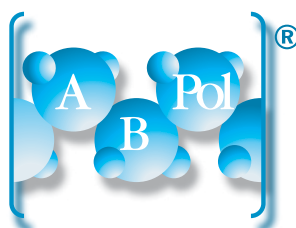


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HYDROPHOBIC AND FLEXIBLE POLYURETHANE FOAMS REINFORCED WITH MICROCRYSTALLINE CELLULOSE FIBERS FOR OIL SPILL CLEAN UP

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Abstract – In this study, open cell polyurethane (PU) foams with the addition of microcrystalline cellulose (MCC) were formulated and chemically modified with organosilane to be used as an absorbent system for oil spill cleanup in water. The influence of MCC concentration on mechanical properties and chemical treatment with organosilane were evaluated. In addition, the sorbents were characterized based on their surface modification and sorption capacity. The main results indicated that the surface treatment on the solid fraction of the foams was effective, pointed out by the contact angle, thus increasing the hydrophobicity of the samples. As the MCC content increases in the composition, the compressive strength tends to be higher and the thickness of the organosilane layer increases, due to the increased roughness of the PU higher the density, which negatively affects the sorption capacity of the samples. However, the results obtained in the samples showed hydrophobic and oleophilic character.

Keywords: Polyurethane foams. Nanocellulose. Oil spill.

Introduction

Oil contamination has been an environmental problem since the beginning of its large-scale extraction and use. The total global volume of tanker oil spill in the year of 2022 was approximately 15,000 tonnes, according to ITOPF (International Tanker Owners Pollution Federation) [1]. Oil spills usually occur during the extraction and transportation process, causing economic, environmental, and social impacts. Oil spilled into water is spread immediately. Its volatile components can undergo evaporation and contaminate the air. Simultaneously, the oil can be emulsified in oil-water, making it difficult to extract and remove [2].

To minimize the impacts caused by oil spills, some techniques for water-oil separation have been studied, such as: flotation, centrifugation, adsorption, gravimetric separation, electrochemical, and biodegradation. The sorption process has been highlighted as a technique for treating industrial effluents and an efficient and economical alternative for remediating areas affected by oil spills. In this process, there are simultaneous involvement of absorption, adsorption, and desorption processes, where in absorption the oil is accumulated within the system and in adsorption the oil is retained on the surface of the solid part of the sorbent.[3]

Polyurethane (PU) foams are formed by a polymerization reaction between a di-isocyanate or tri-isocyanate and a hydroxylated (polyol), generating a polyurethane chain. The PU's application can include upholstery to reinforced materials with sorption capacity. Among the properties of the foams, when produced with high open cell concentrations, viscoelastic properties allow sorption and desorption of oils. The development of the oleophilic and hydrophobic properties are related to sorption and desorption, by the use of certain reagents as organosilanes for modifications during the preparation of the foams [4].

Microcrystalline cellulose (MCC) is generated from purified and partially depolymerized cellulose. MCC can be produced from a lot of cellulosic sources, but cotton and wood are usually the main sources for the fabrication. The most common applications of MCC include a binder and filler in

food, medical tablets, and especially as a reinforcement agent in the development of polymer composites. MCC is considered as a potential reinforcement to turn the composites into a biodegradable material and to reduce the costs, meanwhile keeping the desired properties [5].

In view of the difficulty involved to clean up oil spills in the water sources around the planet, urge the need to create alternative options that are capable of sorption the oil. With the knowledge that polyurethane foams can acquire hydrophobic and oleophilic properties based on the addition of organosilane chemical treatment [6]. Also, when microcrystalline cellulose is added to obtain the composite, there is the goal to improve the mechanical properties.

