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Functionalization of Silicon Carbide (SiC) for Abrasive Filament Production

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Declaration

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Abstract

This thesis addresses the advantages of performing a surface treatment using silane coupling agents to enhance the adhesive bonding performance of silicon carbide, SiC. The surface treatment involves a pre-treatment, followed by the functionalization. Various coupling agent/substrate ratios were studied to find the optimal conditions. Several functionalization tests were carried out with an ethanol/water ratio of 75/25, for alkylsilanes OCTEO, SIVO850 and 9896, and ethanol as the solvent for the silane AMMO. Regarding DAMO-T and 1401, toluene was used as the solvent and 0.5 % (V/V) of n-butylamine was used as a catalyst.

Concerning the surface characterization of the functionalized particles, Fourier-transform infrared spectroscopy (FTIR) analysis, contact angle measurements and X-ray photoelectron spectroscopy (XPS) analysis, were performed.

The FTIR analysis showed that all the organosilanes were present on the surface and unveiled the bond Si-O-Si proving that the organosilane was, in fact, chemically bonded to the SiC substrate. The sample treated with the volume of 10.0 mL of AMMO presented the best performance in the contact angle measurement with the value of 134.4±0.2 º. Considering the achievement of good performance when using a small amount of organosilane, the OCTEO and DAMO-T silanes presented significantly high contact angles of 126.0±0.2 º and 114.4±0.4 º, with the application of 3.0 mL and 2.5 mL respectively. XPS analysis was only executed for the samples with the best contact angle results, concluding that the ones that presented greater coverage were the samples treated with the Dynasylan DAMO-T and AMMO.

Keywords: Silicon Carbide, Organosilane, Surface Functionalization, Nylon, Abrasive Filament.

Resumo

Esta tese trata as vantagens de realizar um tratamento de superfície, funcionalização, com o auxílio de agentes de acoplamento, organossilanos, para aprimorar o desempenho da ligação adesiva do carboneto de silício, SiC. As amostras de SiC foram imersas em diferentes tipos de solventes, de acordo com o organossilano utilizado e várias razões organossilano/substrato foram estudadas, a fim de encontrar as condições ótimas de funcionalização. Vários testes foram realizados com uma razão etanol/água de 75/25, para os alquilsilanos OCTEO, SIVO850 e 9896, para o aminosilano AMMO, etanol foi utilizado como solvente e para os aminosilanos DAMO-T e 1401, o solvente utilizado foi tolueno e como catalisador n-butilamina.

Quanto à caracterização da superfície das partículas funcionalizadas, foram realizadas análises por espectroscopia de infravermelho com transformadas de Fourier (FTIR), medições de ângulos de contato e espectroscopia fotoelectrónica de raios X (XPS),

A análise FTIR mostrou que os organossilanos se encontravam na superfície das amostras corroborando a presença da ligação química, Si-O-Si, entre o silano e o substrato SiC. A amostra que apresentou melhor desempenho na medição do ângulo de contato foi a amostra tratada com o volume de 10.0 mL do organossilano AMMO, exibindo o valor de 134.4 ± 0.2 º. Tendo como objetivo a obtenção de um bom desempenho ao usar a menor quantidade de organossilano possível, os silanos OCTEO e DAMO-T apresentaram ângulos de contato significativamente altos de 126.0 ± 0.2 ° e 114.4 ± 0.4 º, com a aplicação de 3.0 mL e 2.5 mL, respetivamente. A análise XPS foi realizada apenas para as amostras com melhores resultados alcançados de ângulos de contato, concluindo que as amostras que apresentaram maior cobertura foram as amostras tratadas com os silanos AMMO e DAMO-T.

Palavras-chave: Carboneto de Silício, Organossilano, Funcionalização de Superfície, Nylon, Filamentos Abrasivos.

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Acronyms

1401 N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane

9896 Oligomeric short chain alkylfunctional silane

AFM Atomic Force Microscopy

AMMO 3-aminopropyltrimethoxysilane

APDEMS Amino-propyldiethoxymethylsilane

APS 3-aminopropyltriethoxysilane

DAMO-T N-(2-aminoethyl)-3-aminopropyltrimethoxysilane

DRIFT Diffuse Reflectance Infrared Fourier Transform

FTIR Fourier-Transform Infrared Spectroscopy

HF Hydrofluoric Acid

IPNs Interpenetrating Polymer Networks

MPS Methacryloxypropyltrimethoxysilane

NMR Nuclear magnetic resonance

OCTEO Octyltriethoxysilane

ODTMS Octadecyltrimethoxysilane

PA6 Nylon 6

SAM Self Assembled Monolayers

SCA Silane Coupling Agent

SiC Silicon Carbide

SIVO Alkyltrialkoxysilane oligomer in water

XPS X-ray Photoelectron Spectroscopy

List of Symbols

θ – Contact Angle

B.E. – Binding Energy (eV)

m – Mass (g)

M – Molar Concentration (mol /L)

P_{amb} – Ambient Pressure

T – Transmittance (%)

T_{drying} – Temperature of drying (ºC)

T_r – Temperature of reaction (ºC)

t_r – Time of reaction (h)

t_{drying} – Time of drying (h)

t_{pellet} – Time of pellet making (h)

V – Volume (mL)

λ – Wavenumber (cm^{-1})

CHAPTER 1

1. Introduction

Nylon abrasive filaments were developed by the end of the 1950s. The most important features of this thermoplastic are its low cost, adaptability and bend memory recovery, that allied with the abrasive properties of the particles, makes these composites suitable for several applications. Despite these characteristics, in nylon abrasive filaments, when the quantity of abrasive particles loaded into the matrix increases, some of the abrasive particle's properties decrease, like the tensile strength and flex fatigue resistance. Then, the filaments will tend to deform and get a different shape, soften and lose its effectiveness or even fracture when applied in harsh applications, thus an increase in the particle loading leads to a poorer attachment between the abrasive and polymer [1-2].

The weak interfacial interaction between the inorganic particles and the polymer limits the applications of some inorganic particles. Silicon carbide (SiC) or carborundum is an inorganic particle of great interest. It presents high hardness and strength retention at elevated temperatures, good thermal stress resistance and conductivity, high radiation resistance and excellent wear and oxidation resistances, therefore this inorganic particle is suitable for usage under severe conditions, such as high temperature, high power and high frequency [3-4]. Silicon carbide is a very promising material for semiconductor devices, biomedical sensors and abrasive applications, being well suited for demanding applications in harsh environments [5-8], [34]. In this thesis, silane surface modifiers and functionalization processes are investigated for the enhancement of adhesion of a nylon/silicon carbide composite for abrasive filament production.

In order to assure the composites quality for posterior applications, there ought to be a homogeneous dispersion of the silicon carbide particles in the polymer matrix, being surface pretreatment particularly essential in these adhesion complexes [9], [34].

To attain optimal adhesion durability, it is frequently necessary to modify the inherent substrate surface, through chemical or physical approaches. It should be taken into consideration that the physical route will not modify permanently the surface or create a surface layer robust enough to guarantee the adhesion durability. Various organosilanes were used as chemical surface modifiers to improve the adhesion durability, due to their hybrid formula, containing organic and inorganic functional groups. Amongst these surface modifiers, silane coupling agents have gotten more attention considering their exceptional chemical structures, specifically for this case, trialkoxysilanes and dialkoxysilanes [3-4]. An organofunctional alkylalkoxysilane contains both organic and inorganic functionalities, therefore it can act as a chemical channel between two dissimilar materials. The general formula of trialkoxysilanes is $Y\text{-}Si\text{-}(OX)_3$, where Y is a functional group and OX is a hydrolysable group and the general formula of dialkoxysilanes is $Y\text{-}Si\text{-}(OX)_2R$, where R is usually an alkyl group [10-13].

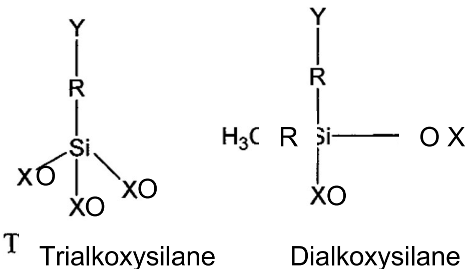


Figure 1 - Schematic representation of alkylalkoxysilanes.

The hydroxyl groups existing on the substrate are the sites at which silanes will be adsorbed and ultimately react. The substrates surface must then be subjected to a pre-treatment step, in order to create the hydroxyl sites for the silane to be deposited and enhance the adhesion performance of the substrate. There are several treatments that can be applied to the fillers surface before the functionalization step used to remove impurities and oxidation layers and after form hydroxyl group sites, such as etching with hydrofluoric acid and several other acidic cleaning solutions, for example an ALNOCHROMIX and sulfuric acid solution [14-16].

1.1. Framework and Thesis Objectives

Previous researches and studies presented in the literature revealed a great capacity given by silicon carbide to act as an abrasive reinforcer in polymers. In order to obtain a better composite several surface treatments can be implemented to guarantee a homogeneous dispersion of the abrasive grains in the matrix. Thus, the present work will be focused on the evaluation of different organosilanes in the surface treatment process of silicon carbide in order to enhance the compatibility between SiC and nylon for abrasive filament production.

The main objectives of this thesis are:

1. Selection of treatment processes for silicon carbide testing different organosilanes;
2. Characterization of the resulting treated surface.

This dissertation work was carried out with an industrial purpose, in partnership with FILKEMP. As part of this work, I was given the opportunity to visit the facilities, in order to closely monitor the production of the abrasive filaments. The process converts nylon and SiC particles in abrasive filaments starting with a mixing and extrusion step in an extruder at temperatures between 100-200 ºC, followed by a cooling step through several rolls and one last cutting step with applied heat.

CHAPTER 2

2. State of the Art

2.1. Adhesion and Adsorption Theory

Mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction theories have been hypothesized as definitions to the mechanisms of adhesion. The mechanical theory states that adhesion occurs by the infiltration of adhesives into pores or cavities or other surface irregularities in the substrate. According to the electrostatic theory, adhesion occurs due to electrostatic effects between the adhesive compound and the adherend. The diffusion theory proposes that through the interdiffusion of molecules in between the adhesive and the adherend, the adhesion is created. At last the adsorption theory states that adhesion results from surface forces that develop from molecular contact between two materials, being this last theory the one that best describes this thesis purposes [17].

The adsorption theory postulates that adhesion results from intermolecular forces existing between the atoms on the surface of the substrate and the atoms of the molecules present in the adhesive material. There are two distinctive types of adsorption: physisorption and chemisorption. Physisorption can be described as the state where a material is connected by secondary forces. These secondary forces comprise London dispersion forces, dipole interactions and hydrogen bonding, thus resulting in strong adhesive bonds as long as the intermolecular distance is short. On the other hand, chemisorption refers to primary bonding throughout the interface, being these forces ionic or covalent. Although it is more challenging to achieve, chemical adhesion is the strongest [18-21], [34].

2.2. Polymer-Abrasive Filler Adhesion

Polymer-Abrasive composites are used in an extensive scope of industries, such as automotive, metal industry, textiles, marble and decorative stone, as well as other more specialized uses [22].

For abrasive types of applications polymer-based composites are of great interest due to their extended aptitudes compared to common polymers. The environment in which these polymers are used, i.e., humidity, temperature and pressure applied, as well as the technical specifications required, such as stiffness, chemical resistance, diameter of the grain and its nature are decisive factors for the choice of materials and stabilizing agents to be used [23-24].

When it comes to polymer composites containing fillers or reinforcements, the usual properties involve great strength to weight ratio, extreme load bearing capability and resistance to extreme working temperature conditions [25]. Generally, it should be taken into account the homogeneous dispersion of the grains in the matrix and the formation of strong bonds between them and the matrix, thus the strong adhesion between polymer and its fillers could be described by the adsorption theory.

2.3. Nylon Abrasive Filaments

Nylon-abrasive filaments, as mentioned previously, have been known and used in the industry for over 60 years. It was not until the late 1950s and early 1960s that the development of nylon abrasive filaments took place. Several advantages of these type of filaments are safety, cleanliness, high cutting speed, finish control, adaptability and ease in design, as well as low cost. The utmost significant characteristics of nylon and other varieties of thermoplastics are their excellent mechanical properties, in particular its bend recovery, and its thermal properties. All these features allied with the abrasive properties of the particles to be incorporated in the matrix, makes the resulting composites ideal for abrasive filament applications. Nevertheless, it should be noted that in filled polymeric composites, as the number of abrasive particles increases, the mechanical properties such as tensile strength and flex fatigue resistance decrease [1], [10].

2.3.1. Nylon 6

Nylon 6 is a nylon Z type of polymer, where the Z is described as the number of atoms of carbon in the original monomer. Nylon 6 is generally produced in the presence of water vapor and an acid catalyst and is formed by the ring-opening chain and growth polymerization of caprolactam, as represented in the following chemical equation [10].

$$[\mathrm{HN}-(\mathrm{CH_2})_5-\mathrm{CO}]+\mathrm{H_2O}\rightarrow \mathrm{H}[-\mathrm{HN}-(\mathrm{CH_2})_5-\mathrm{CO}-]_{\mathrm{n}}\mathrm{OH} \qquad (1)$$

The purity of the caprolactam is critically assessed for the production of nylon 6 (PA6) polymer.

PA6 fibers are produced for textile uses and for industrial uses, which requires higher strength. Most PA6 is applied in the production of furniture, brushes, ropes, apparel, hosiery and tire cords, so it is typically shaped in the form of filament yarns. This broad spectrum of application can be endorsed to the combination of the fiber’s properties. The nylon films can be produced by extrusion, extrusion coating, and blown film [26].

Some of the PA6 characteristics are its chemical and oil resistance, except for strong acids and bases, as well as outstanding long-term heat resistance (maximum temperature ranging between 80 °C and 150 °C). It also offers exceptional gas barrier properties and displays excellent surface finishing even when reinforced. Nylon 6 is also one of the least costly types of nylons, thus, it can be applied for multiple applications, being one of the most suitable polyamides for abrasive filaments [27-28].

2.3.2. Functional Fillers

Abrasive particles are selected depending upon their applications, machining rate and surface finish requests. There are several types and sizes of particles selected to achieve highly wear-resistant polymer composites. These fillers can be polytetrafluoroethylene powders (PTFE), graphite flakes, short aramid fibers, glass or carbon fibers and inorganic particles such as CuS, ZnO or CuO particles, TiO_2, SiO_2 or SiC particles [29-30]. The most commonly used abrasive fillers are aluminum oxide (Al_2O_3), silicon carbide (SiC), glass beads, crushed glass or sodium bicarbonate ($NaHCO_3$), as well as more exclusive particles such as diamond and hexagonal boron nitride and other metal oxides like cerium oxide [31-32].

Some abrasive grits properties may be hardness and stiffness high enough, so the particles do not disintegrate into parts when applied in the working surface. The abrasive grits should also be low cost, readily available and have different shapes and size according to the application. Reuse of abrasives is not suggested in view of the fact that its cutting capacity decreases after first use, resulting in metallic chips clogging in the orifices within the nozzle of the polymeric filament extrusion machine. Silicon carbide is a low-cost extremely stiff and sharp grain that is more friable than aluminum oxide. It is used in blasting of extremely hard materials and very hard work applications. On another hand, its abrasive properties can substantially reduce the nozzle life of the blasting machines taking into account the environment of application. Sand, silicon dioxide and silica breakdown too quickly, therefore, are considered smooth. Alumina applications can be cleaning, cutting and deburring, smoothing, materials with different hardness values. Glass beads are essentially applied for matting surfaces and to reduce the transparency of the surface. Crushed glass can be used for heavy cleaning or peening operations - the process of working a metal's surface to improve its properties. Plastic grit is another soft medium, often made from recycled plastic or plastic waste and is typically used to clean surfaces without harming the substrate [9], [32].

Silicon carbide particles are of great interest for abrasive applications and have been demonstrated to be effective multifunctional materials, especially for the application as polymer reinforcements due to their inexpensive price, high abrasive and hardness properties, and simple synthesis [1], [7], [33].

2.3.3. Silicon Carbide

Silicon carbide, also known as carborundum or SiC is a very promising inorganic particle for various applications in which it is required to work under extreme conditions, since it exhibits mechanical robustness, chemical inertness, it is nontoxic and biocompatible [5-6].

SiC has a 1:1 stoichiometry between silicon and carbon and comprises numerous of the advantages of these components. Some of the properties of this compound are its chemical inertness to acids, bases and salts, it is not expandable in liquids, has a low density, but a high degree of hardness and elastic modulus. It is a wide-bandgap semiconductor that has the ability to operate at high-temperature, high-power, and other kinds of harsh-environments, since it exhibits good thermal conductivity, high radiation resistance and high breakdown voltage. Another one of the most unique properties of this inorganic material is its polytypism, having more than two hundred different crystalline structures [5-7].

On the other hand, silicon carbide may have lower chemical stability when it comes to lasting processes of application since it is prone to form oxides, being vulnerable to diffusion of ions. Upon oxidation, silicon carbide form $\mathrm{SiO_2}$ surface layers. Water molecules are frequently discovered on the surfaces of SiC, as water molecules can interact with the $\mathrm{Si-OH}$ groups present on the surface through hydrogen bonding, and thus the surface of the particles is wettable, as schematized in the following Figure 2 [34].

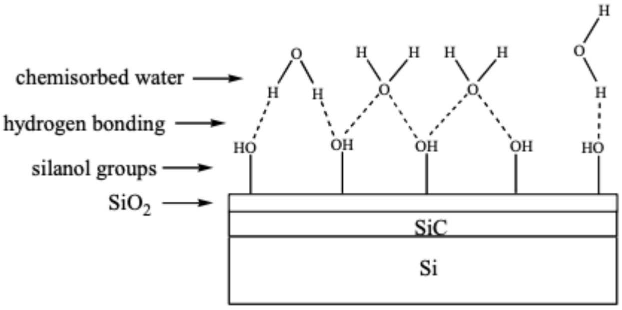


Figure 2 - Schematic representation of a hydrophilic SiC/Si surface covered with a native oxide ($\mathrm{SiO_2}$) and chemisorbed water molecules [34].

Inorganic particles are very prone to agglomerate in media, showing poor dispersion capability in organic solvents or oils as a result of their high surface energy. Due to the bad consistent interfacial interaction, the combination of the inorganic particles is largely limited. The bond of the inorganic SiC particles with the polymer matrix is weak and therefore the applications could be limited due to the bad consistent interfacial interaction. The phenomenon of agglomeration of SiC makes it difficult to disperse the particles in the polymer, however surface modification techniques can be very effective to improve the dispersibility of the particles. In these techniques it is very common to resort to coupling agents which can be connected with the particles on their surface and increase its dispersion in the polymer [3-4], [35].

The surface modification can be obtained on a physical level or a chemical level, and this modification can result from the addition, removal or shift of materials existing on the surface of the particle studied. When it comes to addition of materials to the surfaces, as coatings, there are several techniques such as sol-gel and plasma-spraying, or vapor deposition methods: chemical deposition, evaporation and sputtering. Ion implantation is also commonly used to add material to surfaces, modifying coatings, and change microstructures [36]. For the removal of surface material, mostly for cleaning purposes, there is the etching technique. At last, the properties of the surface can also be changed without any material required. Techniques like laser and electron beam thermal are frequently used for hardening.

Surface modification of inorganic particles by the addition of coupling agents has attracted a great deal of attention since it provides exceptional incorporation in the matrix and an improved interface between the particles and polymer matrices. Surface modification methods for inorganic particles can be divided into two main classes: chemical or physical. The selectable routes of physically modifying powder usually cannot meet the requirements of altering the nature permanently or obtaining thick surfaces. In the case of chemical modification, there are various coupling agents.

Coupling agents are described as the interconnecting compound that forms chemical bonds amid materials, usually an inorganic material and an organic substance. Several examples include silane coupling agents, titanate coupling agents, aluminate zirconium or organic chromium, and polymer coupling agents. Silane coupling agents are the most commonly used and are suitable for abrasive filament production due to the outstanding capacity to integrate an organic-compatible property and an inorganic-compatible functionality within one coupling agent [37].

2.4. Silane Coupling Agents

It has been described in previous literature that inorganic particles like silica, SiO_2, or silicon carbide, SiC, can be effectively modified with coupling agents to enhance their dispersive capacity in polymer matrices. The surface of the powder is converted from hydrophilic to hydrophobic resulting in a significant improvement of the dispersibility of the grains in the matrix and the compatibility of the particles in the organic phase [24]. Silane coupling agents are considered hybrid molecules that comprise both organic and inorganic properties, thus allowing them to act as bridges between two dissimilar materials promoting adhesion between organic and inorganic phases [24], [34].

