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Study of the reaction of γ-methacryloxypropyltrimethoxysilane (γ-MPS) with slate surfaces

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Thermal Analysis (TA) and Fourier Transform Infrared Spectroscopy (FT-IR) were used in order to study the reaction of γ-methacryloxypropyltrimethoxysilane (γ-MPS) with slate surfaces at different temperature conditions (25, 35 and 50 °C), concentrations (0.5–5% weight of silane) and reaction times (1, 3, 5 and 10 min). By these conditions, a typical physical adsorption of the γ-MPS silane on the slate surface has been observed. A monolayer of γ-MPS is firstly adsorbed on the slate surface by hydrogen bonding through the carbonyl group of the silane and after that, silane multilayers are formed where free carbonyl groups are predominant. A concentration of 1% is considered as appropriate for silanization of the slate particles with γ-MPS. © *1999 Kluwer Academic Publishers*

1. Introduction

Slates are compact metamorphic and fine grain rocks formed by regional metamorphism. Slates have homogeneous and penetrative slate cleavage that permits to be separated in parallel thin sheets of smooth surface [1]. These rocks came from clay sediments that were deposited in oceanic basins with other materials. They were transformed to slates by both high pressures and temperatures. Slate mineralogical composition depends on the origin of this material. Generally all of them are constituted by philosilicates (sericite, a silicate aluminium and potassium hydrated, chlorite) and quartz. Kaolinite is a common component in some slates although in less concentration above mentioned minerals. The concentration of other minerals (calcite, iron sulphide, carbonaceous matter...) is very changeable and have not a clear influence on their physical and chemical properties or on applications of this material. Such minerals can come from impurities of primary rock or can be inserted from adjacent rocks in any metamorphism phase. Some of these impurities are harmful. When pyrite or iron sulphide such as pyrrotine or marcasite are in an oxidation state can generate marks on the slate. This prevents the use of slates as ornamental rock. Calcite is harmful impurity too because in sulphurous atmospheres (industrials zones) can be modified occurring white marks. Calcite can also absorb moisture from the atmosphere and then cause volume increase in the slate.

Covering buildings (tiles) is the more traditional application of slates. Slates are used as ornamental rocks both inside and outside for floor tiles, vaults, columns, stair steps, garden tables, electric insulations, etc. Slates are used in asphalt manufacture, painting, cement and plastic industry too [2]. Recently slate wastes have been studied for composite use [3]. Such work made clear the advantages of these new materials inasmuch of their mechanical properties in relation to original materials. This opens a new way for application slates as plastic fillers. It is well known the use of fillers or fibres in reinforcing plastics. In this sense high performance composite materials are developed with both fibres and resins of high properties. On the other hand, when composites are made from an organic matrix reinforced with inorganic fillers, chemical incompatibilities can take place between these dissimilar materials. In these cases, it is necessary to modify some components. One of the modification treatments consists on the silanization of the reinforcement surface by coupling agents [4, 5]. A coupling agent is a chemical compound applied at the interface of a composite in order to improve adhesion between a matrix and reinforcing material. By this, a coupling agent can be considered to be an adhesive used to join two dissimilar surfaces [6]. Silane coupling agents are widely used in fillers reinforced polymer composites to provide a water-resistant bond between a filler and polymer matrix [7–9]. Typical fillers are glass fibres and silica which are siliceous in nature. Two others fillers of commercial importance are alumina trihydrate (a flame retardant additive) and calcium carbonate (due to its low cost). When a solid surface is treated with a coupling agent, the mechanical performance of the composite material is strongly improved under humid environments. Trifunctional silanes such as γ-MPS are compounds of general formula $RSiX_3$, where R is an organofunctional group and X is a readily

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hydrolyzable group. Trifunctional silanes have also been used to functionalise silica for high-performance liquid chromatography [10, 11].

In this work, we have studied the interaction of a silane coupling agent (γ-MPS) with slates, a siliceous filler of low cost. The interaction of the coupling agent with the slate surface may change depending on both the composition of the slate surface and the type of coupling agent. Vanderbilt [12] indicated that different mineral surfaces have different interactions with silane coupling agents. The pH of the treating solution of the slate is an essential factor in controlling the population of acid sites. The chemical stability of silanol groups is highly pH dependent. Thus, the structure of the coupling agent in the treating solution is also strongly influenced. In the present study, differential thermal analysis (DTA) and Fourier Transform Infrared Spectroscopy (FT-IR) have been used in order to characterize the interaction between γ-MPS and slate particles.

