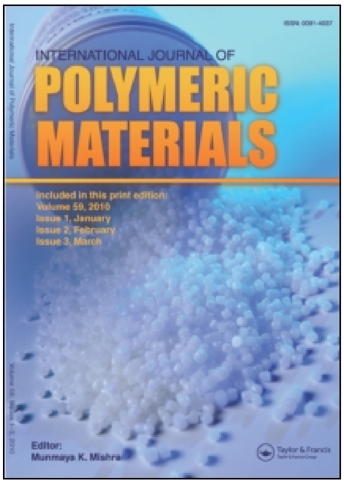

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The Interactions of Silane and Zirconate Coupling Agents with Calcium Carbonate

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The Interactions of Silane and Zirconate Coupling Agents with Calcium Carbonate

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The present work deals with the study of the structure and the form of the deposit on calcium carbonate of two types of silane coupling agents and a zirconate one. The structure of the deposited layers as well as their interactions with the filler were investigated by means of Fourier Transform Infra-Red Spectroscopy. The extent of the recovery was determined using the dissolution method, which allowed the authors to measure the adsorbed quantity and to estimate the molecular area occupied by each coupling agent as well as the orientation of the molecules on the surface of $CaCO_3$*. The structure of the aminosilane layers deposited on calcium carbonate appeared to be greatly influenced by the initial conditions of treatments. These include the pH, the concentration of the aqueous bath of impregnation, duration, and method of application. The results showed the formation of structures polymerized on the surface of* $CaCO_3$ *and the deposit was composed of monomers and oligomers that were both physisorbed and chemisorbed. The study of the chemical structure of the zirconate agent that was deposited on the surface of* $CaCO_3$ *showed that a monomolecular layer was chemically adsorbed. The physisorbed part was mainly constituted of monomers that were soluble in the solvent used for the extraction.*

Keywords: calcium carbonate, coupling agents, dissolution method, surface treatment

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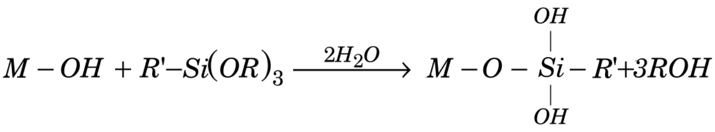
INTRODUCTION

The addition of fillers to polymers has a great importance. In fact, fillers are a major ingredient in many polymer-based formulations. However, due to their low affinity toward the polymeric matrix they are often mixed using high shear means, or they are chemically treated in order to improve their compatibility.

Chemical substances having a surface activity are used as treatment agents for mineral or organic fillers in order to modify the interfacial tension and improve the filler–polymer interactions. A good example of such substances is stearic acid and its metallic salts whose effect is to increase the wetability of the filler particles within the polymer matrix [1]. Owing to this treatment the properties are better than those obtained with untreated fillers. But this advantage is temporary and a loss of physical characteristics would be noted upon storage.

Other types of filler treatment agents are the organosilane coupling agents whose general structure is $R'Si(OR)_3$ where R' and OR are two distinct functions through which many chemical reactions would be possible.

Condensation and hydrolysis reactions of silanes on the surface of a mineral filler are illustrated as follows [1]:



$$M-OH + R'-Si(OR)_3 \xrightarrow{2H_2O} M-O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}-R'+3ROH \qquad \mathbf{(1)}$$

(where M is the mineral substrate).

However, this type of agent is not adsorbed as a single layer but forms an irregular multilayered coating. The efficiency of the silane coupling agent depends greatly on the extent of condensation, which affects the structure of the composite interphase. The interphase structure depends also on many other factors such as the pH, filler concentration, the agent's functionality, solution temperature, type of solvent, drying conditions, duration, and method of application. The filler can also have an influence through its topology and surface properties [2–3].

Aminosilane coupling agents are widely used because of their solubility and their good stability in solutions based on solvents that can form hydrogen bonding such as water and alcohols. This stability is attributed to the formation of zwitterionic and/or cyclic species, which stabilize the molecular structure by limiting the condensation [4–5].

Studies [6–7] have clearly shown, through qualitative and quantitative determinations, the recovery of silane agents in a multilayered structure on the surface of most mineral fillers. This recovery is an evidence of an adsorption that takes place physically as well as chemically. The effect of the physically adsorbed layer on the properties of composites is not yet well understood. In this context, some contradictory results have been reported concerning the effect of the thickness of the adsorbed layer on the mechanical properties of composite materials [8–10].

Other coupling agents that are used with low reinforcing fillers are composed of organometallic agents based on titanium or zirconium. These molecules are exceptional because their reaction with the free protons of the inorganic interface on the surface of which organic monomolecular layers will be formed according to the following alcoholysis mechanism [11]:

$$\begin{aligned} \mathrm{M-O-H + R'-O-Zr(O-X-R-Y)_3} &\longrightarrow \mathrm{M-O-Zr-(\!-O-X-R-Y)_3} \\ &\quad + \mathrm{R'OH} \qquad (2) \end{aligned}$$

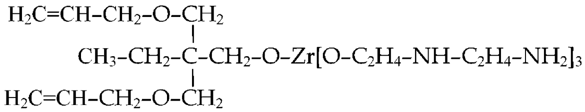
The present work is a contribution toward the study of the structure of the resulting layers formed on the surface of calcium carbonate. The substances used for the treatment of the mineral filler have been chosen so as to create an interface with an increasing structural complexity. These substances are two organosilane agents and an organozirconate agent having all amine functional groups.

The study aims at investigating different factors that could affect the structure of the deposited layers. These include the effect of the pH of the aqueous solution, concentration, duration, and method of application. The testing method is essentially the Fourier Transform Infra-Red Spectroscopy.

