

Study of the Silanization Process in CNFs: Time, Temperature, Silane Type and Concentration Influence

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Abstract. Functionalization of CNFs with silane coupling agents (SCAs) has been studied in this work. APS silane has been used in order to study the influence of temperature and reaction time on the silanization process. Thermal analysis and surface area measurements have revealed that reaction times higher than 1 min. and temperature reaction higher than 25°C do not increase the amount of adsorbed silane on CNFs surface. Silanization process carried with different SCAs (APS, AMO, DMO and GMO) has allowed the study of the concentration and silane structure influence. It has been observed that differences in SCA adsorption are related to the silane structure. Aminosilanes APS and AMO show a very similar behaviour because they have the same functional group. However, the diaminosilane DMO shows lower interaction with CNFs surface due to the length of the diamine chain, that avoid further silane adsorption on the coated CNFs surface. The epoxysilane GMO shows a similar behaviour to other SCAs at low concentrations, while for high silane concentrations epoxysilane GMO forms multilayers.

Introduction

Since the work published by Iijima in 1991¹, who obtained CNTs as a minor by-product of fullerene synthesis, a significant advancement in CNTs investigation has been developed. The extraordinary structural, electronic and mechanical properties of CNTs make them an exceptional material for a great variety of applications, such as field emission devices, lithium batteries, or hydrogen storage devices. Also, the high aspect ratio, high conductivity, high strength and high modulus among other mechanical properties, makes CNTs an excellent material to use as reinforcement in composites. However, the high production cost of CNTs is a disadvantage for using in composites. In this way, the use of CNFs can solve this problem as CNFs have less economical cost, and show also interesting properties for advanced polymer matrix composites^{2,3,4}.

As it is well known, the interface between reinforcement and matrix plays a crucial role in the high performance of composites⁵, since it is necessary to achieve strong interactions between reinforcement and matrix in order to provide the strain transmission from the reinforcement to the matrix. The main procedure to increase the compatibility between reinforcement and matrix is to modify the surface of CNFs in order to create active surface sites with high compatibility with the matrix. In this way, a great variety of scientific researches has been carried out in surface modification of CNTs or CNFs, including oxidizing or plasma treatments. These treatments, although effective, cause damages in CNFs structure or increase highly the procedure cost. In this way, the use of silane coupling agents (SCAs) as surface modifiers of CNFs results an interesting choice.

Silane coupling agents are organofunctional molecules with the general formula $(X)_3SiY$, where X is an hydrolysable group (methoxy or ethoxy group), and Y is a functional group. Since these silanes present two functional groups, they could undergo two chemical reactions, the hydrolysis of the silane coupling agent and the characteristic reactivity of the functional group Y. The hydrolysis of the silanes means the chemical reaction, by condensation, between the hydroxyl groups of the silane hydrolysed molecules and hydroxyl groups in CNFs surface. So that, the silane molecules are chemically bonded to the surface of CNFs, and the silane functional group Y can be chosen to enhance the reactivity of the reinforcement with de polymer matrix^{6,7}. The fact of being able to choose the functional group Y of the silane coupling agent according to the polymer matrix is an advantage of using silane coupling agents instead of other treatments for surface modification of CNFs.

Silane coupling agents have been widely used in surface modification of glass⁶, glass fibres⁸ and carbon fibres^{9,10} in order to provide strong interactions and suitable interfaces with matrix. Works related with the use of silane coupling agents in order to produce surface modifications of glass or glass fibre^{6,8} have been carried out to obtain monolayers of silane covering the glass surface, and the silanization process proposed consist in different treatments before and after the silanization reaction. The formation of monolayers is due to different factors, including the control of the previous surface, the long silanization reaction carried out, or the high concentration of silane coupling agent.