Experimental

Materials

For the development of PU foams, Voranol WL 4010 polyol and Voranate™ T-80 TDI toluene diisocyanate (TDI), supplied by Dow Brasil Sudeste Industrial Ltda., were used. The amine catalyst (Dabco® 2033 Catalyst) was supplied by Air Products, and the organometallic tin octanoate catalyst (Kosmos® 29) was supplied by Evonik Industries. The surfactant, commercially known as Nix silicone L-595, was supplied by Momentive Performance Materials Inc. Methylene chloride, a deionizing agent supplied by Brasil Sudeste Industrial Ltda, and deionized water were used. Microcrystalline cellulose (MCC), Sigmacell Type 20 grade, particle size approximately 20 µm, code S3504, was supplied by Sigma-Aldrich S.A. For the hydrophobic coating of PU foams, triethoxyvinylsilane (TEVS) (supplier code: 175560) and tetraethoxysilane (TEOS) (supplier code: 13190) were used, both supplied by Sigma-Aldrich. The oils used for the sorption tests were as follows: Ipiranga SAE 5W30 oil (lubricating motor oil) with a density of 0.86 g.cm⁻³ at 20 °C and a kinematic viscosity of 70 cSt at 40 °C, soybean oil (vegetable oil-cooking oil) with a density of 0.91 g.cm⁻³ at 20°C and a kinematic viscosity of 32 cSt at 40 °C, kerosene (fuel oil) with a density of 0.78 g.cm⁻³ at 20 °C and kinematic viscosity of 2.2 (max) cSt at 40°C.

Methods

The PU foams formulated with MCC concentration, expressed in parts per hundred polyols (pphp). Four levels of MCC were used in a standard composition of flexible PU foams, considering a theoretical density of 10 kg.m⁻³. The formula consisted in 100 pphp of methylene, 80 pphp of diisocyanate, 6 pphp of water, 0.3 of amine, 3.3 of silicone, 0.5 of octoate, and 22 of chloride. The amounts of MCC varied according to the sample, being for PU 1 without the addition of MCC, PU.C10 with 10 pphp, PU.C20 with 20 pphp, PU.C30 with 30 pphp, and PU.C40 with 40 pphp.

PU foams were produced by the batch method using a Fisaton 715 propeller mixer with a rotational speed of 2500 rpm. Initially, water, amine, silicone, and different concentrations of MCC were added to the polyol and stirred for 80 s. Then, tin octanoate was added and mixed for 40 to 50 s. Thereafter, TDI and chloride were added to the blend with vigorous stirring for approximately 10 to 15 s and then the mixture was poured into a mold for free expansion, to form the foam. Expansion time was approximately 1 min. The foam was cured for 48 h in a controlled temperature of 23 °C. The treatment for PU foam hydrophobization was carried out using an organosilane-based coating. At first, organosilane hydrolysis was carried out by a solution of water:alcohol (70:30) with 1% (mass) of organosilane TEVS and 1% (mass) of TEOS. Acetic acid (approximately 10 mL for each liter of solution) was added dropwise to stabilize the pH of the solution to 4.5. The solution was stirred for 2 h. After this, foam samples (25 x 25 x 25 mm³) were immersed in the solution and stirred slowly with a magnetic bar stirrer for 4 h. Later, the foams were removed from the solution, the excess liquid was drained, and the samples were dried (with the occurrence of concomitant organosilane curing) at 120 °C for 4 h.

Characterization

To perform the analysis of the density of the samples, five specimens, each sized 25 x 25 x 25 mm³, were used per sample, and the densities of the foams were calculated using Eq. 1 as described in ASTM D3574-11.

$$\rho_f = \frac{m_f}{v_f} \times 10^6 \quad (1)$$

Where ρ_f is the foam density (kg.m⁻³), m_f is the mass (g) and v_f is the volume (mm³) of the specimen, which was calculated from the measurement with a caliper. Sample morphology was evaluated by field emission scanning electron microscopy (FEG-SEM) using a Shimadzu device (Superscan SS-550 model) and a Tescan microscope (model Mira3). The test was performed on five specimens, all samples were precoated with gold (Au) and 15 kV voltage was used. The foam area was observed vertically, in the direction of expansion of the samples. The compressive strength tests of the PU foams were carried out in a universal testing equipment EMIC model DL 2000 with specimens measuring 50 x 50 x 25 mm³ and compression speed of 50 mm.min⁻¹. The tension required to reduce the thickness of the specimen by up to 80% of its initial thickness was evaluated, according to ASTM D3574-11. The hydrophobicity of a material can be evaluated by the contact angle of a drop of water deposited on its surface [7]. When this contact angle is greater than 90° it is convenient to define it as hydrophobic

