Study of the functioning time of aluminosilicates for the formation of hydrophobic surfaces

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Abstract. The modification of surfaces for the creation of hydrophobic materials has grown in recent years due to the wettability properties that can be obtained, in this process the chemical environment of the surface is modified. In the case of aluminosilicates, surfaces are generally considered polar, so it is of great interest to create hydrophobic surfaces through the functionalization process, obtaining low wettability; hydrophobicity is determined when a surface comes in contact with a drop of an organic component and contact angles greater than 90° are obtained. The present work describes the results of the study of the contact time between aluminosilicate surfaces and a siloxane as a functionalizing agent, to determine the optimal time in which hydrophobic surfaces are obtained. The results show that after 3 hours of contact between the surface and the functionalizing agent, a surface with a contact angle of 106° is generated, due to the heterogeneous surface of the functionalizing agent that is generated in the aluminosilicate because of the polymerization reaction.

1. Introduction
Aluminosilicates are known as inorganic materials and are located spatially by an alternate network of silicates (SiO₄) and aluminate (AlO₄) [1,2], due to the crystalline structure and the properties that these materials present, they are widely used in the industry for various applications (aviation, electronic construction) [3,4]. Within these properties is the porosity, which depending on the origin of the aluminosilicate and the synthesis treatment that is performed, may be greater, generating an increase in the hydrophilicity of the material, which makes them very useful for applications where exchange or wettability are of great importance [5,6]. However, in the latter years it has been wanted to implement these materials in fields where their affinity with water is unwanted, which is why it is vitally important to modify the surface of these turning them into hydrophobic surfaces.

The hydrophobic effect is the tendency of non-polar molecules to remain bound when they are in aqueous solutions [7]. When the aqueous solution comes into contact with a surface that has non-polar groups, the non-polar molecules of the solution tend to adhere to the surface, generating the adsorption phenomenon; this is why hydrophobic substances, such as hydrocarbons, tend to adhere to non-polar surfaces. Hydrophobic surfaces are characterized by having low wettability, which occurs when the surfaces that come into contact with an organic component, have contact angles greater than 90° [8], to this purpose, chemical functionalization processes are normally used to the industry [9,10].

The chemical functionalization is one of the most common processes in the industry to modify the characteristics of the materials. In this process, a functionalizing agent of apolar character is...
anchored to the surface, providing the necessary apolarity to the surface so that it can retain hydrophilic substances [11-13], that is how in recent years they have been chosen to generate greener processes in order to reduce production costs and carbon footprint. For this reason, this work evaluates the process of chemical functionalization with an apolar agent of highly hydrophobic surfaces at different contact hours, in order to obtain a good hydrophobicity in the shortest possible time.

2. Materials and methods

2.1. Preparation of aluminosilicate material

We worked on nine specimens of an aluminosilicate previously obtained in the “Laboratorio de Química Orgánica y Biomolecular (LQOBio)” which has high hydrophobicity, the material is molded into a cube shape to later perform the functionalization.

The functionalization process occurs in two stages, in the first one the cubes will be stirred in a solution of piranha (3:1) of concentrated sulfuric acid (95% - 97%) and a solution of 35% hydrogen peroxide for 5 minutes (The solution should be prepared at the time when the stirring of the ceramic units will be carried out, in an extraction booth with the appropriate safety fittings. For the mixture, borosilicate glass material will be used, and the peroxide will be added slowly to the acid. (Caution! very exothermic reaction, with a tendency to boil.), to obtain a surface of silanol groups. Following this, a thorough washing with deionized water will be carried out to eliminate any remaining piranha solution. Acetone will then be added to remove water and facilitate the drying process. The aluminosilicates will then be placed in a drying oven, to be subsequently immersed in a solution of hexamethyldisiloxane (Caution! easily flammable substance) that will act as a functionalizing agent and will create the groups of tetraethoxysiloxane). This treatment acts to change the surface of the silane groups. The functionalized aluminosilicates will be washed with toluene and then air dried for 24 hours.

2.2. Functionalization time

Tests were carried out to study the contact time to monitor the formation of the hydrophobic surface, for this, assays were carried out at different contact hours between an aluminosilicate and 1 ml of hexamethyldisiloxane, evaluating the contact angles every 3 hours for 24 hours.