Organofunctional silanes are most often used as coupling agents, as mentioned previously. Various silanes have been previously used for modification of glass or silica surfaces, in order to offer these materials hydrophobic properties. The functionalization process with silanes has been considered for the surface hydrophobization of silicate and other particles, for example carborundum particles. There is a broad array of commercially accessible silanes for the silanization process. Additional fluorinated silane coupling agents are extensively used for this purpose as well. Silica particles functionalized by alkoxysilanes have been significantly studied in great fields of applications, such as chromatographic separation or chemical sensing or used as additives for the improvement of the mechanical resistance of polymers [11], [38-39].

2.4.1. Silane Chemistry

The employment of silanes as coatings and coupling agents depends on their chemical structure. Silane coupling agents have two main functional groups, one that is attracted to the organic polymer and the other one that is attracted to the inorganic surface of the filler thus, enhancing the performance of the composite adhesion.

The general formula for functional silane is $(\mathrm{Y}-\mathrm{Si}{-}(\mathrm{OX})_3)$, being Y the functional group and OX the hydrolysable group. The hydrolysis of $(-\mathrm{Si}-\mathrm{OX})$ will form silanol groups, $(-\mathrm{Si}-\mathrm{OH})$, which can bond to the surface hydroxyl groups of inorganic substrates forming strong siloxane bond $(-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-)$, between the silane coupling agents and the silicon carbide through condensation [11], [40].

The nature of the functional group (Y) will provide the silane the ability to act as surface-modifying agents and coupling agents. A long hydrocarbon chain as the functional group will act as an enhancer of the hydrophobicity of the substrate surface. On the other hand, if (Y) also contains an amine group, $(-\mathrm{NH}_2)$, that will allow the substrate to connect to nylons, epoxy, vinyl acrylate resins and other polyamides and polyesters [11].

2.4.2. Silane and Substrate Activation and Functionalization Reaction

Silane coupling agents can be described as an interphase region maker, between the inorganic filler (glass, metal, or mineral) and the organic substrate (organic polymer, coating, adhesive), acting as a bonding agent. The functionalization process with silanes leads to the enhancement of the dispersion of fillers in the polymer matrix, decrease of the viscosity of the polymer–filler mixture, protection of minerals against cleavage, treatment of defects in the surface, and reinforcement of the polymer at the boundary with the coupling agent forming interpenetrating polymer networks (IPNs) [9]. Organofunctional silanes contain two different reactive functional groups that can react and couple with various inorganic and organic materials.

A fundamental constraint for effective functionalization is the surface activation step, which consists in the modification of the particles terminal groups to $-\mathrm{OH}$ groups that will react with the alkoxy groups of the organosilane molecules (A). Previous studies confirmed that etching of the SiC particles with hydrofluoric acid or other types of acid solution pre-treatments, will result in the development of the hydroxyl termination, thus, this surface activation treatment is suitable for an effective wet chemical functionalization.

After the activation step, the surface modification technique lies on the immersion of the surfaces on an organosilane solution (B). The reaction occurs at room temperature, with the formation of silanol groups from the head groups of the organosilane, which are hydrophilic, in the presence of the solvent (hydrolysis). Following, the reaction of the silanols with the surface hydroxyl groups yields stable oxygen bonds between the organic silane and the inorganic substrate material, $\mathrm{Si-O-Si}$ bonds, as schematized in the following Figure 3.

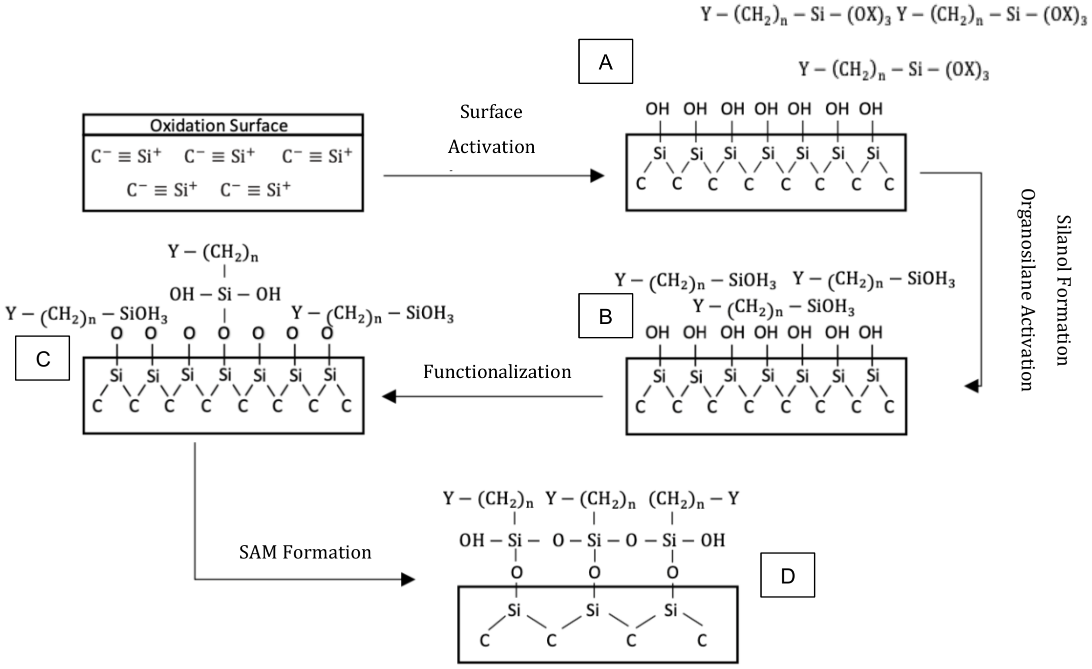


Figure 3 - Surface and Silane Activation and Functionalization Reaction steps [34].

The silane monomers are hydrolyzed in the presence of water yielding reactive silanol groups. It is worth mentioning that the hydrolysis of silane coupling agent proceeds step by step, and its equilibrium equation is as follows (B):

$$\mathrm{Y-Si-(OX)_3+H_2O\rightarrow Y-Si-(OX)_2OH+X-OH} \qquad (2)$$

$$\mathrm{Y-Si-(OX)_2OH+H_2O\rightarrow Y-Si-OX(OH)_2+X-OH} \qquad (3)$$

$$\mathrm{Y-Si-OX(OH)_2+H_2O\rightarrow Y-Si-(OH)_3+X-OH} \qquad (4)$$

Then, the silanol groups when positioned nearby to the hydroxyl groups of the inorganic particles, have the conditions to form chemical bonds (C). As the final step approaches, still under heating conditions, the hydroxyl groups of the inorganic particles and the silanol groups can be converted into covalent bonds releasing free water and the silane monomers can create bonds within, forming a silane self-assembled monolayer (D) [4].

It should be noted that for silane coupling agents that partake an amine group, this group is responsible for the chemical reaction behavior and it is accountable for the high reactivity of the aminosilanes. The electron rich nitrogen center of the amine group can form hydrogen bonding interactions with hydrogen donating groups, such as hydroxyl groups or other organosilanes.

Before the functionalization, another required step is the activation of the silane molecules, by reacting with water adsorbed molecules on the hydrophilic SiC surface, or the water in the solvent to transform the alkoxy groups into silanol groups. The subsequent silanol groups formed will then react with the already surface activated $-\mathrm{OH}$ groups and bond covalently, forming self-assembled monolayers, SAMs. Since the amine group is highly reactive, the functionalization process is often made under inert atmosphere conditions to avoid oligomerization of the silane [15]. The best solvent is one where hydrolysis and self-condensation do not occur, being desirable to have the silane reacting with the hydroxyls on the solid surface instead of with the solvent, or between the silane itself. Anhydrous toluene fulfills this role well for aminosilanes at room temperature and under inert atmosphere conditions. The silanization of particles process using 3-aminopropyltriethoxysilane was described by *Zhenghe et al.* The silanization process was conducted in toluene and water solutions to examine the solvent effect on the molecular orientation and packing density of the silanized films, showing that in acidic environment, the films silanized in toluene were more stable than the films silanized in water [41].

In order to observe the silane functionalization on the sample, there are several methods, for example: Fourier-transform infrared spectroscopy (FTIR) used to study the bonds in the surface of the powder after the silane modification of the SiC surface. X-ray photoelectron spectroscopy (XPS) used to study the surface of modified substrates, silane coverage, orientation of the silane molecules in the surface and to determine whether there was adhesion failure or not. Nuclear magnetic resonance, NMR, was applied for the study of the structures and dynamics of the silane in the surface, thus presenting absence of adhesive on the bonding system. The measurement of the contact angle of the SiC treated surface in order to identify if the surface is treated or not according to its hydrophobicity degree [4], [15], [42].

In a study by *De Haan et al.,* the silanes 3-aminopropyltriethoxysilane (APS) and 3-methacryloxypropyltrimethoxysilane (MPS) were attached to silica powders through covalent bonds and the modified silica surface was analyzed using FTIR and NMR techniques. Previous studies have demonstrated that the covalent bonds between trifunctional silanes and silica substrates could occur from mono to tridentate linkages. Another study by *De Haan et al*. revealed that the nature of the bonds depended on several aspects like the type of solvent, the coupling agent used, the temperature conditions of the treatment and reaction. The study showed that when anhydrous toluene was used as solvent in the silane, deposition resulted in mainly monodentate and bidentate linkages, while when the used solvent was water, the linkages were bidentate and tridentate. In the case using dry toluene as solvent with the silane MPS, mainly monodentate and bidentate structures were found, with minor quantities of tridentate and crosslinking structures, even for higher temperature conditions [43].

Caravajal et al. also observed that the amount of surface coverage and the structure of the silane using dry toluene as solvent were extremely conditioned on the water available on the surface. This finding is revealing that the amino groups in samples prepared in dry toluene can be either hydrogen bonded or protonated by acidic silanols at the silica gel surface. The study also suggested that the amount of the protonated form increases with the amount of water present at the silica surface [34], [38].

Kang et al. resorted to solid phase NMR analysis in order to analyze the structures of aminosilanes attached to Cab-O-Sil surfaces, that are fumed silica particles. The NMR spectra obtained of the treated Cab-O-Sil samples revealed that the silane molecules were chemically attached to the surface through the silanol bonds with surface $\mathrm{Si-OH}$ groups. The hydrolysis rates were determined at ambient temperature (21 °C) and the coupling agent was placed in acetone-water solution followed by the silica surfaces. This study also showed that an increase in the concentration of the treatment solution, led to an increase of the amount of silane chemically adsorbed [42]. This study is coherent with the study conducted by *Okabayashi et al.* of the behavior of 3-aminopropyltriethoxysilane (APS) on silica gel using for characterization of the sample Diffuse Reflectance Infrared Fourier-transform (DRIFT) spectra [43]. DRIFT spectroscopy studies the surface chemistry of high surface area powders, postulating proof that the APS was present on the silica and the silane chemical structure depended on the amount of the silane used and the reaction time. *Okabayashi et al.* found evidence that at low concentrations (0.2-0.3 M), the amine group, was observed mainly in its protonated form, $\mathrm{NH_3^+}$, while at higher silane concentrations (0.6-0.7 M), the amine in its neutral form, $\mathrm{NH_2}$, was observed in more abundance [44]. Low silane concentration will result in unreactive $\mathrm{Si-OH}$ sites in the silicon carbide surface that consequently will interact with the amine in the silane that will take its protonated form. An increase in the amount of silane will result in the increase of silanol groups to react with the silicon carbide, leaving the amine group in its neutral form [34].

Schoell et. al. studied the silanization of silicon carbide surfaces with different crystal structures, with organosilanes through the development of self-assembled monolayers (SAMs). Self-assembled monolayers of amino-propyldiethoxymethylsilane (APDEMS) and Octadecyltrimethoxysilane (ODTMS) were produced through wet chemical modification methods. Their chemical structure and other properties were assessed using various characterization methods such as the measurement of static water contact angle in order to assess the hydrophobicity of the surface, X-ray photoelectron spectroscopy and atomic force microscopy

(AFM). The analysis showed the presence of smooth, even, compact and densely packed organic layers formed. The silanization process was executed starting with a pre-treatment consisting in the ultrasonic cleaning of the particles in acetone and isopropanol, followed by oxygen plasma cleaning, and for the activation of the surface to form hydroxyl groups an etching step in 5 % (V/V) hydrofluoric acid (HF) in water. Functionalization was then achieved with the immersion of the samples in 5 % (V/V) solutions of organosilane molecules in toluene at 14 °C for 90 min [15]. The reaction was executed under Ar atmosphere, with the aim of averting oligomerization of the silane throughout the functionalization procedure. For functionalization with ODTMS, 0.5 % (V/V) butylamine was added to the reaction solution as a catalyst.

Schoell et. al. also contemplated the successful functionalization of SiC with organosilanes by the wet-chemically process, originating self-assembled layers with the two silanes octadecyltrimethoxysilane and aminopropyldiethoxymethylsilane. The chemical properties and structure of the SAMs were assessed by contact angle measurement techniques, atomic force microscopy, X-ray photoelectron spectroscopy and thermal desorption methods. The organic layers were smooth and wetting angles up to 100 º were observed confirming the presence of silane. The self-assembled ODTMS layers were attained via immersion of the particles in a mixture of 5 % (V/V) of the silane ODTMS in the solvent anhydrous toluene, at 14 °C for 2 hours and 30 minutes. It is worth mentioning that in order to support the functionalization, 0.5 % (V/V) n-butylamine was added as a catalyst [45].

Shang et. al. studied two other silane coupling agents, specifically 3-aminopropyltriethoxysilane (KH550) and 3-mercaptopropyltrimethoxysilane (KH590) as primary modifiers to boost the hydrophobic properties of the surface of silicon carbide (SiC) particles as an initial and main step. By measuring the contact angle of the treated samples, the factors that had greater impact in the modification effects were studied. For the reaction, a mixture of 25 % (V/V) deionized water/ethanol was used as solvent and certain amounts of KH550/KH590 were tested at different temperatures and different reaction times on stream. The results disclosed that the functionalization with the silane KH590 incorporated a better effect than KH550. Furthermore, the contact angle improved the most after the SiC powder reacted with 0.3 g KH590, with aqueous/alcohol solution as solvent at 75 ºC for 4 hours. The KH550/KH590 modified particles were characterized via Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS) and the analysis confirmed that the silanes were covalently bonded to the surface of the substrate [4].

At last, *Chunxue et. al.* considered a thermochemical technique for the functionalization of silicon carbide/silica (SiC/SiO_2) powder with methacryloxypropyltrimethoxysilane (KH570) and octylphenolpolyoxyethyleneether (OP-7). For the synthesis of hydrophobic SiC/SiO2-KH570 powder, a mixture containing water (10 mL), ethanol (30 mL), and KH570 (4 g) was stirred for half an hour at room temperature, and then the SiC powder (2 g) was slowly added and agitated in the reactor for 4 h in a 90 ºC water bath. The characterization of the surfaces after functionalization verified that KH570 and OP-7 were bonded to the surface of SiC, through covalent bonds, showing an increase in the hydrophobicity of the particles. The characterization was executed via Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) [46].

2.5. Surface Pre-Treatment

The existence of impurities on the surface of carborundum particles has been previously reported and confirmed by X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy analysis. It has also been previously stated that the surface chemistry of SiC, analyzed by XPS, was affected by characteristics such as chemical composition, morphology, particle density, and primary particle size [47-48].

The properties of the commercially available SiC particles are determined by the production process used by the manufacturer, in particular the purity of the silicon carbide. When the surface is contaminated, the silanization process may not be sufficient and effective for the purpose of the enhancement of the particle's dispersion in a matrix [49].

The hydroxyl terminations present on the substrate surface correspond to the spots on which silanes will be adsorbed and eventually will react, therefore, a pre-treatment step is essential in the particles surface, so that there is a hydroxylated layer and at the same time all the other contaminants are removed. Some types of treatments used to enhance adhesion durability are oxygen and water/oxygen plasma treatments prior to the deposition of the organosilanes, etching of the surface with hydrofluoric acid (HF etching), hydrochloric acid, nitric acid or sulfuric acid and several other cleaning solutions are used to remove contaminants, oxidized surfaces and form the hydroxyl groups [47-51].

The removal of silicon oxide layers is typically achieved by HF etching. This treatment results in dangling bond saturation, unlike the Hydrogen termination of Si subsequent of similar treatments. The etching process results in an oxidized surface with an F-termination and this F-terminated surface compared with the usually obtained H-terminated surface is thermodynamically more stable. In spite of the increase of the stability, the strong Si-Si bond polarization between silicon and the F-termination in the surface may lead to production of volatile SiF_4, due to the large electronegativity difference that results in a further attack by HF in the substrate. The surface is stable in air for up to several hours and have low surface state concentrations [7], [16].

ALNOCHROMIX cleaner is a concentrated inorganic persulfate-based additive to sulfuric acid creating a metal-free and surfactant-free inorganic particle cleaner that is excellent for cleaning glassware and other sensitive cleaning applications, tissue culture, trace metals and enzyme kinetics research. It is a nonmetallic, non-carcinogenic, and a simpler replacement for chromic acid [52]. This solution will not only clean the surface from any contaminants, but also will etch the surface with the presence of the sulfuric acid, resulting in an H-terminated surface.

Although it has not been previously reported, to the best of our knowledge, the use of ALNOCHROMIX cleaner as a surface pre-treatment, its cleaning agents and the use of the strong acid make this solution a suitable candidate for the surface pre-treatment [53].

CHAPTER 3

3. Surface Characterization Methods

3.1. Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) has conventionally been used in material and surface analysis within the chemical industry, as an absorption spectroscopy that requires an incandescent source of light to radiate a bright ray in the IR wavelength range. When the radiation is passed through a sample, some is absorbed by the sample and some is transmitted. The subsequent signal that is detected by the detector is a spectrum characterizing the chemical structure (molecular), since each stretching vibrations corresponds to specific functional groups and each compound produces its own unique pattern of peaks in this region.

The wavenumbers assignments taken from the literature, that are relevant for the chemical structures in this thesis are given in the following Table 1.

Table 1 - FTIR wavenumbers and corresponding assignments [54-56].

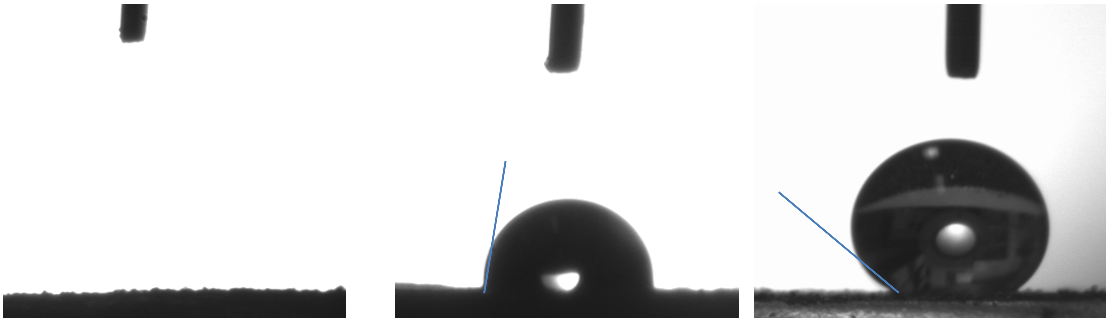
Chemical Bonds	**Wavenumbers (cm^{-1})**
$\mathrm{Si-O-Si}$	1130-1000
$\mathrm{Si-O-CH_2-CH_3}$	1170-1160,1100, 1085-900
$\mathrm{Si-(CH_2)}_x\mathrm{-CH_3}$	1220-1170
Primary Amine	1650-1450, 910-665
$\mathrm{Si-O-CH_3}$	2840, 1190, 1100-1080
$\mathrm{-(CH_2)_x-\quad(C-H)}$	3000–2915, 2880–2840
$\mathrm{Si-OH}$	3400-3200, 950-810
Secondary Amine	910-665
Silicon Carbide	c.a. 800

The FTIR analysis were performed using a PerkinElmer, Spectrum Two, mid-Infrared spectrometer equipped with a Pike Technologies MIRacle® Attenuated Total Reflectance (ATR) accessory. Attenuated total reflectance (ATR) is a sampling method that introduces light onto a sample in order to acquire structural and compositional information. It is quick, non-destructive and requires no sample preparation and it is applied to samples where the composition of the surface needs to be measured. ATR is one of the most used sampling technologies for FTIR spectroscopy, enabling solid and liquid samples to be analyzed straight by simplifying the measurement of all substances significantly decreasing the noise signals [57].

3.2. Contact Angle measurements with Sessile drop Method

The contact angle measurement technique that is mostly used, is the direct measurement of the static angle of wetting, at the point of contact, between three phases resulted from a liquid drop on the substrate. These measurements can be taken with various liquids and may be conducted on goniometers. A drop with a well-defined volume is positioned on the substrate, and then several photographs are taken and the angle between the tangent to the drop and the substrate is measured for each frame.

