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SURFACE MODIFICATIONS OF MONTMORILLONITE FOR TAILORED INTERFACES IN NANOCOMPOSITES

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Different kinds of clays based on sodium montmorillonite have been modified by (1) cationic exchange of alkylammonium ions and (2) covalent grafting of organosilane. We have prepared organophilic clays with different gallery heights (due to alkylammonium ions with alkyl chain length varying from 8 to 18 carbon atoms) and with a specific functionalization (due to the organosilane). The experimental parameters of the cationic exchange process (exchange temperature, initial amine/clay ratio, washing of the clay) govern the quantity of the intercalated alkylammonium ions as well as their organization in the montmorillonite galleries. We have generated organoclays with different kinds of organic layer properties, namely ionically bonded or physically adsorbed alkylammonium ions and covalently grafted organosilane. These different surface treatments will be useful for different applications, varying as a function of the coupling with the matrix and as a function of filler dispersion and resulting properties (thermal stability, mechanical and barrier properties) of the final nanocomposite.

Keywords: Montmorillonite; Organoclay; Alkylammonium ions; Organosilane; Interlayer gallery organization; Surface energy; Nanocomposites

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INTRODUCTION

In the past twenty years, many studies have focused on the incorporation of inorganic clay platelets in organic polymers in order to obtain hybrid materials [1]. These nanostructured composites are of great interest because they present attractive behaviours in terms of stiffness [2], thermal resistance [3], and barrier properties [4]. These properties are related to the high aspect ratio of silicates and to their layered structure. Clays exhibit a specific multiscale organization. At the Angström scale is the platelet, which is 7 Å thick and several hundred nanometers long and wide. At the micron scale, these platelets are stacked into primary particles. At a higher scale, these primary particles are stacked together to form aggregates, as shown in Figure 1.

In order to obtain optimal properties for the nanocomposite, the platelets must be randomly dispersed, i.e., exfoliated, in the matrix to obtain a large contact area with the matrix. However, the hydrophilic nature of the silicate surface primarily limits its dispersion. In order to facilitate exfoliation, surface treatment of the platelets is necessary in order to change their nature from hydrophilic to hydrophobic [5]. Other parameters also govern the dispersion of the layered silicates in the polymer: the type of silicate (which determines the swelling capacity) [6], the method of mixing the clay with the polymer [7], and the curing treatment of the final nanocomposite [7, 8].

The easiest way to make clay minerals hydrophobic is to exchange the intercalated cations with alkylammonium ions [9]. The swelling of clay in an aqueous alkylammonium ion solution leads to an extension of the interlayer galleries due to the hydration of inorganic cations (Na^+ , Ca^{2+}) contained in these galleries, allowing the alkylammonium ions to intercalate between the platelets. Among the different types of clays, montmorillonite presents a high swelling capacity, which makes the surface of its platelets easily accessible for surface treatments. Other clays, such as illites or kaolinites, do not have expandable

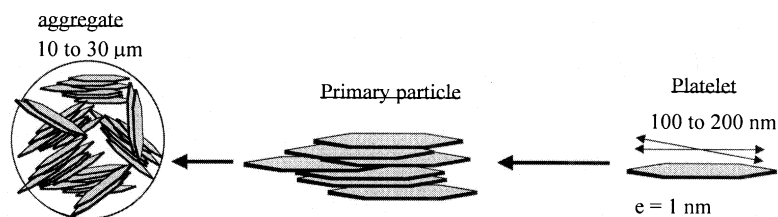


FIGURE 1 Multiscale organization of clay from platelet to aggregate.

galleries due to strong interlayer interactions. The type of cations present in the galleries governs the swelling capacity of the smectic clays. In the case of montmorillonite, these cations are small (Na^+ , Ca^{2+}) and easily hydrated, and that is why montmorillonite is the smectic clay with the highest swelling capacity.

The intercalation of organic cations, such as alkylammonium ions in the galleries, gives montmorillonite hydrophobic behavior and makes it compatible with a polymer matrix. Moreover, the use of long-chain organic cations (18 carbon atoms) leads to extended galleries, which assists the introduction of monomers in the next step of nanocomposite synthesis [6].

Organoclays obtained by cation exchange offer a great diversity of interlayer structures. The interplatelets' structure depends on the alkyl chain length and on the cation exchange capacity, which is the maximum number of monovalent cations exchangeable per 100 grams of clay. Lagaly [10] reported four types of idealized organizations of individual long-chain alkylammonium ions in the galleries of layered silicates as shown in Figure 2: mono-, bi-, and pseudotri-molecular layers and paraffin-like monolayers. The last one is obviously the most interesting structure to separate platelets.

