

Functionalization of Silicon Carbide (SiC) for Abrasive Filament Production

Beatriz Inês Castanheira Mendes

Instituto Superior Técnico, Lisboa, Portugal

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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 $134.4 \pm 0.2^\circ$. 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 $126.0 \pm 0.2^\circ$ and $114.4 \pm 0.4^\circ$, 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.

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, which 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 particles loading leads to a poorer attachment between the abrasive and polymer [1-2].

The weak interfacial interaction between the inorganic particles with the polymer limits the applications of some inorganic particles. Silicon carbide 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 resistance, therefore this inorganic particle is suitable for usages under severe conditions, such as high temperature, high power and high frequency [3-4]. In this study, silane surface modification processes are investigated

for the improvement of the adhesion of a nylon silicon carbide powder composite. Silicon carbide, SiC, is the particle of interest because it is extremely stable, is capable of withstanding high heat, has low thermal expansion and high resistance to acids and bases, being a very promising material for semiconductor devices, biomedical sensors and abrasive applications, being well suited for demanding applications in harsh environments [5-8].

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. Surface pretreatment is particularly essential in most adhesion systems. To attain optimal adhesion durability, it is frequently necessary to modify the inherent substrate surface [9].

To alter the substrates surface there is a chemical or a physical approach. It should be taken into consideration that the physical route will not modify permanently the surface or create a surface tick 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 in 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 $Y-Si-(OX)_3$, where Y is a functional group and OX is a hydrolysable group and the formula of dialkoxysilanes is $Y-Si-(OX)_2R$, where R is usually an alkyl group [10-13].

The hydroxyl groups existing on the substrate are the sites at which silanes will be adsorbed and ultimately react. The substrate 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].

Previous researches and studies 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. In order to further study the effect of coupling agent on the composites interface and obtain hydrophobic SiC particles, the alkylsilanes: octyltriethoxysilane (Dynasylan OCTEO), an oligomeric short-chain alkylsilane (Dynasylan 9896) and an emulsion of an alkyltrialkoxysilane oligomer in water (Dynasylan SIVO850); and the aminosilanes: 3-aminopropyltrimethoxysilane (Dynasylan AMMO), n-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Dynasylan DAMO-T) and n-(2-aminoethyl)-3-aminopropylmethylidimethoxysilane (Dynasylan 1401) were tested as SiC modifiers.

The effects of the treatment were studied by the measurement of the contact angle to establish the respective optimal reaction volume of organosilane used and compare their modification effects. The bonding mechanism between modifiers and SiC was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS).

2. Materials and Methods

2.1. Materials

Silicon carbide was provided by NavarroSiC with an average particle size of 28-70 μm . The silane coupling agents, namely Dynasylan OCTEO, SIVO 850, 9896, AMMO, DAMO-T and 1401 were supplied by EVONIK.

2.2. Surface Pre-Treatment

For the surface pretreatments Hydrofluoric acid etching (HF), and a solution of 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.

Prior to the 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.

For the ALNOCHROMIX and sulfuric acid solution 2 g of ALNOCHROMIX crystals and 50 mL of sulfuric acid (98%) were 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 wash process with water and a vacuum filtration process.

2.3. Surface Functionalization

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 $T_r = 75 \pm 7$ °C. After, the particles were washed with Ethanol in order to remove any physisorbed molecules from the surface, vacuum filtered and dried ($t_{\text{drying}} = 24$ h) in a heating chamber operating at $T_{\text{drying}} = 55$ °C. 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 to 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 ($T_r = 20 \pm 7$ °C). 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 $t_{\text{drying}} = 24$ hours in a heating chamber operating at $T_{\text{drying}} = 55$ °C.

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 the 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 1 it is possible to see the volumes of organosilanes tested.

Table 1 - 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

2.4. Sample Characterization

The degree of hydrophobicity was assessed from an optical water contact angle meter, a Ramé-hart DROPimage Goniometer through the sessile drop method.

In a cylindrical mold with 1.1 cm of diameter and 5 mm of height, the samples were lightly pressed up until the mold was fulfilled. 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. The 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.