2. Experimental

2.1. Materials

Slate samples, average diameter 37 μm, were supplied by Pizarras Villar del Rey, S.A. (Badajoz, Spain). The slate has a surface area of 5.8 m^2/g (BET, dynamic method). Silane coupling agent used in this work was γ-MPS, (A-174, from Union Carbide) which was used as received without further purification.

Aqueous solutions were prepared in deionized distilled water. Reactions were carried out in solutions at pH 6.0 containing from 0.5–5% weight of silane. The reaction times were 1, 3, 5 and 10 min. Previously, the γ-MPS was hydrolysed for one hour at the reaction temperature. Stirring was kept constant during the whole process. The resulting solutions were filtered and dried for 24 h at 50 °C in an oven at room atmosphere. The temperatures of the treating solutions were 25, 35 and 50 °C.

2.2. Instrumentation

A Fourier Transform infrared spectrophotometer (FT-IR, Perkin Elmer, model 1760X) was used for this study. The resolution was 4 cm^{-1} in the spectral range (4000–400 cm^{-1}). Ten scans were used to obtain each spectrum and background was subtracted from all spectra. Solid samples were analysed using high-purity pellets.

The quantification of γ-MPS adsorbed on slate surface was performed by thermal analysis (TA) using a simultaneous thermal analyser model Netzsch STA 409 EP, using platinum crucibles and taking α-Al_2O_3 as reference for TA. About 100–150 mg of sample were used in each measurement. The heating rate was 10 °C/min in air atmosphere.

3. Results

Fig. 1 shows the FT-IR spectra of as-received and silane treated slates with 0.5% and 5% of γ-MPS at the reaction temperature of 35 °C. In the FT-IR spectrum of the as-received slate, the broad band at 3440 cm^{-1} and the medium band located at 1630 cm^{-1} are assigned to the stretching and bending vibrations of OH groups and molecular water respectively. The absorption bands lying at 1165, 1065 and 1025 cm^{-1} are attributed to Si—O—Si, Si—O and Si—O—Al bonds of muscovite [13]. The band at 995 cm^{-1} is attributed to both muscovite and chlorite. The small band close to 933 cm^{-1} is characteristic of muscovite (sericite) which is mostly absent in others micas [13]. In the spectral region between 900–400 cm^{-1} appear the characteristic bands of quartz, muscovite and chlorite (13). A medium sharp absorption doublet located at 798–778 cm^{-1} and a weak sharp band at 695 cm^{-1} are assigned to quartz [14]. The bands close to 754 and 632 cm^{-1} are associated to chlorite [14].

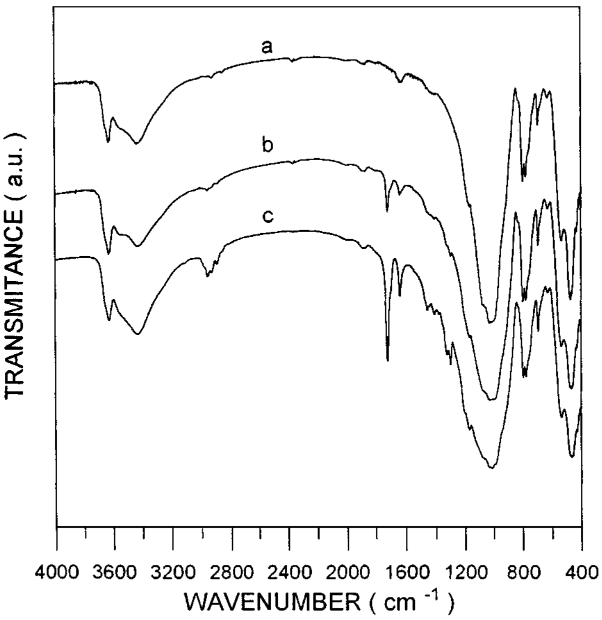

Figure 1 FT-IR spectra at 35 °C: (a) as-received slate, (b) slate treated with 0.5% of γ-MPS and (c) slate treated with 5% of γ-MPS.

The FT-IR spectra of silane treated slates appear new bands which are not present in the as-received slate. These new bands have higher intensity for sample treated with the higher γ-MPS concentration. These bands correspond to the γ-MPS molecules adsorbed on the slate surface. The absorption bands around 2957 and 2894 cm^{-1} are attributed to stretching vibrations of alkyl groups (CH_3 and CH_2) [15]. The bands close to 1720 and 1637 cm^{-1} are associated to the stretching vibrations of C=O and C=C groups respectively [15]. The absorption bands located at 1320 and 1299 cm^{-1} are assigned to the C—O—C bonds and wagging vibration of CH_3 groups of the γ-MPS molecule. The bands lying at 1168 and 1088 cm^{-1} are attributed to stretching vibrations of Si—O—C bonds of the γ-MPS and Si—O—Si bonds of both those of the slate and those formed between the slate and silane coupling agent. The peaks around 1000 cm^{-1} are assigned to bending vibrations of these Si—O—C bonds [15].