Organosilane grafting on the hydroxyl groups present on the edges of platelets is another way to functionalize the clay. Modification of silica with variable geometry, such as divided particles for chromatographic applications or silicon wafers for elaborating molecular devices, has been investigated extensively [11]; however, much less work deals with grafting reactions with clay minerals [12–14]. The grafting of hydroxyl groups on the edges of platelets by organosilanes with different functionalities facilitates production of organically modified clays, where organic moieties are covalently bonded and chosen in accordance with the matrix.

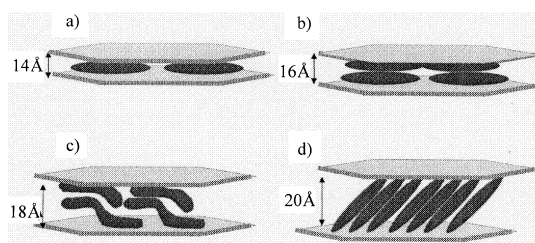


FIGURE 2 Alkyl chain aggregations in 2/1 clay minerals: monolayers (a), bilayers (b), pseudotrimolecular layers of chain lying flat on the surface (c), and paraffin-type monolayer (d). From Kornmann [8].

Much of the work that has been done recently in the polymer/clay nanocomposite field has consisted of introducing clays (mostly commercial organophilic clays) into all kind of polymers and in characterizing the resulting properties of these hybrid materials. Most of the work has focused on the influence of the type of clay, the type of modifier, or the quantity of clay introduced; few have dealt with the influence of the nature of the inorganic/organic interface on macroscopic properties of the composite. The state of the interface is very important for preparation of composite materials. In fact, it is a key problem in increasing the strength of the composite. The effect of the surface treatment of commercial organoclays on mechanical properties of epoxy/clay nanocomposite is shown in Table 1. To obtain an optimal composite, a good dispersion of clay particles and a good chemical compatibility of clay with the matrix are necessary to get a good reinforcing effect from the filler.

In this paper, we report the preparation of modified clays

1. by introducing alkylammonium ions to increase the gallery spacing, to help monomer diffusion between the platelets, and to improve the clay's dispersion, and also
2. by covalent grafting of organic functions liable to react with the epoxy matrix to improve the compatibility.

Organic layers of different types were built by: (1) ionic bonding by the cation exchange process, (2) physical adsorption, and (3) covalent bonding by grafting. We have studied different parameters of the cation exchange process in order to tailor the quantity of intercalated alkylammonium ions and their organization in the galleries. For different alkyl chain lengths we have investigated the exchange

TABLE 1 Evolution of Dynamic Tensile Modulus Determined on an Epoxy Nanocomposite Reinforced With 5 wt% Clay as a Function of the Surface Treatment of the Organoclay

Sample	Modifier	E' dynamic tensile modulus (MPa)
Epoxy matrix	None	2.1
Epoxy matrix + 5 wt% organoclay 1	Dimethyl-tallow-benzyl ammonium	3.2 (+52%)
Epoxy matrix + 5 wt% organoclay 2	Hydrogenodipropyleneoxy-ditallowammonium	2.5 (+19%)
Epoxy matrix + 5 wt% organoclay 3	Dimethylditallow ammonium	2.7 (+29%)

temperature, the initial amine/clay ratio, and the washing step. We have attempted to prepare organophilic clays with well-controlled surface properties (clay modified with specific functions, stable layers with an extended conformation in the galleries) in order to generate different kinds of interfaces as a function of the properties (mechanical, thermal, and barrier) requested for the nanocomposite material.

EXPERIMENTAL

Materials

Na⁺-clay (Optigel EX0255, subsequently called OPT) was obtained from Société Française des Bentonites et Dérivés, France. Its Cationic Exchange Capacity (CEC) is about 100 meq/100 g and its d-spacing is about 12.6 Å (hydrated clay).

A commercial organophilic clay (Tixogel, subsequently denoted TIX), supplied by Société Française des Bentonites et Dérivés, was taken as a reference organophilic clay. This clay was modified with dimethyltallowbenzylammonium ions and its d-spacing is about 20 Å.

The different amines used were octadecylamine CH₃-(CH₂)₁₇-NH₂, hexadecylamine CH₃-(CH₂)₁₅-NH₂, dodecylamine CH₃-(CH₂)₁₁-NH₂, and octylamine CH₃-(CH₂)₇-NH₂. The silane was γ -aminopropyltriethoxysilane H₂N(CH₂)₃Si(OC₂H₅)₃ (subsequently denoted γ -APS). All these products were purchased from Aldrich and used without further purification.