Infrared spectra were collected using PerkinElmer, Spectrum Two, mid-Infrared spectrometer equipped with a Pike Technologies MIRacle® Attenuated Total Reflectance (ATR) accessory.

The surface compositions were characterized by X-ray photoelectron spectroscopy XSAM800 (KRATOS) operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 20 eV, the non-monochromatized radiation $Mg K_{\alpha}$ ($h \cdot \nu = 1253.6$ eV) and a power of 120 W (10 mA \times 12 kV).

3. Results and Discussion

3.1. Surface characterization of Silicon Carbide by FTIR

This chapter focuses on the characterization of the samples treated with the organosilanes OCTEO, SIVO 850, 9896, AMMO, DAMO-T and 1401. Surface characterization analysis was performed via FTIR. Firstly, it should be noted that on a first FTIR analysis, the two types of pre-treatment were tested, hydrofluoric acid etching (HF) and sulfuric acid with ALNOCHROMIX, and the treatment who showed better results was the second one, thus it was applied for all the following treated samples.

It is possible to observe in the Figure 1, that the FTIR spectrum of the unmodified SiC sample is characterized by one adsorption band near 830 cm^{-1} , corresponding to the Si-C silicon carbide bond. In the Figures 1.1, 1.2, 1.3, the spectra of the functionalized SiC are characterized by several peaks including the stretching vibration bands of the C-H at 2934, 2926 and 2855 cm^{-1} , 2957, 2929 and 2872 cm^{-1} and 2958, 2927 and 2872 cm^{-1} respectively.

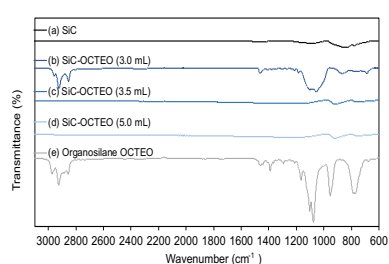


Figure 1.1

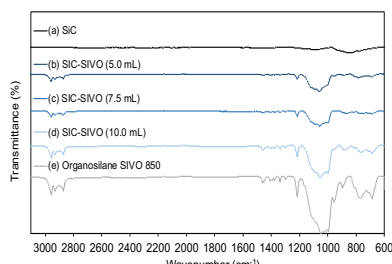


Figure 1.2

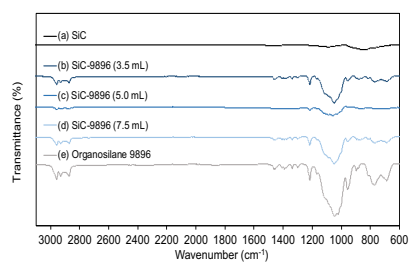


Figure 1.3

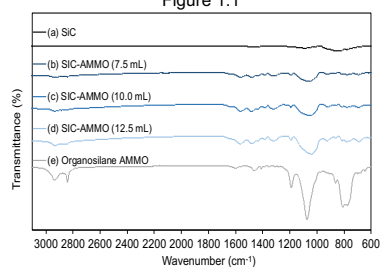


Figure 1.4

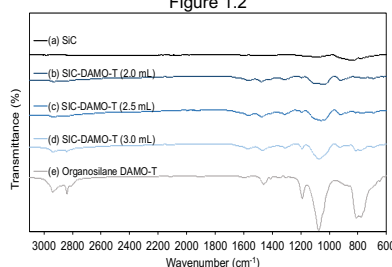


Figure 1.5

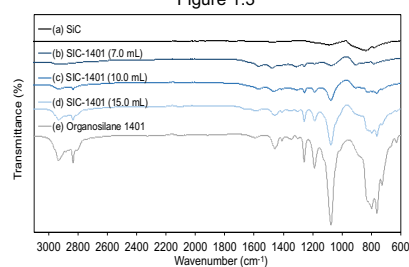


Figure 1.6

Figure 1 – Spectra of functionalized silicon carbide with each organosilane and respective volumes.