EXPERIMENTAL

The calcium carbonate (Alcal UF-5) that was used was supplied by ENG-Algeria and had an average particle diameter of 5 μm and a specific surface area of 2.64 m^2/g (BET, N_2 at 77 K). X-ray diffraction measurements indicated that the calcium carbonate was pure calcite. Its chemical composition is given in a previous publication [12]. The coupling agents used are presented in Table 1. Two methods of surface treatment were applied in this study, namely: adsorption from a solution and dry blending. In the first method the silane coupling agents were hydrolyzed for about 24 h in a bi-distilled water whose pH had

TABLE 1 Structure of the Coupling Agents Used for the Treatment of Calcium Carbonate

Coupling agent	Chemical structure	Trade name	Producer
3-aminopropyltriethoxysilane	$H_2N-CH_2-CH_2-CH_2-Si\ (OC_2H_5)_3$	A-1100	Witco Corp.
N-(2-aminorthyl)-3-amino propyltrimethoxysilane	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si\ (OCH_3)_3$	Z-6020	Dow Corning Corp.
Neopentyl (diallyl)oxy, tri (N-ethylene) diaminoethylzirconate	 $\begin{array}{l} H_2C{=}CH\text{-}CH_2\text{-}O\text{-}CH_2 \\ \qquad\qquad\qquad\quad \vert \\ CH_3\text{-}CH_2\text{-}C\text{-}CH_2\text{-}O\text{-}Zr[O\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH_2]_3 \\ \qquad\qquad\qquad\quad \vert \\ H_2C{=}CH\text{-}CH_2\text{-}O\text{-}CH_2 \end{array}$	NZ-44	Kenrich Petrochemicals Incorp.

been adjusted to values of 3, 6, 9, and 12 by adding acetic acid or sodium hydroxide. The calcium carbonate was then added to these solutions in different vessels and the suspensions were continuously agitated for 1 h at 25°C. The coated product was then filtered on a Büchner filter, washed with tetrahydrofurane (THF), and dried in air for 1 day and for 12 h in an oven at approximately 105°C to complete the condensation process.

The level of coating applied was varied from 0.2 to 2 wt%. The extent of recovery was determined at each concentration using the dissolution method [13–14].

An amount of 10 g of the treated calcium carbonate was stirred in 150 ml tetrahydrofurane and the suspension was then agitated vigorously for about 45 min. After heating in a reflux condenser for 30 min, the suspension was cooled at room temperature and was allowed to settle for 72 h. During this period the flasks were shaken well every day for 15 to 20 min. Finally, the product was filtered and dried briefly at 80°C.

The treatment with the zirconate coupling agent was performed in an isopropanol solution by mixing the coupling agent in the solvent for approximately 60 min. After adding the calcium carbonate to this solution, the slurry was mixed until good dispersion was achieved. The solvent was then extracted under vacuum at 80°C for 12 h. The treated product was washed again with carbon tetrachloride and dried for the same period of time and at the same temperature as was performed with the silane coupling agents.

For the second method of treatment the calcium carbonate was dry-blended with the three coupling agents. The powder was placed in a high intensity solid mixer and the pure silane coupling agents were slowly sprayed for 30 min. The coated calcium carbonate was left standing for various periods of time ranging from 0 to 600 min. Time zero was taken in all experiments as the moment when the spray operation was finished. Contrary to the silanes, the zirconate coupling agent was dissolved in isopropanol in order to reduce its viscosity. Then this solution was pumped and sprayed onto the filler powder while agitating. Finally, the treated $CaCO_3$ was stored in air-proof containers until further analysis.

The chemical structure of the coupling agents was characterized using a Perkin-Elmer FTIR spectrometer with an optical resolution of 4 cm^{-1}. The spectra were obtained in transmission using GRAMS software to analyze the different transmittance bands.

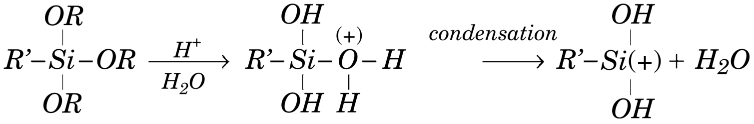
Characterization of the recovered products present on the particles of calcium carbonate was carried out in transmission using the KBr plate method. About 5 mg of particles were mixed with 95 mg of potassium bromide and then compacted into thin plaques with a hydraulic press, using 5 tons of force and maintained for about 4 min. Samples were analyzed by signal averaging 600 scans.

Characterization of the extracted products was also carried out in transmission. The extracts were deposited as a film between two KBr windows after evaporation of the solvents. Samples were analyzed by signal averaging 120 scans at a resolution of $5\,\mathrm{cm}^{-1}$.

The amount of the coupling agents that are bound permanently to the surface of the filler can be calculated by determining the concentration of the solution obtained by the dissolution process and analyzed by FTIR.

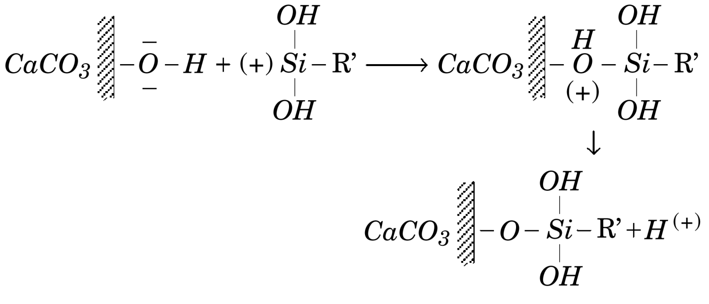
RESULTS AND DISCUSSION

It is evident that the effects of the surface treatment by means of organosilanes depend on their conditions of application and the mechanism through which they act on the inorganic surface. At acidic pH conditions, the silane is rapidly hydrolyzed and is transformed mainly to a silanol. The silane molecule undergoes a protonation of the oxygen, which means the creation of a positive charge on this atom. Therefore, the oxonium cation formed causes the break-up of the Si–O bond and a cation is formed as follows:



$$R'\text{-}\overset{OR}{\underset{OR}{Si}}\text{-}OR \xrightarrow[H_2O]{H^+} R'\text{-}\overset{OH}{\underset{OH}{Si}}\text{-}\overset{(+)}{\underset{H}{O}}\text{-}H \xrightarrow{condensation} R'\text{-}\overset{OH}{\underset{OH}{Si}}(+) + H_2O \qquad (3)$$

