEMI, 2006).

Figure 4. Synthesis of Diisocyanate and Polyol resulting in PU.

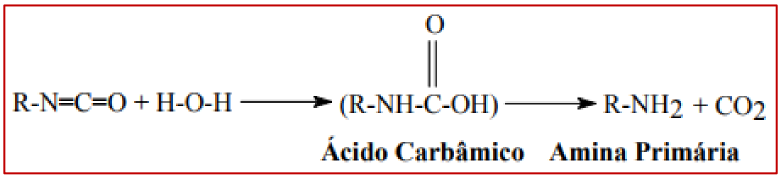


$$O{=}C{=}N\text{-}R_1\text{-}N{=}C{=}O + HO\text{-}R_2\text{-}OH \longrightarrow \cdots O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}\text{-}R_1\text{-}\underset{\underset{H}{|}}{N}\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R_2\text{-}O\cdots$$

Source: Cangemi, 2006.

Cangemi (2006) says that, in addition to the basic isocyanate reaction with hydroxyl, during the polymerization of polyurethanes, parallel reactions involving isocyanate groups can also occur. One of the most common is the reaction of isocyanate with water to form carbamic acid, which in turn decomposes to form primary amine and carbon dioxide (CO_2), which can cause the polymer to expand. Appropriate catalysts and surfactants are used in order to control the cell reaction speed. Follow Figure 5, with the synthesis of a polyurethane foam: the mixture of reagents with the PU formation reaction, which inflates due to the gas released in the reaction medium, and then, Figure 6, with the illustrated representation of the steps of the same synthesis.

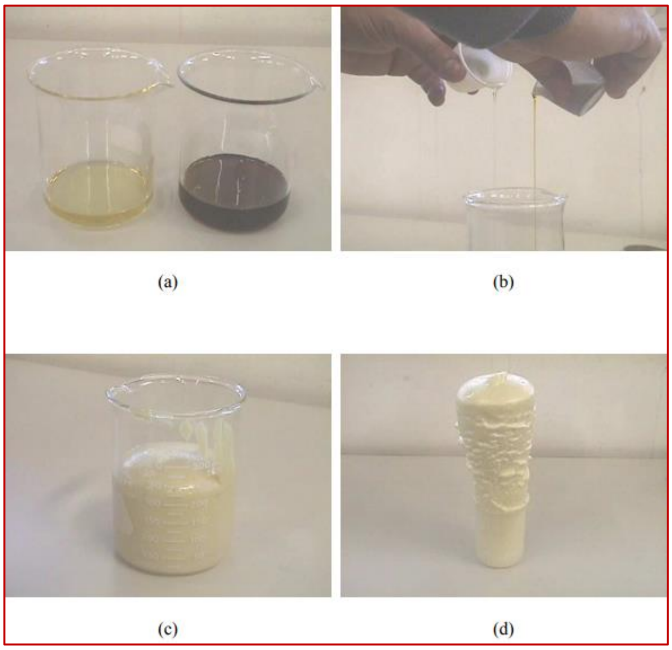
Figure 5. Synthesis of a polyurethane foam: the mixture of reagents with the PU formation reaction, which inflates due to the gas released in the reaction medium.



$$\text{R-N=C=O} + \text{H-O-H} \longrightarrow (\text{R-NH-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH}) \longrightarrow \text{R-NH}_2 + \text{CO}_2$$

Source: Cange mi, 2006.

Figure 6. Steps in the synthesis of polyurethane foam: (a) polyol and prepolymer ; (b) during mixing; (c) beginning of foam formation; (d) finished foam.



Source: Cangemi ; Saints; Claro Neto, 2009.

Oil sorption and retention with PU

According to Gumtz and Meloy apud Pereira et al. (2004) reported on the use of ester-type polyurethane (reused and cross-linked) as an oil sorbent in spills in aquatic systems, where dimensional analysis, mathematical modeling and experimental data were combined to optimize oil sorption rates, through adjustment of model parameters, such as viscosity, selection of different foams and different geometries, in addition, the work showed that flakes with a rectangular parallelepiped shape (½ x ½ x ½) were more efficient in saturation time, with a relationship being found of inverse dependence on the wet perimeter (soaked), and that this time is not directly proportional to the volume of sorbent particles used, where the largest contact area is responsible for the greatest sorption.