The measurement of contact angles allows the characterization of fundamental surface properties of a solid material. The effects of roughness and heterogeneity can easily overshadow the influences of interfacial energetics, so this technique is extremely sensitive to the quality of the substrate surface. It is therefore important, to produce solid surfaces that ensure an accurate measurement of the angle. A perfect wetting means the maximum value of $\cos\theta$, which is obtained when the contact angle is zero, thus the surface is hydrophobic and for contact angles above 90 º the surface is hydrophobic as seen in Figure 4 [58]. In this thesis, it will be used as a technique to identify if the organosilane is attached to the surface or not, since the silicon carbide unmodified is hydrophilic and therefore, has perfect wetting and the coated silicon carbide with the hydrophobic properties of the organosilane will display low or high wetting. The sample characterizations were conducted with a Ramé-hart DROPimage Goniometer through the sessile drop method.



(a)
Contact Angle: $\theta = 0$ °
Perfect Wetting

(b)
Contact Angle: $\theta < 90$ °
High Wetting

(c)
Contact Angle: $\theta > 90$ °
Low Wetting

Figure 4 – Schematic representation of the angle between the solid surface and the edge of the drop [58].

3.3. X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron spectroscopy is a surface sensitive technique that allows the identification and quantification of atomic elements, the study of the electron's interaction with the surface, the loss of their energy exciting vibrational and electronic states and ionization, providing information on the chemical state of the elements in the solids surface. This technique requires an X-ray source, usually $\mathrm{Mg\ K_{\alpha}(1253.6\ eV)}$ or $\mathrm{Al\ K_{\alpha}(1486.6\ eV)}$, to ionize the atoms of the sample, resulting in the emission of photoelectrons. For the samples in study the X-ray source will be $\mathrm{Mg\ K_{\alpha}(1253.6\ eV)}$, because it has lower energy than Al and therefore will only penetrate the surface and not the core of the particles. A sample is placed in a vacuum setting and exposed to the X-ray beam. X-ray photons are absorbed by atoms and the subsequent ionization and emission of core and valence electrons, as well as Auger electrons occur [34], [59-60].

The energy of a photon is given by the equation (5), where h is the Plank's constant $(6{,}62 \cdot 10^{-34}\ \mathrm{J \cdot s})$ and ν is the frequency of the radiation (Hz) of the X-ray. The ionization process of the photons is the outcome of the energy conversion, which can be defined by the equation (6), being $\mathrm{E_K}$ the kinetic energy of the photoelectron and $\mathrm{E_B}$ the binding energy, the energy difference between neutral and ionized atoms. Since every chemical element has a characteristic binding energy associated with each core atomic orbital, the detected signals at specific energies specify the presence of that exact element. Furthermore, the intensity of the detected peaks is associated with the concentration of the element, allowing the quantification of elements at the solid surface and in the present study, to quantitatively observe the silane coverage [60].

$$\mathrm{E = h \cdot \nu} \tag{5}$$

$$\mathrm{E = h \cdot \nu = E_K + E_B} \tag{6}$$

Analytical evaluation of C 1s, Si 2p and N 1s photopeaks were performed by adjusting the obtained XPS curve to peaks through deconvolution. XPS spectra are quantified in terms of peak intensities and positions. The peak intensities measure how much of the elements is on the surface, while the peak positions indicate the elemental and chemical composition. The preeminent way to compare XPS intensities is through atomic concentration percentage. The representation of the intensities of the peaks acquired, as a percentage, is obtained by the ratio between the intensity of that given peak and the total intensity of electrons in the measurement. Transitions from diverse electronic states from the same element will vary in peak area, thus, the peak areas for transitions from different elements must be scaled too. Relative sensitivity factors are necessary for transitions in the element. These sensitivity factors are considered to scale the measured areas hence the atomic concentrations can be attained, regardless of the selected peak [61]. The photopeak assignments used for curve-fitting are given in the following Table 2.

Table 2 - XPS peak assignments for Si, C, O and N photopeaks [34], [48-49], [62-67].

Chemical Bonds	Peak Energy Range (eV)
$\mathrm{Si-C}$	99.8-100.7
$\mathrm{Si-O_x}$	102.0-103.7
$\mathrm{Si-O_2}$	103.1-103.9
$\mathrm{Si-C}$	282.0-283.6
$\mathrm{C-H/C-C}$	284.6-285.0
$\mathrm{C-N}$	286.0
$\mathrm{C-O}$	286.3-287.1
$\mathrm{C=O}$	287.8-288.2
$\mathrm{Si-O-Si}$	531.0-532.7
$\mathrm{C=O}$	531.0-531.6
$\mathrm{Si-O_2}$	532.0-532.2
$\mathrm{Si-O_x}$	532.3-532.9
$\mathrm{C-O}$	532.9-533.3
$\mathrm{H_2O}$	533.7
$\mathrm{N-H_2}$	399.2-400.0
$\mathrm{N-H_3^+}$	401.4-401.9

The used XPS spectrometer was a XSAM800 (KRATOS) operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 20 eV, the non-monochromatized radiation $\mathrm{Mg\,K_\alpha}$ $(\mathrm{h\cdot\nu\ =1253.6\ eV})$ and a power of 120 W (10 mA × 12 kV).

CHAPTER 4

4. Experimental

4.1. Materials

4.1.1. Substrate

Silicon carbide grains were obtained from FILKEMP suppliers Saint-Gobain and NavarroSiC. The SiC grains from NavarroSiC after production are submitted to a demagnetizing process and chemical treatment, since they are produced from a mixture containing high purity silica sand and low sulfur petroleum coke, thus ensuring high-quality silicon carbide particles. Saint-Gobain's produced SiC particles are only submitted to a washing process with water, thus a pre-treatment step is required. The diameter of the grains used during the thesis can be consulted on the following Table 3. The properties of the substrate can also be consulted in Appendix A.

Table 3 - Silicon carbide diameter dimensions [68].

Supplier	Denomination	Diameter (μm)
Saint-Gobain	F046	300-425
NavarroSiC	F046	300-425
	F060	212-300
	F240	28-70

It should be taken into consideration that the silanization process was initially tested with the silicon carbide F046 but considering that the grains with higher dimensions reduce the surface contact coverage with the crystal, it was decided to use a smaller grain to prevent this behavior. Since the relative intensity of ATR-spectrum strongly depends on the amount of material which is in contact with IR-radiation, when the contact of the rough material with the internal reflection element occurs only in several points, the resulting spectra is inevitably distorted and the measurement may not be accurate, as the air between the sample and ATR crystal results in a weaker absorbance signal [57], [71].

Qualitative measurements are not considered problematic as long as the contact area is great enough to guarantee a robust measurement of the signal, thus it was decided to use a smaller grain, silicon carbide F240. Substrates were surface modified with a pre-treatment followed by silane agents, and subsequently characterized.

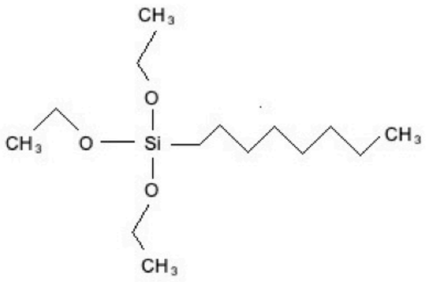
4.1.2. Silane Coupling Agents

Silicon carbide particles were chemically modified using six silane coupling agents, as result of the state-of-the-art studies and the existence of real offer on the market. The chosen silane coupling agents were divided in two main groups, according to the absence or presence of amino functional groups.

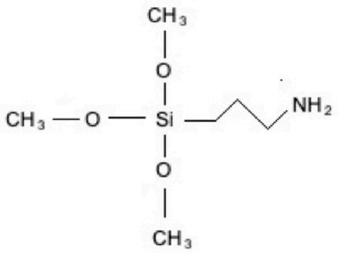
Group a): The alkylfunctional silanes octyltriethoxysilane (Dynasylan OCTEO), an oligomeric short chain alkylfunctional silane (Dynasylan 9896) and an emulsion of an alkyltrialkoxysilane oligomer in water (Dynasylan SIVO850);

Group b): The aminofunctional silanes 3-aminopropyltrimethoxysilane (Dynasylan AMMO), n-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Dynasylan DAMO-T) and n-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (Dynasylan 1401).

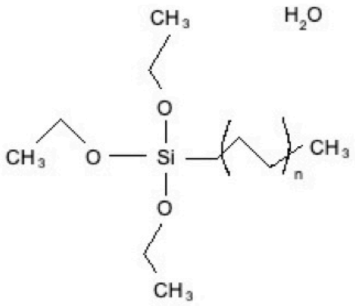
All the silane coupling agents (SCAs) were supplied by EVONIK. The SCAs were applied using a wet-chemical reaction that involved ethanol and water as a solvent for the first three mentioned organosilanes, only ethanol for the Dynasylan AMMO and toluene as solvent and n-butylamine as a catalyst for the two last ones. The structures of the SCAs are shown in Figure 5. See section 4.4 for further reaction details.



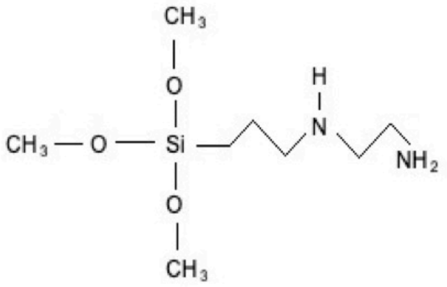
Octyltriethoxysilane
(Dynasylan OCTEO)



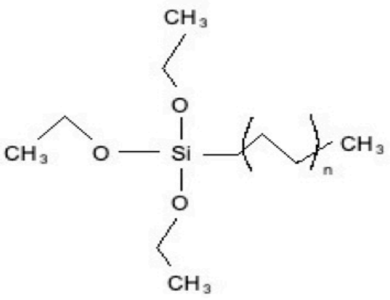
3-Aminopropyltrimethoxysilane
(Dynasylan AMMO)



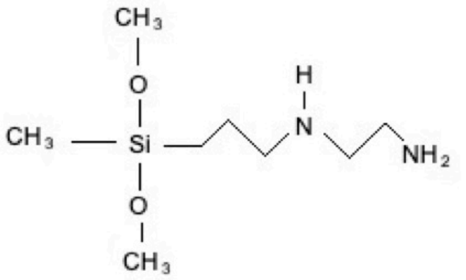
Emulsion of Alkyltrialkoxysilane oligomer in water
(Dynasylan SIVO850)



N-(2-aminoethyl)-3-aminopropyltrimethoxysilane
(Dynasylan DAMO-T)



Oligomeric short-chain Alkylfunctionalsilane
(Dynasylan 9896)



N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane
(Dynasylan 1401)

(a) (b)

Figure 5 - Structures for the silane coupling agents: (a) Alkylsilanes and (b) Aminosilanes.

4.2. Reactor

A three-neck round bottom flask with V = 250 mL of capacity was used as a reactor for the surface functionalization process. For the reactions that required heating, a condenser was built-in in the middle inlet, one of the lateral entrances had a thermocouple controlling the temperature and the third neck was used for the silicon carbide addition after the hydrolyzation step. The thermocouple was connected to a controller engaged with the heating and stirring plate.

For the reactions that required a nitrogen atmosphere, the reactor had an inlet of nitrogen gas an inlet for the silicon carbide addition and also a built-in condenser. Since the reactions did not require heating, only the stirring function of the magnetic hot plate stirrer was used. The reactors are illustrated in Figure 6, where the reactor a) was used for the functionalization with the Dynasylans OCTEO, SIVO 850 and 9896, and the reactor b) was used for the Dynasylans AMMO, DAMO-T and 1401.

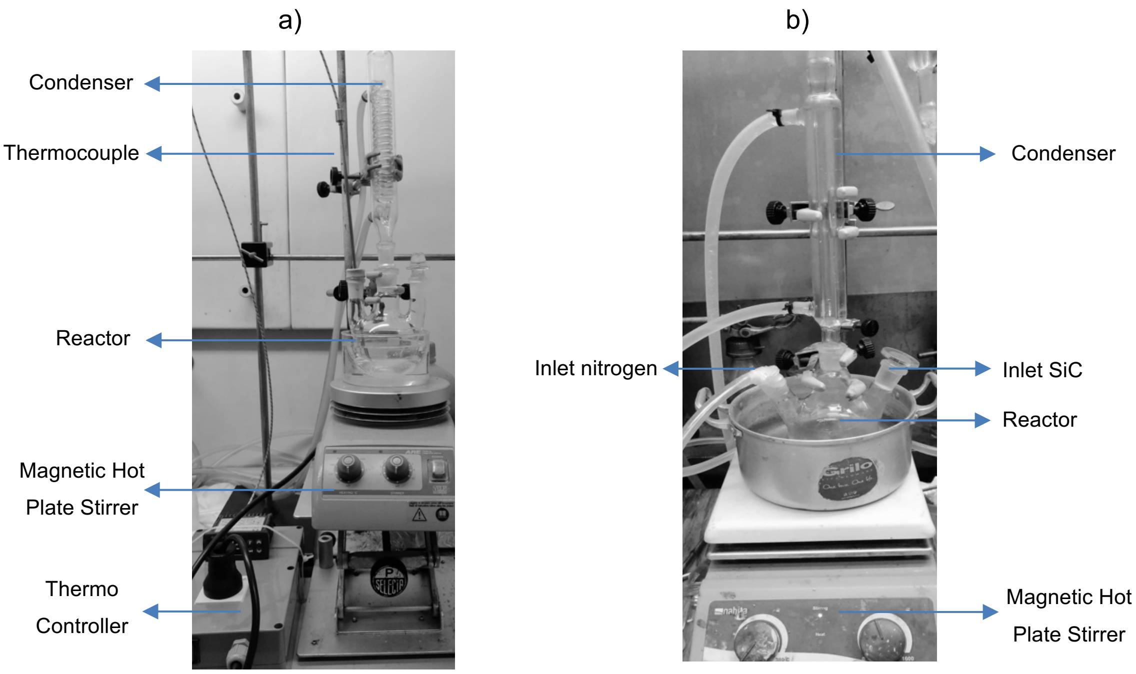


Figure 6 - Reactor used for: a) Alkylsilanes and b) Aminoalkylsilanes.

4.3. Surface Pre-Treatment

Surface pretreatments using hydrofluoric acid etching (HF) and sulfuric acid with ALNOCHROMIX (consists primarily of ammonium persulfate as an oxidizing agent) were applied to the substrate prior to the functionalization process in order to clean the surface.

4.3.1. HF Etching

Prior to reaction, the samples were cleaned in acetone and isopropanol for 10 min each, followed by etching in 5 % (V/V) hydrofluoric acid (HF) in water for 10 min. Surface hydroxylation was achieved by the HF treatment immediately prior to the functionalization reaction. The samples were filtered in a vacuum chamber and added to the reactor. It should be noted that at an initial stage, for the cleaning process, an ultrasound bath and a magnetic stirrer were compared, but no significant differences were observed in the samples after functionalization via characterization by FTIR technique, thus the following samples were cleaned through the magnetic stirring technique. These conclusions were obtained through FTIR analysis, as shown in the Appendix B.

4.3.2. ALNOCHROMIX and Sulfuric Acid Solution

Although this process may seem a little bit unconventional for this application, a solution containing 2 g of ALNOCHROMIX crystals and 50 mL of sulfuric acid (98%) was used as the cleaning process. After all the crystals were dissolved in the acid, the SiC particles were added and stirred lightly for 15 minutes in the solution, followed by a washing process with water and a vacuum filtration process.

This cleaning process removes the contaminants and oxidized layers present in the substrates surface and promotes the formation of hydroxyl groups. This ALNOCHROMIX and sulfuric acid solution showed to be more effective as surface treatment, thus it was chosen as the pre-treatment step for the following samples as seen in section 5.1.1.

4.4. Silane Treatment

A mixture containing deionized water (v = 25 mL), ethanol (v = 75 mL), and organosilane was magnetically stirred for 30 min at room temperature, in order to activate the silane by the formation of silanol groups. This step was followed by the addition of the silicon carbide into the reactional medium where the functionalization reaction would occur. The parameters time and temperature of the reaction were $t_r = 4$ h and $T_r = 75 \pm 7$ ºC. Afterwards, the particles were washed with ethanol in order to remove any physisorbed molecules from the surface, vacuum filtered and dried ($t_{drying} = 24$ h) in a heating chamber operating at $T_{drying} = 55$ ºC. This process was only applied for the organosilanes OCTEO, SIVO850 and 9896.

For the organosilane AMMO, a mixture containing ethanol (100 mL) and organosilane was stirred for 30 min at room temperature under a nitrogen atmosphere, in order to activate the silane by the formation of silanol groups and prevent oligomerization. This step was followed by the addition of 10 g of silicon carbide into the reactional medium and the functionalization reaction phase occurred for t_r = 1.5 h at room temperature (T_r = 20±7 ºC). After, the reaction the steps were similar to the ones applied to the other silanes. The particles were washed with the reaction medium solvent, ethanol, vacuum filtered and dried for t_{drying} = 24 hours in a heating chamber operating at T_{drying} = 55 ºC.

At last for the organosilanes DAMO-T and 1401, a mixture containing toluene (100 mL), a catalyst, 0.5 % (V/V) n-butylamine, and the organosilane, was stirred for 30 min at room temperature under a nitrogen atmosphere. The following steps are the same as the used for the organosilane AMMO, except for the solvent used for the washing step after the reaction, that was toluene. All the samples were stored in closed containers until further characterization. All reactions were executed at atmospheric pressure, P_{amb}.

Samples were immersed in different types of solvents, according to the chemical structure of the coupling agent and various coupling agent/substrate ratios were studied in order to find the optimal conditions. In the Table 4 it is possible to see the volumes of tested organosilanes.

Table 4 – Designations of organosilanes and volume added for functionalization tests.

Organosilane	**$V_{organosilane}$ (mL)**	**Organosilane**	**$V_{organosilane}$ (mL)**
Dynasylan OCTEO	3.0	Dynasylan AMMO	7.5
	3.5		10.0
	5.0		12.5
Dynasylan SIVO 850	5.0	Dynasylan DAMO-T	2.0
	7.5		2.5
	10.0		3.0
Dynasylan 9896	3.5	Dynasylan 1401	7.0
	5.0		10.0
	7.5		15.0

4.5. Sample Preparation – Pellet for Goniometer Test

After dried, the sample was placed in a cylindrical mold with 1.1 cm of diameter and 5 mm of height and is lightly pressed up until it fulfilled the mold. Then it was subjected to a pressing process, with the applied force of 3 metric tons, for t_{pellet} = 2 min, forming a compact tablet of functionalized SiC particles. This tablet was placed in a heating chamber for at least 8 hours and then in a desiccator for 24 hours to ensure that the sample was completely free of humidity. The tablet was then ready for the measurement of the contact angle. This entire process was necessary to ensure that the sample was completely free of moisture.

CHAPTER 5

5. Results and Discussion

5.1. Surface characterization of Silicon Carbide by FTIR

In this chapter, the first part of the discussion focuses on the characterization of the modified silicon carbide testing the two pre-treatments described in the previous chapters. The second part of the chapter focuses on the characterization of the samples treated with the organosilanes OCTEO, SIVO 850, 9896, AMMO, DAMO-T and 1401 with the volume of organosilane presented in the previous Table 4. Surface characterization analysis was performed via FTIR.

5.1.1. Pre-Treatment

The FTIR spectra can be used to identify the functional group by showing different vibrational modes of various bonds that are related to the SiC surface. Samples of functionalized silicon carbide particles prepared with 3.5 mL of organosilane OCTEO were prepared for the two studied types of pre-treatment, the etching solution of HF and the cleaning solution ALNOCHOROMIX. These samples were analyzed by Fourier-transform infrared spectroscopy (FTIR), as shown in Figure 7.

