

Polysiloxane-*g*-TiNbO₅ Nanocomposites: Synthesis via in Situ Intercalative Polymerization and Preliminary Characterization

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New organic–inorganic hybrid materials, prepared via in situ intercalative polymerization of cyclosiloxanes in the presence of $(R_4N)_xH_{1-x}TiNbO_5$, are described. The polysiloxane-*g*-TiNbO₅ nanocomposites were identified mainly by Fourier transform infrared absorption spectroscopy, X-ray diffraction, transmission electron microscopy, and differential scanning calorimetry. All of these techniques confirm the proposed structure and show exfoliation of the initial mineral sheets in the polymer matrix is largely achieved. Elemental analysis indicates that grafting yields lie in the range 100–200% (w/w), corresponding to nanocomposites in which the mineral phase occupies between 50 and 25% of the total volume.

Introduction

Nanocomposites are hybrid organic–inorganic materials with at least one dimension in the nanometric range, quite lower than that of usual composite materials. The field of nanocomposites has attracted considerable attention as a tool for enhancing polymer properties and extending their uses. As reported earlier, organic–inorganic hybrid materials have improved mechanical, thermal, or barrier properties and fire resistance, for example, compared to pure polymers.^{1–9}

A special case of nanocomposites consists of a polymer material associated with dispersed lamellar mineral compounds. Several methods of nanocomposite preparation have been described, resulting in both intercalated and exfoliated nanostructures (Figure 1).

In the first class, denoted intercalated hybrids, one or more organic molecules are inserted between the host layers, generating ordered lamella with a repeat distance of a few nanometers. In the second class, described as delaminated or exfoliated hybrids, mineral layers are dispersed in the polymer matrix. Exfoliated polymer–mineral nanocomposites are especially desirable for improving most physical properties because of the homogeneous dispersion of the mineral phase and the

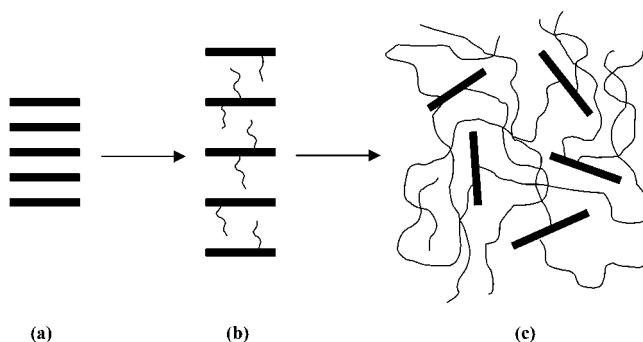


Figure 1. Schematic representations of (a) layered mineral, (b) intercalated hybrid, and (c) exfoliated hybrid.

huge interfacial area between the polymer and the mineral.

In the present study, we report the grafting of polysiloxane chains onto surface of a single-sheet mineral layer using an original method.

The oxide HTiNbO₅ is the mineral compound chosen for its lamellar and well-defined structure,^{10,11} and the ion-exchange properties of this compound allow its structure to receive quite different ions without destroying the bidimensional layers.¹² It can be considered as a very interesting model compound for intercalation studies as it can accept up to one organic molecule per proton. This titanium–niobium oxide is characterized by an orthorhombic system, with *a*, *b*, and *c* crystallographic parameters equal to 6.53, 3.78, and 16.70 Å, respectively. Several studies have demonstrated the

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great flexibility of the HTiNbO₅ structure and the possibility of intercalation of more or less voluminous cations and primary alkylamines. Intercalation leads to a drastic increase of the *c* parameter, which can be considered as a function of the inserted cation size or alkyl chain length in amines. The *a* and *b* parameters determined by the geometry of the TiNbO₅ layers remain independent of the cation nature. HTiNbO₅ is not a natural mineral, but its synthesis is easy, as reported in Experimental Section.