There are studies that studied the sorption and oil retention capacity of polypropylene nonwoven fabric and observed that the fiber diameter, sorbent porosity and oil properties are the most important factors in the oil sorption performance of this material (WEI et al. Apud PEREIRA et al., 2004).

Silva Júnior and Mulinari , PU presents several of the characteristics of a sorbent material , due to its large surface area, high porosity, good oleophilic character , as well as good oil retention capacity and ease of application. One of the advantages of macromolecules in relation to mineral sorbents is the possibility of adjusting the geometric structure and its pores.

Tanobe apud Bara (2011) tested flexible polyurethane foams with different densities as petroleum and marine diesel sorbents with artificial seawater. The tests were carried out in a static and dynamic system where good sorption results were verified at around 58.2 g of oil per g of sorbent.

PU foam obtained from Castor Oil

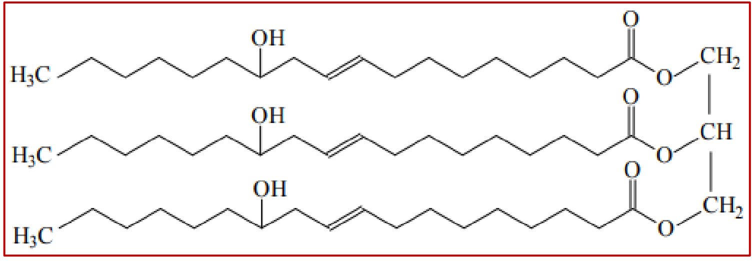
Polymeric composites reinforced by vegetable fibers have been the subject of great academic and industrial interest as they replace, generally with cost and lightness advantages, parts made from conventional polymer composites or even parts made entirely from plastic. Composites derived from vegetable products, both in the matrix and reinforcement, are part of the policy of using renewable, less aggressive and toxic resources, as raw materials of vegetable origin, such as: oils, fibers, polymers, dyes, etc., in addition to coming from renewable sources, they meet the requirements of biodegradability and environmental preservation throughout their life cycle. According to Neto, De Carvalho, Araújo (2007) apud Jayabalan and Lizymol addressed the importance of polyurethanes as biomaterials and Neto, De Carvalho, Araújo (2007) apud Melo and Pasa reported that the presence of ester bonds, hydroxyl groups and unsaturations promote sites reaction in castor oil, which allows the preparation of important industrial derivatives such as polyurethane.

A promising option is biodegradable polymers which, unlike synthetic ones derived from petroleum, undergo biodegradation relatively easily, fully integrating with nature. In recent years, there has been a growing interest, worldwide, in biodegradable polymers, especially when considering the development of new products that cause less environmental impact. Cellulose compounds, poly (vinyl alcohol), polyesters such as poly (lactic acid) (PLA), poly(εcaprolactone) and poly(β-hydroxybutyrate-co-valerate) (PHPV) are some of the examples. For a biodegradable polymer to be used for a certain application, it must degrade in the environment in which it will have its final destination, after disposal, and not necessarily degrade in any other environment (VERONESE, 2009). Studies have demonstrated the biodegradability of PU foam obtained from castor oil, using, for example, the halo zone technique, which makes it possible to evaluate the biodegradation of polymers by certain strains of microorganisms, since the activity of the enzymes produced allows the visualization of transparent halos, which indicate the degradation of polymer particles around the microorganism colonies (CANGEMI; SANTOS; CLARO NETO, 2009).

Another important factor for using porous polymers is the advantage of the possibility of chemical modification of their surface, being castor oil or castor oil, a pale yellow liquid of high viscosity extracted from castor beans, the seed of the castor bean plant (Ricinus communis L.), a very popular plant almost all over the world, found in tropical and subtropical regions, being more abundant in Brazil. From this natural and renewable resource, it is possible to synthesize polyols and prepolymers with different characteristics that, when mixed, give rise to polyurethane. They have great application versatility with properties superior to petroleum-derived polymers. In this way, organic polymers, in addition to being biodegradable, do not harm the environment in the same way that a synthetic polymer does, which makes it economically viable for applications such as resources when containing oil spills (MULINARI; SILVA JÚNIOR).

Due to the presence of rhinoleic acid, seen in Figure 7, castor oil has unique chemical characteristics when compared to most vegetable oils. This acid has the peculiarity of being one of the few natural fatty acids whose chemical structure has three highly reactive functional groups: the hydroxyl group on the 12th carbon, the unsaturation on the 9th carbon and the carbonyl group on the 1st carbon, where, starting from rhinoleic acid, polyester polyol, raw material for the synthesis of polyurethanes, can be obtained (CANGEMI, 2006).