In the spectral region of 1000–400 cm^{-1} the γ-MPS give weak absorption bands which cannot be distinguished from those of the slate.

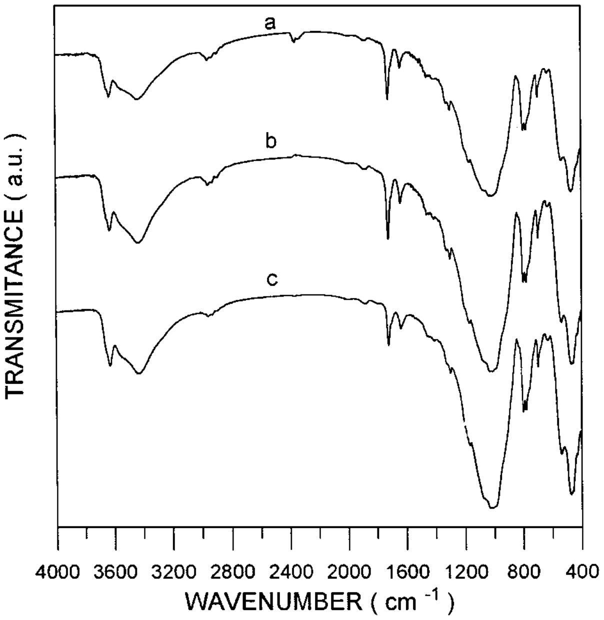

Figure 2 FT-IR spectra of treated silane slate with 1% of γ-MPS and 10 min contact time: (a) 25 °C, (b) 35 °C and (c) 50 °C.

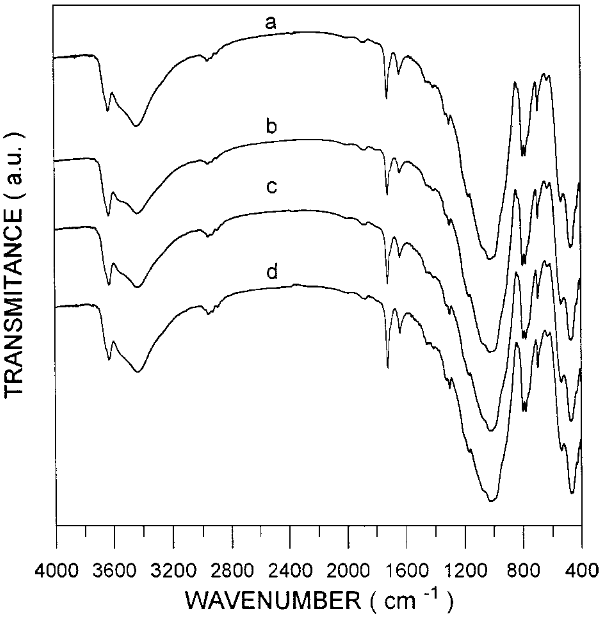

Figure 3 FT-IR spectra of treated slates at 35 °C and 1% of γ-MPS: (a) 1 min contact time, (b) 3 min contact time, (c) 5 min contact time and (d) 10 min contact time.

FT-IR spectra of slates treated with γ-MPS at different temperatures and different reaction times are shown in Figs 2 and 3. In all of these spectra appear the characteristic bands of the slate sample and the bands attributed to the silane coupling agent discussed above.

Differential thermal analysis (DTA) and thermogravimetric (TG) thermograms for the slate sample and for the slate treated with γ-MPS are shown in Fig. 4. Similar thermograms were obtained for other treatments.