The cation that is formed will be added onto the hydroxyl group of the inorganic substrate, followed by a spontaneous elimination that restores the H^+ ions according to the following reaction:

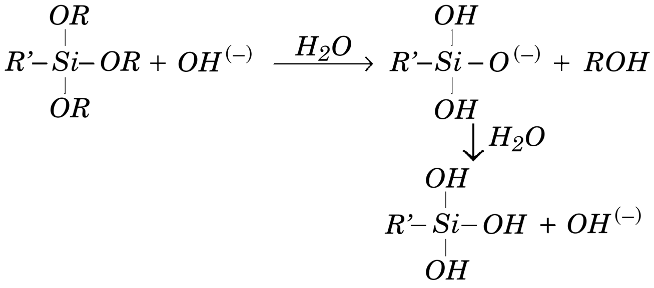


$$CaCO_3\,|\!-\overset{-}{\underset{-}{O}}-H + (+)\overset{OH}{\underset{OH}{Si}}-R' \longrightarrow CaCO_3\,|\!-\overset{H}{\underset{(+)}{O}}-\overset{OH}{\underset{OH}{Si}}-R'$$

$$\downarrow \qquad (4)$$

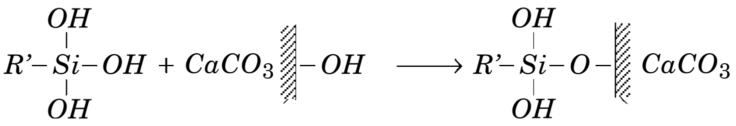
$$CaCO_3\,|\!-O-\overset{OH}{\underset{OH}{Si}}-R' + H^{(+)}$$

In basic catalysis, OH^- ions cause the formation of a nucleophilic entity that reacts immediately with water. This is followed by an elimination reaction that regenerates back the OH^- ions according to reaction (5):



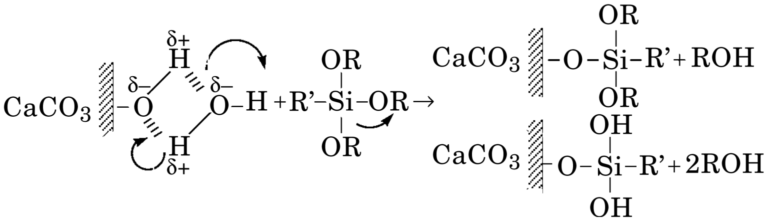
$$R'-\underset{OR}{\overset{OR}{Si}}-OR + OH^{(-)} \xrightarrow{H_2O} R'-\underset{OH}{\overset{OH}{Si}}-O^{(-)} + ROH \xrightarrow{H_2O} R'-\underset{OH}{\overset{OH}{Si}}-OH + OH^{(-)} \qquad (5)$$

The condensation reaction takes place according to the following reactional scheme:



$$R'-\underset{OH}{\overset{OH}{Si}}-OH + CaCO_3\,|\!-OH \longrightarrow R'-\underset{OH}{\overset{OH}{Si}}-O-\!|\,CaCO_3 \qquad (6)$$

The second treatment technique that was investigated consists of impregnating the filler with nonhydrolyzed pure products. In this case it is supposed that the water physisorbed at the surface of the filler would be sufficient to hydrolyze the reactive species. This is illustrated in the following reactional scheme:



(7)

Parameter Optimization Tests

The Effect of pH

Figure 1 shows the variation of the amount of A-1100 and Z-6020 coupling agents adsorbed on calcium carbonate as a function of pH. The adsorption is achieved inside the aqueous bath of impregnation with a concentration of 0.6 wt% of the coupling agents for a period of 60 min. The results show that the amount of the adsorbed matter decreases as the pH increases. Such a behavior was expected because

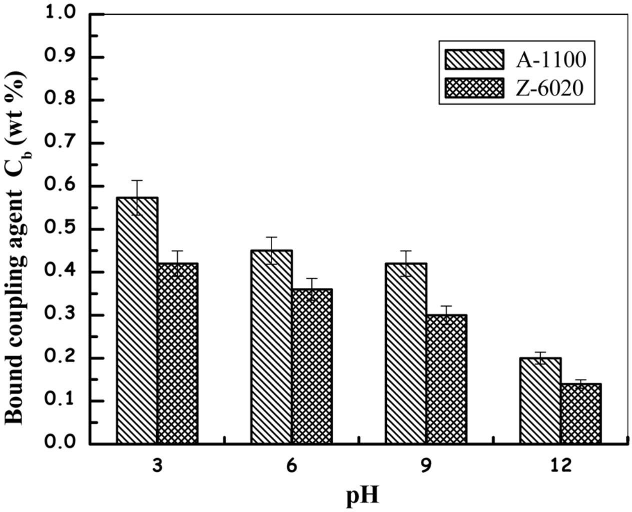


FIGURE 1 Effect of pH on the amount of the A-1100 and Z-6020 adsorbed onto $CaCO_3$: for an initial concentration of the silane coupling agents in the solution of 0.6 wt%.

it had been reported that treatment by means of aminosilanes in aqueous media could be achieved throughout a large interval of pH values [15–16].

The Effect of Concentration

The study of the variation of the amount of the bound matter as a function of the initial concentration of the coupling agent was carried out for the same conditions of measurements. The surface treatment of $CaCO_3$ with the silane coupling agent was achieved at different concentrations for a $pH = 3$ during a period of 60 min.