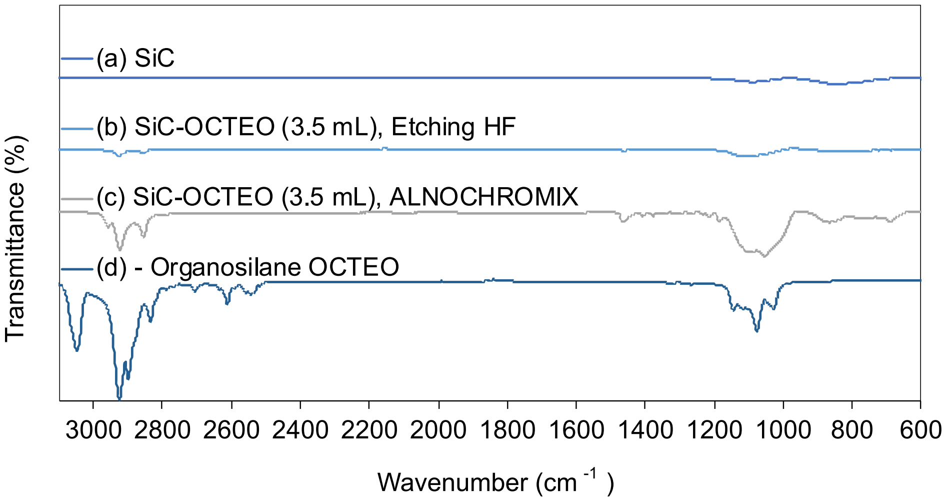
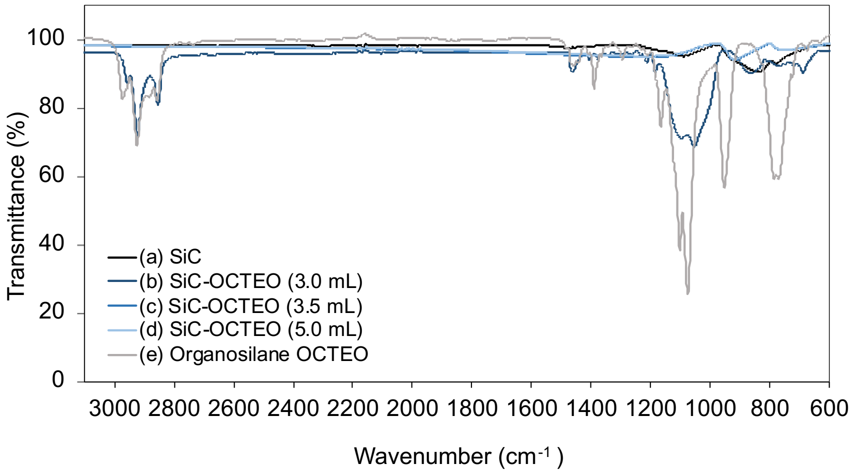


Figure 7 - FTIR spectra of (a) SiC, (b) SiC-OCTEO (3.5 mL), Etching HF, (c) SiC-OCTEO (3.5 mL), ALNOCHROMIX and (d) Dynasylan OCTEO.

It is possible to observe in the Figure 7, that the FTIR spectrum of the unmodified SiC sample is characterized by one adsorption band near 830 cm^{-1}, corresponding to the $\mathrm{Si-C}$ silicon carbide bond. The samples were submitted to the two different pre-treatments and then functionalized in the same conditions. The spectra corresponding to the sample treated with HF etching, Figure 7 (b) , shows a lower intensity of the organosilane characteristic functional groups compared to the sample that was treated with the ALNOCHOROMIX solution, Figure 7 (c), meaning that the surface of the silicon carbide is not covered as much, comparing with the treated sample with the ALNOCHROMIX pre-treatment. This interpretation led to the decision to treat all samples with this second process, since it showed to be more effective for the later on functionalization step.

5.1.2. Organosilane Dynasylan OCTEO

Samples of the functionalized particles of silicon carbide prepared with 3.0 mL, 3.5 mL and 5.0 mL of organosilane OCTEO were observed by Fourier-transform infrared spectroscopy (FTIR), having obtained the images presented in Figure 8. This organosilane is a octyltriethoxysilane, being characterized by its linear carbon chain (octyl), and the alcoxy group.



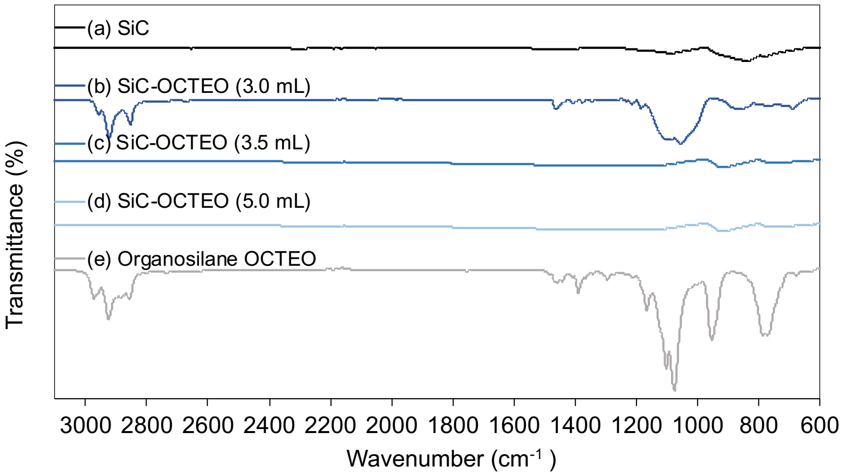


Figure 8 - FTIR spectra of (a) SiC powder, (b) SiC-OCTEO (3.0 mL), (c) SiC-OCTEO (3.5 mL), (d) SiC-OCTEO (5.0 mL) and (d) Dynasylan OCTEO.

Observing the Figure 8, the FTIR spectra of the coupling agent Dynasylan OCTEO and silicon carbide before and after modified by the organosilane. The spectra of the organosilane OCTEO, Figure 8 (e), is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 2971, 2925, 2881 and 2855 cm^{-1}, values within the range of the literature (3000–2840 cm^{-1}), $\mathrm{Si-O-CH_2-CH_3}$ stretches between 1167-951 cm^{-1} and 954 cm^{-1}, being characterized by the strong doublet at 1100 cm^{-1} and 1076 cm^{-1}, as well as the bond $\mathrm{Si-(CH_2)}_x\mathrm{-CH_3}$ from the alkyl group at 1165 cm^{-1} and $\mathrm{Si-OH}$ stretches at 862 cm^{-1}.

In the Figure 8 (b), the spectra of the functionalized SiC is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 2934, 2926 and 2855 cm^{-1}, being within the range in the literature of 3000–2840 cm^{-1}. These stretches are mainly related to the alkyl group introduced by the organic functionalization with the Dynasylan OCTEO. The chemical bonds, $\mathrm{Si-O-CH_2-CH_3}$ correspond to the stretches between 1161-978 cm^{-1}, as well as the bond $\mathrm{Si-(CH_2)}_x\mathrm{-CH_3}$ from the alkyl group at 1165 cm^{-1} and $\mathrm{Si-OH}$ stretches at 862 cm^{-1}. Besides, the absorption peak at 1050 cm^{-1} belongs to the stretching vibration of $\mathrm{Si-O-Si}$, which demonstrates that the organosilane is chemically bonded to the silicon carbide particles effectively.

It should also be taken into consideration that the added amount of the silane coupling agent will influence the modification of the SiC powder. By increasing the amount of the silane coupling agents, the $\mathrm{Si-OH}$ group generated by the hydrolysis process will attack the Si atom of the silane coupling agent which is already bonded to the surface of the particle [69-70]. As a result, the grafted coupling agents are detached from the surface. The samples of silicon carbide functionalized with (c) 3.5 mL and (d) 5.0 mL do not show the presence of the organosilane, but should not be discarded, thus more characterization tests should be done in order to observe the presence or not of the organosilane, since it is difficult to guarantee that through this method the surface is in fact treated, as the quality of the signal depends on the contact area between the sample and the FTIR crystal. When the contact of the sample with the internal reflection element does not occur in a way that the crystal is fully covered, the resulting spectra shows inevitably lower intensity. At higher frequencies, thus lower wavenumbers, due to the dependence of the absorbance intensity on the penetration depth, the spectral information can be lost [71]. It should be taken into consideration that the relative intensity of ATR-spectrum strongly depends on the amount of material which is in contact with IR-radiation. As mentioned previously in the section 4.1.1, when the contact of the rough material with the internal reflection element occurs only in several points, the resulting spectra is inevitably distorted and the measurement may not be accurate, as the air between the sample and ATR crystal results in a weaker absorbance signal.

5.1.3. Organosilane Dynasylan SIVO850

Samples of the functionalized particles of silicon carbide prepared with 5.0 mL, 7.5 mL and 10.0 mL of Dynasylan SIVO850 were observed by Fourier-transform infrared spectroscopy (FTIR), having obtained the images presented in Figure 9. Since this organosilane is an emulsion composed of an alkyltrialkoxysilane oligomer in water, the main groups observed should be similar to the ones from the Dynasylan OCTEO being the linear carbon chain (alkyl), and the silane group.

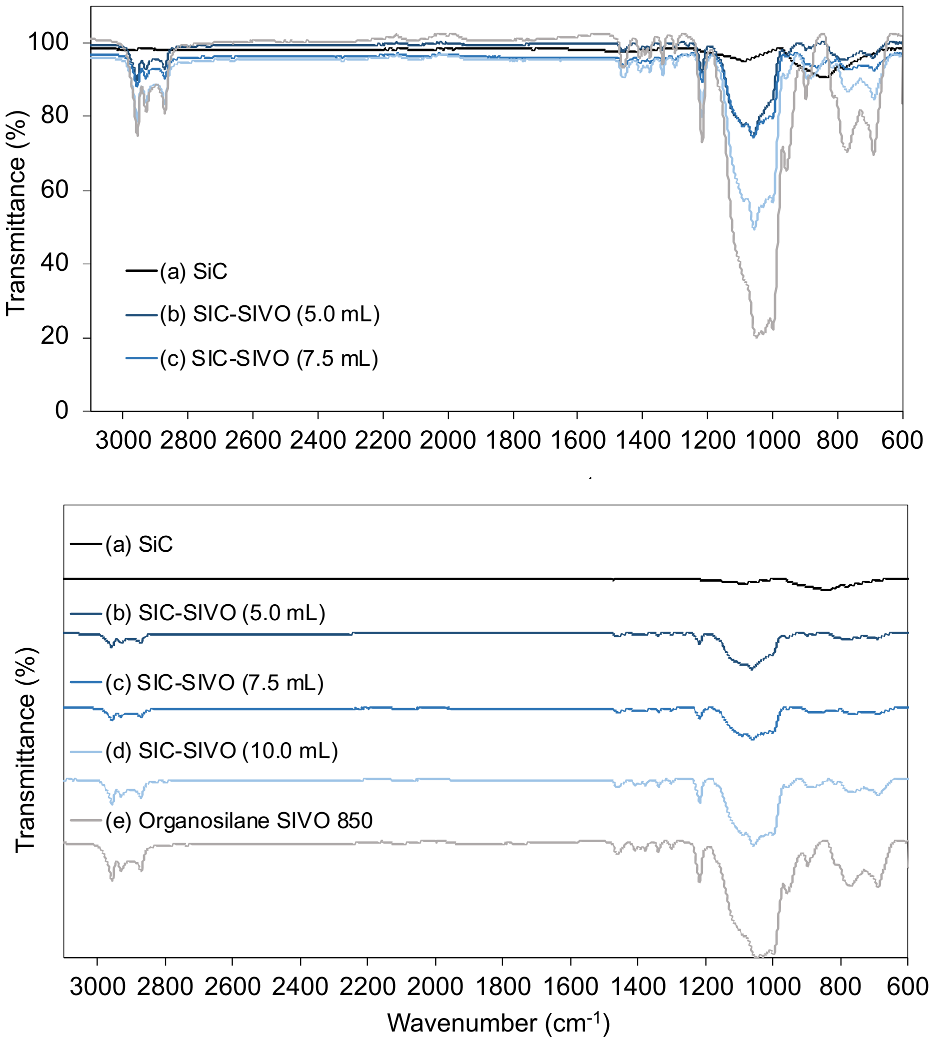


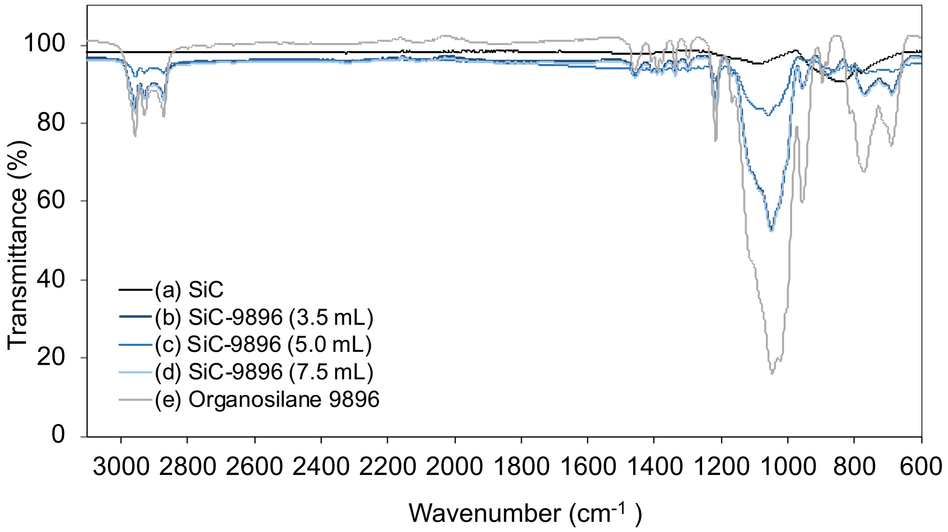
Figure 9 - FTIR spectra of (a) SiC powder, (b) SiC-SIVO (5.0 mL), (c) SiC-SIVO (7.5 mL), (d) SiC-SIVO (10.0 mL) and (d) Dynasylan SIVO850.

It is possible to observe in the Figure 9, the FTIR spectra of the coupling agent Dynasylan SIVO850 and silicon carbide before and after modified by the organosilane. The spectra of the organosilane SIVO850 is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 2957, 2929 and 2872 cm^{-1}, being within the range in the literature of 3000–2840 cm^{-1}, $\mathrm{Si-O-CH_2-CH_3}$ stretches between 1167-973 cm^{-1} and 997 cm^{-1}, with the strong 1047 cm^{-1} and 1027 cm^{-1} doublet. The bond $\mathrm{Si-(CH_2)}_x\mathrm{-CH_3}$ from the alkyl group at 1216 cm^{-1} and $\mathrm{Si-OH}$ stretches at 897 cm^{-1}. It should be noted that the longer the alkyl group is, the band attributed to this bond moves to lower frequencies. Although the number of carbons present in this silane is not known, the fact that it shows a higher frequency for this bond than the Dynasylan OCTEO, which is an octylsilane, is a guide that this silane has less carbons in the alkyl functional group.

In the Figure 9 (b), (c) and (d), the presence of $\mathrm{C-H}$ stretch at 3000–2840 cm^{-1} is mainly related to the alkyl group introduced by the organic functionalization of the Dynasylan SIVO 850 being a strong indication of the presence of the silane in the surface. The stretching vibration of $\mathrm{Si-O-Si}$, on the other hand, is located at 1056 cm^{-1}, corroborating that the organosilane is chemically bonded to the silicon carbide successfully.

5.1.4. Organosilane Dynasylan 9896

Samples of the functionalized particles of silicon carbide prepared with 3.5 mL, 5.0 mL and 7.5 mL of Dynasylan 9896 were observed by FTIR, having obtained the spectra presented in Figure 10. This organosilane is a short chain alkyltrialkoxysilane, thus the main groups observed should be similar to the ones from the Dynasylan OCTEO and SIVO 850.



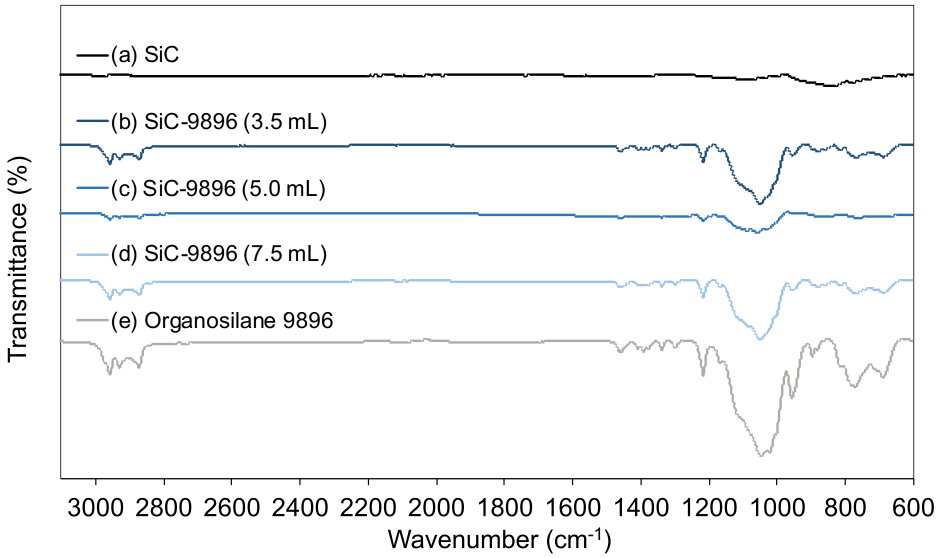


Figure 10 - FTIR spectra of (a) SiC powder, (b) SiC-9896 (3.5 mL), (c) SiC-9896 (5.0 mL), (d) SiC-9896 (7.5 mL) and (d) Dynasylan 9896.

It is possible to observe in the Figure 10, the FTIR spectra of the coupling agent Dynasylan 9896 and silicon carbide before and after modified by the organosilane. The spectra of the organosilane 9896 is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 2958, 2927 and 2872 cm^{-1}, being within the range in the literature of 3000–2840 cm^{-1}, $\mathrm{Si-O-CH_2-CH_3}$ stretches at 1108 cm^{-1}, 1043 cm^{-1} ,1021 cm^{-1} and 957 cm^{-1}, from the alkoxy groups to be activated, the bond $\mathrm{Si-(CH_2)}_x\mathrm{-CH_3}$ from the alkyl group at 1217 cm^{-1} and $\mathrm{Si-OH}$ stretches at 897 cm^{-1}.

In the Figure 10 (b), (c) and (d), once again the presence of $\mathrm{C-H}$ stretch at 2983–2852 cm^{-1} is mainly related to the alkyl group introduced by the organic functionalization of the Dynasylan 9896. Besides, the absorption peak at 1046 cm^{-1} belongs to the stretching vibration of $\mathrm{Si-O-Si}$, which demonstrates the organosilane is chemically bonded to the silicon carbide particles, aside from the other stretches present in the organosilane and the functionalized samples [72-74].

5.1.5. Organosilane Dynasylan AMMO

Samples of the functionalized particles of silicon carbide prepared with 7.5 mL, 10.0 mL and 12.5 mL of organosilane were observed via FTIR, having obtained the Figure 11. This organosilane is a 3-aminopropyltrimethoxysilane, being characterized by its linear carbon chain (propyl), the amine functional group and the silicon bonds.

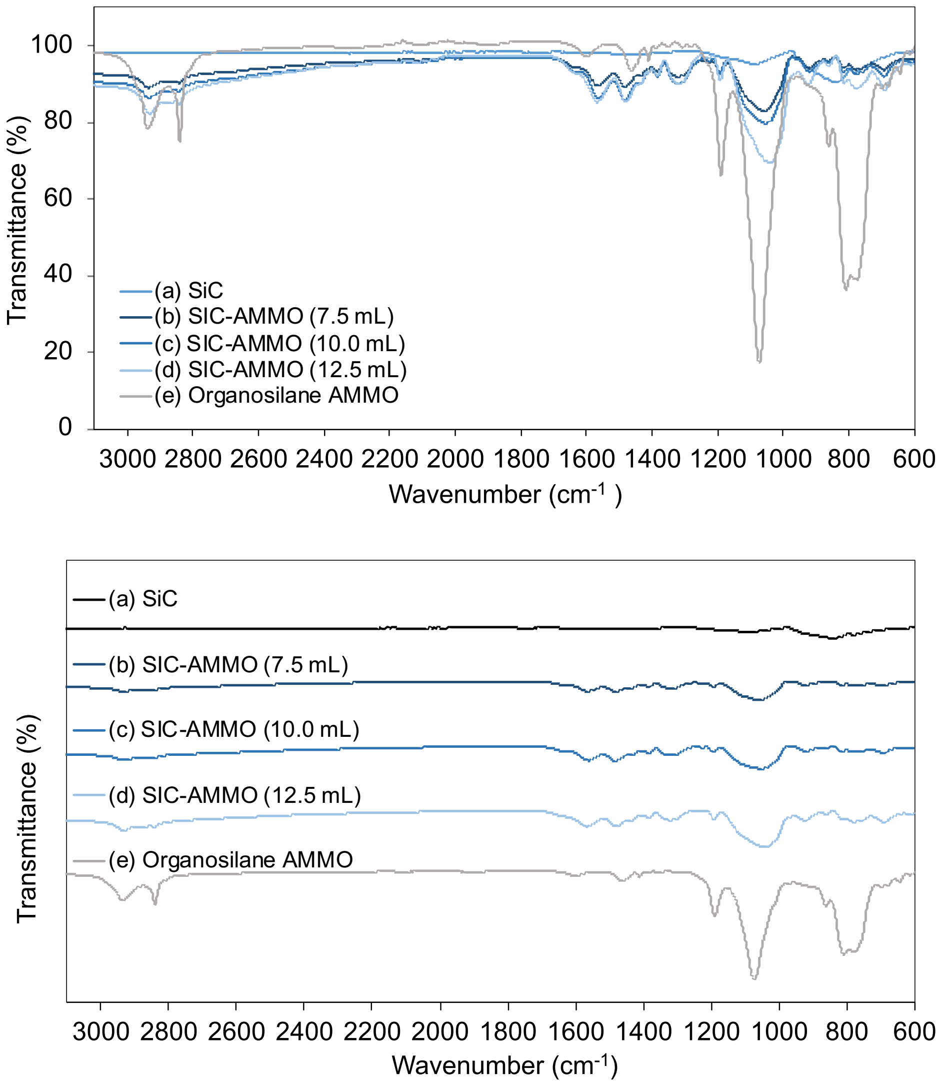


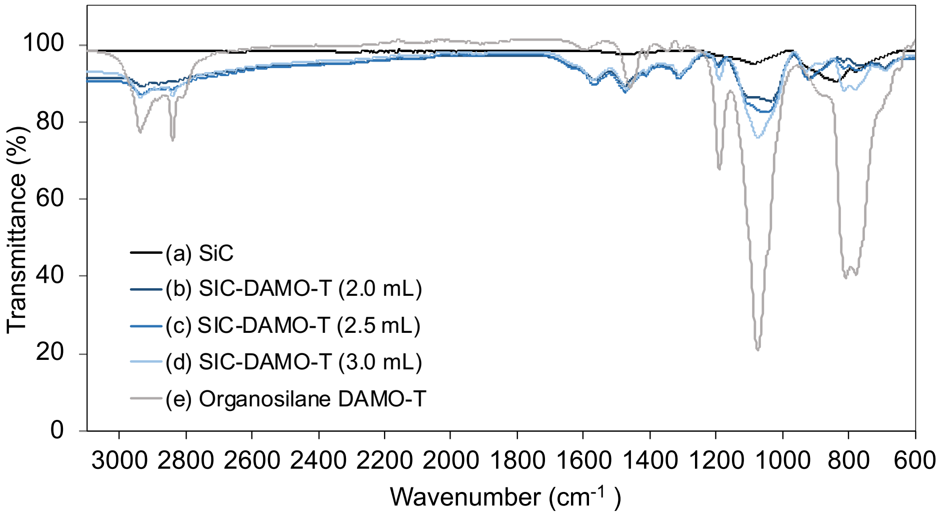
Figure 11 - FTIR spectra of (a) SiC powder, (b) SiC-AMMO (7.5 mL), (c) SiC-AMMO (10.0 mL), (d) SiC-AMMO (12.5 mL) and (d) Dynasylan AMMO.