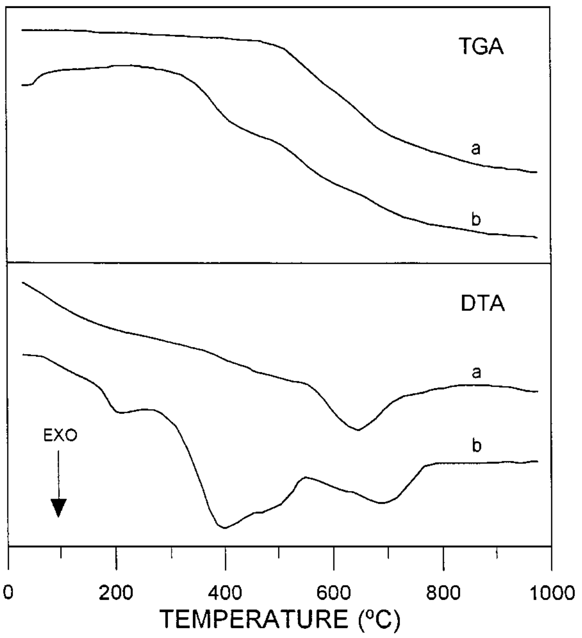

Figure 4 TGA and DTA curves of the studied samples: (a) as-received slate and (b) 5% γ-MPS treated slate at 25 °C and 3 min of reaction time.

The DTA curve of the slate shows an exothermic peak at 650 °C due to the recrystalization of the muscovite mineral existing on the slate sample. By using X-ray diffraction analysis the presence of muscovite, chlorite and quartz on the studied slate have been found [16]. The DTA of the γ-MPS treated slate shows also this exothermic peak but shifts up to 690 °C. At 210 and 400 °C appear two new exothermic peaks and a shoulder at 488 °C. The first peak at 210 °C is due to the oxidation of C=C bonds of the γ-MPS molecule [17]. Oxygen induced polymerization of the vinyl group of γ-MPS was found to occur over at a temperature above 210 °C by Ishida *et al.* [18]. This exothermic peak is associated with an increase of the weight observed in the TG curve, as it will be shown later. The exothermic peak at 400 °C and the shoulder at 488 °C are associated with the combustion of the γ-MPS molecules adsorbed on the slate surface.

The TG curve of the slate sample shows an important weight loss between 500 and 1000 °C due to the elimination of hydroxyl groups of muscovite and chlorite (19). On the other hand, the TG curve of the γ-MPS treated slate shows a little increase of weight at 210 °C (in accordance with the exothermic peak of the DTA curve) and then a continuous weight loss between 350 and 1000 °C. This weight loss is carried out in different stages as it may be observed by the different changes of the slope of the TG curve. These weight losses correspond to the combustion of the silane molecules adsorbed on the slate surface and also to the elimination of hydroxyl groups of the slate sample.

4. Discussion

In order to obtain quantitative information about the interaction of γ-MPS silane on the slate surface, the FT-IR spectra were deconvoluted assuming gaussian profile for the IR bands. Since the IR bands of the slate sample overlap most of those of the silane, we have chosen the 1840–1580 spectral region, where carbonyl stretching (1780–1660 cm^{-1}) and C=C stretching and H—O—H bending (1660–1580 cm^{-1}) appear as

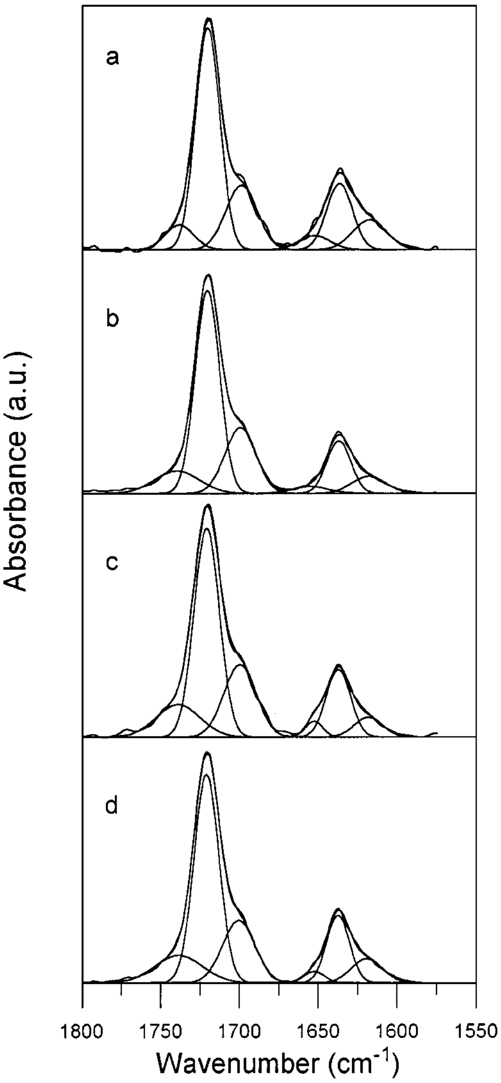

Figure 5 Spectral deconvolution of the γ-MPS treated slate at 25 °C: (a) 0.5% of γ-MPS, (b) 1% of γ-MPS, (c) 3% of γ-MPS and (d) 5% of γ-MPS.

well-defined isolated bands. Fig. 5 shows a typical spectral deconvolution for the slate treated with γ-MPS at different concentrations.