2.3. Characterization

Microstructure of aluminosilicate and its functionalization was evaluated by SEM using the field emission scanning electron microscope Tescan Mira3 of the “Universidad Pontificia Bolivariana”. With thermal gravimetric analysis (TGA) technique and differential scanning calorimetry (DCS), the thermal stability of the surface modification of the aluminosilicate and of the material without functionalization was studied, under temperature conditions from 30 °C to 1000 °C in a nitrogen atmosphere, at a heating rate of 5 K/min on an SDT-Q600 (TA Instruments). Contact angle measurement was performed to evaluate the wettability of the surfaces using the Dataphysics OCA E15 equipment. For this, using the sessile method, a drop of distilled water of 2 μL was placed on the surface of the aluminosilicate by slow injection, after 10 seconds the contact angle between the surface and the drop, was taken.

3. Results and discussion

3.1. Analysis by scanning electron microscopy

Scanning electron microscopy was taken to the surface of the aluminosilicates without treatment as seen in Figure 1(a) and after the six-hour functionalization process as shown in Figure 1(b), the cubes were covered with a carbon layer to confer conductivity to the sample. In Figure 1(a) it is observed that the aluminosilicate has a homogeneous surface with some porosities which is indicative that the aluminosilicate network (Si-O-Al) was properly formed during the process of synthesis of the material, in turn the porosity it can be attributed to the presence of organic matter that was initially in the precursor
and which after the synthesis process due to temperature disappears, leaving spaces in the network that are observed as pores, which are favorable for the removal processes.

In Figure 1(b), the aluminosilicate is observed after 6 hours of contact with the functionalizing agent, with a significant change in the surface of the material, this new surface is not found homogeneously in the micrograph, which indicates that the functionalizing agent accumulates and begins to branch into specific areas of the material as indicated by the authors, the process of functionalization is given by the displacement of hydroxyl groups that are on the surface, and that in aluminosilicates these groups would meet united in the network due to the presence of Si and Al, in turn it can be inferred by the measure of contact angle, that the longer the contact time the surface becomes more homogeneous, causing the contact angles to decrease.

3.2. Thermal gravimetric and differential scanning calorimetry analysis
Thermograms and differential scanning calorimetry was taken to the surface of the aluminosilicates without treatment (Figure 2(a)) and after six-hour of functionalization process (Figure 2(b)). TGA of aluminosilicate shows a great stability of the material when it is subjected to high temperatures, presenting a loss of mass of less than 3%, which, according to DSC line, indicates a physical transformation [14], which can be attributed to water molecules, that are found both superficially and interstitially, in the structure [15].

In Figure 2(b), the TGA and DSC of functionalized aluminosilicate are shown. TGA shows that once the polymerization process of the functionalizing agent is carried out, the material shows low stability when it is subjected to high temperatures showing 3 large losses of mass. The first loss of mass occurs in the range of 30 °C - 125 °C, with a value of 6.9%, which, based on the DSC data, corresponds to a physical transformation [14] attributed to the loss of water molecules that found on the surface of the material [15]; followed by this, a loss of mass of 11.8% it is evident in the range of 125 °C - 400 °C, temperature range at which the functionalizing agent, in according to the DSC curve, presents a physical transformation, hinting at the decomposition of chains of this agent. There is a third loss of mass of 11.5% in the range of 400 °C - 600 °C, which corresponds to the decomposition of longer or more complex chains of functionalizing agent, product of the polycondensation process, these chains are also observed by scanning electron microscopy (Figure 1(b)) [16], so this mass losses, as the previous one, is due also to a physical transformation. Finally, in the range of 600 °C - 1000 °C the loss of mass is less than 3% and the DSC shows that a chemical transformation occurs, which may be due to the phase transition process of the functionalizing agent chain.

Figure 1. (a) Aluminosilicate. (b) functionalized aluminosilicate.
3.3. Analysis by contact angle

The contact angle measurements were taken for 9 surfaces, the first one being the non-functionalized aluminosilicate, with this surface it was not possible to have a measure of the angle generated by the drop when touching the surface due to the hydrophilic nature of it, which at the moment the contact was generated sipped the drop. For the remaining 8 surfaces the measurement of contact angle was successful, managing to have the image after 10 seconds of contact between the surface and the water.