These stretches are mainly related to the alkyl groups introduced by the organic functionalization with the alkylsilanes. The chemical bonds Si-O-CH₂-CH₃ in Figure 1.1 and in the Figures 1.2 and 1.3 other alkoxy groups correspond to the stretches between 1161-978 cm⁻¹, as well as the bond Si-C from the alkyl group at 1165, 1216 and 1217 cm⁻¹ respectively and Si-OH stretches around 862 cm⁻¹, correspond to the unreactive silanol groups of the silane. At last, the absorption peaks at 1050, 1056 and 1046 cm⁻¹ respectively belong to the stretching vibration of Si-O-Si, which demonstrates that the organosilane is chemically bonded to the silicon carbide particles effectively. In the Figure 1.4 it is possible to detect the presence of C-H stretch at 3000–2840 cm⁻¹, mainly related to the alkyl group introduced by the organic functionalization of the aminosilanes. Besides, the absorption peak approximately at 1042 cm⁻¹ belongs to the stretching vibration of 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 with the corresponding peak at 1568 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 Si-OH as expected.

In the Figure 1.5 the C-H bonds are then again represented by stretches at 3000–2840 cm⁻¹, corresponding to the alkyl group introduced by the organic functionalization of the Dynasytan DAMO-T. Besides, the absorption peaks at 1070 cm⁻¹ belong to the stretching vibration of Si-O-Si, confirming that the organosilane is chemically bonded to the silicon carbide particles. Another indicator of the organosilane existence is the amine group corresponding peak at 1595 cm⁻¹. It is also possible to observe the bond Si-(CH₂)_x-CH₃ from the alkyl group around 1200 cm⁻¹, evidencing that the organosilane is indeed in the sample.

In the Figure 1.6 it is possible to observe the presence of C-H stretch at 3000–2840 cm⁻¹ that is mainly related to the alkyl group introduced by the organic functionalization of the Dynasytan 1401. Furthermore, the absorption peak of approximately 1073 cm⁻¹ belongs to the stretching vibration of Si-O-Si, which proves the organosilane is chemically bonded to the silicon carbide particles successfully. Additional markers of the organosilane presence is the amine group corresponding peak at 1460 cm⁻¹, 798 and 763 cm⁻¹, and the bond Y-(CH₂)_x-Si-CH₃ from the alkyl group 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 did not show its presence, other characterization tests were executed to corroborate or not its existence. Overall, it can be stated that the technique 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.

3.2. Surface characterization of Silicon Carbide by Contact Angle Measurement

In order to compare the alteration effect by the organosilane, as well as to obtain the optimum reaction condition by the effect of modification of the amount of organosilane, this study was focused on the experimental parameter of the contact angle. Samples of the silicon carbide pellets with and without the surface functionalization after the pre-treatment were observed by Goniometer.

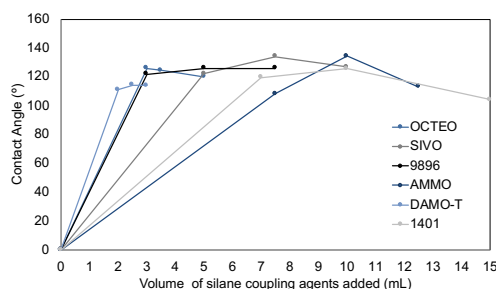


Figure 2 - Effect of silane coupling agent amount on the contact angle.

Figure 2 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°, and the hydrophobicity has improved clearly in different degrees after modification by the different organosilanes. The average contact angle was determined from fourteen different measurements in each sample. Table 2 presents these values, as well as the respective standard deviations.

Table 2 - Average contact angles and respective standard deviations for the functionalized samples.

Organosilane	V _{Organosilane} (mL)	Contact Angle (°)	Organosilane	V _{Organosilane} (mL)	Contact Angle (°)
Dynasytan	3.0	126.0±0.2	Dynasytan	7.5	108.3±0.1
OCTEO	3.5	124.7±0.2	AMMO	10.0	134.4±0.2
	5.0	120.1±0.2		12.5	113.3±0.2
	5.0	122.2±0.5	Dynasytan	2.0	111.2±0.4
Dynasytan	7.5	134.2±0.2	DAMO-T	2.5	114.4±0.5
SIVO 850	10.0	127.0±0.2		3.0	114.1±0.3
	3.5	122.0±0.9	Dynasytan	7.0	119.6±0.5
Dynasytan	5.0	126.0±0.3	1401	10.0	125.7±0.2
9896	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 Dynasytans 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.