Organoclay Preparation

Cation Exchange Process

The alkylamine (10⁻² mol. L⁻¹) was dissolved in 1 liter of 0.01 M hydrochloric acid solution (based on deionized water). The solution was stirred at 60 or 80°C for 3 h. Then, ten grams of OPT were added to the solution which was then stirred at the same temperature for 3 more hours. Introducing 10 g of OPT led to an approximate stoichiometric ratio equal to 1 between alkylammonium ions and exchangeable inorganic cations. We will subsequently denote this type of organoclay as 1CEC-modified clay. If only 5 g of OPT were introduced, it will be denoted as 2CEC-modified clay. The alkylamine concentration was 10³ times higher than the CMC, which was about 10⁻⁵ mol/L⁻¹.

The solution was then filtered and washed with hot deionized water or a hot ethanol:water (1:1) mixture until no chloride was detected upon adding 0.1 M aqueous AgNO₃. The resulting organoclay was then dried at 85°C for 36 h and kept dry in a vacuum box.

Covalent Grafting

The organosilane (0.3 wt%) was introduced in a water:ethanol mixture (25:75). The solution was stirred at 80 °C for 1 h. Ten grams of TIX were added to the silane solution, which was stirred at the same temperature for 6 h. The solution was then filtered and washed with a hot ethanol:water mixture. The grafted organoclay was then dried at 85 °C for 1 h.

Characterization

X-ray diffraction (XRD) spectra were obtained with a Siemens D500 diffractometer with a back monochromator and a Cu anticathode. The 2θ angles were varied between 1 and 10° in order to measure the d_{001} spacing of the modified montmorillonites.

Thermogravimetric analysis experiments were performed using a TGA2950 from TA Instruments. The samples were brought from 25 °C to 800 °C at a scanning rate of 20 °C/min under helium atmosphere in order to evaluate the thermal stability of the modified clays and the quantity of intercalated alkylammonium ions.

Wetting measurements were completed on a GBX device. From contact angle measurements performed with water and diiodomethane as test liquids, we determined polar and dispersive components of surface energy by using Owens-Wendt theory [15, 16].

RESULTS AND DISCUSSION

Optimization of Cation Exchange Process

Influence of the Exchange Temperature

Temperature is one of the cation exchange process parameters, which has an effect on the layer structure in the clay gallery. We have modified the clays at two different exchange temperatures. Figure 3 shows the XRD spectra of the organoclays, designated OPTC18A and OPTC18B, prepared at 60 and 80 °C, respectively, from the cation exchange reaction between Na⁺-montmorillonite and octadecylamine with an amine/clay ratio of 1CEC. The basal spacing was obtained from the (001) peak position. After intercalating the montmorillonite with alkylamine, there is no remnant of the original 12.6 Å spacing of Na-montmorillonite, and the basal spacing has strongly increased. Thus, this means that the alkylammonium ions have been successfully intercalated in the clay gallery.

At first sight, both modified clays show two peaks; however, the layer structure in the gallery is clearly different. The spectrum of the

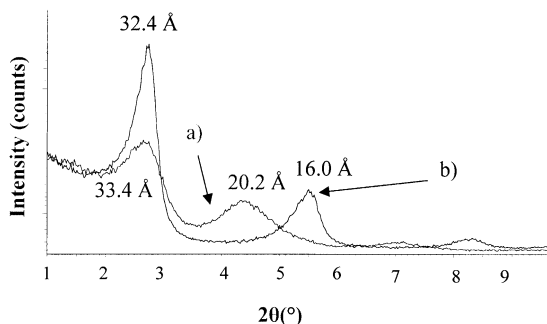


FIGURE 3 XRD spectra (from $2\theta = 0$ to 10°) of (a) OPTC18A (1CEC/ 60°C) and (b) OPTC18B (1CEC/ 80°C).

OPTC18 A presents two quite broad peaks, which means that two organizations coexist in the galleries. By referring to the layer organizations proposed by Lagaly [17], the first peak ($d_{001} = 33.4 \text{ \AA}$) is related to intercalated ions with a paraffin-like structure (see Figure 2d), whereas the second one ($d_{001} = 20.2 \text{ \AA}$) is rather significant of a pseudotrilayer structure (see Figure 2c). The OPTC18B spectrum presents two peaks as well, but they are significant of only one single organization because the peak at 16 \AA is a second-order peak of the first peak at 32 \AA . Moreover, these peaks are much narrower than those of OPTC18A, which reveals a very stable and very well-defined paraffinic structure.