Observing the Figure 11, the FTIR spectra of the coupling agent Dynasylan AMMO and silicon carbide before and after modified by the organosilane are shown. The spectra of the organosilane AMMO is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 3000–2840 cm^{-1}, $\mathrm{Si-O-CH_3}$ stretches at 1190 cm^{-1} and 1075 cm^{-1} and a sharp peak at 2840 cm^{-1}, the bond $\mathrm{Si-(CH_2)}_x-$ from the propyl group at 1189 cm^{-1} and $\mathrm{Si-OH}$ stretches at 950-800 cm^{-1}. It is also possible to observe the $\mathrm{N-H}$ stretch at 1564 and 774 cm^{-1}.

In the Figure 11 (b), (c) and (d) it should be expected to observe the presence of $\mathrm{C-H}$ stretch at 3000–2840 cm^{-1} is mainly related to the alkyl group introduced by the organic functionalization of the Dynasylan AMMO. Besides, the absorption peak approximately at 1042 cm^{-1} belongs to the stretching vibration of $\mathrm{Si-O-Si}$, which demonstrates the organosilane is chemically bonded to the silicon carbide particles successfully. Another indicator of the organosilane presence is the amine group corresponding peak at 1568 cm^{-1}, in the range 1650-1580 cm^{-1}. It is possible to observe that the strong peak seen in the organosilane spectra corresponding to the methoxy group at 2840 cm^{-1} disappeared in the functionalized samples, which reveals that the silane activation was successful, and this group was converted to reactive $\mathrm{Si-OH}$.

5.1.6. Organosilane Dynasylan DAMO-T

Samples of the functionalized particles of silicon carbide prepared with 2.0 mL, 2.5 mL and 3.0 mL of Dynasylan DAMO-T were observed by Fourier-Transform Infrared Spectroscopy (FTIR), having obtained the images presented in Figure 12. This organosilane is a n-2-aminoethyl-3-aminopropyltrimethoxysilane, being characterized by its linear carbon chain (propyl), the amine functional groups, having one primary and one secondary amines and the silicon bonds.



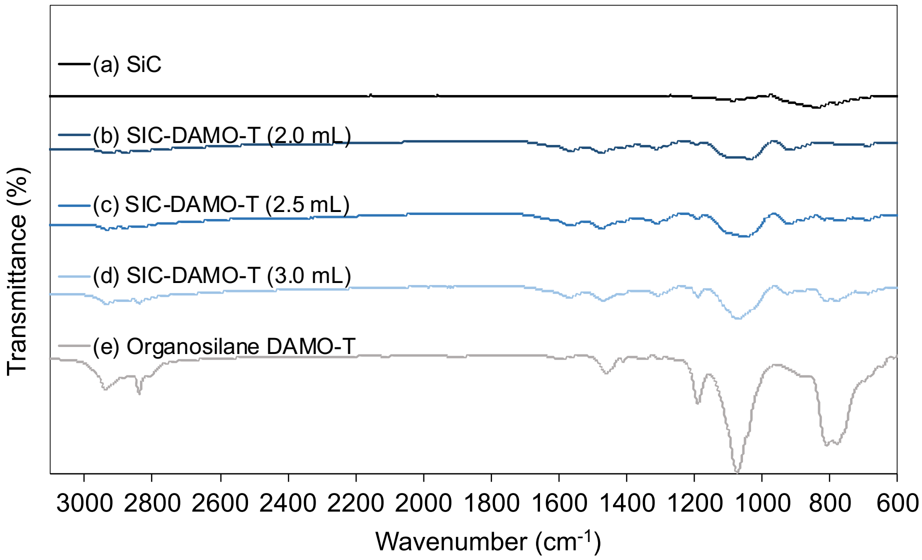


Figure 12 - FTIR spectra of (a) SiC powder, (b) SiC-DAMO-T (2.0 mL), (c) SiC-DAMO-T (2.5 mL), (d) SiC-DAMO-T (3.0 mL) and (d) Dynasylan DAMO-T.

It is possible to observe the Figure 12, the FTIR spectra of the coupling agent Dynasylan DAMO-T and silicon carbide before and after modified by the organosilane. The spectra of the organosilane is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 3000–2840 cm^{-1}, $\mathrm{Si-O-CH_3}$ stretches,1190 and 1075 cm^{-1} strong doublet and a sharp peak at 2840 cm^{-1}, as well as the bond $\mathrm{Si-(CH_2)}_x-$ from the alkyl group around 1200 cm^{-1} and $\mathrm{Si-OH}$ stretches at 950-800 cm^{-1}. A peak at 1595 cm^{-1} is attributed to the primary amine and the band at 774 cm^{-1} observed corresponds to the primary and secondary amines.

In the Figure 12 (b), (c) and (d) it should be expected to observe the presence of $\mathrm{C-H}$ stretch at 3000–2840 cm^{-1} which is mainly related to the alkyl group introduced by the organic functionalization with the Dynasylan DAMO-T. Besides, the absorption peaks at 1070, 1040 and 1052 cm^{-1} belong to the stretching vibration of Si-O-Si, for each (b), (c) and (d) spectra respectively, which demonstrates the organosilane is chemically bonded to the silicon carbide particles successfully. Another indicator of the organosilane presence is the amine groups corresponding peaks at 1595 cm^{-1}, in the range of 1650-1580 cm^{-1} and the bands at 774 cm^{-1}. It is also possible to observe the bond $\mathrm{Si-(CH_2)}_x-$ from the alkyl group around 1200 cm^{-1}, evidencing that the organosilane is indeed in the sample.

5.1.7. Organosilane Dynasylan 1401

Samples of the functionalized particles of silicon carbide prepared with 7.0 mL, 10.0 mL and 15.0 mL of Dynasylan 1401 were observed by Fourier-transform infrared spectroscopy (FTIR), having obtained the images presented in Figure 13. This organosilane is a n-2-

aminoethyl-3-aminopropylmethyldimethoxysilane, being characterized by its linear carbon chain (propyl), the amine functional groups, having one primary and one secondary amines and the silicon bonds and a methyl group bonding with the silicon.

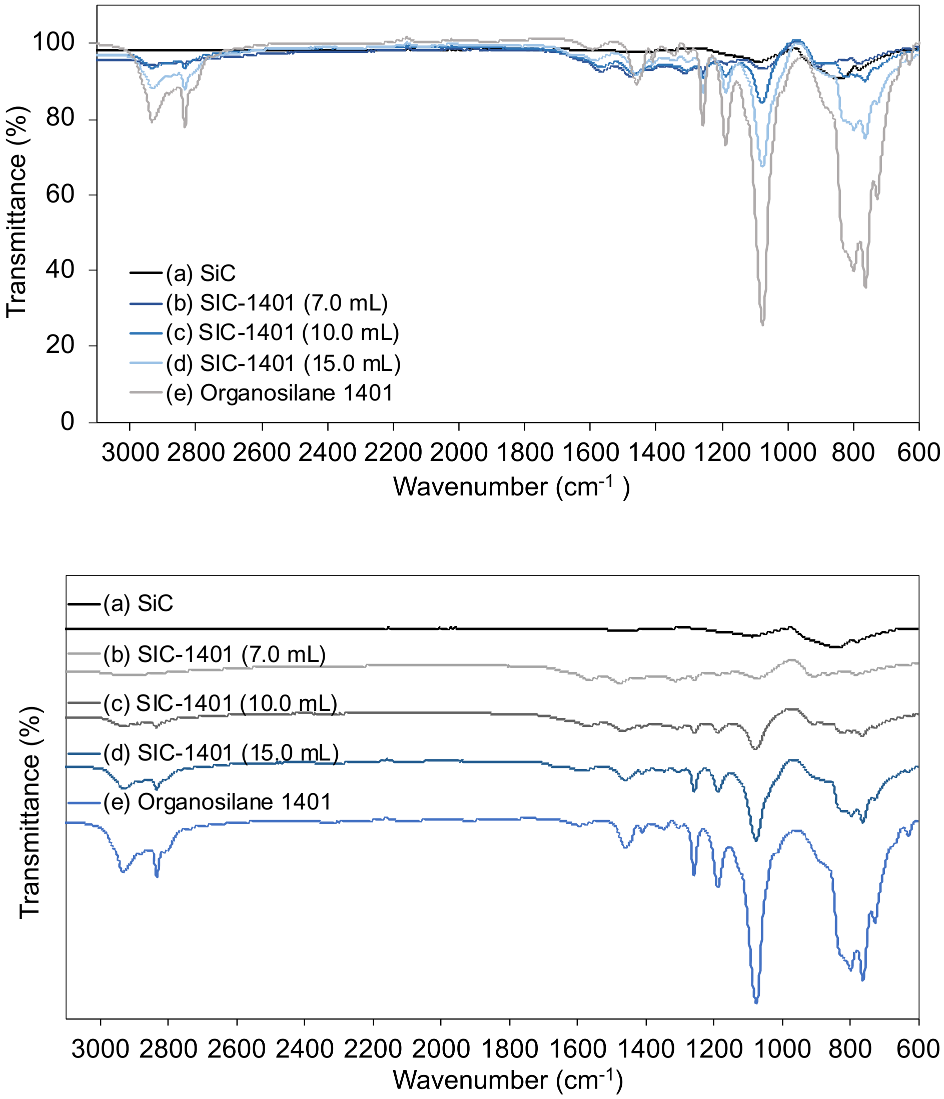


Figure 13 - FTIR spectra of (a) SiC powder, (b) SiC-1401 (7.0 mL), (c) SiC-1401 (10.0 mL), (d) SiC-1401 (15.0 mL) and (d) Dynasylan 1401.

Observing the Figure 13, the FTIR spectra of the coupling agent Dynasylan 1401 and silicon carbide before and after modified by the organosilane. The spectra of the organosilane 1401 is characterized by several peaks including the stretching vibration bands of the $\mathrm{C-H}$ at 3000–2840 cm^{-1}, $\mathrm{Si-O-CH_3}$ stretches,1185 and 1075 cm^{-1} strong doublet and a sharp peak at 2834 cm^{-1}, as well as the bond $\mathrm{CH_3-Si-(CH_2)}_x-$ from the alkyl groups around 1258 cm^{-1} and $\mathrm{Si-OH}$ stretches at 850-800 cm^{-1}. A peak at 1460 cm^{-1} and at 798 and 763 cm^{-1} can be observed corresponding to the amine groups, primary and secondary amines.

In the Figure 13 (b), (c) and (d) it should be expected to observe the presence of $\mathrm{C-H}$ stretch at 3000–2840 cm^{-1} is mainly related to the alkyl group introduced by the organic functionalization of the Dynasylan 1401. Furthermore, the absorption peaks of approximately 1073 cm^{-1} belong to the stretching vibration of $\mathrm{Si-O-Si}$, which proves the organosilane is chemically bonded to the silicon carbide particles successfully. Additional markers of the organosilane presence are the amine groups corresponding peak at 1460 cm^{-1}, 798 and 763 cm^{-1}, and the bonds from the alkyl groups around 1200 cm^{-1}, evidencing that the organosilane is indeed in the sample.

Summarizing, the functionalization of the SiC surface showed to be successful with every silane studied. Although several samples treated with the silane OCTEO didn't show its presence, other characterization tests will be executed to corroborate or not its existence. Overall, it can be stated that the techniques employed to modify the surface properties based on the chemical adsorption of silanes in the surfaces of SiC powder is effective and all the silanes showed to be promising for the SiC functionalization. Further characterization tests are needed to identify the silane chemical bonds with the surface, to quantify the surface coverage and to determine the volume of organosilane which shows higher hydrophobicity results, accessing which silanes are the most promising.

5.2. Surface characterization of silicon carbide by Contact Angle Measurement

The pellets obtained upon applying pressure on the particles of functionalized silicon carbide were positioned in a leveled surface and then a water droplet was placed onto the pellet. This way, the contact angle against water on a horizontal surface of the pellet was obtained. The wetting experiments were done for each sample.

The contact angle characterization has been used very often as a relatively simple method to assess the properties of surfaces as a result of their chemical or physical modification. The water contact angle can indicate if the surface is hydrophobic or hydrophilic. In order to compare the change by the presence of the organosilane, as well as to obtain the optimum reaction condition by the effect of modification by the amount of organosilane, this study was focused on the experimental parameter of the contact angle. Samples of silicon carbide pellets with and without the surface functionalization after the pre-treatment were observed with a goniometer, having obtained the images presented in Figure 14. Before the functionalization process the surface is still hydrophilic, which is corroborated by the obtained contact angle obtained of 0 º. After the functionalization process, the hydrophobic property of the organosilane that bonded with the SiC surface was granted to the surface, which can be verified by the contact angle over 90 º.

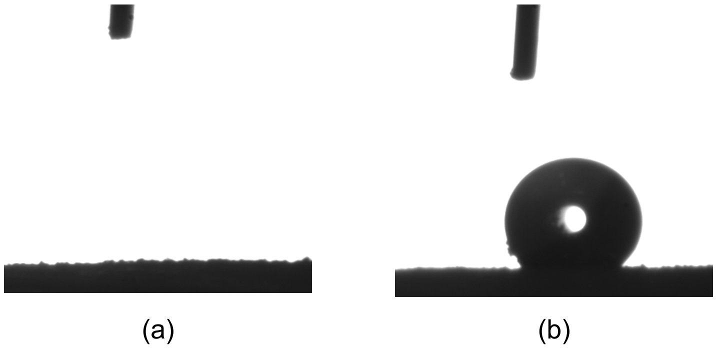

(a) (b)

Figure 14 – Evolution of the contact angle obtained by the Sessile Drop Method: (a) SiC after Pre-treatment and (b) SiC after functionalization.

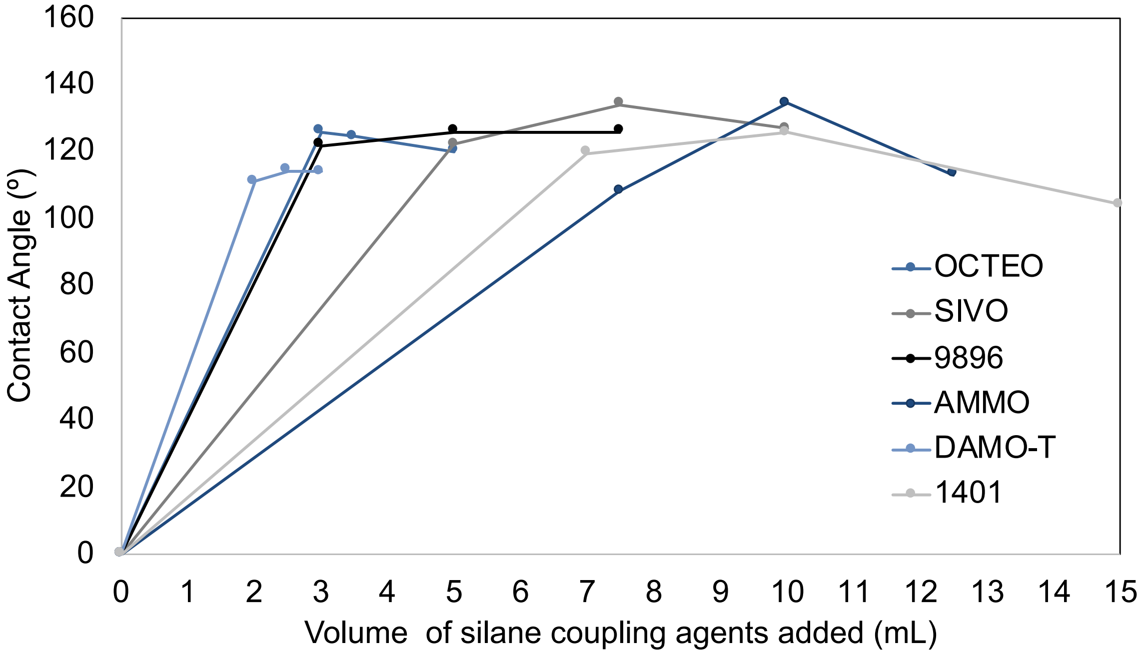


Figure 15 – Effect of silane coupling agent amount on the contact angle.

Figure 15 shows the effect of silane coupling agent amount on the contact angle. The SiC particles before modification can be considered as hydrophilic due to a water contact angle of 0 º, and the hydrophobicity has increased obviously in different degrees after modification by the different organosilanes. The average contact angle was determined from fourteen different measurements in each sample. Table 5 presents these values, as well as the respective standard deviations.

Table 5 - Average contact angles and respective standard deviations for the functionalized samples.

Organosilane	$V_{organosilane}$ (mL)	Contact Angle (º)	Organosilane	$V_{organosilane}$ (mL)	Contact Angle (º)
Dynasylan OCTEO	**3.0**	**126.0±0.2**	Dynasylan AMMO	7.5	108.3±0.1
	3.5	124.7±0.2		**10.0**	**134.4±0.2**
	5.0	120.1±0.2		12.5	113.3±0.2
Dynasylan SIVO 850	5.0	122.2±0.5	Dynasylan DAMO-T	2.0	111.2±0.4
	7.5	**134.2±0.2**		**2.5**	**114.4±0.5**
	10.0	127.0±0.2		3.0	114.1±0.3
Dynasylan 9896	3.5	122.0±0.9	Dynasylan 1401	7.0	119.6±0.5
	5.0	**126.0±0.3**		**10.0**	**125.7±0.2**
	7.5	126.0±0.2		15.0	104.3±0.4

It can be clearly observed that the contact angles of modified SiC increase first and then decrease with the increasing silane coupling agent amount, reaching maximum values at 7.5 mL, 5.0 mL, 10.0 mL, 2.5 mL and 10.0 mL for Dynasylans SIVO850, 9896, AMMO, DAMO-T and 1401, respectively. For the organosilane OCTEO, it is only possible to observe a decrease of the contact angle meaning that at the lowest volume tested of 3.0 mL, the contact angle is at its maximum.

As mentioned before, the results demonstrate that when the amount of silane coupling agent increases too much, the contact angle decreases, so the silane volume parameter is very important when it comes to the modification of the SiC powder surface. Before the silanization step, the major functional group in the surface is the hydroxyl group ($\mathrm{Si-OH}$). The silane added is constantly forming silanol groups that will react with the hydroxyl surface groups. If the silane coupling agent amount increases, the more silanol groups will be formed and will bond with the surface via condensation and more and more silanes will be grafted to the SiC surface contributing with the hydrophobic property, thus an increase in the contact angle value is verified [4], [69-70]. Even though in the section 5.1, it was not possible to observe, for all the treated samples, the presence of the organosilane, this analysis proves that the organosilane is in fact present in the surface of silicon carbide. In order to guarantee the presence of the chemical bond between the organosilane and the silicon carbide another method of surface characterization was used, XPS analysis.