It is possible to observe 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 (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 adding the hydrophobic property to the surface, thus an increase in the contact angle value is verified.

When the amount of silane coupling agent is in surplus, the silanol that is formed during the hydrolysis step, attacks the Si atom of the neighboring silane coupling agent that was already bonded to the SiC surface and breaks the functionalization bond, resulting in the detachment of the once grafted coupling agents, thus causing a decrease of the contact angle [4].

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 and one sample with the linear chain will be evaluated. The sample tested with the organosilane AMMO (10.0 mL), which showed the highest value of contact angle, was submitted to the next characterization test. The sample with DAMO-T (2.5 mL), requiring a low amount of organosilane volume needed and with the contact angle achieved of $114.4 \pm 0.5^\circ$ was also analyzed since it has a great volume vs performance achievement. At last, the sample tested with the organosilane OCTEO (3.0 mL), was submitted to the next characterization test since it has a high contact angle value ($126.0 \pm 0.2^\circ$) and the volume of organosilane required was very low. All in all, the modification is considerably advantageous to enhance the surface hydrophobicity of the SiC particles.

3.3. Surface characterization of Silicon Carbide by XPS

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. In this section, the first part of the discussion focuses on the characterization of the unmodified silicon

carbide as a basis of comparison for the surface after the ALNOCHROMIX and sulfuric acid pre-treatment. In the second part, the samples treated with the organosilanes OCTEO, AMMO and DAMO-T are presented and at last compared.

The silicon carbide sample without any treatment and the sample after the ALNOCHROMIX and sulfuric acid solution treatment were characterized via XPS. The following Table 3 lists the surface bonds contribution for the unmodified SiC substrate and for the SiC substrate after pre-treatment.

Table 3 - Composition (atomic %) corresponding to the Si bonds in the unmodified and in the pre-treated surface.

Sample	% Si-C	% Si-O _x	% Si-O ₂
SiC Unmodified	80.4	8.9	10.7
SiC Pre-Treated	82.6	17.3	-

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 silicon suboxides, (SiO_x, x<2), interpreted as Si-OH bonds present on the surface as expected from the surface activation step. It is possible to verify that the contribution of the elemental Si bonds disappeared indicating that the silicon carbide surface in which all the research work is developed is mostly the inorganic Si-C bond and the Si-OH layer ready to chemically bond to the silane in the posterior silanization step and some minor amount of oxidized Si.

3.3.2. Organosilane Dynasylan OCTEO

XPS analysis of the Dynasylan OCTEO functionalized substrate with the silane volume of 3.0 mL showed the presence of the elements carbon, oxygen, silicon, nitrogen. In the Figure 3, 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. 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, (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.

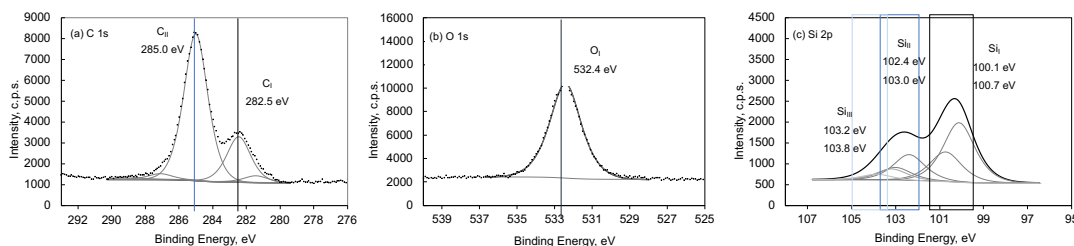


Figure 3 - Photopeaks of SiC-OCTEO (3.0 mL) substrate: (a) C 1s, (b) O 1s and (c) Si 2p.