Figure 7. Structure of rhinoleic acid triglyceride .



Source: Cangemi , 2006.

METHODOLOGY

DESCRIPTION OF THE TYPE OF RESEARCH CARRIED OUT

There were two means used for this research: bibliographic, according to Gil and Vergara (2015), this is the investigation carried out using books, articles and other texts of a scientific nature already published as sources. In this type of investigation, predominantly theoretical in nature, the aim is to unveil the relationships between concepts, ideas and characteristics of an object, where various positions on a problem are compared; and experimental, a procedure in which variables are manipulated to evaluate the impact of one on another, normally two groups are separated, where one of them is isolated, while the other is influenced by a certain variable, after a comparison is made between both groups, to evaluate the impact of the variable (GIL; VERGARA, 2015).

Two samples of particulate materials were studied. One being A and the other B, both in their natural state and modified in the laboratory. They were obtained and produced in the PMT Department Laboratory.

METHODS PERFORMED

- Particulate moisture

Moisture was determined in three aliquots of approximately 1.00 g each, dried at 110 ºC for a minimum of 24 hours, using the formula below:

$U(\%) = \frac{Pu - Ps}{Ps}$ x 100 (Wet base moisture) Where Pu = wet weight and Ps = dry weight.

Production of particulate matter

The sample obtained was produced and modified in a laboratory, provided by the PMT Department Laboratory. In the amount of 2.2 kg in powder form, light brown in color, involving processes with low humidity.

Polyurethane Production

The polymerization of urethanes occurs when a compound with two or more isocyanates reacts with a polyol, that is, a polyfunctional alcohol (CANGEMI, 2006). Thus we produce a 1:1, 1:2, 1:3, 1:4 and 1:5 mixture of Isocyanate and Polyol, respectively. Mixing them, with a Hamilton Beach shaker, weighing on the Shimadzu scale (with 3 decimal places). Seeking an optimal polyurethane mixture, the samples were cured for 24 hours. Below is Table 1, showing the quantities of mixture of Polyol and Isocyanate:

Table 1. Polyurethane produced with 10 second agitation Hamilton Beach Agitator.

Equivalences (respectively)	Isocyanate (grams)	Polyol (grams)
1:1	10 g	10 g
1:2	5 g	10 g
1:3	5 g	15 g
1:4	5 g	20g
1:5	5 g	25

Inclusion of particulate matter

The best samples, with high porosity and larger contact area, were 1:1 and 1:2. Therefore, Table 2 follows, with their respective equivalences, quantities in grams of the substances involved and names of the samples:

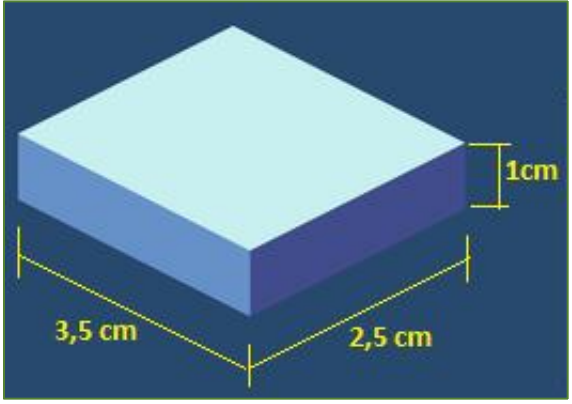
Table 2. Samples A and B and their substance concentrations.

Samples	Equivalences (respectively)	Isocyanate (grams)	Polyol (grams)	Particulate matter (grams)
A	1:1	40 g	40 g	-
TO 1	1:2	25 g	50 g	-
B	1:1	38 g	38 g	4 g
B1	1:2	25 g	46.25 g	3.75g

Cutting samples

With cutting of 3 blocks of each equivalence. The samples were cut, according to Figure 8, after curing for 24 hours, in the pattern 1cm x 2.5cm x 3.5cm, with a total volume of 8.75cm³.

Figure 8. Representation of the cut sample pattern .



Immersion of samples in engine oil

The 3 samples of each respective equivalence were placed in plastic pots with the same standard dimensions, containing 200 ml of crude engine oil, seen in Figure 9, below.

Figure 9. Arrangement of cut samples in engine oil.