In order to obtain the minimum deviation between theoretical and experimental spectra, three components were included for the carbonyl region, and three components were also included for the C=C stretching and H—O—H bending region. For the carbonyl region these three components appear at 1730, 1720 and 1700 cm^{-1}, and may be associated with the non-hydrogen- bonded nonresonance-stabilized carbonyl, the non-hydrogen-bonded resonance-stabilized carbonyl and the hydrogen-bonded resonance-stabilized carbonyl respectively [17].

In the C=C stretching and H—O—H bending region three components were also needed for obtaining the minimum deviation between experimental and theoretical spectra. In this case the two components, C=C and H—O—H, are highly overlapped and separated by only a few wavenumbers: 1639 cm^{-1} for C=C and 1629 cm^{-1} for H—O—H. Since the presence of H—O—H from of KBr used for the preparation of the IR pellet and from the H_2O adsorbed on and existing in the slate, we have preferred to use the carbonyl region for studying the interaction of γ-MPS with the slate.

As we have mentioned before, we have assumed Gaussian profile for the IR bands. The area of a Gaussian band can be easily obtained by integrating over a wide range of wavenumbers when the position (wavenumber), intensity and half width values are known.

The area of a Gaussian band is then related to the concentration of their chemical bonds which are contributing for. In order to avoid sample weight differences, band areas were normalized by the area of the quartz peak situated at 796 cm^{-1}, because quartz do not react with water at $pH = 6$ during short periods of time [20].

Figs 6–8 show the evolution of the non-hydrogen-bonded resonance-stabilized carbonyl band (1720 cm^{-1}) as a function of the silane concentration at the reaction temperatures of 25, 35 and 50 °C respectively. These figures show that the amount of γ-MPS adsorbed on the slate surface depends on: (1) the silane

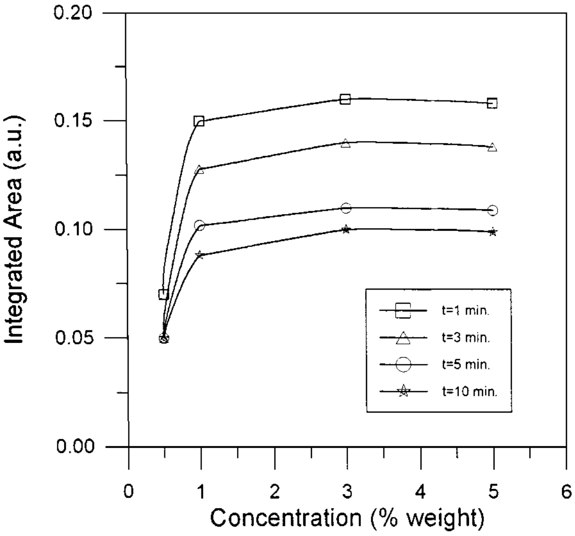

Figure 6 Evolution of the band at 1720 cm^{-1} with the γ-MPS concentration at 25 °C.

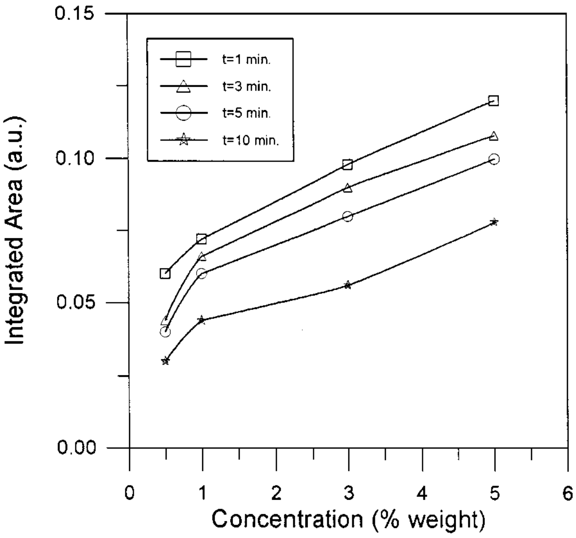

Figure 7 Evolution band at 1720 cm^{-1} with γ-MPS concentration at 35 °C.