Taking into account that the organosilanes with the amino functional group have been reported in the literature as most promising for the SiC-nylon adhesion, on the next analysis two samples functionalized with aminosilanes will be evaluated and one sample with the alkylsilane. The sample tested with the organosilane AMMO (10.0 mL), which showed the highest contact angle value, will be submitted to the next characterization test. The sample with DAMO-T (2.5

mL), requiring a low amount of organosilane volume and with the contact angle achieved of 114.4 ± 0.5 º should also be analyzed since it has a great volume vs performance achievement. At last, the sample tested with the organosilane OCTEO (3.0 mL), will be analyzed since it has a high contact angle value (126.0 ± 0.2 º) and the required volume of organosilane required was very low.

5.3. Surface characterization of silicon carbide via XPS

In this chapter, the first part of the discussion focuses on the characterization of the unmodified silicon carbide as a basis of comparison for the surface-modified samples. The second part of the chapter focuses on the characterization of the sample after the ALNOCHROMIX/ sulfuric acid pre-treatment. In the final part, the samples treated with the organosilanes OCTEO, AMMO and DAMO-T are presented. It should be noted that only the samples with the volume of organosilane who showed the highest values of contact angle were submitted to this characterization test.

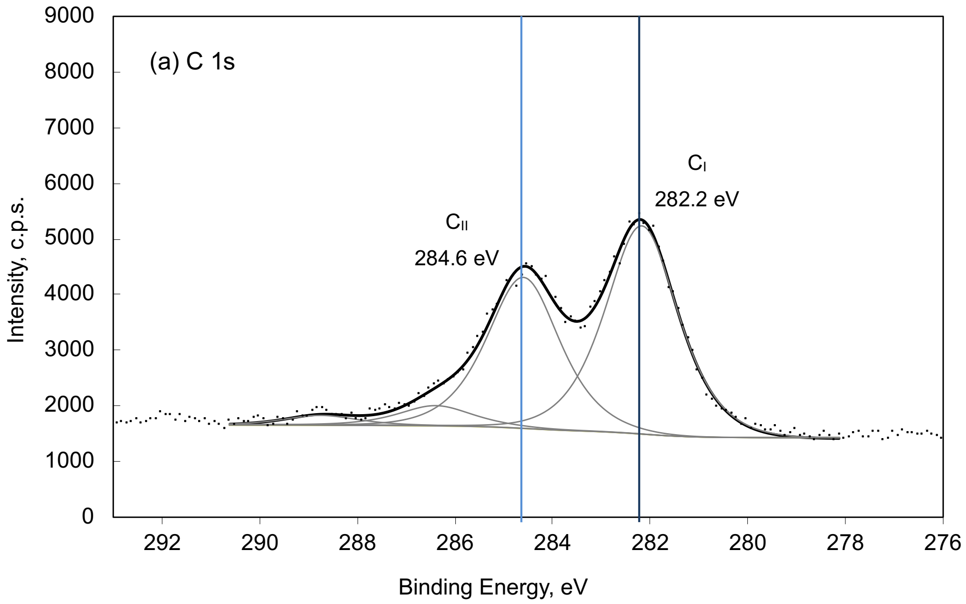
5.3.1. XPS Analysis for non-surface modified SiC

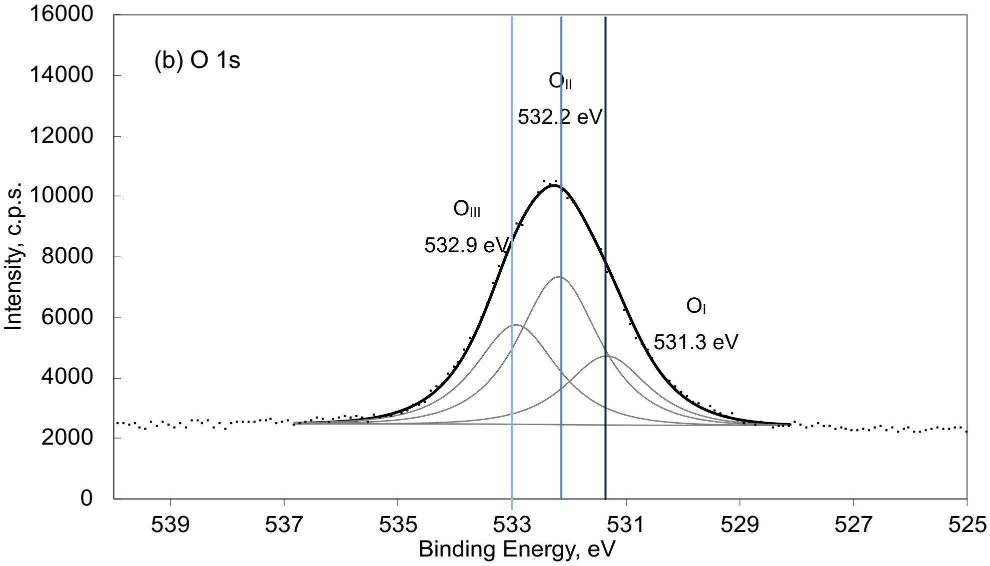
The silicon carbide sample without any treatment showed the presence of carbon, oxygen and silicon in the wide scan spectrum. The following Table 6 lists the elemental surface composition for the unmodified SiC substrate.

Table 6 - XPS analysis for the unmodified SiC substrate (atomic %).

Sample	% C	% O	% Si
Unmodified SiC	45.4	29.7	24.9

The analysis of the data in Table 6 implies that the SiC surface has organic contaminants and an oxidized layer. The carbon composition value observed is really high, 45.4 %, suggesting the presence of organic carbon as a surface contaminant, since the SiC surface is 1:1 (Si:C), and the percentage of silicon shown of 24.9 % is low compared to the carbon. To better understand the bonds in the SiC surface, it is possible to observe in the following Figure 16 the XPS survey scans of the SiC surfaces C 1s, O 1s and Si 2p and the corresponding peak assignments. It should be noted that if the surface was ideally clean, the surface atomic composition should be approximately 50/50 % (Si/C %).


(a) C 1s
C$_I$
282.2 eV
C$_{II}$
284.6 eV
Intensity, c.p.s.
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
292
290
288
286
284
282
280
278
276
Binding Energy, eV


(b) O 1s
O$_{II}$
532.2 eV
O$_{III}$
532.9 eV
O$_I$
531.3 eV
Intensity, c.p.s.
16000
14000
12000
10000
8000
6000
4000
2000
0
539
537
535
533
531
529
527
525
Binding Energy, eV

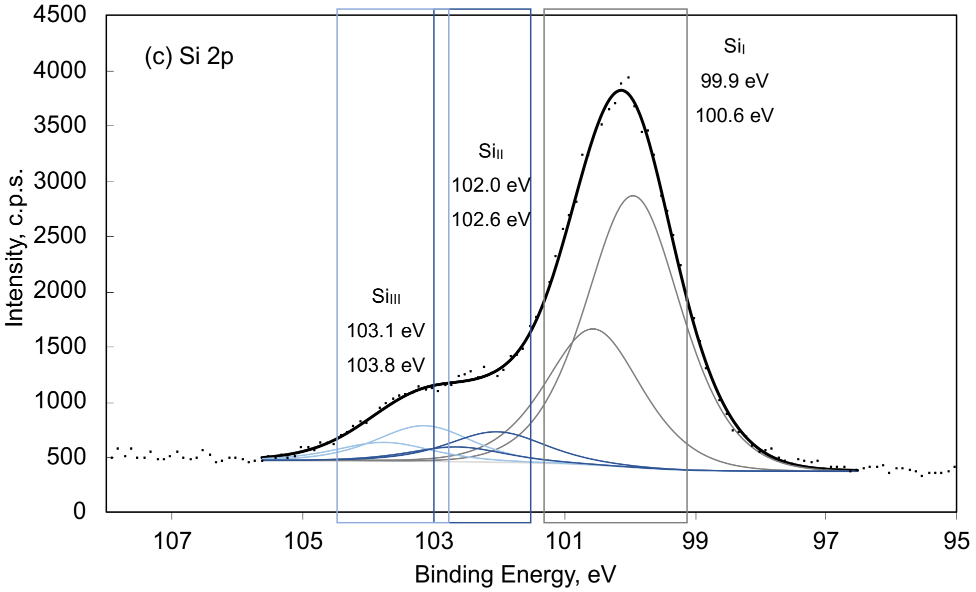


Figure 16 - XPS survey spectra of unmodified SiC. (a) C 1s, (b) O 1s and (c) Si 2p core level spectra.

The C 1s spectrum was resolved into two main peaks. Peak C$_{\mathrm{I}}$ at a binding energy (BE) of 282.2 eV was attributed to carbide carbon in $\mathrm{C-Si}$, while peak C$_{\mathrm{II}}$ at 284.6 eV was assigned to adventitious carbon, comprising a variety of short chain, perhaps polymeric hydrocarbons species with small amounts of both singly and doubly bound oxygen functionality ($\mathrm{C-H/C-C}$) or maybe from the contact with other surfaces like polythene bags, or the gloves used for handling the samples. The high intensity of the organic carbon peak explains the high carbon percentage observed in the Table 6.

The O 1s spectrum consists of three peaks at 531.3 eV which corresponds to $\mathrm{C=O}$ bonds in the SiC surface and a peak at 532.9 eV corresponding to the $\mathrm{C-O}$ bond, from oxidation of the carbide or from contaminants, and at last, a 532.2 eV peak corresponding to the $\mathrm{Si-O_2}$ bond.

The Si 2p spectrum was resolved into three main peak doublets. Peaks Si$_{\mathrm{I}}$ at 99.9 eV and 100.4 eV are attributed to Si bonded to C from the silicon carbide and peaks Si$_{\mathrm{II}}$ at 102.0 eV and 102.6 eV are attributed to silicon suboxides, $\mathrm{Si-O_x}$, (x<2), interpreted as $\mathrm{Si-OH}$ bonds present on the surface. There is also a Si$_{\mathrm{III}}$ peak doublet at 103.1 and 103.8 eV indicating traces of oxidized silicon carbide, $\mathrm{Si-O_2}$ [75]. All the binding energy values are consistent with the reported values mentioned in the Table 2 from section 3.3.

The Si to C atom ratio associated with SiC was also calculated from the area ratio of the Si$_{\mathrm{II}}$ peak to the C$_{\mathrm{I}}$ peak divided by their respective sensitivity factors, 0.32 for C 1s and 0.37 for Si 2p. The resultant atom ratio Si$_{\mathrm{SiC}}$/C$_{\mathrm{SiC}}$ was 1.0 which is in agreement with the theoretical value. The experimental ratio indicates there is exactly the same amount of silicon atoms relative to carbon atoms on the surface.

The sensitivity factors for the elements in question are supplied by the instrument manufacturer and this sensitivity factor with the curve fitting of the spectrum, give the relative percentages corresponding to each element.

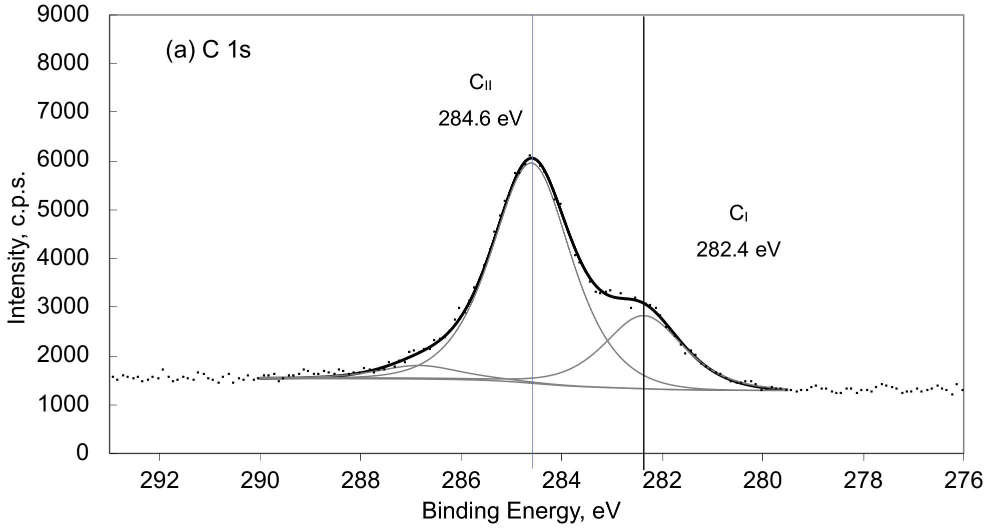
5.3.2. XPS Analysis for SiC after the selected surface pre-treatment

The silicon carbide sample after the ALNOCHROMIX and sulfuric acid solution treatment showed the presence of carbon, oxygen, silicon, but also of nitrogen in the wide scan spectrum. The Table 7 lists the elemental surface composition for the SiC substrate after pre-treatment.

Table 7 - XPS analysis for the SiC substrate after pre-treatment (atomic %).

Sample	**% C**	**% O**	**% Si**	**% N**
SiC Pre-Treated	46.4	38.8	11.7	3.1

From the analysis of the SiC surfaces atomic composition in the Table 7 it should be expected to have a lower percentage of carbon present in the surface and higher silicon content. Since the oxygen composition is then again really high, 38.8 %, compared to the silicon 11.7 %, maybe this value is due to the formation of hydroxyl groups, $\mathrm{Si-OH}$, resulting from the acid pre-treatment. The presence of nitrogen can be justified by the ALNOCHROMIX solution that included ammonium persulfate. Since no direct conclusions can be taken from the analysis of the atomic composition, in the following Figure 17 the XPS survey scans of the SiC pre-treated surfaces C 1s, O 1s, Si 2p and N 1s will give more information about the exact bonds existing in the surface.



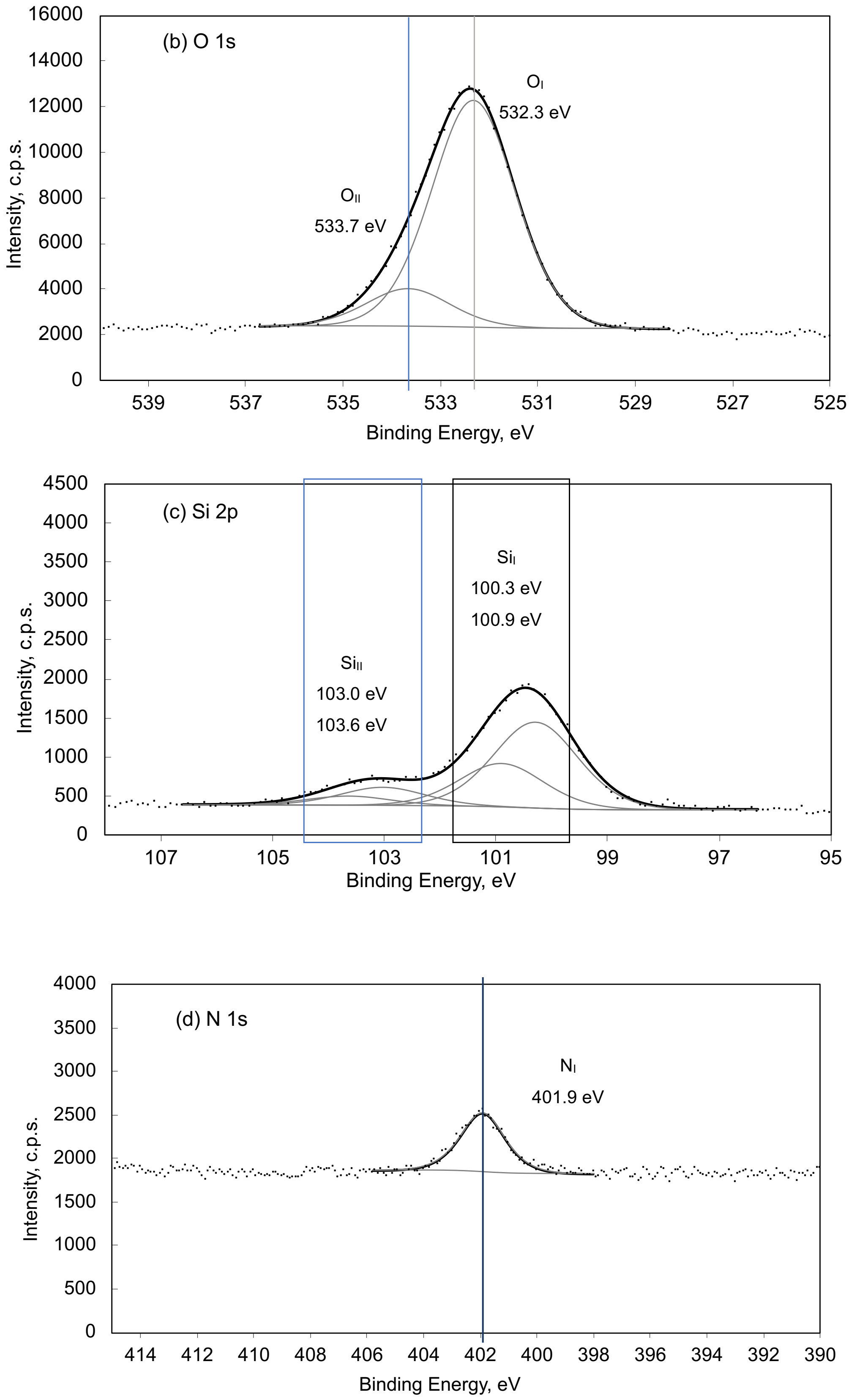


Figure 17 - Photopeaks of SiC after pre-treatment: (a) C 1s, (b) O 1s, (c) Si 2p. and (d) N 1s.

The C 1s spectrum was resolved into two main peaks. Peak C_I at a binding energy (BE) of 282.4 eV was attributed to carbide carbon, $\mathrm{Si-C}$, peak C_{II} at 284.6 eV was assigned to adventitious carbon, $\mathrm{C-H/C-C}$. The high amount of organic carbon seen can be explained by the *eppendorf* container in which it was stored or re-adsorption of adventitious carbon from the atmosphere.

The O 1s spectrum consists mainly of an O_I peak at 532.3 eV which corresponds to the suboxides $\mathrm{Si-O_x}$ bond at the surface of the silicon carbide samples. Another secondary O_{II} peak appears at 533.7 eV, corresponding to residual water after the pre-treatment used to wash off the acid solution. The Si 2p spectrum was resolved mainly into two doublet peaks. Peak Si_I at 100.3 eV and 100.9 eV was attributed to the $\mathrm{Si-C}$ bond in the silicon carbide and the peak doublet Si_{II} at 103.0 eV and 103.6 eV was attributed to Si bonded to O from the suboxides formed, mainly $\mathrm{Si-OH}$. The new presence, nitrogen, consists on a single peak at 401.9 eV that corresponds to a protonated amine and the ALNOCHROMIX solution used in the pre-treatment justifies this new element since it is has ammonium persulfate. All the binding energy values are consistent with the reported values mentioned in the section 3.3 as well.

On a final note, comparing the atomic percentages corresponding to the bonds containing Si, of the unmodified surface and of the surface after pre-treatment, it is possible to observe a significant increase in the presence of $\mathrm{Si-OH}$ bond present on the surface as expected from the surface activation step. In Table 8 it is possible to verify that the contribution of the oxidized Si bonds disappeared indicating that the silicon carbide surface in which all the research work is developed is mostly the inorganic $\mathrm{Si-C}$ bond and the $\mathrm{Si-OH}$ layer ready to chemically bond to the silane in the posterior silanization step and some minor amount of oxidized Si. The chosen pre-treatment is, thus, efficient. These values were obtained from the fraction of area corresponding to each bond and the overall contribution.

Table 8 - Composition (atomic %) corresponding to the Si bonds in the unmodified surface and in the surface after pre-treatment.

Sample	% SI-C	% Si-O_x	% Si-O_2
SiC Unmodified	80.4	8.9	10.7
SiC Pre-Treated	82.6	17.3	-

5.3.3. XPS Analysis of Treated Surfaces of SiC

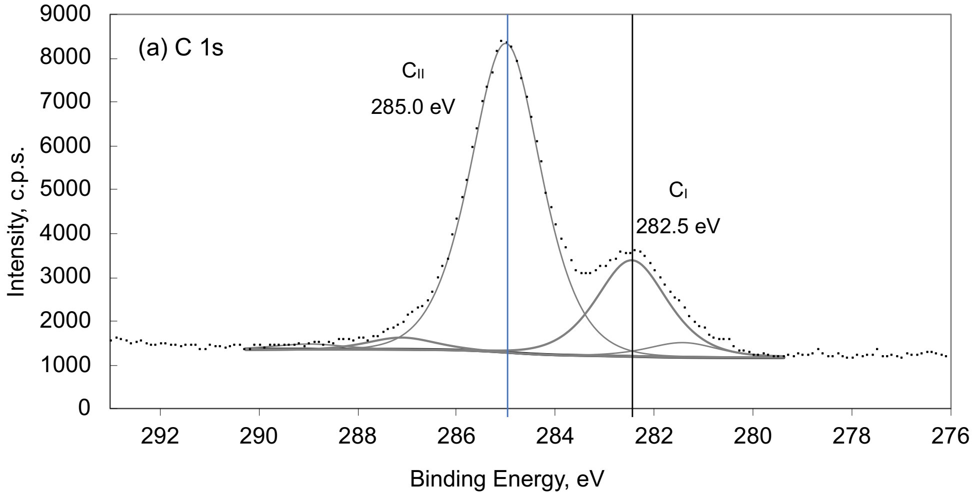
The properties of the SCAs depend on the organofunctional silane itself, the substrate surface and the application parameters. Some of the silicon carbide samples functionalized with the organosilanes were characterized via XPS analysis. As previously mentioned, the samples treated with the organosilanes OCTEO, AMMO and DAMO-T with the volume of organosilane who showed the highest values in the contact angle analysis were submitted to the XPS characterization test.