Figure 3 shows the aluminosilicate specimens images and contact angles obtained for each of the surfaces as the contact time with the functionalizing agent increased, this being increments of 3 hours for 24 hours. It is evidenced that the greatest contact angle was obtained at 3 hours being 106° (Figure 3(a)) and as the functionalization time increases, it is observed that there is a decrease, being 104° in the first 15 hours (Figure 3(b) to Figure 3(e)) followed by a stabilization at 97° at 18 remaining until 24 (Figures 3(f) to Figure 3(h)). These decreases in the contact angle may be due to the non-growth of the apolar chain of the functionalizing agent generating the respective ramifications, but to the homogeneous
distribution that can change on the surface; in turn it can be attributed to surface chemistry because when the measurement is made, specifically of the type of surface, a space is generated between the rough structure and the drop, in which air is trapped and the pressure generated by this air in the drop, the interface will generate a measurement with a greater or lesser contact angle [17], however it can be verified that by this process hydrophobic surfaces are obtained and, in turn, the fact that a functionalized surface is obtained in such short times compared to what the literature reports (24 hours) is of great importance, since it reduces production costs and times of obtaining said materials.

4. Conclusion
The functionalization of aluminosilicates through chemical treatments to obtain hydrophobic surfaces is successful, taking into account the shorter contact times between the functionalizing agent and the surface, the greater the contact angle which attributes greater hydrophobicity. The best hydrophobic surface was obtained at 3 hours with a contact angle of 106°.

The functionalization process showed hydrophobic surfaces which, as the contact time between the functionalizing agent and the surface increased, decreased the contact angle. By means of scanning electron microscopy, the structural change can be observed by forming a coating on the surface of the aluminosilicate, product of the process of functionalization with silanes and the thermal characterization of the material shows that this process is presumably driven by a polymerization reaction.

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References
[1] Mysen B, Richet P 2019 Chapter 9 Structure of aluminosilicate glass and melt Silicate Silicate Glasses and Melts eds Mysen B and Richet (Amsterdam: Elsevier)
[2] Maesen T, Marcus B 2001 The zeolite scene -An overview Studies in Surface Science and Catalysis eds Van Bekkum H, Flanigen E M, Jacobs P A and Jansen J C (Amsterdam: Elsevier) Chapter 1
[3] Rozo Rincón S M, Sánchez Molina J, Gelves Díaz J F 2015 Revista Facultad de Ingeniería 24(38) 53
[4] Montaño A M, González C P, Castro D, Baron G C, Atencio R 2017 Journal of Physics: Conference Series 935(1) 012016:1
[5] Ramírez Llamas L A, Jacobo Azuara A, Martínez Rosales J M 2015 Acta Universitaria 25(3) 25
[6] Castillo Lara R, Antoni M, Alujas Díaz A, Scrivener K and Martirena Hernández J F 2011 Revista Ingeniería de Construcción 26(1) 25
[7] Espinosa Silva R 2015 Journal de Ciencia e Ingeniería 7(1) 1
[8] Narayanan P, Ravirajan A, Umasankaran A, Prakash D G, Kumar P S 2018 Journal of Industrial and Engineering Chemistry 63 1
[9] Reza Razavi S M, Oh J, Sett S, Feng L, Yan X, Hoque M J, Liu A, Haasch R T, Masoomi M, Bagheri R, Miljkovic N 2017 Sustainable Chemistry and Engineering 5(12) 11362
[10] Zhang Z, Ge B, Men X, Li Y 2016 Colloids Surfaces A: Physicochemical and Engineering Aspects 490 182
[11] Hoshian S, Jokinen V, Somerkivi V, Lokanathan A R, Franssila S 2015 Applied Materials and Interfaces 7(11) 941
[12] Hu M Z, Bischoff B L, Morales Rodriguez M E, Gray K A, Davison B H 2019 Industrial and Engineering Chemistry Research 58(2) 1114
[13] Liu J, Huang W, Xing Y, Li R, Dai J 2010 Journal of Sol-Gel Science and Technology 58(1) 18
[14] Granados Cristancho Y 2015 Importancia de los Ensayos TGA y DSC en el Estudio de las Propiedades Térmicas de Mezclas Asfálticas (Bogota: Universidad Distrital Francisco Jose de Caldas)
[15] Vieira C, Sanchez R, Monteiro S 2008 Construction and Building Materials 22(5) 781
[16] Muñoz Velez M F, Hidalgo Salazar M A, Mina Hernandez J H 2014 Biotecnología en el Sector Agropecuario y Agroindustrial 12(2) 60
[17] Cheng C, Weng D, Mahmood A, Chen S, Wang J 2019 ACS Applied Materials and Interfaces 11(11) 11006