The originality of this study lies in the choice of polymerization method used to graft polysiloxane onto TiNbO₅ layers obtained after an acid–base reaction between HTiNbO₅ and tetraalkylammonium hydroxide (see below). An organically modified layered mineral is produced by dispersing HTiNbO₅ in water and then treating the mixture with a quaternary ammonium hydroxide solution. This process converts the hydrophilic mineral into an organophilic compound by increasing the distance between the mineral layers and opens a route to the synthesis of a wide variety of polymers. The oxygen anions associated with quaternary ammonium as a counterion resulting from this exchange can initiate the anionic ring-opening polymerization of cyclosiloxanes in aqueous medium.

According to Hémery et al., cyclosiloxanes can be polymerized in aqueous emulsion using a cationic emulsifying agent.¹³ These researchers obtained polysiloxanes in yields higher than 90% without macrocyclic polysiloxanes and with the remaining products essentially being composed of low-molecular-weight cyclosiloxanes (D₄–D₆), which are easily removed. This method leads, in a very simple way, to poly(dimethylsiloxane)s (PDMS) with a controlled molecular weight.

This paper deals with the development of an experimental protocol that allows for the synthesis of PDMS-intercalated and exfoliated TiNbO₅ by the reaction of the organophile TiNbO₅ with a cyclosiloxane through anionic ring-opening polymerization. The resulting products are characterized by elemental analysis, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC).

PDMS-*g*-TiNbO₅ materials¹⁴ are single-sheet nanocomposites different from the usual double-sheet clay–polymer composites. These new nanocomposites could provide access to the physical influence of such isolated inorganic sheets incorporated in composite materials. Another objective of this work is the study of polysiloxane suspensions and/or networks containing isolated inorganic sheets to test their fire resistance and mechanical, optical, and rheological properties.

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(14) Added note: A complex issue is the nomenclature of such composites. The starting structures are made of negatively charged inorganic sheets associated with quaternary ammonium ions. Polysiloxane chain growth results in the movement of the negative charges to the molecular ends (or active sites). The termination reaction induces negative charge neutralization through coupling with the quenching agent (alkyl halide, SN₂-type reaction). The precise name should describe both the PDMS grafting through covalent bonds to inorganic sheets and the presence of the eventually remaining hydroxyl groups on the TiNbO₅ phase surface. Thus, we have preferred PDMS-*g*-TiNbO₅ as a common name, although a more precise formula would have been [(PDMS-*g*-]_xH_{1-x}TiNbO₅.

Experimental Section

Products. Titanium oxide (Alfa), niobium oxide (ABCR), and potassium carbonate (Merck) were used as received to synthesize first KTiNbO₅ and then HTiNbO₅ through an exchange reaction between KTiNbO₅ and aqueous hydrochloric acid.

Hexamethylcyclotrisiloxane (D₃), tetramethylammonium and tetrabutylammonium hydroxide, and methyl iodide were purchased from Acros and used without purification.

Synthesis of HTiNbO₅ and Intercalation by Tetraalkylammonium Ions. HTiNbO₅ (*M* = 221.8 g mol⁻¹, *d* = 3.55) was prepared from KTiNbO₅, as previously described.¹⁵ To prepare intercalated HTiNbO₅, a typical synthesis consisted of mixing HTiNbO₅ and tetrabutylammonium or tetramethylammonium hydroxide, under stoichiometric conditions, in a methanol/water mixture (1/1 by volume) and heating at 50 °C for several hours. The reaction was activated by ultrasonification for 2 h. The separation of the solid from the liquid phase was performed by centrifugation, and the resulting solid was washed several times with water and then methanol to remove all remaining unintercalated tetraalkylammonium hydroxide. Finally, the product was dried under vacuum at 40 °C.

Polymerization. Into a stirred reactor were placed dry intercalated (R₄N)_xH_{1-x}TiNbO₅ and a 1/1 (v/v) mixture of methanol and deionized water. The mixture was stirred efficiently for 30 min to disperse the intercalated mineral phase. During emulsification, the mixture temperature was increased to about 50 °C. Nitrogen was bubbled through the solution for a few minutes, and then cyclosiloxane monomer was introduced into the reactor. The mixture was submitted to ultrasonification for 3 h. The reaction temperature (50 °C) was adjusted with a regulated oil bath. Polymerization was carried out under a slight nitrogen flow and stirring. Polymerization was quenched by methyl iodide addition, and the organic–inorganic material was recovered by filtration, washed many times with toluene to eliminate all residual siloxane and ungrafted polymer, and dried under a vacuum at 40 °C.