Few research papers have been developed related with surface modifications of CNFs with silane coupling agents^{7,11,12}. Velasco-Santos et al.⁷ studied the surface modification of CNTs with 3-mercaptopropyltrimethoxysilane (3-MPT), and showed that the silanization process did not change the crystalline structure of CNTs. Ma et al.¹¹ used the silane 3-glycidoxypropyltrimethoxysilane (GMO) for surface modifications of CNTs, and they found FTIR evidences for GLYMO epoxy groups. In such way, Kathi and Rhee¹² carried out surface modifications of CNTs with 3-aminopropyltrimethoxysilane (APS), and showed results indicating the attachment of APS molecules on the surface of CNTs. The silanization procedures described for surface modification of CNFs with silane coupling agents have been carried out over CNTs treated to create surface hydroxyl groups to condensate with hydrolysed silane molecules. As well, those procedures are based in the reactivity of silanes with glass that show surface properties quite different to CNTs or CNFs, and proposed the use of long time reactions and high silane concentrations, in order to produce, at least, monolayer coatings.

The aim of this work is to study the silanization reaction of the silane coupling agent APS with CNFs and then study the influence of different concentrations of different silane coupling agents. Different techniques have been used in this study, such as point of zero charge and Boëhm method in order to study the surface of original CNFs, and thermal analysis, surface area measurements, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in order to characterize the silanized CNFs.

Experimental

The CNFs used in this work (GANF CNFs) were supplied by Grupo Antolín Ingeniería S.A. Those CNFs were synthesized based on the floating catalyst method¹³. In this method, the pyrolysis of gaseous hydrocarbons, in the presence of metallic particles of catalyst produces the growth of CNFs. In this case, the carbon source was natural gas, and nickel was used as catalyst. The synthesized CNFs were treated in N_2 at 350°C for 2 hours for purification.

The silane coupling agents used in this work were supplied by Gelest. They have been kept at low temperature and away from UV light, as it spoils them. Four silane coupling agent have been used in this work without further purification: 3-aminopropyltriethoxysilane (APS), 3-aminopropyltrimetoxysilane (AMO), N-(2-aminoethyl)-3-(aminopropyltrimethoxysilane) (DMO) and 3-glycidoxypropyltrimethoxysilane (GMO). The structures of these silanes are presented in Fig. 1.

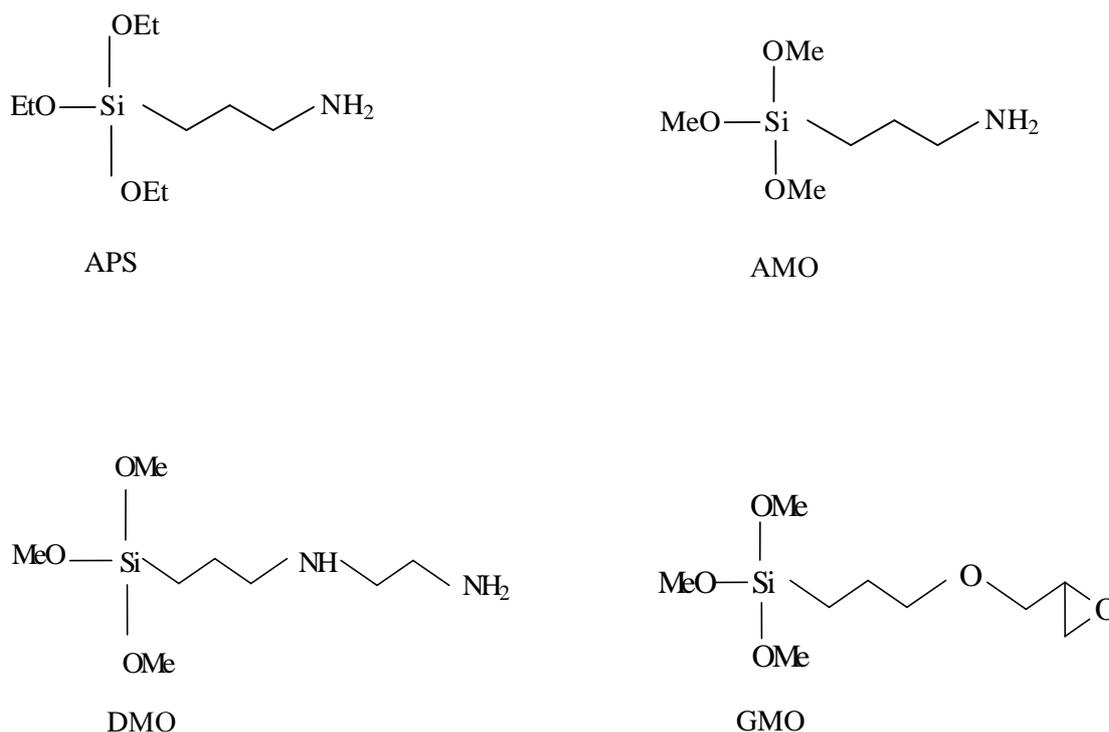


Fig.1 Structures of studied SCAs.