The extent of recovery was determined using the dissolution method described earlier. From the difference between the initial quantity C_0 and the final amount C_f the amount of the bound matter formed on the surface of the filler can be deduced, which is referred to as C_b. Figure 2 presents the dissolution curves of the A-1100 agent. A linear part can be distinguished in these curves, where the adsorbed amount is proportional to the initial concentration, which is designated as C_{100}. In the horizontal part of these curves the adsorbed amount does not vary with the initial concentration. In this case the maximum recovery is achieved and is noted as C_{max}. The results show that the adsorbed amounts of A-1100 formed on the surface of calcium

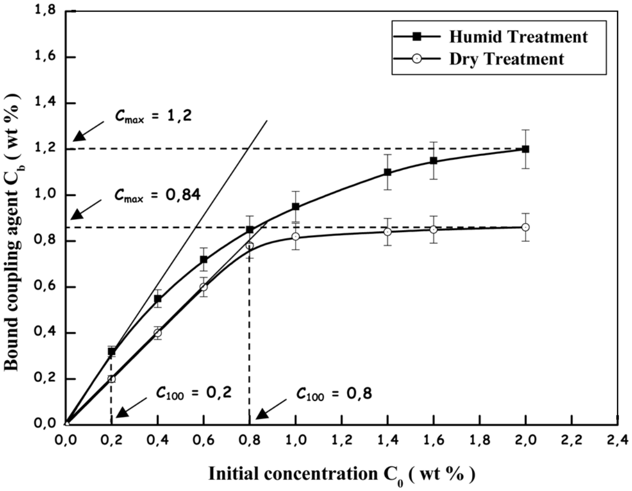


FIGURE 2 Effect of the initial concentration of the A-1100 agent on the amount adsorbed onto $CaCO_3$.

carbonate increase rapidly up to a concentration of the aqueous bath of impregnation of 0.2 wt% in the case of humid treatment, and to a value of 0.8 wt% for the case of dry treatment. Then, this increase becomes slower until the maximum recovery is reached. The values of C_{max} are 1.2 wt% for the humid treatment and 0.8 wt% for the dry treatment. These results are in agreement with those reported by Johanson and coworkers [16] and those of Chabert [17].

If it is assumed that C_{100} corresponds to the amount necessary for the formation of the monolayer, and knowing the value of the BET specific area of the filler, then one can estimate the surface that is occupied by an adsorbed molecule and which is noted as (a_m). The value of a_m calculated was found to be 0.30 nm^2 in the case of humid treatment. This supposes that the silane molecules are adsorbed by bringing the amino groups into contact with the hydroxyls of the $CaCO_3$ surface resulting in cyclic structures. Concerning the second mode of treatment, that is the dry method, the values of a_m were found to be close to 0.075 nm^2. In this case the adsorbed molecules are oriented vertically with respect to the surface of $CaCO_3$. This result is in agreement with those of Demjen and co-workers [6].

A completely different behavior was noted with the Z-6020 agent, as shown in Figure 3. The trend of these curves is comparable to the adsorption isotherm of the S type according to the classification

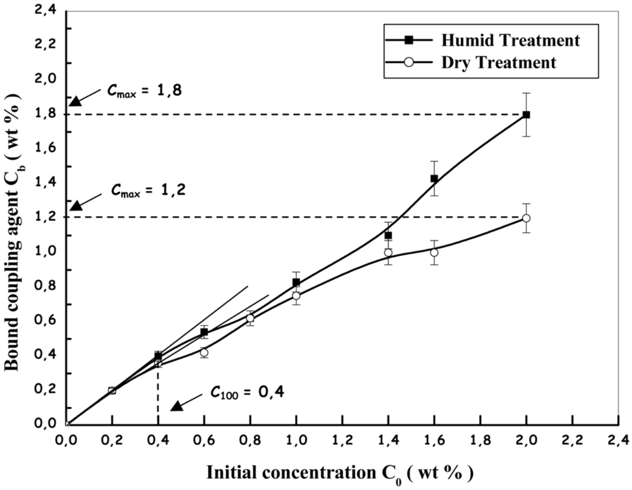


FIGURE 3 Effect of the initial concentration of the Z-6020 agent on the amount adsorbed onto $CaCO_3$.

established by Gilles and coworkers [18]. This indicates that the interaction of this agent with calcium carbonate is much more complicated.

The characteristic value of C_{100} is 0.4 wt% for the two modes of treatment. However, the values of C_{max} are 1.2 wt% and 1.8 wt% for humid treatment and dry treatment, respectively. The calculated area occupied by the Z-6020 molecule was found to be 0.21 nm^2, which means that the molecules are oriented perpendicularly to the surface of $CaCO_3$.

Figure 4 presents the dissolution curves of NZ-44 agent. They point out an increase of the amount of bound matter with the increase in the initial concentration but in a noncontinuous manner. Two distinct plateaus are noted, which reflect the complexity of the phenomena. If it is considered that the first plateau corresponds to the formation of a monolayer, the second one would therefore mean the deposition of an additional layer. The values of C_{max} for each plateau were found to be 0.48 wt% and 0.6 wt% for the humid treatment. Concerning the dry treatment, the values of C_{max} were 0.35 wt% and 0.4 wt% for the corresponding first and second plateau.

It is also shown through these curves that the adsorbed quantity is proportional to the initial concentration within the range up to 0.4 wt%. The estimated area that is occupied by the molecule is 0.62 nm^2. This result means also that the adsorbed NZ-44 molecules are perpendicularly oriented with respect to the surface of the filler.