Characterization. FTIR analyses were performed using a Perkin-Elmer Spectrum 1000 apparatus. Spectra were recorded in transmission mode using KBr pellets in the 4000–400 cm⁻¹ range with 2 cm⁻¹ resolution.

X-ray diffraction data were collected using a Philips PW3710 diffractometer equipped with a goniometric X'PERT system. The instrument used radiation from a copper target tube (Cu K α radiation, λ = 1.541817 Å), and the resulting data were treated with the X'PERT program (version 2.1).

For MET analysis, the different samples were dehydrated in ethanol solution (up to 100%), then in 50% Epon, and finally in 100% Epon. After polymerization, the blocks were sectioned, and the ultrathin sections were observed in a Philips CM12 microscope operating at 120 kV.

Glass transition temperatures were determined on a Perkin-Elmer Pyris 1 differential scanning calorimeter using Pyris V 3.0 software on a Windows NT 4.0 platform for data collection and treatment.

Results and Discussion

Intercalation of HTiNbO₅ by Tetraalkylammonium Hydroxides. According to the process described in the Experimental Section, the reactive organophilic HTiNbO₅ was prepared by exchanging interlayer hydrogen atoms by tetramethylammonium or tetrabutylammonium ions through a reaction (Figure 2).

HTiNbO₅ can be considered as a Brönsted acid, and it reacts with organic Brönsted bases. It must be pointed out that the presence of water (or a protic solvent) is necessary for intercalation because of the acid–basic

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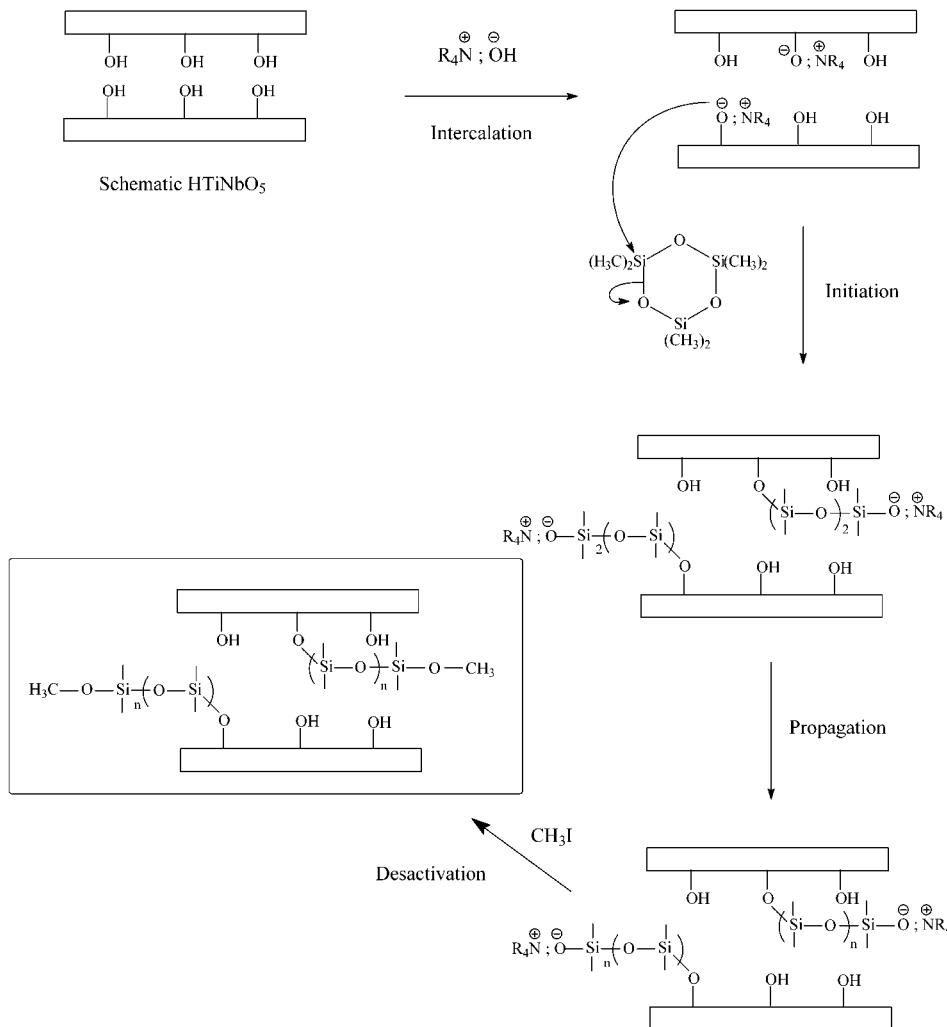