The silanization process consisted in the coupling agent hydrolysis in an aqueous environment and the subsequent reaction of the hydrolysed SCA molecules with the CNFs. The hydrolysis was carried out mixing 100g of distilled water and a given amount of SCA at room temperature for 60 minutes. According to bibliography this process is usually complete within one hour, giving the hydrolysis of the SCA molecules¹⁴. This process was maintained under vigorous stirring. After hydrolysis process CNFs were added, and the mixture was continuously stirred for a given time according to the required studies. Then, CNFs were filtered and dried in an oven at 110°C for 48h. In every experiment, the CNF mass used was of 5g. The amount of SCA needed to obtain a monolayer was calculated in terms of the specific surface area BET of CNFs and the specific wetting surface of each SCA. The ratio, in weight is 2:5 (40% w/w).

On one hand, we have studied the influence of both temperature and reaction time on the silanization process. The SCA used for this purpose was APS, as it has been widely analysed in several works^{15, 16}. Table 1 presents the experimental conditions used for the study.

Table 1: Experimental conditions used to study the influence of both temperature and reaction time on the silanization process.

Sample	APS (g)	Reaction time (min)	Reaction T (°C)
APS-2-1-25	2	1	25
APS-2-5-25	2	5	
APS-2-10-25	2	10	
APS-2-20-25	2	20	
APS-2-40-25	2	40	
APS-2-1-35	2	1	35
APS-2-1-45	2	1	45

On the other hand, the concentration effect of different SCAs (APS, AMO, DMO, GMO) has been studied. Table 2 presents the experimental conditions for such studies. Since every sample has

been obtained in different reaction conditions, a rigorous nomenclature has been chosen in order to simplify. This nomenclature shows in first place the SCA type, the SCA mass added to the reaction, the reaction time and, finally, the reaction temperature. So that, the nomenclature indicates: SCA-mass-time-temperature.

Pristine CNFs were characterised in terms of their surface functional groups, by the Boëhm method, and the point of zero charge (pzc). The procedure carried out in the determination of surface groups was a variation of Boëhm method¹⁷ adapted to carbon materials. For that, 50 mg of CNFs were mixed and stirring for 16 hours with 40 mL of four different bases 10^{-3} M. The bases were NaHCO_3 , Na_2CO_3 , NaOH , and NaOC_2H_5 . Then, the samples were filtered, and the solution obtained was titrated with $\text{HCl } 10^{-3}$ M. The pzc of CNFs were determined by pH measurements¹⁸. For that, dispersions of increasing amounts of CNFs in distilled water were prepared and stirred for 24 hours. The amounts of CNFs were 0.01%, 0.1%, and 1% w/w. After that, the pH of each sample was measured. For both Boëhm and pzc methods, a pHmeter Metrohm 827 equipped with Ag/AgCl electrode was used. Before carrying out any measurement, the pH meter was calibrated with two standard buffer solutions at pH 4 and pH 7.

Table 2: Experimental conditions used to study the influence of both silane type and silane concentration in the silanization process.

Sample	SCA (g)	Reaction time (min)	Reaction T (°C)
SCA*-001-1-25	0.01	1	25
SCA*-003-1-25	0.03		
SCA*-01-1-25	0.1		
SCA*-05-1-25	0.5		
SCA*-1-1-25	1		
SCA*-2-1-25	2		
SCA*-5-1-25	5		

*SCA: APS, AMO, DMO, GMO

Pristine and silanized CNFs were also characterized by scanning and transmission electron microscopy. Scanning electron microscopy characterization was carried out using a field emission scanning microscope (FE-SEM, Hitachi 4700), operating at 20 keV. Transmission electron microscopy was carried out in a Hitachi H-120 microscope, operating at 125 kV with resolution of 1.5 nm.