Influence of the Amine/Clay Ratio

The amine/clay ratio is another parameter that governs the cation exchange of montmorillonite. We have modified sodium montmorillonite with octadecylamine at 80°C with a stoichiometric amine/clay ratio (1CEC) and with an excess of amine (2CEC). These organoclays are called OPTC18B and OPTC18C, respectively.

The XRD spectra reported in Figure 4 of OPTC18B and OPTC18C show exactly the same type of organization as the one described previously. As a result, the amine/clay ratio seems to have no influence on the organization of the ions in the galleries.

On the other hand, the influence of the amine/clay initial ratio is revealed by the TGA measurements. A TGA spectrum, which reports the first derivative of the weight loss as a function of temperature performed on a modified montmorillonite, usually shows three main peaks. The first peak, located in the $25\text{--}150^\circ\text{C}$ range, is linked to the vaporization of water. The weight loss in the $150\text{--}300^\circ\text{C}$ range can be attributed to the vaporization of physisorbed alkylammonium ions or

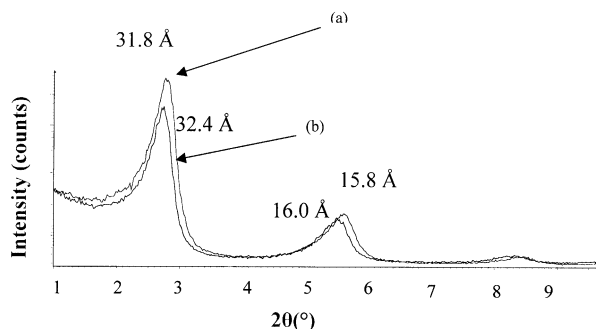


FIGURE 4 XRD spectra (from $2\theta = 0$ to 10°) of (a) OPTC18B (1CEC/ 80°C) and (b) OPTC18C (2CEC/ 80°C).

alkylamines. The last peak, located from 300 – 500°C is linked to the vaporization of the ionically bonded species. Integrating this peak allows us to calculate the CEC of the clay (with these kinds of ions, under these conditions).

By analyzing the thermograms shown in Figure 5, we can deduce that an excess of amine is necessary to complete the layer of ions ionically bonded to the platelet surface. Indeed, the surface of the weight loss peak between 300 and 500°C increases, which is evidence that the number of exchanged ammonium ions is much higher. The results of the analysis of these thermograms are given in Table 2. We observe that the CEC is strongly dependent on the exchange parameters. Indeed, the CEC has risen to 101 meq/ 100 g just by increasing the amine/clay ratio. This value is relatively close to those given in the literature for a Na-montmorillonite [18]. We can conclude that an excess of amine is necessary to complete the first layer of ionically bonded alkylammonium ions. Moreover, we can say that our method is quite efficient in determining the CEC of the clay. The CEC determined in this way is related to the capacity of the inorganic cation of the clay to be exchanged with one kind of ion and with specified exchange parameters.

Moreover, the hydrophobic behaviour of the clay seems to be related to the quantity of ions physisorbed on the particles (very low water amount, no peak in the 20 – 150°C range when no ions are physisorbed); that is why it is of great interest to study the influence of the washing treatment after the exchange process.

Influence of the Washings after the Exchange

The washing step is an important step in the process because it allows one to obtain well-structured layers by removing the