Results and Discussion

Fig. 2 shows the results of bulk density of PU foams with different content of MCC and after treatment with organosilane, where the samples containing organosilane represented by PU.S. Increasing the content of MCC causes an increase in the bulk density of the samples, a result already expected, since cellulose is an additional composition. It is also necessary to consider that, with the addition of cellulose to polyol, there is a proportional increase in the viscosity of this phase, which impacts the restriction of the expansion capacity of the foam, coupled with the fact that cellulose fibers occupy the empty spaces within the polyurethane molecules and can promote an increase in foam density [8].

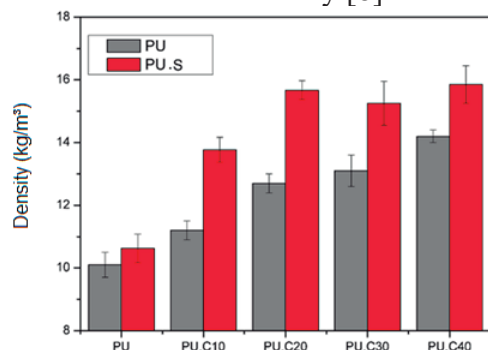


Figure 2: Density of PU samples with different MC contents and with (PU. S) and without (PU) organosilane-based hydrophobic treatment.

It is also observed that after the hydrophobic chemical treatment, all samples showed higher density values in relation to their analogues without the treatment, a fact associated with the incorporation of organosilane layers on the surface of the solid fraction of the foam. It is noteworthy that, compared to the pure PU sample (that had approximate increase of 7%), and the samples containing MCC, after chemical treatment, showed a more expressive increase in density, with an increase of 27% for PU.C10, 29% for PU.C20, 20% for PU.C30 and 14% for PU.C40. The increase in density of the foams with MCC may be associated with the higher surface roughness of the solid fraction, which may have caused the formation of thicker layers of organosilane on the surface of the foam solid fraction.

Fig. 4 presents the micrographs obtained by SEM of the PU samples with different levels of MC and with and without hydrophobic treatment. It is possible to observe that, after the treatment with

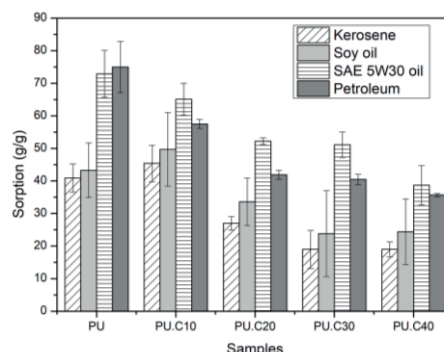


Figure 3: Static sorption capacity of PU foams with different cellulose contents.

organosilane (a), the samples presented a rigid coating layer, in which during the cutting of the samples, it was fragmented, exposing more evident the organosilane coating layer, as seen in the images (b) and (c). The pure PU (a), before chemical treatment presents a smoother surface, which may contribute negatively to the adhesion of the organosilane on the surface, and under mechanical stress, deteriorate and can be removed more easily. The presence of MCC at figure (d) and (e), thicker layers of organosilane were observed, and no significant tricks and detachments were found, comparatively to the PU and as observed in the micrographs.