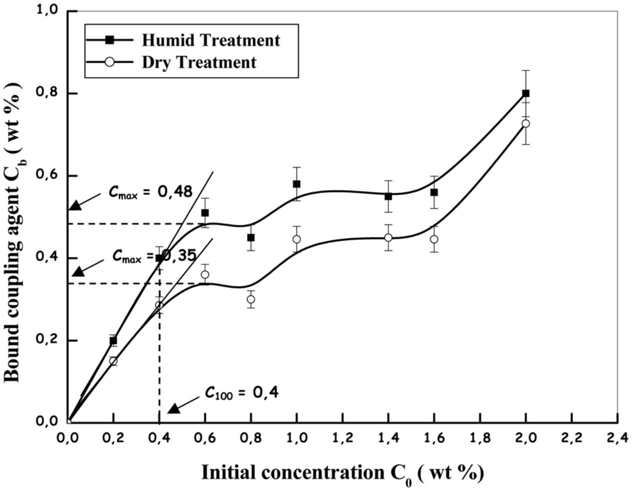


FIGURE 4 Effect of the initial concentration of the NZ-44 agent on the amount adsorbed onto $CaCO_3$.

The Effect of Treatment Time

Figure 5 shows the effect of treatment time on the quantity of A-1100 agent that was adsorbed on calcium carbonate from aqueous baths of impregnation adjusted to pH values of 3, 6, and 12 for an initial concentration of 2 wt%. The adsorption has revealed the existence of a succession of upward steps characterized by three distinct plateaus. For a basic bath of impregnation ($pH = 12$), the adsorbed quantity increases rapidly after going through a long induction period. Overall, at equal times of impregnation the adsorbed quantities remain lower than those noted in an acidic medium.

Similar results were obtained with the Z-6020 agent, especially at pH values of 3 and 6, as shown in Figure 6. A rapid increase of the adsorbed quantity is observed after the first plateau. This could be attributed to the formation of polymolecular layers after the deposition of the first layer. The decrease of the adsorbed amount, which is noted after the second plateau, is certainly due to a complex phenomenum.

In the case of a basic bath of impregnation and as shown in Figure 7, which presents the variation of the adsorption quantity of the NZ-44 agent as a function of time, the curve is characterized by a long induction period followed by two plateau regions. These results show that the adsorbed amount remains constant for a long period before ultimately rapidly increasing. After passing through the first increase

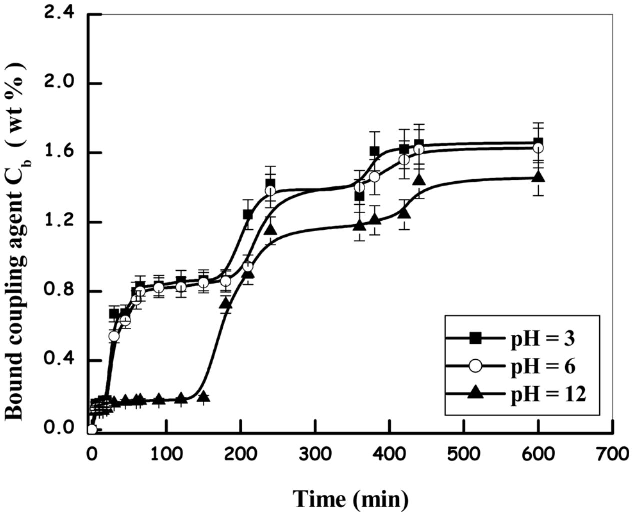


FIGURE 5 Effect of treatment time on the amount of the A-1100 agent adsorbed onto $CaCO_3$: for an initial concentration of the coupling agent of 2 wt%.

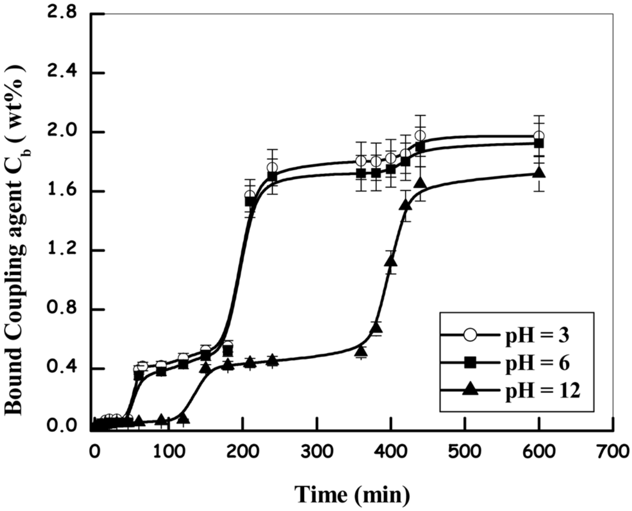


FIGURE 6 Effect of treatment time on the amount of the Z-6020 agent adsorbed onto $CaCO_3$: for an initial concentration of the coupling agent of 2 wt%.

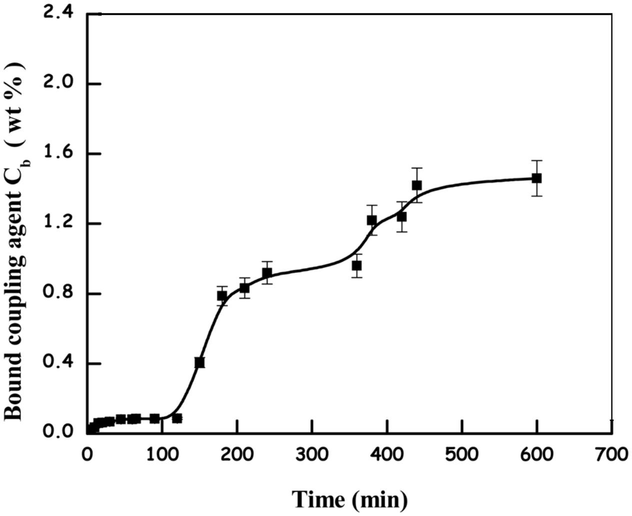


FIGURE 7 Effect of treatment time on the amount of the NZ-44 agent adsorbed onto $CaCO_3$: for an initial concentration of the coupling agent of 2 wt%.

region, three other plateaus are observed; a behavior that reflects again the complexity of the phenomena.