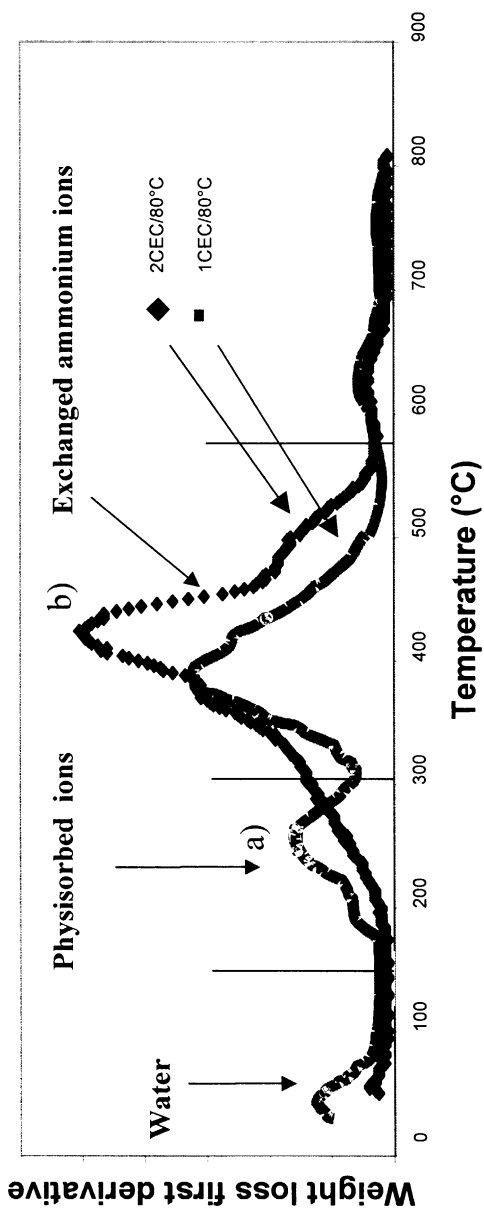


FIGURE 5 First derivative of weight loss as a function of temperature for (a) OPTC18A (1CEC/60°C) and (b) OPTC18B (1CEC/80°C).

TABLE 2 Quantity of Intercalated or Physisorbed Ions Deduced From the TGA Experiments for OPTC18B (1CEC/80°C) and OPTC18C (2CEC/80°C)

Sample	Intercalated products	% by weight in the sample	Deduced CEC (meq/100 g)
OPTC18B (1CEC)	Water	2.44	56.4
	Physisorbed ions	6.10	
	Ionicly bonded ions	15.21	
OPTC18C (2CEC)	Water	0.42	101
	Physisorbed ions	4.32	
	Ionicly bonded ions	27.38	

physisorbed alkylammonium ions and by keeping only the ions intercalated in the galleries. The sodium montmorillonite was exchanged with octadecylamine at 80°C with an amine/clay ratio of 2CEC. The first sample, OPTC18W1, was washed only with hot deionized water ($\rho > 20 \text{ M}\Omega/\text{cm}$), and the second one, OPTC18W2, was washed an additional four times with a hot ethanol:water (1:1) mixture.

The TGA thermograms are shown in Figure 6. In the TGA curve of the OPTC18W1, the two weight losses due to the two kinds of ions present in the clay (i.e., physisorbed and intercalated ions) are clearly observable. Comparison of the TGA curves between OPTC18W1 and OPTC18W2 shows that repetitive washings with a hot ethanol:water mixture lead to a complete disappearance of the physisorbed ions without removing the ionically bonded ions in the galleries. As the basal spacing measured by XRD remains the same after the repetitive washings, we confirm that the physisorbed ionic species are located outside the galleries (on the edges of the platelets or around the primary particles). By keeping only the strongly bonded ions (intercalated ions) in the galleries, the thermal stability of the exchanged clay is increased up to 300°C. This is a very interesting characteristic because these organoclays can be incorporated in thermoset or thermoplastic polymers without being degraded during their curing treatment or their transformation process.

Clay Modification by an Optimized Cation Exchange Process

The alkyl chain length was varied from octyl (OPTC8), to dodecyl (OPTC12), hexadecyl (OPTC16), and octadecyl (OPTC18). We chose

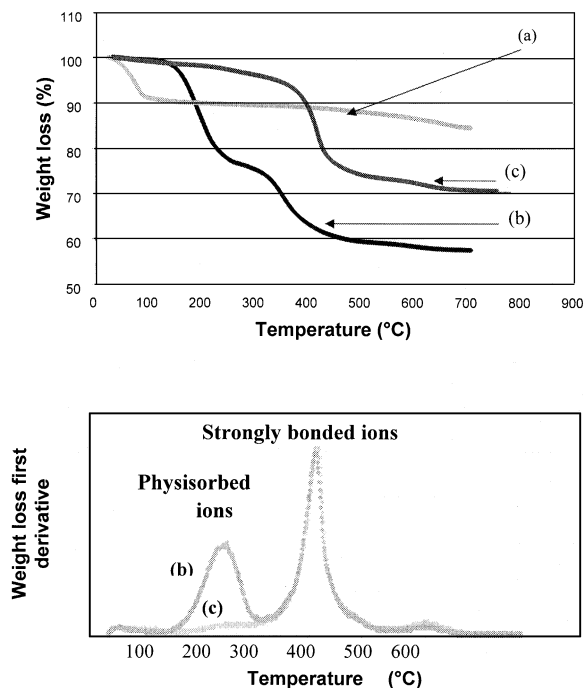


FIGURE 6 TGA experiments on the pristine clay OPTIGEL EXO255 (a), OPTC18W1 (b), and OPTC18W2 (c); weight loss and first derivative of weight loss as a function of temperature.

primary amines because Zilg *et al.* [19] demonstrated that organoclay modification with protonated primary amines gives a much better toughness/stiffness balance with respect to those modified with protonated secondary and tertiary amines or quaternary ammonium cations.

As shown by the data in Table 3, basal spacings measured by XRD increase in proportion to the alkyl chain length of the ammonium cations.