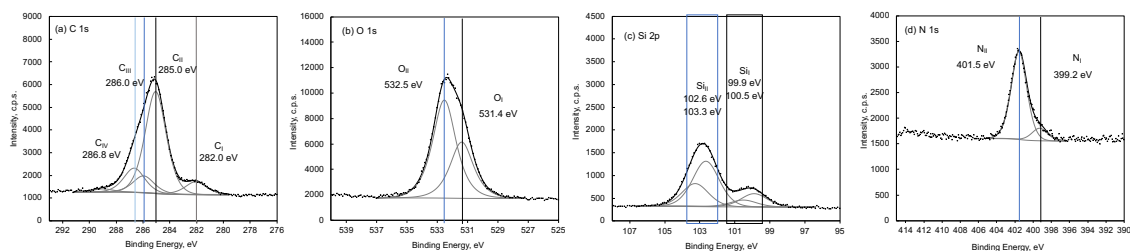


Figure 4 — Photopeaks of SiC-AMMO (10.0 mL) substrate; (a) C 1s, (b) O 1s, (c) Si 2p and (d) N 1s.

The O 1s spectrum consists only of an O_I peak at 532.4 eV which corresponds to the Si-O-Si bond that proves that the organosilane is chemically bonded to the substrate.

At last, 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 Si-C bond. Si-O-Si bond from the silanol group bondage with the surface of the SiC particles, Si_{III}, is at 102.4 eV and 103.0 eV, proving that the silane was successfully attached to the surface. The peaks doublet Si_{III} at 103.2 eV and 103.8 eV is attributed to silicon suboxides in the SiC surface.

3.3.2. Organosilane Dynasytan AMMO

XPS analysis of the Dynasytan AMMO functionalized substrate with the organosilane volume of 10.0 mL showed the presence of the elements carbon, oxygen, silicon and nitrogen. In the following Figure 4, 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 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, (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 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 Si-O-Si bond between the silane and the surface, corroborating that the organosilane is chemically bonded to the substrate. 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 Si-C bond in the

substrate, and peaks Si_{II} at 102.6 eV and 103.3 eV are attributed to the 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 (NH₃⁺). 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 modified SiC by this organosilane requires a detailed knowledge of the nature of the coupling agent attachment to the surface. The behavior of the NH₂ group strongly depends on the concentration of the silane in the solvent toluene used for the modification. It has been previously shown that the NH₃⁺ 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%, thus 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 and bonding with the hydroxylated surface resulting in the protonated amine form as schematized in Figure 5 [17-19].

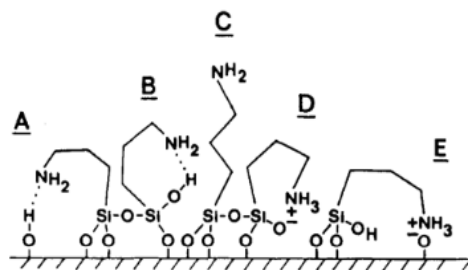


Figure 5 – Structural possibilities of the SiC-AMMO system [17].

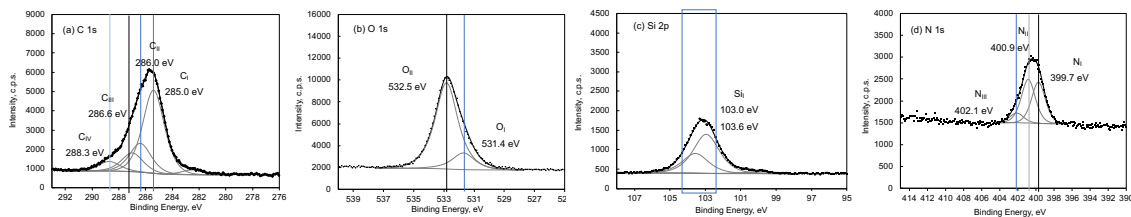


Figure 6 - Photopeaks of SiC: SiC-DAMO-T (2.5 mL) substrate: (a) C 1s, (b) O 1s, (c) Si 2p and (d) N 1s.

3.3.3. Organosilane Dynasytan DAMO-T

At last, the XPS analysis of the Dynasytan DAMO-T functionalized substrate with the organosilane volume of 2.5 mL showed the presence of the elements carbon, oxygen, silicon and nitrogen, Figure 6.