Fourier Transform Infra-Red Spectroscopy

Figure 8 presents the FTIR spectra of $CaCO_3$ treated with the A-1100 agent by the humid way, and that of the product extracted with THF solvent, in comparison to the reference spectra, which are those of the pure coupling agent and the untreated $CaCO_3$.

Spectrum 8(c) shows a polymerized structure of the A-1100 on calcium carbonate. This is evidenced by the absorption bands at 1142 and 1030 cm^{-1}, which are attributed to the siloxane bonds linked to the formation of oligomers (dimers, trimers, tetramers) and linear and cyclic chains [19].

The band appearing between 3600 and 3300 cm^{-1} corresponds to the vibration of the N–H bond in the NH_3^+ ion, which means the presence of an amine salt resulting from the formation of a $H_2N^+ \cdots H \cdots {}^-O\text{–}Si$ type of a complex.

Spectrum 8(d) of the product extracted with THF points out the existence of oligoaminosilanes through the absorption bands at 1070, 1030, and 1180 cm^{-1}. The residual presence of $-CH_3$ groups

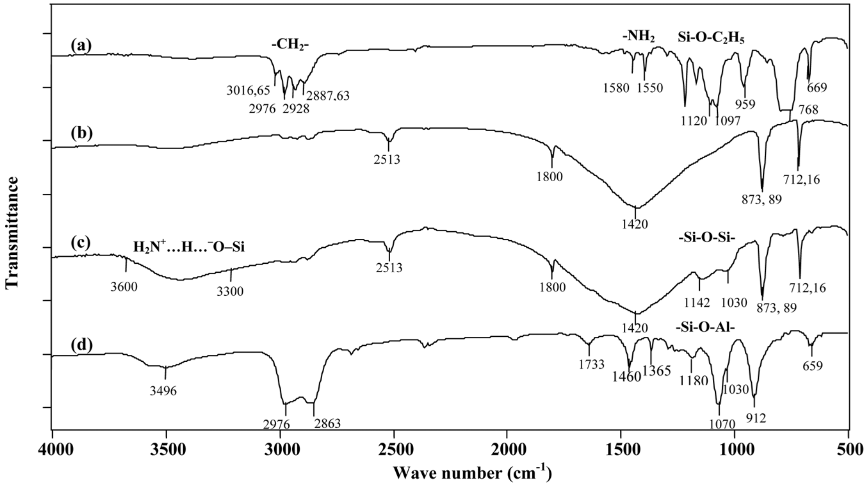


FIGURE 8 FTIR spectrum of (a) A-1100, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with A-1100 by the humid method, (d) product extracted with THF.

(absorptions at 2976, 1863, and 1365 cm^{-1}) could be attributed to the presence of ethyl acetate, which is characterized by the absorption bands due to the carbonyl group of the ester functional group at 1733 cm^{-1} and 1250 cm^{-1}.

The absorption band at 1630 cm^{-1} is probably an indication of the presence of water despite a prolonged drying that was carried out for 24 h at 105°C. It is therefore probably a consequence of a stable fixation of water with a salt.

Figure 9(c) shows the infrared spectrum of $CaCO_3$ that was treated with the A-1100 agent by the dry method. The double absorption appearing between 1142 and 1030 cm^{-1} confirms the presence of oligomers resulting from the condensation of silanes into siloxanes. The analysis of the extract given by Figure 9(d) shows a broad band at 3480 cm^{-1}, which could be attributed to the stretching vibrations of the N−H or O−H groups that are fixed in hydrogen bridges. The elbowed band at 3600 cm^{-1} is probably due to the presence of OH groups that are not associated.

The absorption at 1070 cm^{-1} could be assigned to the elongational vibrations of the Si−O−Al bonds, as was proposed by Boerio [20] who studied the deposit of the aminosilane (A-1100) on alumina. This supposes the condensation of the hybrid network into a polyaluminosiloxane structure. The interpretation of this result admits that the aluminum ions migrate from the surface toward the interior. This is

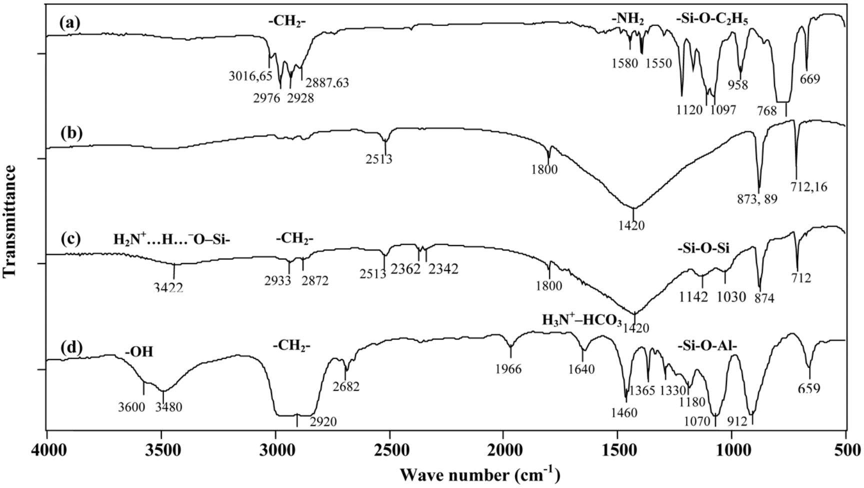


FIGURE 9 FTIR spectrum of (a) A-1100, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with A-1100 by the dry method, (d) product extracted with THF.

in agreement with the observations reported by Wang and Jones [21]. The three bands located at 1570, 1470, and 1310 cm^{-1} could be attributed to the vibrations of the N–H and C=O bonds from the amine salts of $H_3N^+{-}HCO_3$ type. The presence of this species is apparently due to the passage of bicarbonate ions HCO_3^{2-} in the solution resulting from the washing operation of $CaCO_3$. But it is also possible that this species resulted from the absorption of carbon dioxide from the air as was proposed by Boerio [20], and Chabert and co-workers [17].