To evaluate the conformation of the chains in the clay galleries, we have reported the theoretical length when the chain adopts an all-*trans* conformation. The theoretical extended chain length, l_t , can be calculated as follows:

$$l_t(\text{\AA}) = 1.265(n_c - 1) + 3.0,$$

where $(n_c - 1)$ is the number of methylene groups in the alkyl chain, 1.265 Å is the contribution due to the $-\text{CH}_2-$ chain segments by

TABLE 3 Interlayer Distance (d_{001} , Å) of Alkylammonium-exchanged Montmorillonites

Sample name	Alkylammonium ion ^a	d_{001} spacing (Å) ^b	Calculated value, l_c (Å)	Tilt angle α (°)
OPTIGEL EXO255	none	12.6	—	—
OPTC18	CH ₃ -(CH ₂) ₁₇ -NH ₃ ⁺	31.6	24.5	50
OPTC16	CH ₃ -(CH ₂) ₁₅ -NH ₃ ⁺	29.6	22	50
OPTC12	CH ₃ -(CH ₂) ₁₁ -NH ₃ ⁺	22.3	18.2	32
OPTC8	CH ₃ -(CH ₂) ₇ -NH ₃ ⁺	13.6	11.9	4

^a Exchange conditions are 80°C and a clay/amine ratio of 2CEC.

^b Measured by XRD at 0.1°/min.

assuming that the chains adopt an all-*trans* configuration, and we add the dimension of the methyl end group (3 Å) as proposed by Lagaly [17].

For OPTC8 and OPTC12 the measured basal spacing is somewhat smaller than the value calculated with an extended chain perpendicular to the platelet, suggesting that these shorter chain ions do not adopt a paraffin-like structure. For alkylammonium ions with $n > 12$, the basal spacing is very near the theoretical extended chain length, which suggests that the chains adopt a paraffin-like structure in a tilted arrangement with respect to the silicate surface. The tilt angle, α , can be calculated as follows [17]:

$$\alpha = \arcsin((d_{001} - 12.8)/l_t),$$

where d_{001} is the d-spacing measured by XRD and 12.8 is the thickness (in Å) of a clay platelet with ammonium groups on its surface.

By using the Scherrer formula, the analysis of X-ray spectra allows us to complete our insight on the organization of these multiscale materials. From the half-height width of the X-ray peak, we can determine the dimensions of the primary particles and therefore the number of platelets contained in a particle:

$$L = \frac{0.9\lambda}{\Delta(2\theta_0) \times \cos \theta_0},$$

where L is the diffracting object size, λ is the wave length, θ_0 is the diffraction angle corresponding to the main peak, and $\Delta(2\theta_0)$ is the half-height width of the main peak.

From the tilt angle calculations, we can confirm that the octylammonium ion chains lie on the surface of the platelets. The OPTC12 presents a intermediate structure, somewhere between the

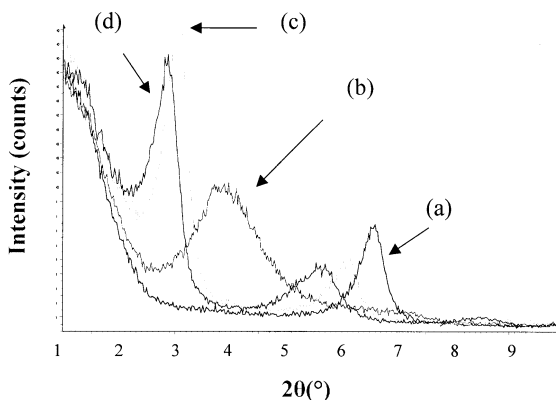


FIGURE 7 XRD spectra of alkylammonium-exchanged montmorillonite: OPTC8 (a), OPTC12 (b), OPTC16 (c), and OPTC18 (d).

monolayer-structure and the paraffin-like structure. This is confirmed by the width of the peak as it can be seen on Figure 7. OPTC18, OPTC16, and OPTC8 present much narrower peaks, and we can deduce from the Scherrer formula that the number of platelets in the primary particles decreased from 12 to 6, which means that the platelets have been intercalated regularly by the alkylammonium ions.