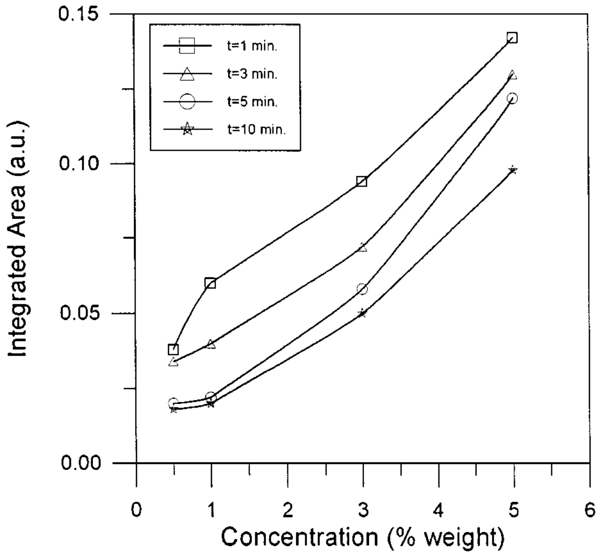

Figure 8 Evolution band at 1720 cm^{-1} with γ-MPS concentration at 50 °C.

concentration in the treating solution; (2) the reaction time and (3) the reaction temperature. The silane adsorption on the slate increases as the concentration of the treating solution increases. This trend was formerly observed by Johanson *et al* [21] in the adsorption of γ-MPS on E-glass fibres, and has also been found for different silane-substrate systems [22–24]. It may be observed in Fig. 6 that a strong break point appears at a silane concentration of 1%. Above this point a flattening of the curve occurs. This result has also been observed in different systems [22–24] and has been assigned as a result of the evaporation of a significant portion of the deposited γ-MPS silane [25] during drying for leaving off the alcohol formed in the reaction. The concentration of the silane solution at which appears the breaking point depends on the kind of silane and kind of substrate. For example, Ishida and Miller [24] have found breaking points at 3 and 2% of γ-MPS concentration in the treating solution for clay and calcium carbonate substrates respectively.

Figs 7 and 8 show the same break point at a silane concentration of 1%, however, the flattening of the curve is not so strong as in the lower temperature is. In accordance with Ishida and Miller [24] the break point represents the maximum silane concentration to be useful for silanization of mineral reinforcements. This indicates that in our case surface treatments above 1% on slate are ineffective in depositing additional γ-MPS.

Comparing Figs 6, 7 and 8 it may be observed that band areas decrease when both treating temperature and reaction time are increased. This decrease of the band area when increase the treating temperature correspond with a classical phenomenon of physical adsorption. Many studies have shown the existence of both chemisorbed and physisorbed layers of γ-MPS on different substrates [24, 26–28]. The relative amount of chemisorbed and physisorbed layers depends on a number of complex interacting phenomena, and one of them is the acid-base characteristics of the mineral surface. Ishida and Miller [24] have shown that the pH of an aqueous slurry of the particulate is a realistic value with respect to the acid-base influence of the substrate. They have found that a clay sample has an acidic surface of pH = 4.1 and a calcium carbonate sample has a basic surface of pH = 9.4. When the clay sample (pH = 4.1) is silanized with γ-MPS, a 66% of the methacryl silane is chemisorbed (34% physisorbed), while the silanization of calcium carbonate (pH = 9.4) gives only 19% chemisorbed (81% physisorbed) silane. Ishida and Miller have given different aqueous slurry pH values for various particulate mineral substrates [24], where mica mineral has values of pH between 9.0 and 9.3. In our previous study [29] of the studied slate sample we have found that this sample is formed by muscovite (mica), chlorite (mica) and quartz, and therefore the aqueous slurry pH must be close to 9. We have measured by a pHmeter (Radiometer, model PHM82) the pH value of a slate slurry and the obtained pH was 8.8, as it was expected. A base surface gives a great percentage of physisorbed silane as we have found in Figs 6–8.

As we have mentioned before, the band areas decrease with the reaction time. This result shows a rapid adsorption of the γ-MPS molecules on the slate surface, and after that, the H_2O molecules of the aqueous solution interact with the slate removing some adsorbed silane molecules. Ishida and Koenig [30] have shown a direct evidence on the molecular level of hydrolysis by water of the Si—O—Si bonds of the silane-filler system, and therefore, layers of coupling agent are removed during hydrolysis by water molecules.