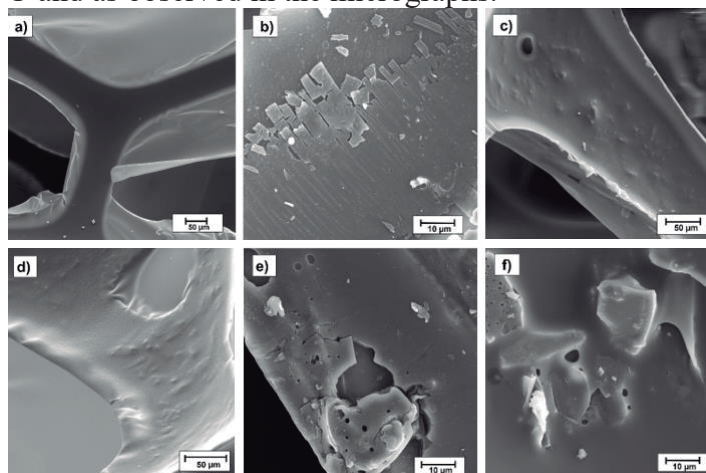


Figure 4: SEM microscopy of (a) untreated pure PU, (b) pure PU with organosilane, (c) and (d) untreated PU.C40 and (e) and (f) PU.C40 with organosilane.

The hydrophobic character of the PU foams was determined by measuring the contact angle of their previously pressed foam obtained by a mechanical press surface, with water (polar liquid), which is defined as the angle between the solid surface and the tangent line of the liquid phase at the solid phase interface. The contact angle obtained in all samples silanized with the liquid of maximum surface tension was greater than 110° at time $t=0$, indicating a surface with hydrophobic characteristics. The cellulose-reinforced foams showed a slight increase in the angle, due to the greater interaction of the foam surface with the organosilane and the stability that the addition of cellulose brings to the foam. The contact angle of the water with the substrate surface is related to the functional groups present on the solid surfaces of the PU foam. After 5 min of the test, the water droplet measurements on the silanized PU foam showed a slight decrease in the contact angle compared to $t=0$, probably due to the migration of water into the compensated porous structure [9]. The foam without the chemical treatment showed higher water migration into the foam after 5 minutes.

According to the results all the samples treated with the organosilane showed hydrophobic character. The larger the contact angle, considering water as the fluid, the greater the selectivity and the interaction of the foam with the oil, enabling greater efficiency in oil removal, as well as playing an important step in the beginning of the oil sorption process [10]. Fig. 4 presents the static sorption capacity of PU foams with different cellulose contents, coated with organosilane and evaluating the influence of different types of oils. Firstly, a higher sorption capacity is observed for PU foams with more viscous oils. This phenomenon is mainly attributed to oil desorption after removal from the system. More viscous oils have greater difficulty in flowing out of the foam and require longer desorption times, thus a greater amount of oil is retained inside the foam. As the adopted desorption time was 30 s for all samples, it was expected that the foams would have a higher sorption capacity for more viscous oils. The sorption process is directly influenced by the viscosity of the oil, and oils with high viscosity have an easier anchorage and retention in porous polymer systems compared to less viscous oils [11]

In a comparative analysis between the samples studied, with increasing cellulose content in the PU foams there is a tendency for the sorption capacity of all the oils to decrease. This reduction is

directly associated with the raise in density of the foams with increasing MCC content since the morphology of the cell structure of the foams was similar. Duong & Burford [12] studied the effect of sorption capacity of PU foams by evaluating the density of PU foams, the viscosities of oils and temperature on the sorption behavior of oils in different PU foams. They reported that the sorption capacity increases significantly with decreasing density of the foams, due to the raise in the number of open cells, cell morphology and, that this behavior also depends on the oil viscosity as well as the oil temperature (test temperature). The data presented in Fig. 3 show the sorption capacity in grams of oil per gram of sorbent, i.e., as the foam density increases, there is a tendency for the sorption capacity to decrease, because the increase in sample mass (constant volume) is directly related to the sorption capacity of the foam.

Conclusions

The development of the polyurethane foams reinforced with microcrystalline cellulose chemically modified with organosilane was succeed as an absorbent system, as it is possible to visualize in the results of the contact angle test and in the sorption capacity of the samples. Creating a mechanism that meets part of the need for oil-in-water removal. It was also observed that the content of MCC increases the compressive strength, and the thickness of the foams. Although, the use of MCC in the composition is responsible for a higher density which negatively affects the sorption capacity of the samples, that was seen during the characterization stage. Nevertheless, the samples obtained showed hydrophobic and oleophilic character designed for the research conducted. Turning the use of microcrystalline in polymeric foams attractive, especially attached to the relatively low-cost and lower density when compared to the inorganic fillers conventionally used.

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