The exchanged organoclays display a large dispersive component and a poor nondispersive component of the surface energy, as shown by the values calculated from the contact angle measurements using the Owens-Wendt theory (Figure 8). The dispersive component is more or less independent of the alkyl chain length. On the other hand, the polar component is higher for clays exchanged with short chains (OPTC8 and OPTC12) because the short chains cover less of the silicate surface and make more polar groups, such as sodium ions or hydroxyl groups, appear on the silicate surface. The analysis of thermogravimetric experiments, presented in Table 4, explains the wetting behaviour. The clays exchanged with longer chains (from $n = 12$) show more important physisorbed and intercalated ions giving a high-dispersive component (close to a paraffin-dispersive component) and a very low polar component. The increase in the physisorbed and intercalated ions amount might be explained by the fact that increasing chain length leads to a quicker surface coverage of the platelets and the excess of ions are physisorbed outside the galleries (on the platelets edges or around the primary particles, for instance).

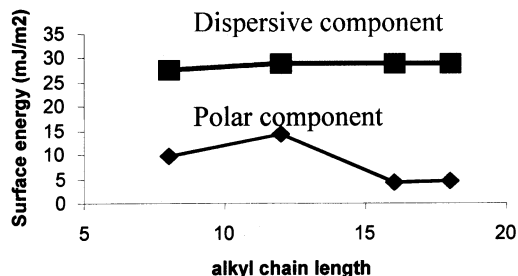


FIGURE 8 Surface energy determined on exchanged clays as a function of alkyl chain length of ammonium ions.

Clay Functionalization by Covalent Grafting

We have functionalized a commercial organoclay with amino groups to make the organoclay reactive towards an epoxy matrix. The Tixogel, already exchanged with dimethylbenzyltallowammonium ions, allows us to have a swollen clay with a d-spacing of about 20 Å. The grafting reaction is described in Figure 9.

After surface modification, the organic chains are covalently bonded to the clay minerals and the surface properties are changed. The results in Table 5 show that the polar component of the surface energy increases after treating because of polar functions, i.e., amino functions. The surface energy values are quite similar to values determined on a γ -APS grafted glass fiber.

The silane grafting takes place on the hydroxyl groups situated on the edges of the platelets, which explains why there is no effect on the d-spacing of the gallery. The X-ray spectra obtained on Tixogel before and after grafting are similar (Figure 10), which means that the conformation of the chains in the galleries is not affected.

TABLE 4 Quantity of Intercalated or Physisorbed Ions Deduced From the TGA Experiments for Optigel Modified by Ions With Alkyl Chain Length Varying From 8 to 18 Carbon Atoms (2CEC/80°C)

Sample name	Physisorbed ions % by weight	Ionically bonded ions % by weight
OPTC18	19.5	17.0
OPTC16	16.9	13.5
OPTC12	13.3	9.2
OPTC8	1.8	9.3

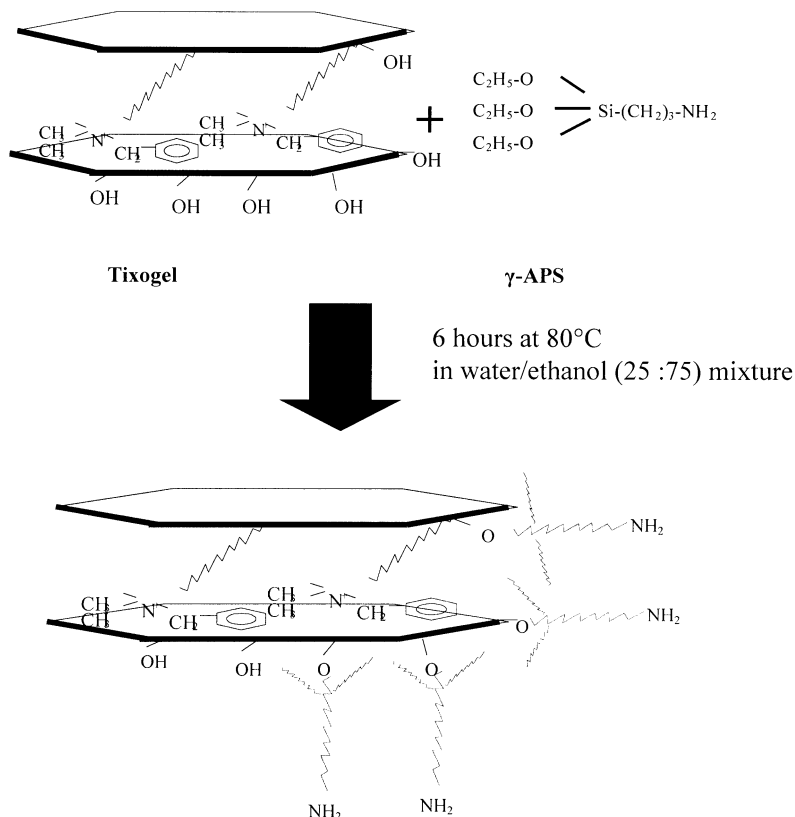


FIGURE 9 Grafting reaction of aminosilane on an organoclay.