Silanized CNFs were characterized by means of thermal analysis and adsorption-desorption isotherms. The amount of SCA on CNFs surface was determined by means of a Thermogravimetric Analyzer Pyris 1 TGA (Perkin-Elmer), heating at $10^\circ \text{C}/\text{min}$ up to 800°C in air. The specific surface areas (SAs) of pristine and silanized CNFs were obtained from nitrogen adsorption-desorption isotherms using a Tri-Star 3000 (Micromeritics) equipment, at 77K. Previously to the measurements, the samples were degassed at 120°C for 20 hours.

Results and Discussion

Surface characterization of pristine CNFs has been of great interest in order to check the capability of CNFs for bounding with hydrolysed SCAs, as the condensation reaction should occur between surface hydroxyl groups in CNFs and hydrolysed SCAs. So that, hydroxyl surface groups on CNFs surface are necessary to bond with hydrolysed SCA molecules. Results obtained for the determination of acidic surface groups by Boëhm method are presented in Table 3.

Table 3. Acidic surface functional groups in CNFs.

Base	Vol. HCl [mL]	Funct. Group	Funct. Group Conc. [mmol/g CNF]
NaHCO ₃	10.75	Carboxyl	0.52
Na ₂ CO ₃	8.8	Lactone	0.052
NaOH	0.45	Phenol	0.22
NaOC ₂ H ₅	0.25	Carbonyl	0.0053

As can be observed, carboxyl groups are the majority among the acidic surface groups determined by this method. The presence of phenol groups is also considerable. Both carboxyl and phenol groups present in their structures OH functionalities, which are suitable groups for bounding with hydrolysed SCAs. Due to the trend showed by carbonaceous materials to adsorb oxygen from atmosphere^{17, 19} and the acidic character of these oxygenated groups, here we have applied the Boëhm method for characterising acidic groups instead of basic ones, as is expected most of surface groups are oxygenated acidic groups. So that, in order to study the acidic or basic character of CNFs surface we have determined the pzc of pristine CNFs. Fig. 2, presented below, shows the pH dependence with increasing amounts of pristine CNFs dispersed in distilled water. As can be seen, for a pH of 7.8, increasing amounts of CNFs do not increase the pH, so that, 7.8 is considered the pzc of pristine CNFs, showing a basic surface of pristine CNFs.

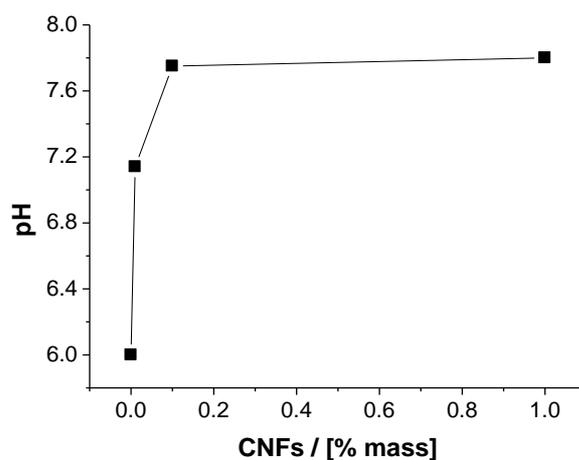


Fig. 2. pH dependence with increasing amounts of pristine CNFs dispersed in distilled water.

As it was expected, like other authors have shown previously^{20,21} surface characterization carried out over pristine CNFs has shown the presence of oxygenated acidic surface groups and an overall basic surface, which could present also basic functional groups as hydroxyl ones. That means that pristine CNFs present a suitable surface to react with hydrolysed SCAs, without any further requirements, as previous surface treatments.

As it has been mentioned before, APS has been used to study the influence of both temperature and the reaction time during the coating process. Table 1 presents the experimental conditions used in this study.