Figure 2. Schematic representation of different steps leading to polysiloxane-*g*-TiNbO₅ nanocomposites.

Table 1. Experimental Results for the Exchange Reaction between Hydrogen Atoms of HTiNbO₅ and Tetraalkylammonium Ions^a

tetraalkylammonium ion ^b	mass increase (%)	substitution degree <i>x</i> (%)
Me ₄ N ⁺	12.1	36.7
	13.3	40.4
	15.5	47.1
Bu ₄ N ⁺	16.2	14.9
	23.8	21.9
	31.5	28.9

^a *T* = 50 °C; reaction time, 72 h; HTiNbO₅, 1 g (4.50 × 10⁻³ mol). ^b In stoichiometric proportions relative to the number of moles of HTiNbO₅.

character of the reaction. The exchange reaction efficiency is easily evaluated from the increase in the sample mass. The substitution of hydrogen atoms by tetraalkylammonium groups leads to a large mass increase, which allows the intercalation percentage *x* (Table 1) to be calculated according to eqs 1 and 2 for tetramethyl ion insertion

$$(Me_4N)_xH_{1-x}TiNbO_5 \quad M = 221.8 + 73.1x \text{ (g mol}^{-1}) \quad (1)$$

$$x = \frac{221.8(m_f - m_i)}{73.1m_i} \quad (2)$$

where *m_i* is the initial mass of HTiNbO₅ and *m_f* is the final mass of (Me₄N)_xH_{1-x}TiNbO₅, and to eqs 3 and 4 for tetrabutylammonium ion insertion

$$(Bu_4N)_xH_{1-x}TiNbO_5 \quad M = 221.8 + 241.5x \text{ (g mol}^{-1}) \quad (3)$$

$$x = \frac{221.8(m_f - m_i)}{241.5m_i} \quad (4)$$

where *m_i* is the initial mass of HTiNbO₅ and *m_f* is the final mass of (Bu₄N)_xH_{1-x}TiNbO₅.

Two series of experiments were carried out. The first involved the substitution of hydrogen atoms by tetramethylammonium groups, and the second used tetrabutylammonium ions. The experimental results show that the substitution degree *x* is higher for Me₄N⁺ ions than for Bu₄N⁺ ions. In the Me₄N⁺ ion case, the intercalation rate ranges from 0.35 to 0.50 within experimental error. Concerning Bu₄N⁺ groups, the substitution degrees are in the range 0.15–0.29. These two different behaviors can be explained by the greater steric hindrance due to the presence of four butyl groups on each nitrogen atom in the second case. Thus, tetramethylammonium hydroxide was selected for further investigation because its exchange reaction efficiency was higher, and the elaboration of nano-