As a result, there was a time of 48 hours for them to be removed, with a drain time of 15 seconds before weighing the samples. Using the formula below, to calculate the absorbed oil values:

$$\textbf{Peso de absorção}_{\text{(g)}} = \textbf{Peso}_{\textbf{seco }(g)} - \textbf{Peso}_{\textbf{óleo (g)}}$$

$$\textbf{Porcentagem de absorção}_{\text{(\%)}} = \left(\frac{\textbf{Peso}_{\textbf{óleo}} - \textbf{Peso}_{\textbf{seco}}}{\textbf{Peso}_{\textbf{seco}}}\right) * 100$$

The weighing of the cut samples, carried out on a Shimadzu scale with precision of 3 decimal places, is shown in Table 3:

Table 3. Dry weight (g) of samples after a period of 48 hours.

Samples	Equivalences	Cut samples	Isocyanate (grams)	Polyol (grams)	Particulate matter (grams)	Dry weight (grams)
A	1:1	1	40 g	40 g	-	0.371 g
		two	40 g	40 g	-	0.412 g
		3	40 g	40 g	-	0.391 g
TO 1	1:2	1	25 g	50 g	-	1.044 g
		two	25 g	50 g	-	1.029 g
		3	25 g	50 g	-	1,348 g
B	1:1	1	38 g	38 g	4 g	0.244 g
		two	38 g	38 g	4 g	0.254 g
		3	38 g	38 g	4 g	0.235g
B1	1:2	1	25 g	46.25 g	3.75g	1.055 g
		two	25 g	46.25 g	3.75 g	1.064 g
		3	25 g	46.25g	3.75 g	1.061 g

Cutting samples for the oil/water experiment

With cutting of 3 blocks of each equivalence. The samples were cut, after curing for 24 hours, in the 2cm x 3.5cm x 3.5cm pattern (Figure 10), with a total volume of 24.5cm³ (cuts related to groups A and B of 1:1) and 2cm x 3cm x 3cm (Figure 11) with a total volume of 18cm³ (related to the cuts of groups A and B of 1:2).

Figure 10. Representation of samples A and B.

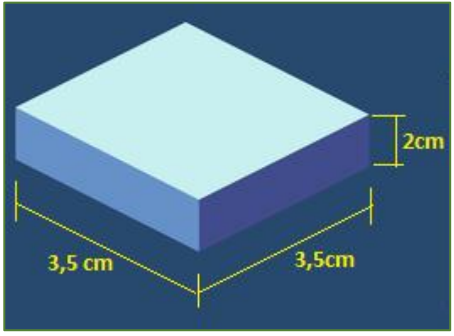
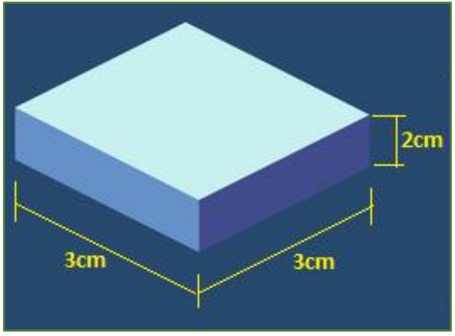


Figure 11. Representation of samples A1 and B1.



Immersion of samples in the heterogeneous oil/water solution

The 4 samples were placed, one in each respective equivalence, in a beaker, containing 400 ml of running water and 100 ml of crude engine oil, that is, with the same heterogeneous water/oil solution (Figures 12 and 13). As a result, there was a time of 24 hours for them to be removed, with a drain time of 15 seconds before weighing the samples, shown in Table 4.

Table 4. Dry weight (g) of samples after 24 hours.

Sample	Equivalence	Isocyanate (grams)	Polyol (grams)	Particulate matter (grams)	Dry weight (grams)
A	1:1	40 g	40 g	-	0.836 g
TO 1	1:2	25 g	50 g	-	1,270 g
B	1:1	38 g	38 g	4 g	0.900 g
B1	1:2	25 g	46.25 g	3.75g	2,024 g

Figure 12. Arrangement of oil and water in the beaker according to samples A and A1.

Figure 13. Arrangement of oil and water in the beaker according to samples B and B1.