Fig. 3 shows the TGA curves for the above mentioned samples. As can be seen, all TGA curves show a weight loss between 25 and 200°C which can be assigned to moisture adsorbed on pristine CNFs. Between 200 and 500°C, pristine CNFs do not show any weight loss, indicating that such CNFs are stable for such temperature interval. On the other hand, the APS treated CNFs show an important weight loss for this temperature range. This weight loss is due

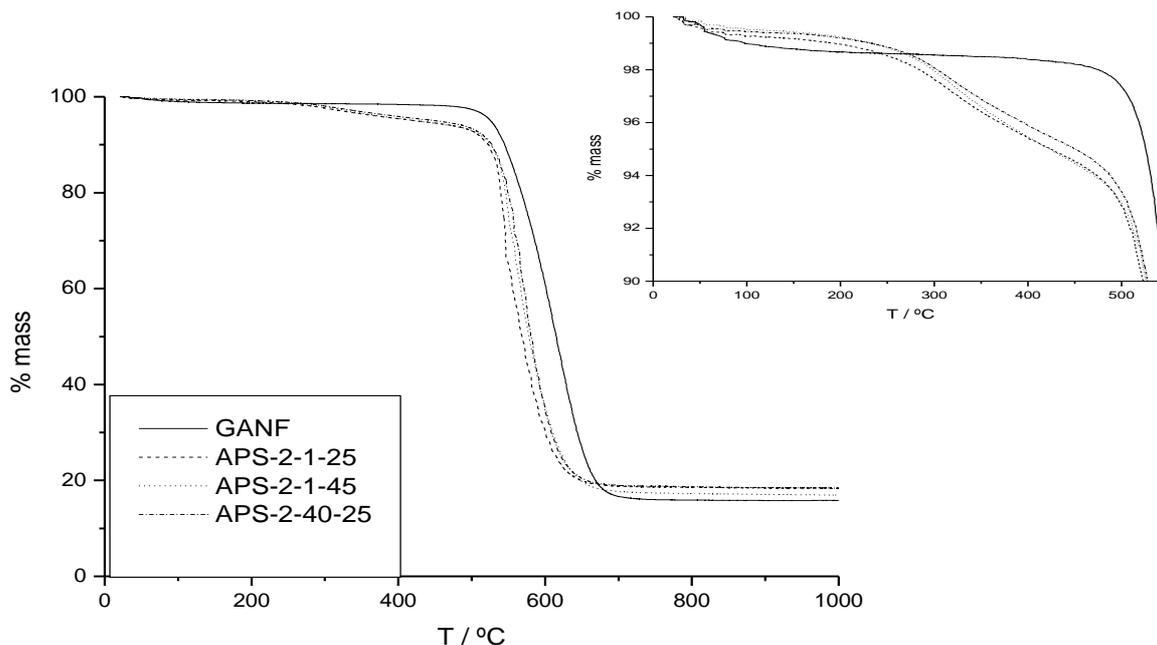


Fig. 3. TGA curves of pristine CNFs and APS coated CNFs for different temperature and reaction times.

to the combustion of aminopropyl groups of the APS molecule. Table 4 presents the weight loss values obtained for APS coated CNFs prepared at different reaction times.

As can be seen in Table 4, the amount of APS incorporated to CNFs shows an important increase in the first minute of reaction and after that it increases more slowly reaching a value close to 3% at 40 minutes of reaction time. This result shows a rapid interaction between APS and the surface of CNFs and after that, the interaction takes place more slowly reaching equilibrium between the surface adsorbed silane and the free one existing in the solution. According with these results, it must be concluded that the surface of CNFs is coated with APS silane molecules. The presence of these molecules must influence the CNF surface area (SAs). Table 4 also gives SAs values for non-coated and APS treated CNFs. The SAs value for pristine CNFs is very close to that obtained for different CNFs and CNTs of similar diameters^{22, 23, 24}. Such value decreases when CNFs are coated with the silane showing that the APS has filled the pores of these CNFs. It can be observed in Table 4 that the weight loss follows the SAs opposite trend, showing that the higher APS coating, the lower SAs of CNFs. In accordance with these results, it is not necessary to use reaction times higher than 1 min. at 25° C for obtaining a good coating on CNFs.

Table 4. Weight loss and surface area (BET) of CNFs coated with APS at different reaction times.