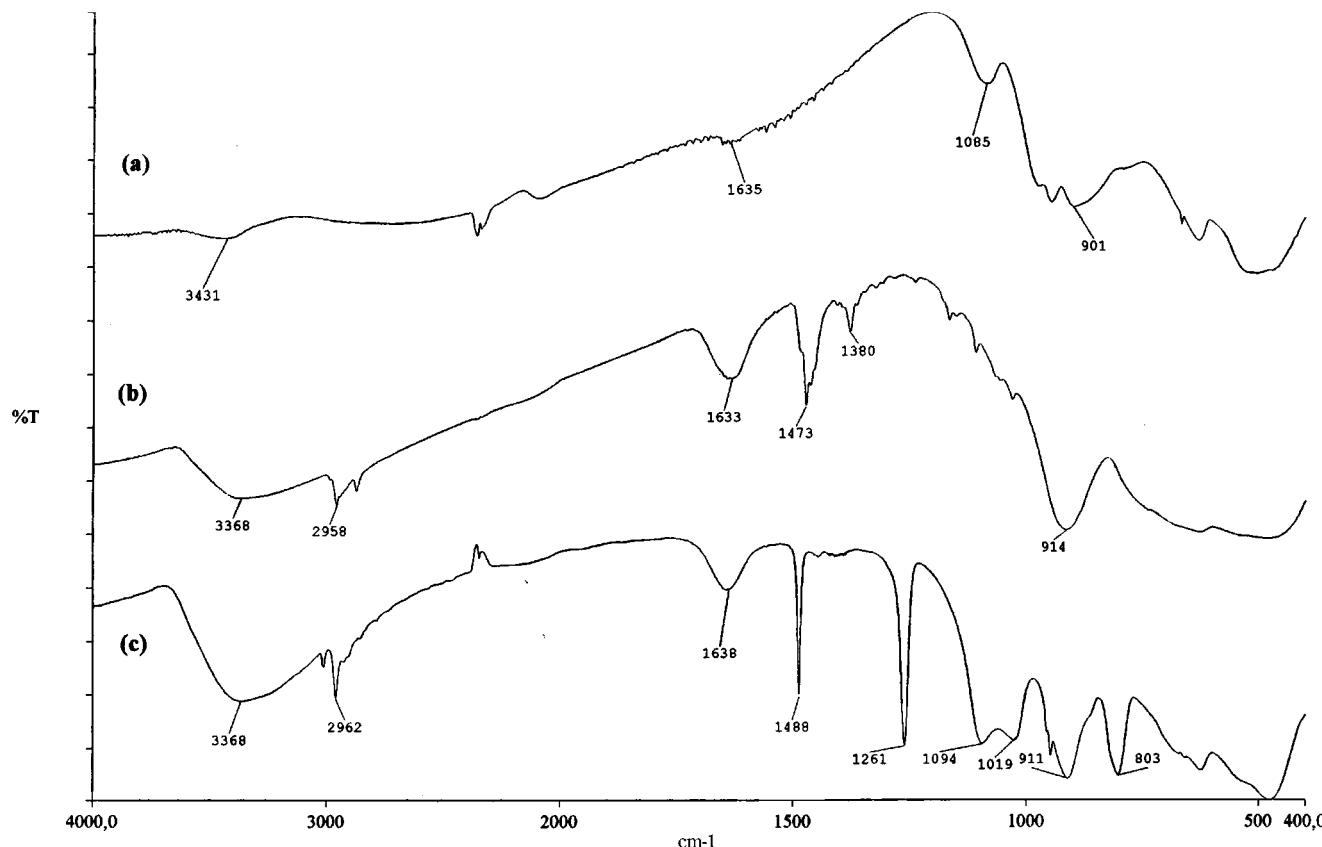


Figure 3. Evolution of FTIR spectra after the intercalation reaction and subsequent polymerization: (a) HTiNbO_5 , (b) $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$, (c) final nanocomposite $\text{PDMS-}g\text{-TiNbO}_5$

composites was based mainly on $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ ($0.35 \leq x \leq 0.50$).