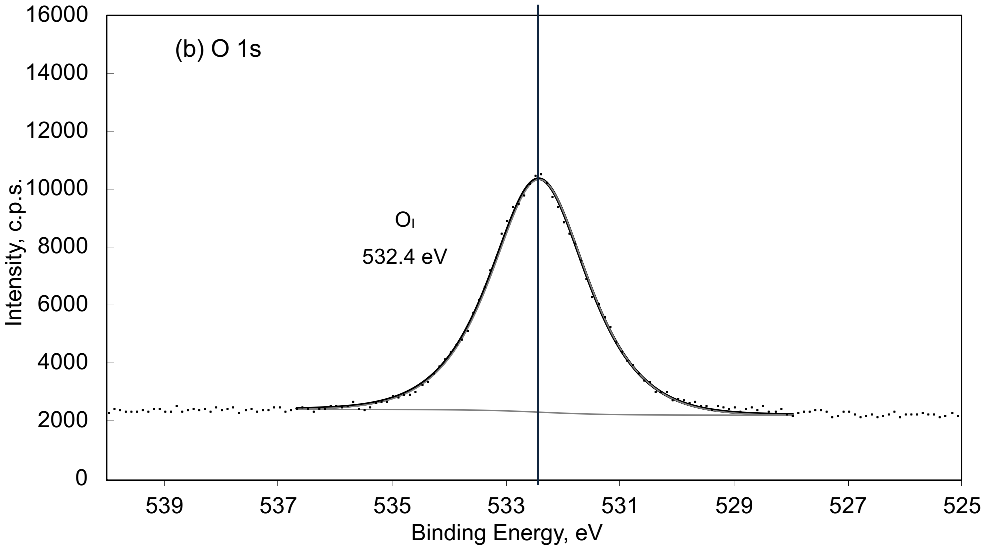
5.3.3.1. Organosilane Dynasylan OCTEO

XPS analysis of the Dynasylan OCTEO functionalized substrate with the organosilane volume of 3.0 mL showed the presence of the elements carbon, oxygen, silicon, nitrogen. In the following table and figure, it is possible to assess the contribution of each element in the surface as well as the XPS survey scans for C 1s, O 1s and Si 2p and the corresponding peak assignments. Although the element nitrogen is in the sample, its contribution is extremely small and only due to the protonated amine from the previous pre-treatment.

Table 9 - XPS analysis for the SiC-OCTEO (3.0 mL) substrate (atomic %).

Sample	% C	% O	% Si	% N
SiC OCTEO (3.0 mL)	55.5	24.0	17.6	1.0





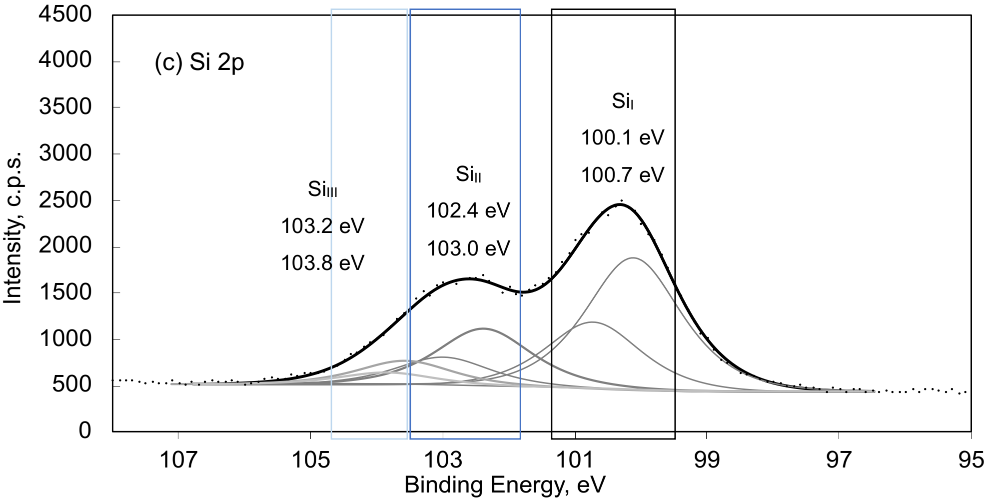


Figure 18 - Photopeaks of SiC-OCTEO (3.0 mL) substrate: (a) C 1s, (b) O 1s and (c) Si 2p.

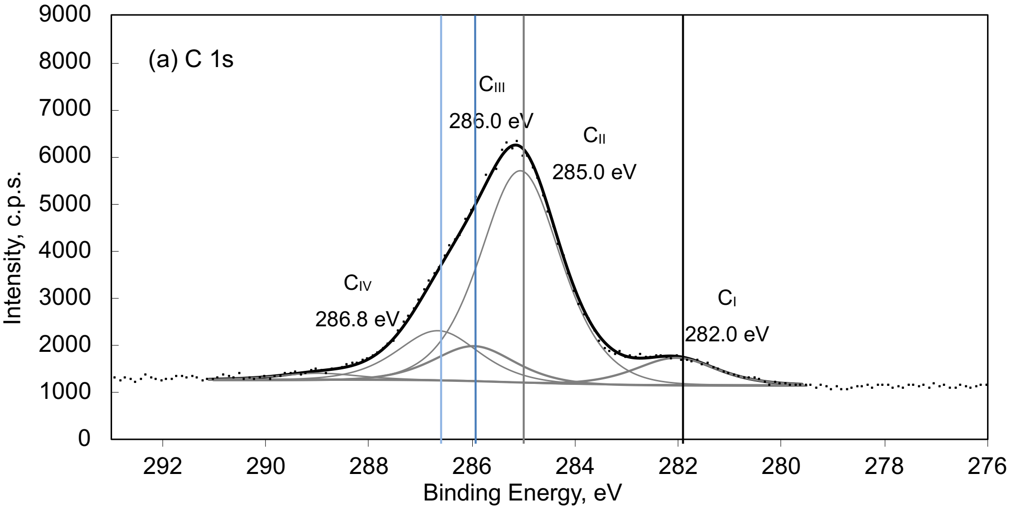
The C 1s spectrum was resolved into two main peaks. Peak C$_I$ with a binding energy of 282.5 eV was attributed to carbide carbon in SiC, peak C$_{II}$ at 285.0 eV was assigned to organic carbon, $(\mathrm{C-H/C-C})$. It is possible to observe that the peak with the highest intensity is the C$_{II}$ corresponding to the Hydrocarbon chain from the organosilane OCTEO. The higher value of the carbon atom seen in Table 9 (55.5 %) compared to the value presented in Table 7 (46.4 %) also suggests that the organosilane is indeed connected to the substrate corresponding to the octyl group existent in the SCA. The O 1s spectrum consists only of an O$_I$ peak at 532.4 eV which corresponds to the $\mathrm{Si-O-Si}$ bond that proves that the organosilane is chemically bonded to the substrate. The Si 2p spectrum was resolved mainly into four peaks. Peaks doublet Si$_I$ at 100.1 eV and 100.7 eV are attributed to silicon carbide $\mathrm{Si-C}$ bond. $\mathrm{Si-O-Si}$ bond from the silanol group in the silane attached to the surface of the SiC particles, Si$_{II}$, is at 102.4 eV and 103.0 eV. The peaks doublet Si$_{III}$ at 103.2 eV and 103.8 eV is attributed to silicon suboxides in the SiC surface. All the binding energy values are consistent with the reported values mentioned in the section 3.3 as well.

5.3.3.2. Organosilane Dynasylan AMMO

XPS analysis of the Dynasylan AMMO functionalized substrate with the organosilane volume of 10.0 mL showed the presence of the elements carbon, oxygen, silicon, nitrogen. In the following Table 10 and Figure 19, it is possible to assess the contribution of each element in the surface as well as the XPS survey scans for C 1s, O 1s, Si 2p and N 1s and the corresponding peak assignments. The presence of 8.9 % of nitrogen is an indication that the Dynasylan AMMO was adsorbed onto the surface. The high oxygen atomic percentage of 35.1 % may result from the silanol groups in the silane and the carbon percentage of 45.8% due to the propyl group existing in the silane.

Table 10 – XPS analysis for the SiC-AMMO (10.0 mL) substrate (atomic %).

Sample	**% C**	**% O**	**% Si**	**% N**
SiC AMMO (10.0 mL)	45.8	35.1	10.2	8.9



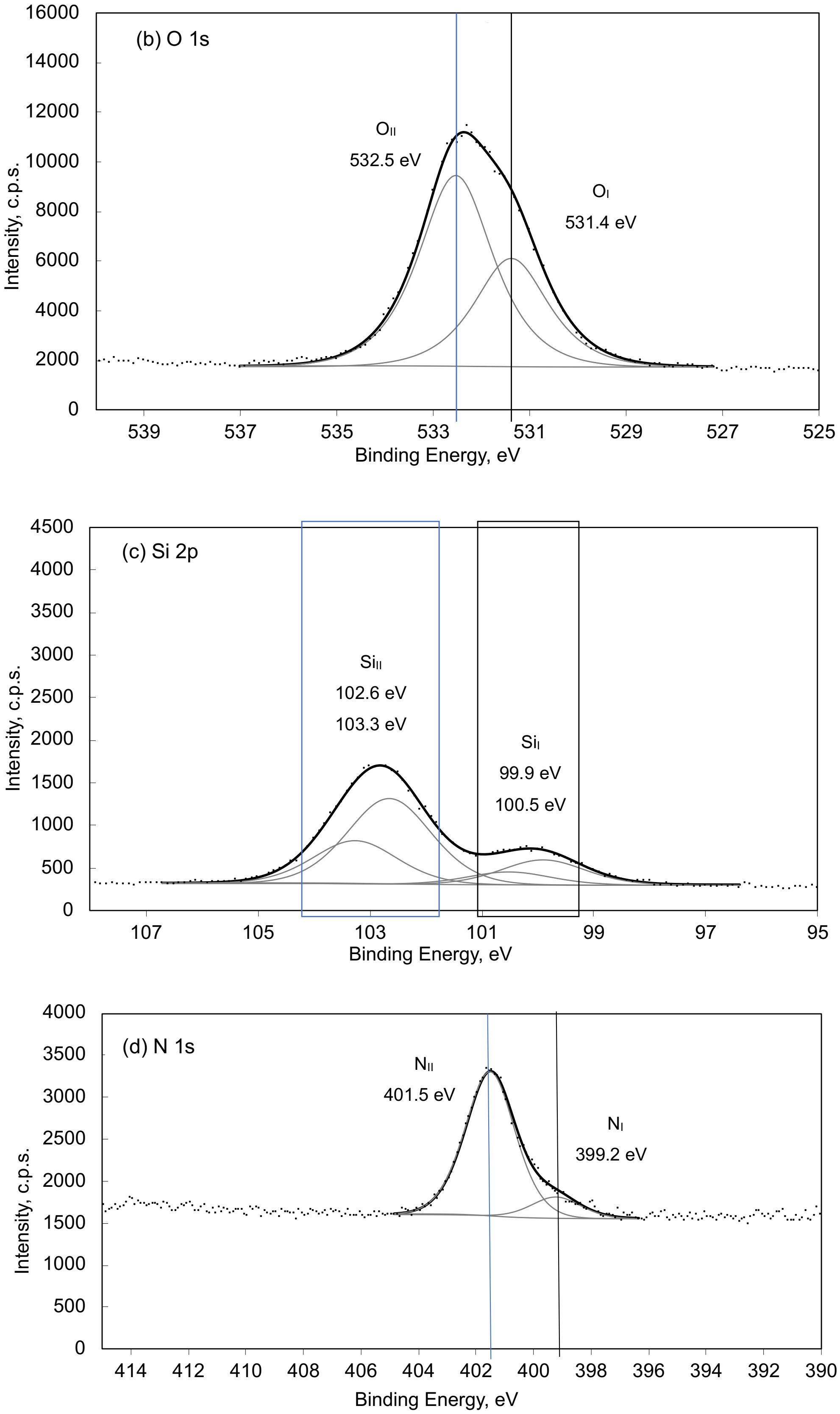


Figure 19 – Photopeaks of SiC-AMMO (10.0 mL) substrate: (a) C 1s, (b) O 1s, (c) Si 2p and (d) N 1s.

The C 1s spectrum was resolved into four main peaks. Peak C_I with a binding energy of 282.0 eV was attributed to carbide carbon in SiC, peak C_{II} at 285.0 eV was assigned to organic carbon, $(\mathrm{C-H/C-C})$ from the silane propyl group, resulting in a high intensity peak. The peak C_{III} at 286.0 eV was assigned to the bond $\mathrm{C-N}$ existing in the silane and at last the peak C_{IV} at 286.6 eV was assigned to the bond C-O existing maybe due to unreactive silanol groups. The O 1s spectrum consists of two peaks: O_I peak at 531.4 eV corresponding to the oligomerization between the silanol groups in the silanes, and peak O_{II} at 532.5 eV corresponding to the $\mathrm{Si-O-Si}$ bond between the silane and the surface, corroborating that the organosilane is chemically bonded to the substrate, as expected from the analysis of the Table 10.

The Si 2p spectrum was resolved mainly into four peaks, divided in two doublets. Peaks for Si_I at 99.9 eV and 100.5 eV are attributed to $\mathrm{Si-C}$ bond in the substrate, and peaks Si_{II} at 102.6 eV and 103.3 eV are attributed to the $\mathrm{Si-O-Si}$ bond between the silanols and the silanols and the SiC surface.

At last, the N 1s curve-fit consists of two peaks, N_I at 399.2 eV that corresponds to the functional group amine of the organosilane and the peak N_{II} at 401.5 eV that corresponds also to the amine from the organosilane, but in a protonated form $(\mathrm{NH_3^+})$. aminoalkylsilanes, such as 3-aminopropyltrimethoxysilane, are extensively used for the chemical modification of various silica and alumina surfaces. The complete characterization of the chemical state of silicon carbide modified by this organosilane requires a detailed knowledge of the nature of the organosilane attachment to the surface. The study of this complex system allowed the representation of the variety of possible chemical structures in this system and can be observed in the Figure 20, explaining the high contribution of the protonated amine seen in the Figure 19 (d). As previously mentioned in the section 2.4, the behavior of the NH_2 group strongly depends on the concentration of the silane in the solvent toluene used for the modification. It has been previously shown that the $\mathrm{NH_3^+}$ group is predominant on the surface of the substrate if the concentration of the organosilane is very low. Being the volume of organosilane used of 10.0 mL, the % (V/V) (silane/solvent) is of 10%, for this low concentration it was expected to observe such a high intensity corresponding to the protonated amine. All the results point to the inference that the silanes are coupling with each other and the amine group of the silane is facing the SiC surface resulting in the protonated amine form. All the binding energy values are consistent with the reported values mentioned in the section 3.3 as well [76-78].

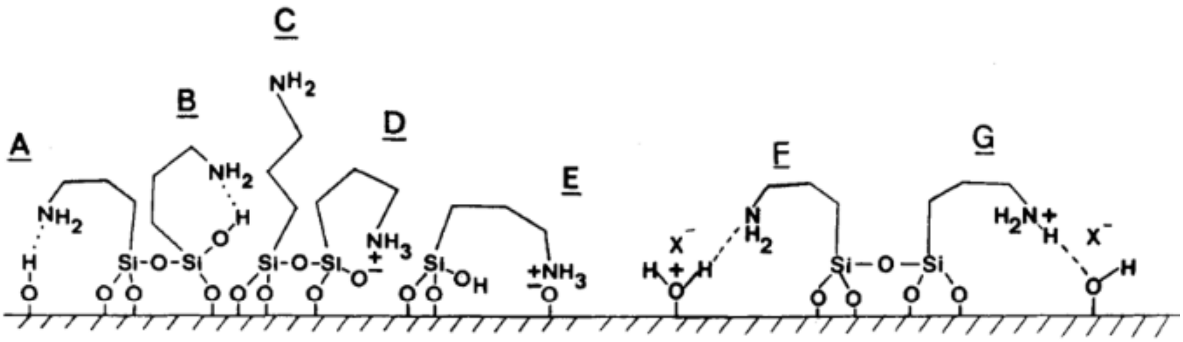


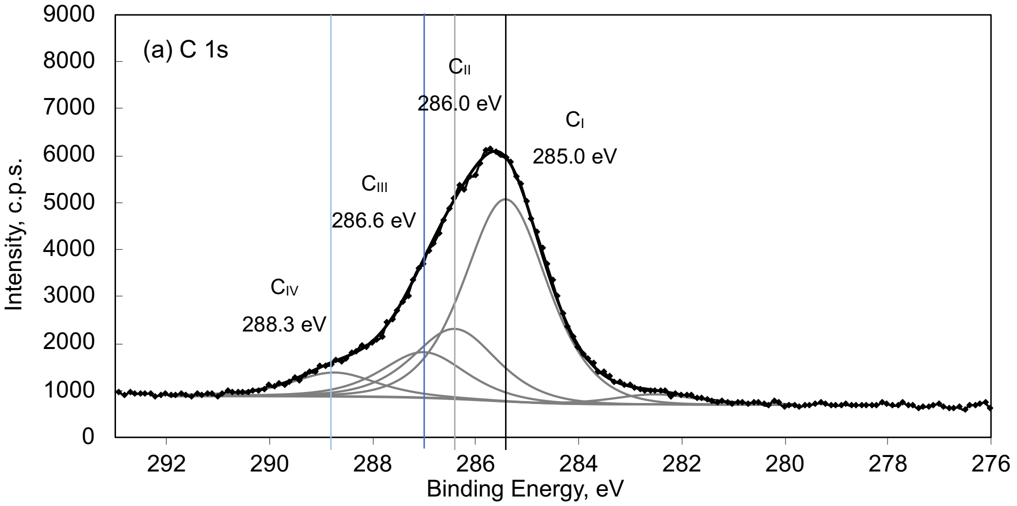
Figure 20 - Structural possibilities of the SiC-AMMO system [76].

5.3.3.3. Organosilane Dynasylan DAMO-T

At last, the XPS analysis of the Dynasylan DAMO-T functionalized substrate with the organosilane volume of 2.5 mL showed the presence of the elements carbon, oxygen, silicon, nitrogen. In the following Table 11 and Figure 21, it is possible to assess the contribution of each element in the surface, as well as the XPS survey scans for C 1s, O 1s, Si 2p and N 1s and the corresponding peak assignments. Once again, the presence of 9.0 % of nitrogen is an indication that the Dynasylan DAMO-T was bonded onto the surface. The oxygen atomic percentage of 28.7 % may result from the silanol groups in the silane and the carbon percentage of 53.3 % is most certainly due to the propyl group existing in the silane.

Table 11 - XPS analysis for the SiC-DAMO-T (2.5 mL) substrate (atomic %).