Figure 10 presents the infra-red spectra of $CaCO_3$ that was treated with the Z-6020 agent by means of the humid way, and those of its THF extract, in comparison with the spectra of the pure coupling agent and untreated $CaCO_3$.

Spectrum 10(c) shows two additional bands at 1120 cm^{-1} and 1035 cm^{-1}. Such bands characterize the siloxane bonds. The absorption bands at 2932 and 2872 cm^{-1} are essentially owing to the stretching vibrations of C–H bonds from the CH_2 group of the aminoethyl or aminopropyl segments.

The broad band centered at 3340 cm^{-1} is an important one and suggests the presence of H_3N^+ ions, which means the formation of an amine salt of a $H_2N^+\cdots H\cdots {}^-O{-}Si$-type. The presence of the C=O group of the ester function is demonstrated by two bands with a low intensity at 1733 and 1250 cm^{-1}, which makes it possible to suppose that the methylic alcohol resulting from the hydrolysis of

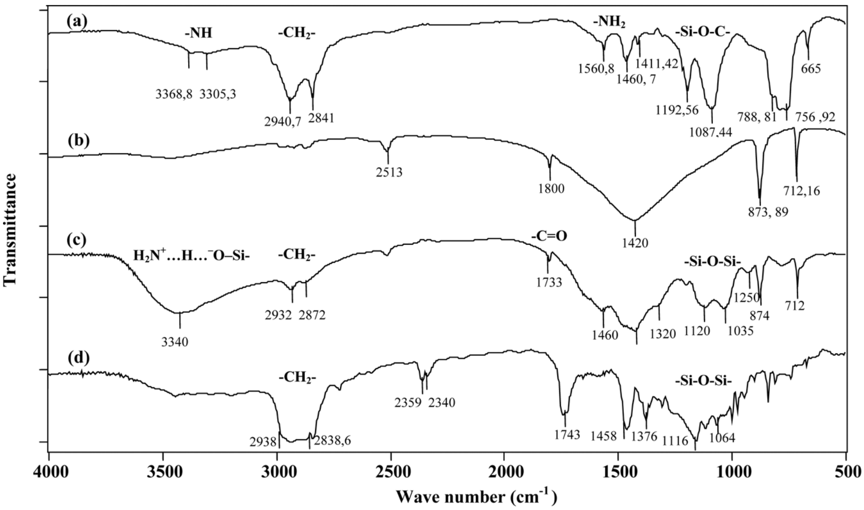


FIGURE 10 FTIR spectrum of (a) Z-6020, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with Z-6020 by the humid method, (d) product extracted with THF.

the aminosilane has not totally disappeared but remained in other forms such as, most probably, methyl acetate. In fact, the hydrolysis of the coupling agent was carried out in an acetic acid medium and it is possible that the drying of $CaCO_3$ was not enough to completely get rid of the acetate.

The infrared analysis of the product extracted with THF, shown in spectrum 10(d), shows two characteristic peaks at 1116 cm^{-1} and 1064 cm^{-1}, which appear to correspond to cyclic oligomers.

Figure 11 presents the infrared spectra of the calcium carbonate treated by means of the dry method with the Z-6020 and its THF extract, in comparison to those of pure coupling agent and untreated $CaCO_3$. The presence of oligoaminosilanes is confirmed in this spectrum through the absorption bands at 1180 and 1070 cm^{-1}. The 1070 cm^{-1} band characterizes the formation of polyaluminosiloxane bonds. This result is based on the chemical composition of $CaCO_3$ filler, particularly the migration of the aluminum ions from its surface toward the hybrid network.

The analysis of the infrared spectrum of the $CaCO_3$ that was treated with the NZ-44 agent by the humid way, which is shown in Figure 12(c), has revealed the presence of a large band appearing between 2933 and 2862 cm^{-1}. This band could be attributed to the $–CH_2–$ groups of the organozirconate agent. The multiplicity of the bands situated

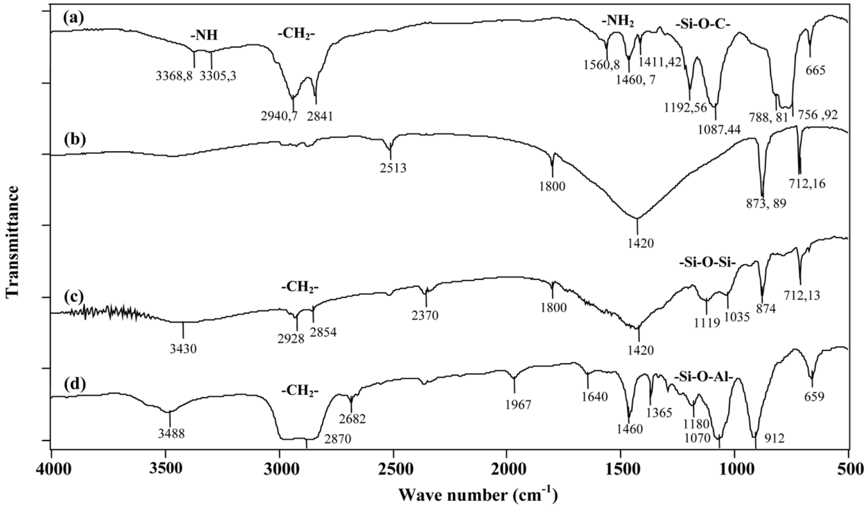


FIGURE 11 FTIR spectrum of (a) Z-6020, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with Z-6020 by the dry method, (d) product extracted with THF.

at 1062, 997, 972, and 937 cm^{-1} are likely due to the Zr–O–C and Zr–O–M groups, where M represents the metallic impurities inside calcium carbonate [22]. In fact, the set of bands that spreads