Preparation of Polysiloxane-*g*- TiNbO_5 Materials from $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$. Nanocomposites were synthesized by emulsion polymerization of hexamethylcyclotrisiloxane (D_3) from the previously prepared organophilic $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$. Anionic ring-opening polymerization was initiated by the mineral-supported oxygen anions associated with the Me_4N^+ counterions acting as a phase-transfer catalyst. At the end of the reaction, the resulting product was treated with excess methyl iodide (Figure 2). A preliminary study of the influence of experimental parameters (ultrasonification time, reaction time, temperature) was performed. Then, the sonication time and reaction temperature were fixed at 3 h and 50 °C, respectively. The reaction is achieved in about 70 h. The most influential parameter seemed to be the sonication time, which had to be at least 3 h to obtain good results. Moreover, polymerization yields were better if the monomer was added progressively to maintain the propagation reaction. Finally, the resulting compound had to be washed several times with toluene to separate the eventually formed ungrafted polymers and residual monomer from the nanocomposite. Under these conditions, the experimental results show a significant increase in sample mass, demonstrating that the new polysiloxane-*g*- TiNbO_5 materials can be prepared in aqueous media according to this original process (Table 2).

Characterization. Elemental Analysis. First, the mass increases of the $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ and $(\text{Bu}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ samples were confirmed by nitrogen elemental analysis (Table 3).

Table 2. Experimental Results for the Preparation of Polysiloxane-*g*- TiNbO_5 Materials from Organophilic $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ ($x = 0.4$) in Water-Methanol Medium (1/1 by Volume)^a

$(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ initial mass (g)	nanocomposite final mass (g)	mass increase (%)
0.291	0.537	84
0.597	1.208	102
0.513	1.180	130
0.525	1.480	182
0.503	1.550	208
0.501	1.862	272

^a $T = 50$ °C; ultrasonification time, 3 h; reaction time, 72 h; large excess of D_3 ; quenching agent, CH_3I .

Table 3. Comparison of the Experimental Results Obtained by Mass Increase and Nitrogen Elemental Analysis

intercalated compound	nitrogen content (%)	x^a	x^b
$(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$	1.83	0.32	0.33
$(\text{Bu}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$	0.86	0.16	0.19

^a Calculated from the nitrogen percentage obtained by nitrogen elemental analysis. ^b Calculated from the sample mass increase.

Within experimental error, the substitution degrees determined by these two different methods are in good agreement.

Fourier Transform Infrared (FTIR) Spectroscopy. All of the prepared materials were systematically characterized by IR absorption spectroscopy. The IR spectra of the compounds show all of the characteristic bands of their respective substitutions.

The initial HTiNbO_5 spectrum presents two characteristic bands around 3400 and 1085 cm^{-1} , respectively

assigned to O–H bond vibrations (antisymmetric and symmetric stretchings) and to bending vibrations of M–O–H, where M is Ti or Nb.¹⁶ We can also see a band representing M–O–H bending at 1635 cm⁻¹.

In the cases of (Me₄N)_xH_{1-x}TiNbO₅ and (Bu₄N)_xH_{1-x}TiNbO₅, it is important to specify that the band around 1100 cm⁻¹ decreases with increasing intercalation rate. The band around 3400 cm⁻¹ does not completely disappear because of the presence of residual OH groups. The spectrum also exhibits a weak but characteristic band related to C–N bond distortion at 1380 cm⁻¹ and a second significant band attributed to C–H bond bending at 1473 cm⁻¹. C–H bond stretching leads to an absorption at 2958 cm⁻¹.

The specific absorptions of poly(dimethylsiloxane)s appear at 1261, 1094, and 1019 cm⁻¹ in IR spectra of polysiloxane-*g*-TiNbO₅ nanocomposites. These three bands are assigned to Si–CH₃ bending vibrations (1261 cm⁻¹) and Si–O stretching vibrations (1094 and 1019 cm⁻¹) typical of poly(dimethylsiloxane) units. Thus, all of the characteristic bands of the polysiloxane-*g*-TiNbO₅ hybrid compound can be observed.

The characteristic evolution of the FT-IR spectra after the intercalation reaction and after polymerization is reported in Figure 3.

X-ray Diffraction (XRD). XRD analysis is a powerful tool for examining the crystal structure of inorganic compounds. The lattice parameters of HTiNbO₅ were calculated from the X-ray diffraction pattern depicted in Figure 4a using the 200, 020, and 002 reflections assuming an orthorhombic cell. The *a*, *b*, and *c* parameters can be calculated from Bragg's law to be equal to 6.511, 3.769, and 16.689 Å, respectively. These values are the same as documented in the literature, and the *a* and *b* parameters are practically independent of the type of intercalated cation.^{9,10} The interlayer distance *d*₀₀₂ corresponding to $1/2$ *c* in an orthorhombic system can be considered as equal to 8.345 Å.