Nevertheless, after grafting the TGA spectrum of Tixogel is modified (Figure 11). The peak indicative of the physisorbed dimethylbenzyltallowalkylammonium ions of Tixogel nearly disappears. By

TABLE 5 Polar and Dispersive Components of the Surface Energy of a Commercial Organoclay (Tixogel) Before and After Aminosilane Grafting

Modified clay	θ water ($^{\circ}$)	θ CH ₂ I ₂ ($^{\circ}$)	Polar component (mJ.m ⁻²)	Dispersive component (mJ.m ⁻²)
Tixogel	64.8 ± 1.2	50.4 ± 0.6	14.9 ± 1.1	27.3 ± 0.9
Aminosilane grafted Tixogel	39.8 ± 0.4	44.4 ± 1.0	31.3 ± 0.8	27.4 ± 0.7
Aminosilane grafted glass fiber	37.6 ± 1.1	32.8 ± 0.4	30.6 ± 0.7	30.3 ± 0.3

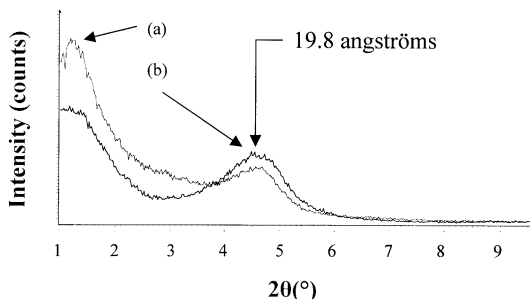


FIGURE 10 XRD spectrum of Tixogel before aminosilane grafting (a) and after aminosilane grafting (b).

considering the excess of ions adsorbed on hydroxyl groups or around the primary particles, it is not surprising to note their removal during grafting since the grafting process in a water:ethanol mixture is similar to repetitive washings, as explained previously. The two other peaks (about 300 and 380°C) are related to the degradation of intercalated modifying ions of Tixogel. A distinct knee at 420°C that appeared after grafting can be attributed to covalent coupling with silane.

We have also characterized the silane grafting on the clay mineral surface by infrared spectral analysis. Since the γ -APS molecules are bound to the clay mineral, the strength of the Si-O vibration absorption should be increased and the vibration of amino groups should be identified. However, Si-O vibration absorption is very strong, and the broad band centered at 1100 cm^{-1} , which is attributed to tetrahedral layers of silica, hides the vibration peak of amino groups.

The correlation between wetting measurements, thermogravimetric analysis, and infrared spectra shows that the silane grafting is

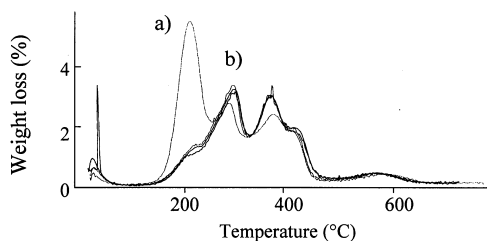


FIGURE 11 TGA experiments on Tixogel (a) before γ -APS grafting and (b) after γ -APS grafting.

successful. However, to find evidence of covalent grafting, only the ^{29}Si CP-MAS NMR can actually characterize the siloxane bond, and measurements are currently in progress.

CONCLUSIONS

The performance of composites is not only related to the nature of their components but also to the reinforcing mechanism of filler and the preparation conditions. These conditions must be carefully worked out to reach an optimum effect. In this work, we have prepared organophilic and functionalized clays by appropriate surface modifications to be introduced in an epoxy matrix.

We have built different nanostructures in the clay galleries by cationic exchange. The galleries of the clay will be the interface between montmorillonite platelets and the polymeric matrix in nanocomposites. That is why it is of great interest to study these structures. Chain length, temperature, amine/clay ratio, and washings after modification are the key parameters of the final clay-gallery structure. Chain length governs the ability of the ion to adopt paraffin-like organization by means of steric hindrance. Temperature governs the organization (bilayer, paraffin-like, tilt angle) of the alkylammonium ions. The amine/clay ratio is responsible for the number of organic cations that can intercalate the clay and create ionic bonds with it. Finally, the number and the type of washings generate different interfaces by controlling the quantity of alkylammonium ions physisorbed on the organoclay primary particles. In order to achieve chemical compatibility between matrix and clay, we have also prepared amine-functionalized clays by covalent grafting on the hydroxyl groups to react toward the epoxy groups of the matrix.

Tailoring the surface modification of clays leads to the elaboration of tailored, well-structured and well-known interfaces in polymer/clay nanocomposites.

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