We have also analysed the evolution of the hydrogen bonded C=O band (1700 cm^{-1}) and have observed an analogous behaviour as the free C=O band (1720 cm^{-1}). The 1700 cm^{-1} band is due to hydrogen bonding between coupling agent molecules and slate surface [24]. Therefore, the ratio 1720/1700 can give information about to the preferential orientation of the adsorbed silane molecules. If such ratio decreases means that the hydrogen bonding of the γ-MPS predominates on the slate surface. Fig. 9 shows the evolution of the 1720/1700 ratio for different silane

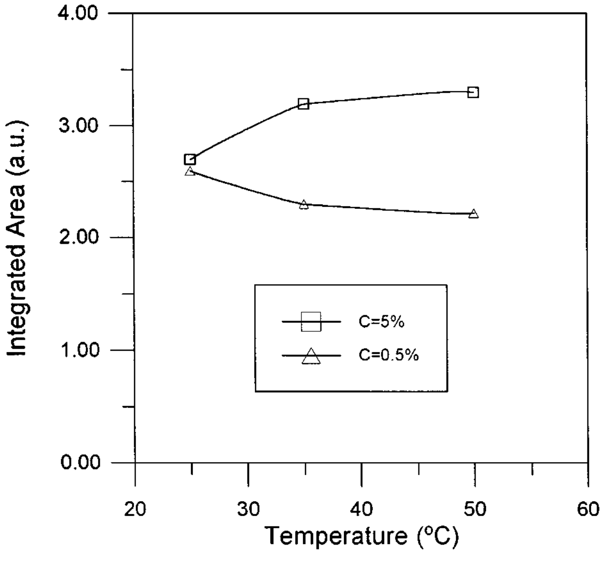

Figure 9 Evolution 1720/1700 ratio with temperature for minimum and maximum γ-MPS concentration used.

concentration as a function of the reaction temperature. It may be observed that at high silane concentration, the free carbonyl groups increase with the reaction temperature, and the opposite is observed for low silane concentration. This result shows that for low silane concentration the hydrogen bonding between the carbonyl groups of the silane and the hydroxyl groups of the slate is favoured as the reaction temperature is increased. When high silane concentration is used, the amount of silane gives a multilayer on the slate surface, and free carbonyl is highly present on such multilayers. Monolayer equivalent surface coverage is defined as the % treatment at which the free carbonyl band (1720 cm^{-1}) just begins to appear [24]. Since we have observed the 1720 cm^{-1} band at the lowest silane concentration, the existence of multilayers is then confirmed. By assuming that one γ-MPS molecule occupies 48 Å of the surface [24], a monolayer coverage on the slate sample, which has a specific surface area of 5.8 m^2/g, should occur at 0.49% silane modification. This is in well agreement with the presence of multilayers at the lowest silane modification and with the observation of free carbonyl band (1720 cm^{-1}) in all spectra.

Since the FT-IR analysis is only semiquantitative, complementary information can be obtained from TG curves. TG analysis is a quantitative technique where the amount of adsorbed silane may be determined from the weight loss of the thermogram. However, the substrate (slate) gives also an important weight loss in the same temperature range. Since the chemical and physical adsorption of the γ-MPS on the hydroxyls of the slate surface, the DTA and TG thermograms can vary in intensity and position (temperature), therefore, we have subtracted the weight loss obtained for the γ-MPS treated slate from that of the as-received slate when both samples have been heated at the high temperature of the measurement, i.e. 1000 °C.

If we assume the reaction:

$$\gamma\text{-MPS-(h)} + \text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2\uparrow + \text{H}_2\text{O}\uparrow$$

where γ-MPS- (h) is the hydrolysed silane, then we could calculate the number of molecules adsorbed on the slate surface. However, two factors must be taken into account: first, the adsorption of water from the solution by the slate and second, the leaching of the slate by the treating solution. The slate sample formed by quartz, muscovite and chlorite has a specific surface area of 5.8 m^2/g, principally due to the muscovite and chlorite minerals which have a layered structure [31]. Water molecules from the treating solution can adsorb between these mineral layers, and temperatures higher than 100 °C are needed for removing off. Besides, water of the treating solution can eliminate cations from the slate by a leaching process. Both factors are dependent on both silane concentration and reaction time. The quantification of both factors on the weight loss obtained from TG analysis is a very difficult task, and therefore the obtained results are only semiquantitative, and are used to corroborate the FT-IR results.