During the cation-exchange process, tetramethylammonium cations penetrate in the interlayer space, replacing hydrogen atoms. Figure 4b shows that the peaks, in particular the 002 peak, are shifted to lower angles and clearly indicate the intercalation of tetramethylammonium ions between TiNbO₅ layers. The *c* parameter increases from 16.689 (*d*₀₀₂ = 8.345 Å) to 30.186 Å (*d*₀₀₂ = 15.093 Å), and it is interesting to note that the results obtained from different (Me₄N)_xH_{1-x}TiNbO₅ samples demonstrate that the interlayer distance *d*₀₀₂ is unaffected by the intercalation degree *x* in the range studied (0.35 ≤ *x* ≤ 0.50). The *a* and *b* parameters that characterize the TiNbO₅ layers are very similar for the two forms, whereas the *c* parameter corresponding to the spacing of the layers differs greatly. Nevertheless, the crystalline structure of (Me₄N)_xH_{1-x}TiNbO₅ remains (Figure 4b).

In contrast, for polysiloxane-*g*-TiNbO₅ materials, the presence of Bragg diffraction peaks that are very small and broad implies that the mineral has been exfoliated in the polymer matrix (Figure 4c). Each layer of the mineral is dispersed homogeneously in the polysiloxane matrix, although a small amount of unexfoliated layers

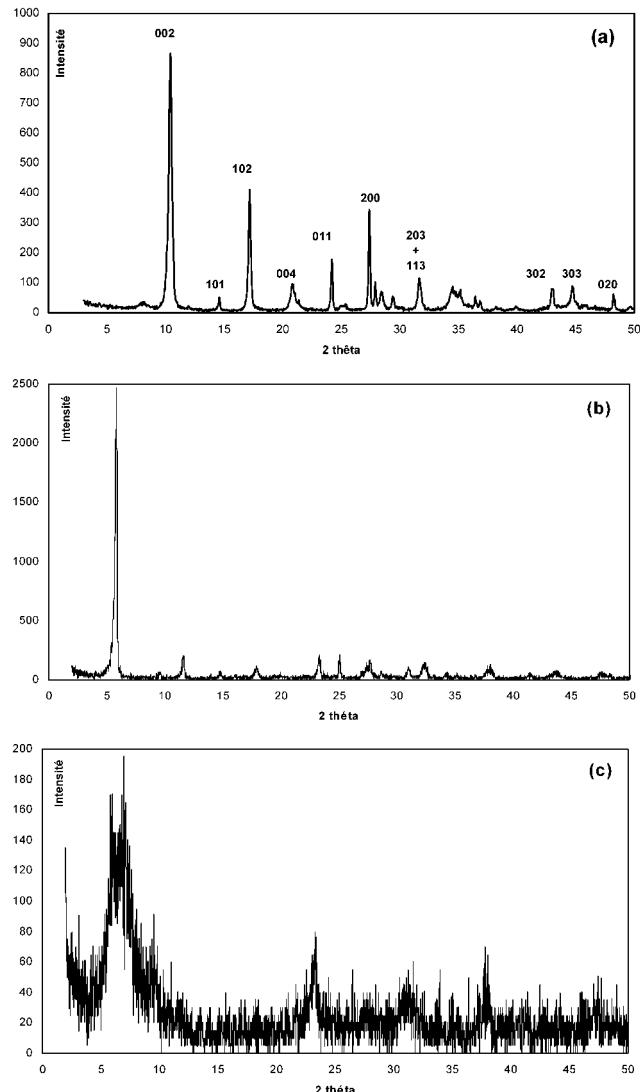


Figure 4. Evolution of X-ray diffraction diagrams after the intercalation reaction and subsequent polymerization: (a) HTiNbO₅, (b) (Me₄N)_xH_{1-x}TiNbO₅, (c) final nanocomposite PDMS-*g*-TiNbO₅.

probably still exists. The existence of these very small peaks in the XRD patterns should be attributed to these few unexfoliated layers, as well as to diffraction by isolated mineral layers.