RESULTS AND DISCUSSIONS

ENTERING THE PARAMETERS

The problems or effects resulting from oil spills on coastal and marine environments are determined by several factors, defined as the following: chemical composition of the oil and quantity spilled, meteorological and oceanographic conditions (winds, currents and tides), geographical situation and dimensions of the affected area. With changes in the reproductive cycle, the entire food chain is affected, which will consequently cause irreparable damage to the ecosystem (CRAIG et al., 2012; CANTAGALLO; MILANELLI; DIAS-BRITO, 2007).

Analyzing these facts reflected in the world's fauna and flora, we introduced a particulate material, produced in the laboratory, into the mixture of Polyol and Isocyanate for the production of Polyurethane, where this polymer will be used to contain oil spills, through its hydrocarbon absorption properties. and hydrophobic.

RESULTS WE OBTAINED IN THE TWO GROUPS

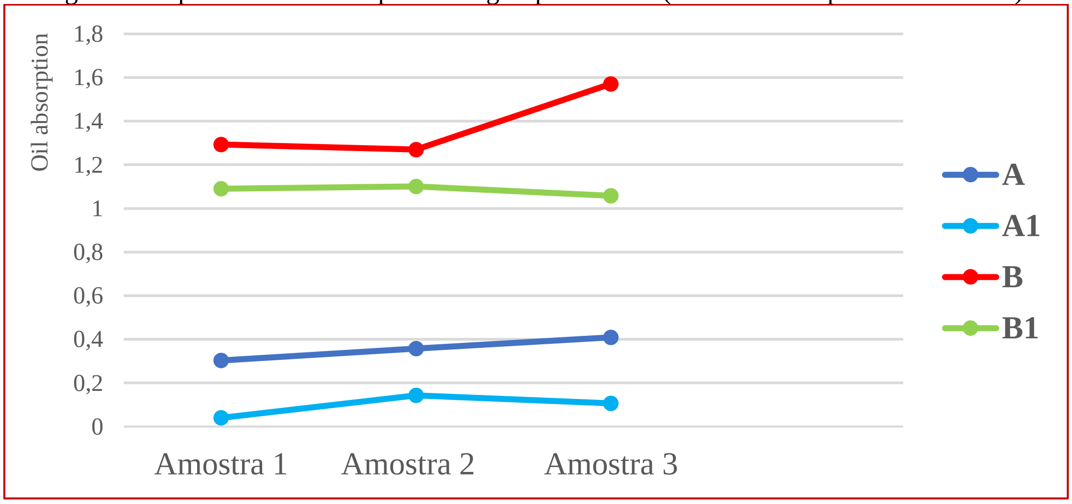
Seeking an optimal polyurethane mixture, with the greatest possible absorption and the smallest amount of material, the samples were cured for 48 hours. Thus, after this period, we found that samples 1:3, 1:4 and 1:5 had very low volume, a sticky appearance and were extremely malleable, unsuitable for the purposes in question. However, the 1:1 and 1:2 equivalences were plausible for a contact area with usable porosity and volume, in addition to the more rigid aspect. Based on the results obtained, we selected samples 1:1 and 1:2 to repeat a new test with engine oil and also to include particulate matter. Below is Table 5 of the optimal branched cut samples, their dry weights (grams) and their weight after immersion in oil (grams):

Table 5. Weight of each sample with oil (g) absorbed.

Sample	Equivalence	Cut samples	Isocyanate	Polyol	Particulate matter	Dry weight	Oil weight
A	1:1	1	40 g	40 g	-	0.371 g	0.879 g
		two	40 g	40 g	-	0.412 g	1.011 g
		3	40 g	40 g	-	0.391 g	1.077 g
TO 1	1:2	1	25 g	50 g	-	1.044 g	1.114 g
		two	25 g	50 g	-	1.029 g	1,269 g
		3	25 g	50 g	-	1,168g	1,348 g
B	1:1	1	38 g	38 g	4 g	0.244 g	2,412 g
		two	38 g	38 g	4 g	0.254 g	2,382 g
		3	38 g	38 g	4 g	0.235g	2,868g
B1	1:2	1	25 g	46.25g	3.75g	1.055 g	2,883g
		two	25 g	46.25g	3.75g	1.064 g	2.909g
		3	25 g	46.25g	3.75 g	1.061 g	2.835 g

In table 5, considering the density of the crude engine oil, and its weight in 200 ml of 167.549 grams, where there were the respective absorptions of the samples of the total weight of the oil, leading to the optimizations of the samples in group B and B1 (where there is particulate matter) of better use. We observe this phenomenon in the graph below (Figure 14):

Figure 14. Optimization of samples from group B and B1 (where there is particulate matter).