Figs 10–12 show the weight loss as a function of the silane concentration in the treating solution. It is

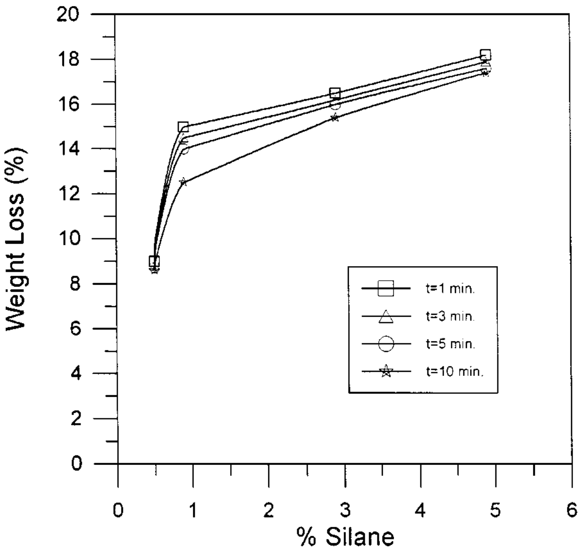

Figure 10 Weight loss as a function of silane concentration at 25 °C.

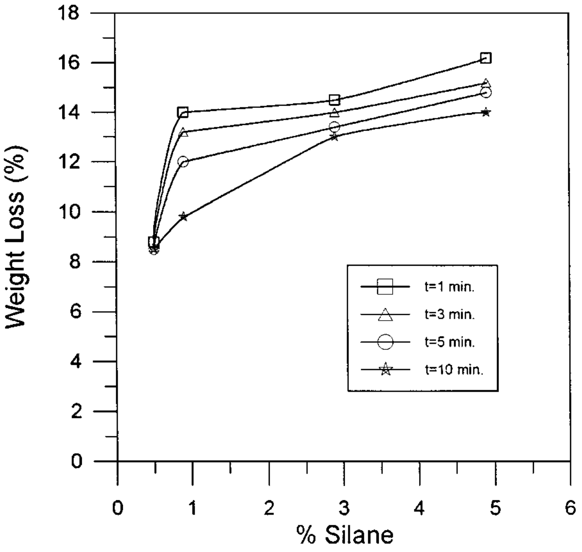

Figure 11 Weight loss as a function of silane concentration at 35 °C.

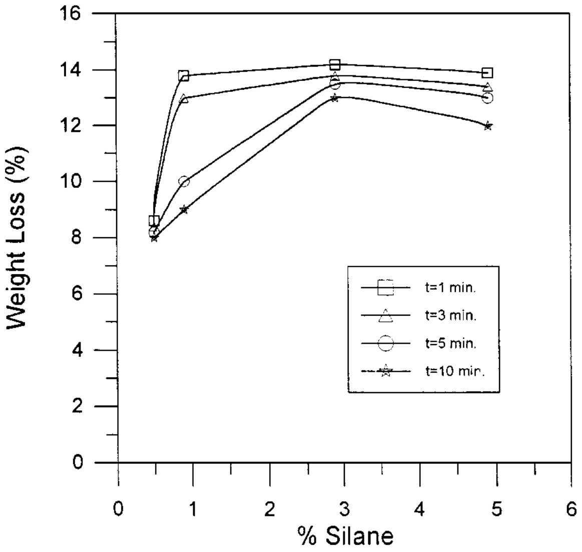

Figure 12 Weight loss as a function of silane concentration at 50 °C.

here observed the same trend as the above mentioned FT-IR results. The weight loss increases with the silane concentration in the treating solution, and for a given concentration the weight loss decreases with both temperature and time of reaction.

5. Conclusions

The silanization of slate particles with γ-MPS has been study by FT-IR and DTA/TG techniques. It has been observed that the amount of the γ-MPS adsorbed on slate particles depends on the concentration of the treating solution, temperature and reaction time. The IR bands of free carbonyl (1720 cm^{-1}) and hydrogen bonded carbonyl (1700 cm^{-1}) appear for the low silane concentration and increase with it. This corresponds to the formation of silane multilayers on the slate surface even at 0.5% of silane in the treating solution.

The adsorbed silane decreases as the reaction temperature increases. This corresponds to a physical adsorption phenomenon. The amount of silane adsorbed by hydrogen bonding through the carbonyl group on the slate surface is observed mainly at low silane adsorption. This suggests that a monolayer of γ-MPS is firstly formed on the slate surface where the silane interacts through hydrogen bonding and then multilayers are formed where free carbonyl can be detected.

A breakpoint appears at a silane concentration of 1% for all studied temperature and reaction times. This concentration of 1% may represent the maximum silane concentration to be useful for silanization slate particles with γ-MPS.

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