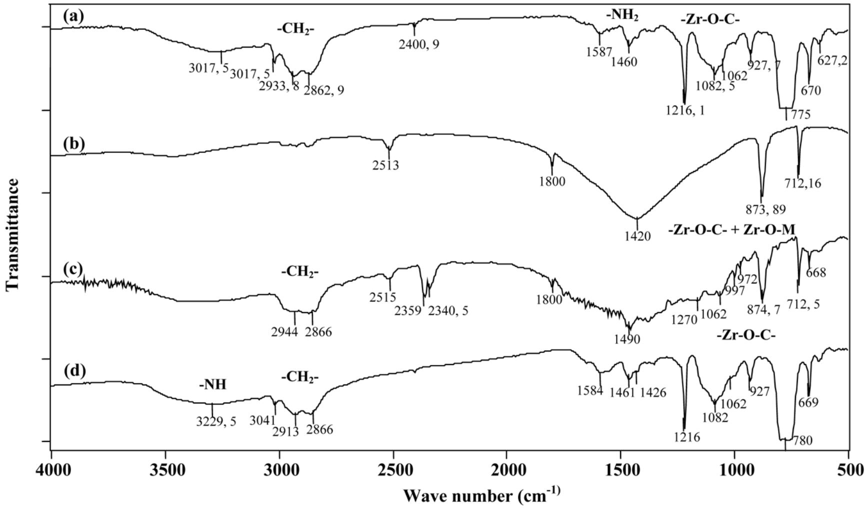


FIGURE 12 FTIR spectrum of (a) NZ-44, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with NZ-44 by the humid method, (d) product extracted with CCl_4.

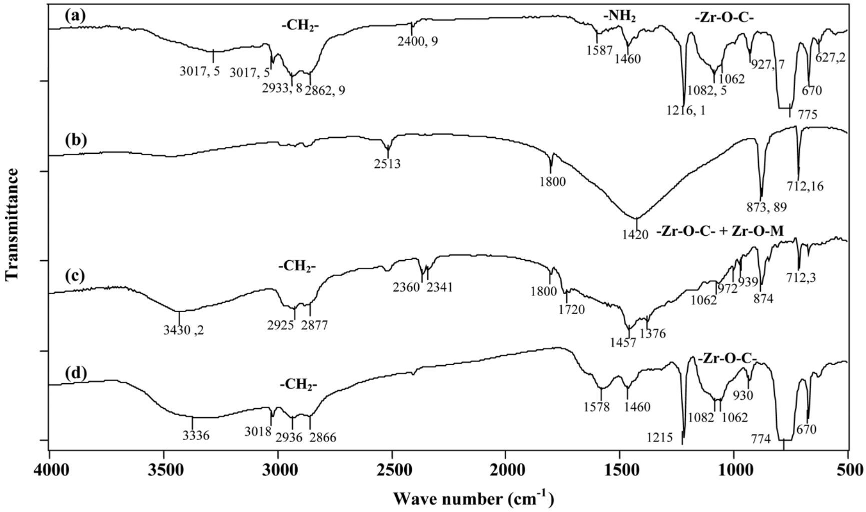


FIGURE 13 FTIR spectrum of (a) NZ-44, (b) untreated $CaCO_3$, (c) $CaCO_3$ treated with NZ-44 by the dry method, (d) product extracted with CCl_4.

throughout the absorption region of calcium carbonate is composed of progression bands. These bands are produced by the great number of the NZ-44 molecules that are adsorbed on the surface of $CaCO_3$.

The infrared analysis of spectrum 12(d) of the extract shows that the additional layers are mainly composed of monomers that are only physisorbed (absorption bands at 1082, 1062, and 927 cm^{-1}).

The results of the infrared analysis of $CaCO_3$ that was treated with NZ-44 by the dry method are illustrated in Figure 13. No further comment is to be made concerning spectrum 13(c) except that a reduced number of the progression bands can be observed, which is attributed to the fact that the number of the deposited molecules under these conditions remains lower than those deposited on the first method of treatment.

Finally, the analysis of the spectrum of the extract (Figure 13[d]) confirms that the deposit took place in a multilayer form. This constitutes an evident proof that the adsorption process of the upper layers, those adsorbed on the first layer, is physical.

CONCLUSIONS

The structure of the layers of the coupling agents that were deposited as well as their interactions with $CaCO_3$ particles were studied by means of Fourier Transform Infra-Red Spectroscopy.

The extent of the recovery was determined using the dissolution method, which allowed the authors to evaluate the area occupied by each coupling agent and to deduce the orientation of the molecules with respect to $CaCO_3$ surface.

The amount of the adsorbed aminosilanes is greatly influenced by different factors such as the pH, the structure of the coupling agents, time, the concentration of the aqueous bath of impregnation, and the mode of treatment.

The study of the adsorption of the aminosilane A-1100 has shown that the initial conditions of the treatment have a great effect on the structure of the deposited layers. It was found that a cyclization of the oligomers on the surface of $CaCO_3$ particles in the form of trimers was noted in the case of humid treatment. However a vertical orientation of the adsorbed molecules is favored in the case of dry treatment. The obtained results were completed through the FTIR spectroscopic analysis of the physisorbed part, which is soluble in THF. It was found that the extract was essentially composed of monomers and oligomers having linear or cyclic chains, which supposes the formation of a structure profile that gets more polymerized further away from the surface.

A vertical orientation of the adsorbed molecules with respect to the surface of $CaCO_3$ was observed for the two coupling agents Z-6020 and NZ-44. This form of orientation concerns only the chemisorbed part. The physorbed part, which was adsorbed much more slowly on calcium carbonate, seemed to be constituted, in the case of Z-6020, of linear and cyclic oligomers. In the case of treatment with NZ-44 the physisorbed fraction was composed mainly of monomers that were completely eliminated through solvent extraction.

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