Then, we made 4 more samples, in the same groups A, A1, B and B1, with the same concentrations of substances, however, with different dimensions from the first experiment, where the absorbed oil was weighed and the samples did not sink. in the liquid, where they maintained a lower density than water, they only absorbed the spill. Below, Table 6 with the weights of oil absorbed by them:

Table 6. Amount of oil absorbed (g), highlighting samples B and B1.

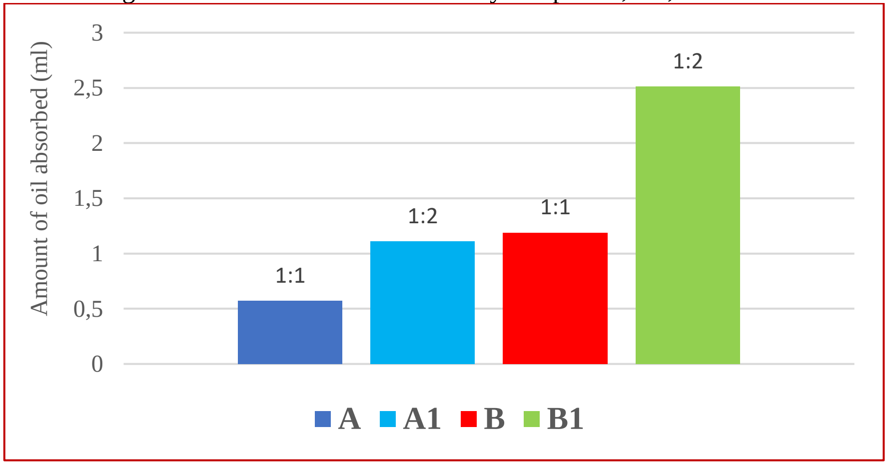
Sample	Equivalence	Isocyanate (grams)	Polyol (grams)	Particulate matter (grams)	Dry weight (grams)	Oil weight (grams)
A	1:1	40 g	40 g	-	0.836 g	1,311 g
TO 1	1:2	25 g	50 g	-	1,270 g	2.183g
B	1:1	38 g	38 g	4 g	0.900g	1.879 g
B1	1:2	25 g	46.25g	3.75 g	2,024 g	4.092 g

Taking into account the amount of oil absorbed by the samples, and the weight of the engine oil in 100 ml of 82.380 grams, we obtained significant amounts of absorption for the samples that contained particulate matter, B and B1, as we can see in the following graph. Figure 15, through calculation shown below, using the values in Table 6:

$$\mathbf{Q_{oa}} = \frac{\mathbf{Q_{óleo}} * \left(\frac{\mathbf{P_{óleo}}}{\mathbf{P_s}}\right)}{\mathbf{T_{óleo}}}$$

Q_{oa}: Quantidade de óleo absorvido (ml)
$T_{óleo}$: Total de óleo no béquer (g)
$Q_{óleo}$: Quantidade de óleo (ml)
P_s: Peso seco (g)
$P_{óleo}$: Peso óleo (g)

Figure 15. Amount of oil absorbed by samples A, A1, B and B1.



Considering the percentage of oil absorption in relation to the size of the foam, we obtain the following values that can be notoriously related to samples B and B1 again, with very high absorption rates per contact area, using the calculation below and shown in Table 7:

$$\textbf{Porcentagem de absorção}_{(\%)} = \left(\frac{\mathbf{Peso_{óleo}} - \mathbf{Peso_{seco}}}{\mathbf{Peso_{seco}}}\right) * 100$$

Table 7. Calculated percentage of oil absorption highlighting samples B and B1.

Samples	Equivalences	Dry weight (grams)	Oil weight (grams)	Calculated percentage (%)
A	1:1	0.836 g	1,311 g	56.81%
TO 1	1:2	1,270 g	2.183 g	71.89%
B	1:1	0.900g	1.879g	108.7%
B1	1:2	2,024 g	4.092 g	101.92%

Below, Table 8, referring to the relationship between the amount of oil absorbed and its respective volume of samples, which are different, thus changing their amount in grams absorbed per g/cm ^{3} .