Time (min)	Weight loss (%)	BET area (m ² g ⁻¹)
0	0	143
1	2.2	106
5	2.0	106
10	1.9	107
20	2.7	117
40	2.8	110

In order to study the influence of the reaction temperatures on the coating process, the above mentioned conditions have been chosen i.e., 2 g of silane and reaction time of 1 minute. Table 5 presents the values of weight loss and SA of APS coated CNFs obtained at a given reaction temperature. It can be observed that the reaction temperature does not influence the coating process.

Table 5. Weight loss and surface area (BET) of CNFs coated with APS at different temperatures.

T [°C]	Weight loss [%]	BET area [m ² g ⁻¹]
25	2.2	106
35	2.7	102
45	2.7	109

According with the results showed before, APS is coating CNFs surface. Both SEM and TEM were utilized to study the morphology of the coatings. Fig. 4 presents SEM images from pristine and silanized CNFs. There is no apparent change in the morphology, although it is observed that pristine CNFs do not present agglomerated nanofibres, while silanized CNFs show small CNFs agglomerates. TEM images for pristine and silanized CNFs are shown in Fig. 5. As can be seen in this case, the TEM image of silanized CNFs shows the presence of a rough discontinuous layer not appearing in pristine CNFs TEM images. This rough layer must be the APS coating formed in CNFs surface.

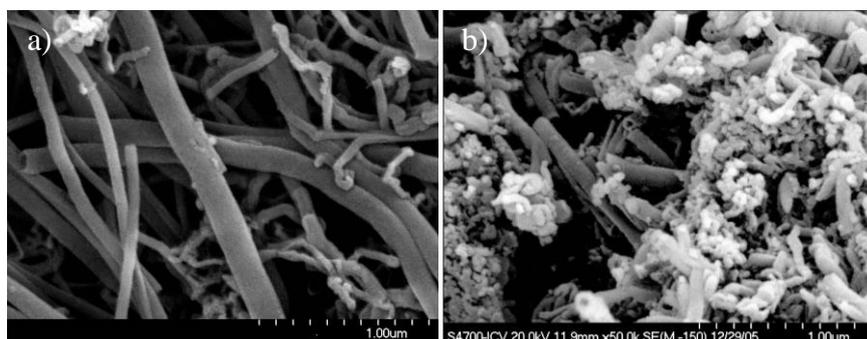


Fig. 4. SEM images of a) pristine CNFs and b) silanized CNFs.

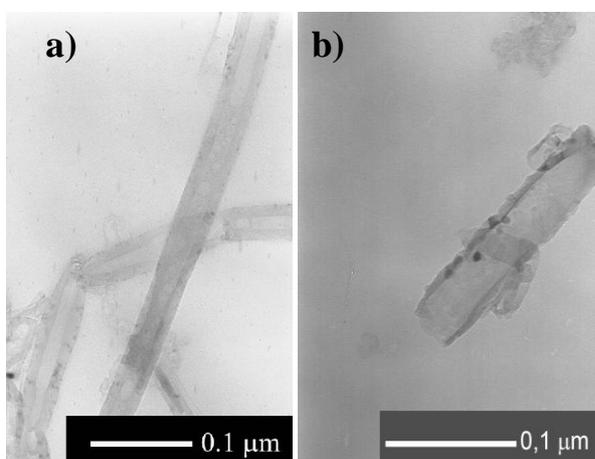


Fig. 5. TEM images of a) pristine CNFs and b) silanized CNFs.

In order to study the influence of both concentration and silane structure on the surface modification of CNFs, the coating reactions were carried out at room temperature for 1 minute (see

Table 2). The influence of the silane structure was studied by using the above mentioned SCAs: APS, AMO, DMO and GMO. To study in more detail the amount of the SCAs deposited on CNFs surfaces, both TGA and SA determinations have been carried out for such samples.