Sample	**% C**	**% O**	**% Si**	**% N**
SiC DAMO-T (2.5 mL)	53.3	28.7	9.0	9.0



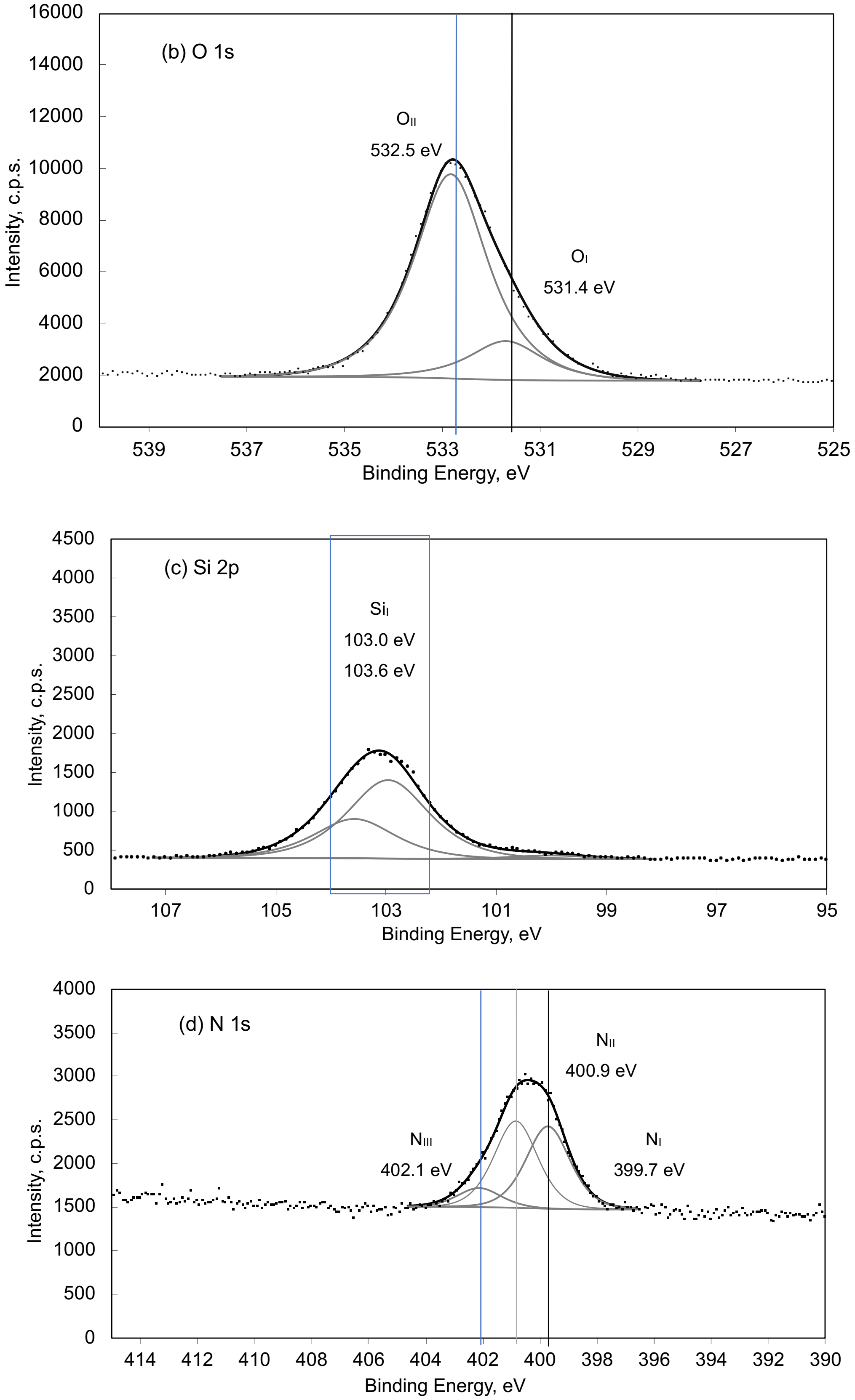


Figure 21 - Photopeaks of SiC: SiC-DAMO-T (2.5 mL) substrate: (a) C 1s, (b) O 1s, (c) Si 2p and (d) N 1s.

The C 1s spectrum was resolved into four main peaks. Peak C_I at 285.0 eV is assigned to organic carbon, $(\mathrm{C-H/C-C})$ from the silane propyl group, resulting in a high intensity peak, peak C_{II} at 286.0 eV is assigned to the bond $\mathrm{C-N}$ existing in the silane. The peak C_{III} at 286.6 eV is assigned to the bond $\mathrm{C-O}$ existing in the silane and at last the peak C_{IV} at 288.3 eV corresponding to a carboxyl group. It should be noted that in this sample, unlike the others analyzed, the silicon carbide bond, $\mathrm{Si-C}$, was hardly detectable, thus this sample treated with the organosilane DAMO-T shows a high surface coverage. The exact origin of the carboxyl group is uncertain. Several articles point to crosslinking, but there are other variables, such as the solvent used (Toluene and n-Butylamine as a catalyst), the pre-treatment solution (mostly oxidizing agent of inorganic persulfate with sulfuric acid and water) and the impossibility of carrying out the reaction in a closed atmosphere of nitrogen. The presence of CO_2 may have led to the reaction of the silane or the silanized surface with CO_2, leading to the presence of an amino-bicarbonate salt as reported previously in the previous literature [79-85].

The O 1s spectrum consists of two peaks: O_I peak at 531.4 eV corresponding to the silane oligomerization between the silanol groups, and peak O_{II} at 532.5 eV corresponding to the $\mathrm{Si-O-Si}$ bond between the silane and the surface, corroborating that the organosilane is chemically bonded to the substrate, as expected from the analysis of the Table 10.

The Si 2p spectrum is resolved mainly into two peaks resulting in a single doublet Si_I at 102.6 eV and 103.2 eV attributed to the $\mathrm{Si-O-Si}$ bond, once again allowing the conclusion that the organosilane is indeed connected with the substrate.

At last, the N 1s curve-fit consists of three peaks, N_I at 399.7 eV that corresponds to the functional group amine of the organosilane, the peak N_{II} at 400.9 eV that corresponds also to the amine from the organosilane, but in a protonated form $(\mathrm{NH_3^+})$ and the peak N_{III} at 402.1 eV that corresponds to the secondary amines. The high contribution of the neutral amine seen in the Figure 21(d) contrary to the prediction of an high protonated form due to low concentration may be explained by steric effects due to the presence of the second amine. The bonds observed through this analysis lead to the assumption that the silane is bonded with the surface and the amine functional group is facing up, creating hydrogen bonds between the electronegative nitrogen atom and the positive hydrogen atom in the other amine. The configuration of this SiC-silane complex may result in a better performance of the functionalized silicon carbide in the adhesion with the nylon for the abrasive filament production since the functional group is positioned facing the nylon. The study of this system allowed the exemplification of the variety of possible chemical structures obtained for a similar silane, 3-aminopropyltriethoxysilane [44].

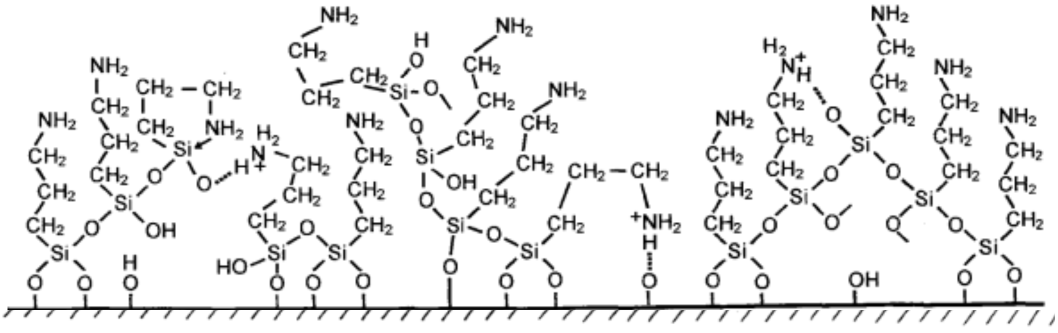


Figure 22 - Structural possibilities of the SiC-DAMO-T system [44].

5.3.3.4. Silane Coupling Agents: XPS Comparison

A final comparison of the XPS photopeaks for the three organosilanes tested, OCTEO, AMMO and DAMO-T was executed for the most critical elements, carbon and silicon.

The XPS spectrums for the carbon 1s element 17 a), 18 a), 19 a) and 21 a) were combined, Figure 23, in order to compare the samples coverage. All the silanes can be seen in the sample due to the high contribution of the alkyl group, $\mathrm{C-C/C-H}$ bond. The Dynasylan OCTEO has an octyl group so the intensity of the peak regarding this bond was expected to be higher than the other silanes that have a propyl group as observed. Regarding the silane coverage, the sample of silicon carbide treated with the organosilane DAMO-T shows a higher coverage by the silane and a lower intensity of the signal corresponding to the silicon carbide carbon, at 282.4 eV, followed by the AMMO treated sample and at last the sample treated with the alkylsilane OCTEO showed the highest intensity of this peak at 282.4 eV, therefore a lower coverage.

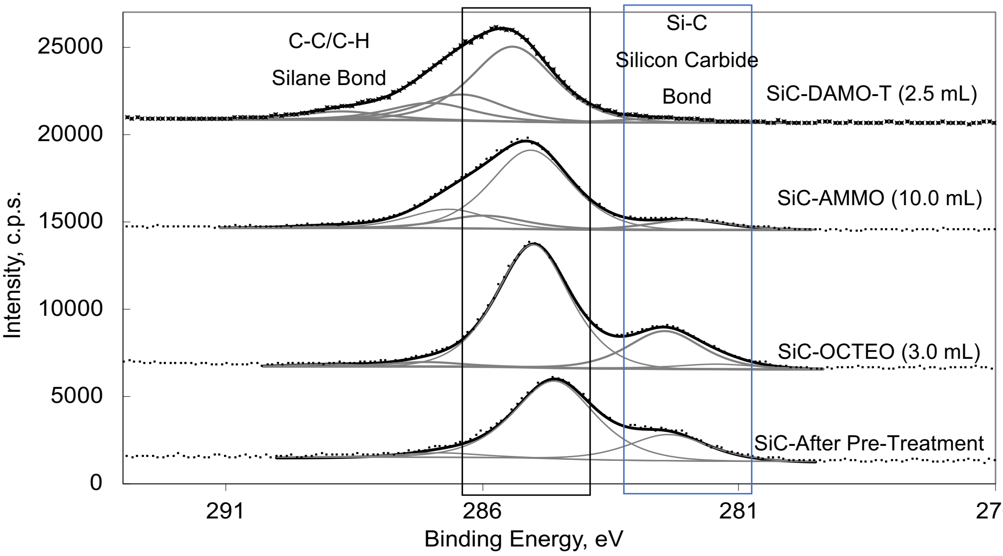


Figure 23 - Photopeaks of SiC substrate C 1s: SiC-DAMO-T (2.5 mL), SiC-AMMO (10.0 mL) and SiC-OCTEO (3.0 mL).

The XPS spectrums for the silicon 2p element 17 c), 18 c), 19 c) and 21 c) were combined, Figure 24, in order to compare the samples coverage. The sample of silicon carbide treated with the organosilane DAMO-T show a slightly higher intensity of the signal for the chemical bond, $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$ accountable of the chemical functionalization than the samples with the organosilane AMO at 102.6 eV. The samples functionalized with the organosilane OCTEO showed the lowest intensity of this peak signal at 102.4 eV. Thus, the XPS evaluation permitted the deduction that the most promising organosilane is the DAMO-T, followed by the silane AMMO and at last the silane OCTEO.

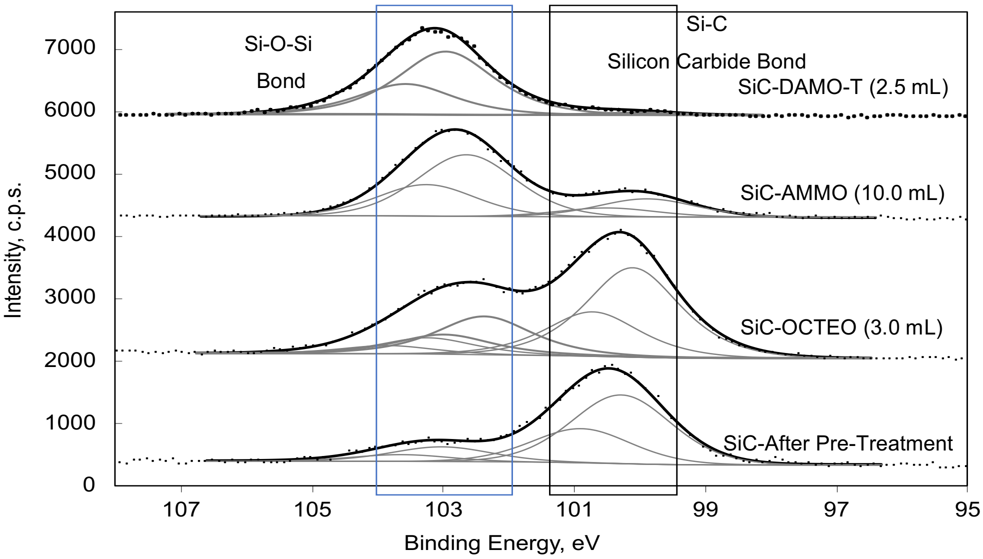


Figure 24 - Photopeaks of SiC substrate Si 2p: SiC-DAMO-T (2.5 mL), SiC-AMMO (10.0 mL) and SiC-OCTEO (3.0 mL).

CHAPTER 6

6. Conclusion

Different types of coupling agents were tested in order to functionalize silicon carbide enhancing its compatibility with nylon, for abrasive filament production. The organosilanes tested were divided in two groups according to their chemical structure. The first group composed by three alkylsilanes, Dynasylan OCTEO, SIVO850 and 9896 and the second group composed by the aminoalkylsilanes Dynasylan AMMO, DAMO-T and 1401.

For the reaction's execution, a first step containing the solvent mixture ethanol/deionized water 75/25 % (v/v) and the alkylsilanes OCTEO, SIVO850 and 9896 was performed in order to activate the silane by the formation of silanol groups. The second step was the addition of the silicon carbide for the functionalization reaction. For the organosilane AMMO, the solvent was ethanol and the reactions were conducted at room temperature under a nitrogen atmosphere, in order to activate the silane by the formation of silanol groups and to prevent oligomerization. For the organosilanes DAMO-T and 1401, the reaction mixture contained toluene (100 mL), a catalyst, and organosilanes, also under nitrogen atmosphere. All reactions were executed at atmospheric pressure, P_{amb} and for each silane various volumes were tested in order to optimize the reaction conditions.

The effects of surface treatments on the surface chemistry were examined using, Fourier-transform infrared spectroscopy (FTIR), contact angle measurement and X-ray photoelectron spectroscopy (XPS). On a first FTIR analysis, two types of pre-treatment were tested, hydrofluoric acid etching (HF) and sulfuric acid with ALNOCHROMIX, and the treatment which showed better results was the second one, thus it was applied for all the following treated samples.

In the second part, the goal was to compare all the silanes and the different tested volumes in order to find the optimal conditions for surface functionalization. From the FTIR analysis for each silane it was possible to observe the influence of the organosilane volume added in the modification of the SiC powder. The increase in the organosilane content led to an increase of the intensity of the signal, allowing to see the presence of the organosilane in the samples, being a good indicator of the silane presence in the substrate, as well as the manifestation of the characteristic silane groups peaks was examined and the silane-SiC bond was also observed. The second characterization analysis carried out was the measurement of contact angle, in order to assess the wettability of the samples. It should be noted that the inorganic particles SiC are hydrophilic and the hydrophobic head of the organosilanes when incorporated in these particles gives them this characteristic. It can be clearly observed that the contact angles of modified SiC increase first and then decrease with the increasing silane coupling agent amount, reaching maximum values at 7.5 mL, 5.0 mL, 10.0 mL, 2.5 mL and 10.0 mL for Dynasylans SIVO850, 9896, AMMO, DAMO-T and 1401, respectively. For the organosilane OCTEO, it is only possible to observe a decrease of the contact angle meaning that at the lowest tested volume of 3.0 mL, the contact angle is at its maximum. When the amount of silane coupling agent is in surplus, the organosilane attacks the Si atom of the silane coupling agent already attached to the SiC surface resulting in the detachment of the coupling agent from the surface and therefore resulting in a decrease of the contact angle value. Even though, through the FTIR analysis, it was not possible to observe, for all the samples treated, the presence of the organosilane, this analysis proves that the organosilane is in fact present in the surface of silicon carbide. In order to guarantee the presence of the chemical bond between the organosilane and the silicon carbide another method of surface characterization was used. The samples with the organosilanes OCTEO (3.0 mL), AMMO (10.0) and DAMO-T (2.5 mL) who showed the highest values of contact angle of 126.0 ± 0.2 °, 134.4 ± 0.2 ° and 114.4 ± 0.5 ° respectively, were submitted to the next characterization test.

Regarding the XPS analysis, only the silane treated samples with the organosilanes OCTEO, AMMO and DAMO-T were tested, since they showed the highest values of contact angle. The sample of silicon carbide treated with the organosilane DAMO-T showed a slightly higher coverage of the surface and higher intensity of the signal for the chemical bond, Si-O-Si accountable of the chemical functionalization, than the samples with the organosilane AMMO. The samples functionalized with the organosilane OCTEO showed the lowest intensity of this peak, thus, the XPS evaluation allowed to conclude that the most promising organosilane is the DAMO-T, followed by the silane AMMO.

CHAPTER 7

7. Perspectives for Future Work

Firstly, to better understand the results it would be important to perform further characterization and compatibility tests, reassuring that in fact the functionalized silicon carbide is evenly distributed within the polyamide matrix. Adhesion durability tests should also be executed in order to evaluate the performance of the composite when submitted to possible work environments. X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) analysis would be performed to guarantee that there is a significant enhancement of the adhesion between the particles and the matrix, providing information about the chemical composition of the surface of the composites. In order to understand the viability of the composite, by determining its mechanical properties, the composites should be subjected to tensile, compression, shear and flexural tests. It would also be interesting to analyze the influence of pH and temperature and test the composite stability and how it is affected in harsh environments.

Another important step would be to perform the reactions with the amine-silanes in a nitrogen atmosphere, since it showed to be the most problematic step not being able to guarantee this atmosphere during the functionalization reaction. The goal would be to perform in a sealed chamber preventing any carbon dioxide and oxygen presence.

Another interesting aspect could be to test the silanization process with particles with different dimensions optimizing the organosilane content for the best performance possible. For particles with higher diameter, since the specific surface area decreases, a smaller organosilane content should be expected.

At last, since this work was developed with industrial purposes, the silanization process should be made in order to test the behavior of the particles in an industrial extruder, thus a batch of 2kg minimum should be tested in the facilities of FILKEMP.

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Appendix A

Silicon Carbide Properties

Table 12 - Properties of the silicon carbide according to the supplier NAVARROSiC [86].

Property	Test	Value
Physical properties		
Color		black, dark, green, grey
Hardness	UNE EN ISO 4545-1:2006	2500-2800 MPa
Density	ASTM C20	3.21 g.cm^{-3}
Moisture absorption	ASTM C373	0.0 %
Refraction Index n_0		2.65
Mechanical Properties		
Resistance to compression	ASTM C773	1725-2500 MPa
Resistance to traction	ACMA Test #4	310 MPa
Young's elasticity modulus	ASTM C848	420 - 476 GPa
Flexural rupture modulus	ASTM F417	324 - 450 MPa
Toughness to fracture	Three-point flexural test	2.3 – 4.0 MPa·m$^{1/2}$
Thermal Properties		
Thermal stability		1400 ºC (air)
Resistance to thermal stress	Tempering	350 - 500 ºC
Thermal conductivity (298 K)	ASTM C408	41 - 90 W·m^{-1}·K^{-1}
Linear thermal expansion	ASTM C372	4.7 – 5.1·10^{-6} K^{-1}
Average specific heat	ASTM C351	0.15 – 0.22 cal·g^{-1}·K^{-1}
Electrical Properties		
Dielectric constant	ASTM D150	10.2 MHz
Electrical resistivity	ASTM D1829	108 W·cm

Appendix B

Pre-Treatment - Cleaner sonicator and Magnetic stirrer

The pre-treatments performed on the silicon carbide surfaces under study, were tested with two kinds of stirrers, an ultrasonic bath and a magnetic stirrer. Both cleaning processes were characterized by FTIR technique. The spectra, Figure 25, were compared, but no significant differences were observed in the samples, thus all the silicon carbide surfaces were cleaned through the magnetic stirring technique.

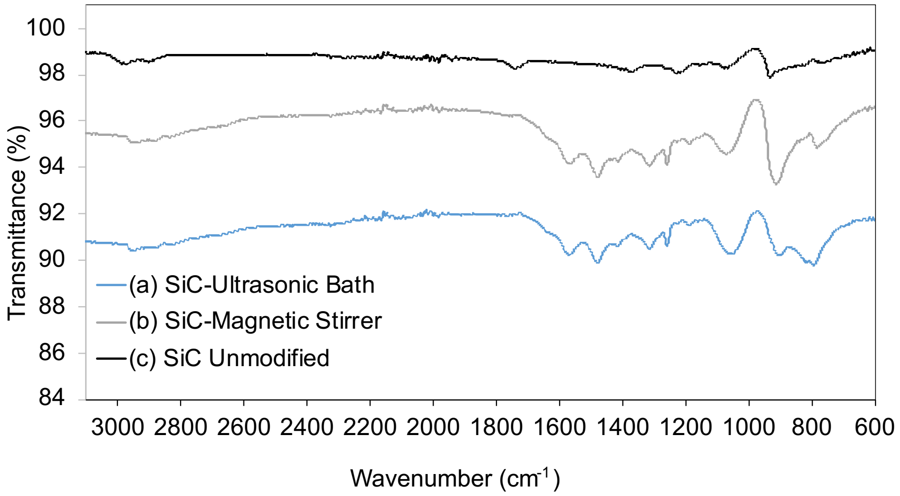

Figure 25 - FTIR spectra of (a) SiC-Ultrasonic Bath, (b) SiC-Magnetic Stirrer, (c) SiC Unmodified.