Using the equation below, we can calculate the amount of crude oil absorbed for each 1 cm ^{3} of volume, where we highlight sample A1, due to its absorption performance slightly above sample B, in relation to its smaller volume. Considering that samples containing 1:2 equivalences are much more usable than 1:1 ones, and those containing particulate material intensify the objective of absorbing leaks, therefore, all 1:2 samples that homogenized particulate matter, have an optimized solution for the appropriate purposes.

$$\mathbf{Q}_a = \frac{\mathbf{P}_{\text{óleo}} - \mathbf{P}_s}{V_{am}}$$

Q$_{\mathbf{a}}$: Quantidade absorvido (g) por cm^3
P$_{\mathbf{s}}$: Peso seco (g)
P$_{\mathbf{óleo}}$: Peso óleo (g)
V$_{\mathbf{am}}$: Volume da amostra

Table 8. Quantity in grams of oil absorbed per g/cm ^{3} .

Sample	Equivalence	Dry weight (grams)	Oil weight (grams)	Absorbed (grams)	Volume (^{cm3})	Quantity (g) absorbed per cm ^{3}
A	1:1	0.836 g	1,311 g	0.475g	24.5 cm^3	0.0194 g/ ^{cm3}
TO 1	1:2	1,270 g	2.183 g	0.913 g	18 cm^3	0.05072 g/ ^{cm3}
B	1:1	0.900 g	1.879 g	0.979g	24.5 cm^3	0.03996 g/ ^{cm3}
B1	1:2	2.024 g	4.092 g	2,068 g	18 cm^3	0.1148 g/ ^{cm3}

We observed in the following images that samples A1 and B1 apparently absorbed more oil than the others, maintaining their density lower than water.

Figura 16. Amostras A e A1 após o período de 24 horas.

Figura 17. Amostras B e B1 após o período de 24 horas.

ECONOMIC FEASIBILITY OF THE MATERIALS INVOLVED

The materials involved in the tests carried out were low cost (Table 9), which resulted in great opportunities for industrial branches that use some type of oily fluid in their demands, optimizing their processes aimed at sustainability.

Table 9. Economic viability of the materials used.

Material	Price (R$)	Amount
Polyol (B)	R$ 35.00	1 kg
Isocyanate (A)	R$ 35.00	1 kg
Particulate matter	-	-

Table 10 shows the equivalent price used for a spill of 100 ml of hydrocarbons:

Table 10. Yield of materials by values (R$) + Particulate material.

Sample	Isocyanate (grams)	Polyol (grams)	Particulate matter (grams)	Sample volume (cm³)	Percentage absorbed in oil (%)	Equivalent price (R$)
B	38 g	38 g	4 g	24.5 cm³	108.7%	2.66+4g MP
B1	25 g	46.25g	3.75 g	18 cm³	101.92%	2.50+3.75g MP

FINAL CONSIDERATIONS

Petroleum is a natural compound that has high toxicity. This pollution, caused by maritime transport accidents, annually contributes 10% to the global pollution of the oceans, where 600 thousand tons of crude oil are spilled with serious economic and environmental consequences.

To minimize damage caused by oil spills, several cleaning methods are used. In this article, the main objective was the development of nanocomposites with a polyurethane polymer matrix interspersed with produced and modified particulate material. To obtain the nanocomposites, treatments were carried out on the particulate for hydrophobization and the influence of polar compatibilizers on the mechanical properties was evaluated, with the aim of absorbing oil leaks. The tests carried out in groups A and B, we obtained, in the samples with particulate matter, large proportions absorbed, where those containing equivalences of 1:2 were more usable than those of 1:1, and those containing particulate material, they intensified the absorption objective, therefore, all 1:2 samples that homogenized the particulate had an optimized solution for the appropriate purposes.

In samples B and B1, there was an absorption of 108.7% in a volume of 24.5 cm³ and 101.92% in 18 cm³, respectively, that is, group B in the 1:1 equivalence absorbed its total weight in oil with a volume of 22.54 cm³ of material, and 1:2, absorbed with a volume of only 17.66

cm³. In addition to these collected data, we observed the phenomenon of densities between oil and water, where there was no decantation of the materials, as the density of the samples after final absorption was not greater than that of water and the particulates only absorbed the oil, repelling water (hydrophobization). It was found that the greater the surface contact area of the samples in the oil stains, the greater their absorption speed.

In short, the economic viability of applying this material in industrial branches that use some type of oily fluid in their demands, optimizing their processes aimed at sustainability, would be low cost, through calculations of the proportion and yield of the materials involved, and of great value for the environment.

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