Transmission Electron Microscopy (TEM). To definitively confirm the hybrid structures, the dispersion of the mineral layers in the polysiloxane matrix was observed by TEM (Figure 5). The efficiency of the intercalation reaction can be seen in Figure 5a. As revealed in this image, tetramethylammonium cations do not penetrate into all of the interlayer spaces. Two zones can be distinguished: a first zone unaffected by intercalation and a second one where intercalation of tetramethylammonium cations induces an increase in the interlayer spacing. It is important to note that the interlayer distance measured directly on the TEM images corresponds approximatively to the distances calculated from XRD patterns (interlayer distance ranging from 8 to 10 Å for nonintercalated layers and from 15 to 18 Å for intercalated layers). TEM images show a nanodispersed morphology in the polysiloxane-*g*-TiNbO₅ nanocomposite (Figure 5b). In this image, the light and

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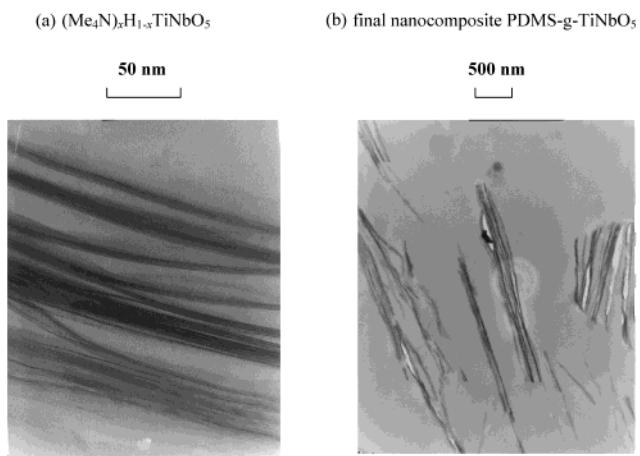


Figure 5. MET images of (a) intercalated compound $(\text{Me}_4\text{N})_x\text{H}_{1-x}\text{TiNbO}_5$ and (b) final nanocomposite PDMS-*g*- TiNbO_5 .

dark regions represent polysiloxane and mineral thin sheets, respectively, and we can observe a heterogeneous disordered nanostructure. These results suggest that an exfoliated polysiloxane-*g*- HTiNbO_5 nanocomposite was obtained, in good agreement with the XRD patterns.

Differential Scanning Calorimetry (DSC). DSC experiments were performed on hybrid materials. The thermograms clearly indicate only one transition phase near -115°C , which let suppose a significant reduction of polysiloxane chain mobility in the nanocomposite. This curve confirms the efficiency of nongrafted polysiloxane extraction steps and, thus, the absence of residual homopolysiloxane [$T_g = -125^\circ\text{C}$ in poly(dimethylsiloxane)] in the final nanocomposite. The purified composite does not present a clear thermal

transition around -125°C . Thus, all of the polysiloxane chains present in final structure seem to be grafted on mineral layers.

Finally, the silicon elemental analysis carried out on polysiloxane-*g*- TiNbO_5 materials allows the ratio of silicon-containing polymer incorporated in the nanocomposite to be calculated (Si content of up to 18%). The average number of $[(\text{CH}_3)_2\text{SiO}]$ units grafted onto the mineral layers can be evaluated as 8–10 (relative to each TiNbO_5 unit). Further investigations are in progress to evaluate the polysiloxane chain length and distribution.

Conclusion

New hybrid organic–inorganic materials based on polysiloxane and a lamellar niobium–titanium oxide have been prepared via *in situ* intercalative polymerization. The experimental conditions allow for the anionic ring-opening polymerization of hexamethylcyclotrisiloxane in aqueous medium. The structural characterization confirms the formation of an intercalated nanocomposite and the exfoliation of the mineral layers in an amorphous polymer matrix.

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