The C 1s spectrum was resolved into four main peaks. Peak C_I at 285.0 eV is assigned to organic carbon, (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 C-N existing in the silane. The peak C_{III} at 286.6 eV is assigned to the bond 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, 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 CO₂ may have led to the reaction of the silane or the silanized surface with CO₂, leading to the presence of an amino-bicarbonate salt which has been previously reported in the literature [20-26]. 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 Si-O-Si bond between the silane and the surface, corroborating that the organosilane is chemically bonded to the substrate. 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 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 (NH₃⁺) 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 6 (d) contrary to the prediction

of a 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 led to the assumption that the silane is bonded with the surface and the amine functional group is facing up, creating hydrogen bonds between the lone pair on the very electronegative nitrogen atom and the slightly 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, as schematized in Figure 7 [27].

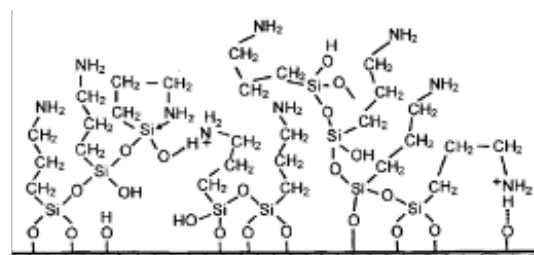


Figure 7 - Structural possibilities of the SiC-DAMO-T system [27].

3.3.4. Silane Coupling Agents: XPS Comparison

The XPS spectra for the carbon 1s element were combined, Figure 8, 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, C-C/C-H bond. The Dynasytan 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.

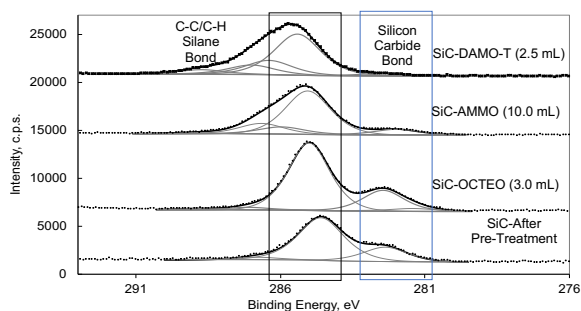


Figure 8 - Photopeaks of SiC substrate C 1s: SiC-DAMO-T (2.5 mL), SiC-AMMO (10.0 mL), SiC-OCTEO (3.0 mL) and SiC-After Pre-Treatment.

The XPS spectrums for the silicon 2p element were combined, Figure 9, 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, Si-O-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.

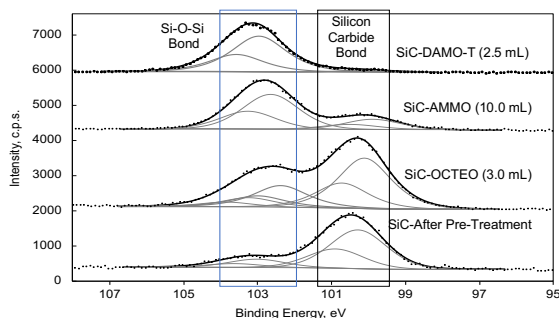


Figure 9 - Photopeaks of SiC substrate Si 2p: SiC-DAMO-T (2.5 mL), SiC-AMMO (10.0 mL), SiC-OCTEO (3.0 mL) and SiC-After Pre-Treatment.

4. Conclusions

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 used

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, 0.5 % (V/V) n-Butylamine, and the 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 surface chemistry were examined using, Fourier-transform infrared spectroscopy (FTIR), contact angle measurement and X-ray photoelectron spectroscopy (XPS). On a first FTIR analysis, the two types of pre-treatment were tested, hydrofluoric acid etching (HF) and sulfuric acid with ALNOCHROMIX, and the treatment who 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 is possible to see the influence of the organosilane volume added in the modification of the SiC powder, The increase in the organosilane content lead 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.

The second characterization analysis carried out was the contact angle measure, 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 volume tested of 3.0 mL, the contact angle is at its maximum. When the amount of silane coupling agent is in excess, the organosilane attacks the Si atom of the silane already bonded to the SiC, resulting in the detachment of the coupling agents from the surface and therefore a decrease of the contact angle. 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.

5. 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 aminosilanes 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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