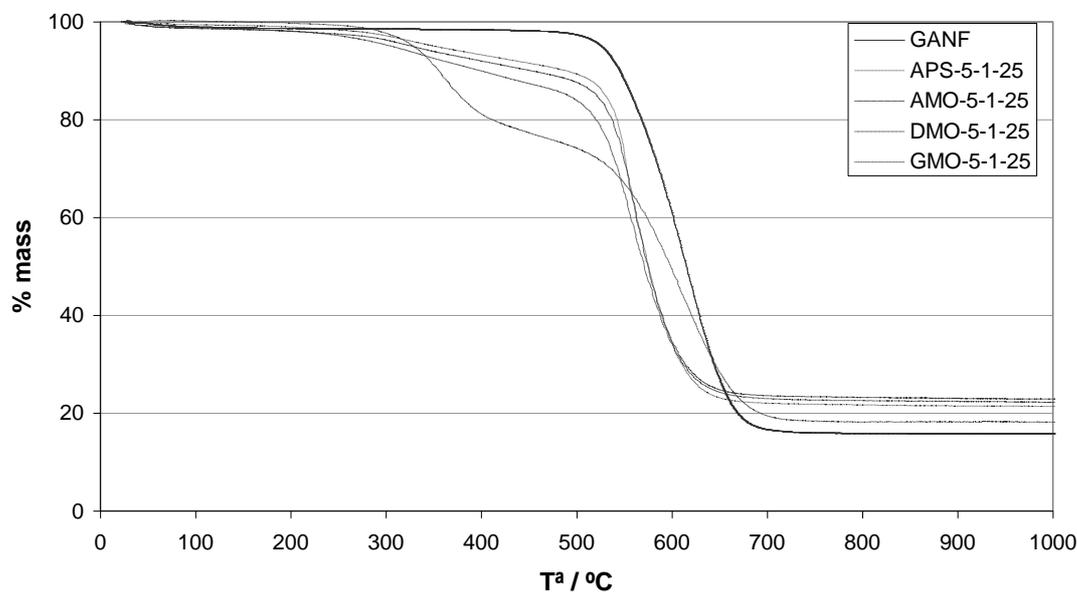


Fig. 6. TGA curves of pristine CNFs and CNFs coated with the higher concentrations of different SCAs.

Fig. 6 shows the TGA curves of pristine and silane coated CNFs after treating with different SCAs. As it was mentioned earlier (Fig. 3), all silane coated CNFs show a weight loss when are heated between 200 and 500°C which corresponds to the combustions of the silane organic chain. In the case of the GMO silane, this combustion takes place in the 250-550°C temperature range. This could indicate that a) the combustion of the epoxy chain of GMO occurs at higher temperatures than the combustion of amine groups present in APS, AMO and DMO silanes or, b) the epoxy chain gives a stronger interaction with the CNFs surface than other silanes.

Fig. 6 also shows that weight losses depend on the silane structure. Thus, GMO shows the higher weight loss and DMO the lower one. These differences in weight losses are due to both silane organic chain weight and the silane adsorbed amount. Fig. 7 shows the weight losses obtained for CNFs treated with the different studied silanes. It can be observed that for low silane concentrations in the hydrolysed solution, the adsorbed amounts on the CNFs are very close (between 0.5 and 2.0%). However, for high silane concentrations, the adsorbed amounts show three mainly behaviours. First of all, DMO gives the lowest interaction with CNFs reaching a value of 1.63%, and this fact is due to the presence of the diamine organic chain. Secondly, APS and AMO show similar behaviours with 3.98% and 4.45% weight losses respectively, because both have the same organic group (3-aminopropyl). And finally, GMO shows a high increase (close to 15%) in the weight loss. These results indicate that monolayer and multiplayer coatings may be obtained on the CNFs surfaces.

As it has been mentioned earlier, the presence of the adsorbed SCAs on the surface of CNFs modifies the corresponding SAs due to the pore coating. SA values obtained from adsorption-desorption N_2 isotherms are given in Table 6.

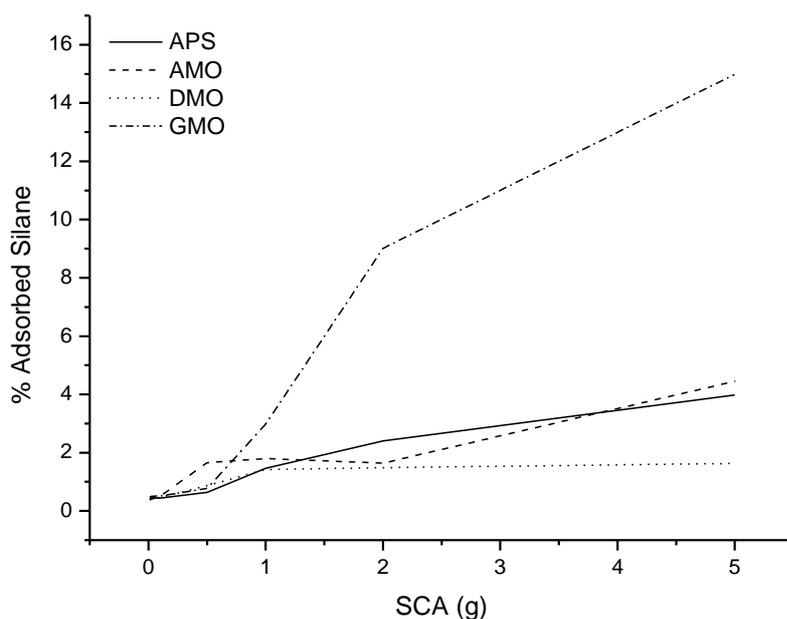


Fig. 7. Concentration of adsorbed silane versus silane concentration in solution.

According to Table 6, the SAs of CNFs decrease when are coated with any SCA. For SCA amounts lower than 0.1 g, the SAs give similar values, however, for higher SCA amounts some differences can be observed. When the amount of SCA is 5 g, the SA has decreased widely, about 50% in the case of APS, AMO and DMO, and about 80% for GMO. This result indicates again, that GMO shows a stronger interaction with CNFs surface than the other studied SCAs.

Therefore, these interactions are due to differences in the molecular silane structure, in both the functional and hydrolysable groups. As it has been mentioned previously, GMO has an epoxy functional group while the functional one in other silanes is amine. Such epoxy group and the fact of having a hydrolysable methoxy group (more easily to hydrolyse than the ethoxy group) give to this SCA the capability of having a stronger interaction than other SCAs studied. On the other hand, the diamine functional group of DMO gives to this SCA the less capability of interaction with CNFs. In summary, according to TGA and SAs results, CNFs give different interaction with epoxy or amine silanes.

Table 6. SA (BET) values of CNFs treated with different amounts of studied SCAs.

SCA added [g]	APS	AMO	DMO	GMO
0	143			
0.01	130	122	116	136
0.03	138	122	120	136
0.1	142	119	119	131
0.5	131	119	109	99
1	118	106	79	86
2	106	88	64	61
5	80	62	62	27

Conclusions

In this paper, we have studied the silanization process of CNFs with different SCAs. First, we have characterized the CNFs surface, in order to evaluate the capability of pristine CNFs to bond with hydrolysed SCAs, founding that pristine CNFs present an overall basic surface, and acidic oxygenated functional groups, making possible the condensation reaction with hydrolysed SCAs.

Secondly, we have employed APS silane in order to evaluate the influence of both reaction time and reaction temperature in the silanization process. It has been concluded that the silane concentration adsorbed on CNFs surface does not increase for reaction times higher than 1 min. At the same time, it has also been observed that the reaction temperature does not influence the adsorbed silane concentration in the range 25°C to 45°C.

Finally, a more detailed study of the silanization process has been carried out for increasing amounts of different SCAs. Two aminosilanes (APS, AMO), one diaminosilane (DMO) and one epoxy silane (GMO) have been used in this study. It has been observed that the different interactions of these silanes on the CNFs surface are due to the silane structure. In this sense, APS and AMO silanes have shown very similar behaviours reaching silane concentrations close to 4% adsorbed on the surface of CNFs. This result is related to the silane structure since both silanes present the same functional non-hydrolysable group and, after hydrolysis they are similar molecules. These silanes interact through Si-OH and OH groups existing on CNFs surface. On the other hand, the diamine DMO silane shows the lowest interaction on the CNFs surface reaching an adsorbed silanes amount close to 1.6%. This diamine silane interacts on CNFs surface as amine silanes do, however, the length of the diamine chain gives the lower adsorbed amount. Finally, the epoxy GMO silane presents two trends. In this case for low silane concentrations in solution, the silane coating process is similar to those for APS; AMO and DMO. However, when the silane concentration in solution increases, multilayers of GMO are formed on CNFs surface, leading to a rapid increase of the silane adsorbed amount.

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