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Stability of hybrid inorganic-organic particles based on Poly(4-Vinylpyridine) adsorption on micron-sized mica platelets

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Abstract

A growing interest has been developed around the preparation of the organic-inorganic composites materials. Because of their numerous technological and fundamental applications, many procedures of synthesis were described. They are based on physical and/or chemical interactions. Thus, we synthesized for the first time two hybrid composite materials P4VP@Mica containing MICA, as mineral material and poly(4-vinylpyridine) [P4VP] polymer, with respectively ratios R=0.2 and R=0.5. These materials were characterized in previous article using, Thermogravimetric analysis (TGA), Fourier transformed infrared (IRTF) and Scanning Electron Microscopy coupled with Energy dispersive X-Ray Spectroscopy (SEM-EDX). In this article we study a stability of these materials by potentiometry and conductimetry.

Key words: Mica, poly(4-vinylpyridine) P4VP, composite.

1. Introduction

These last years, a great number of organic-inorganic composites have been developed using many procedures of synthesis from the literature [1-6]. In fact, they have a multiple technological and fundamental applications. On the other hand, they has been based on both the physicochemical and on the polymerization methods. The most effective means of the synthesis of these hybrid materials is based on the specific interactions at the interface between the two organic and inorganic phases. The deposited polymers on inorganic surface have a potential interest for the modification of its interfacial properties and the preparation of composite materials [7-11]. Thus, a certain inorganic number of hybrids and organic nanocomposites were deferred in the literature [12-16]. The latter are intended for a large variety of fields of application such as adhesives, chromatography, protein immobilization, colloidal stabilization, medicine, dentistry and beauty products. [17-19]

Our work intends to reproduce a multilayered structure by creating at the surface of a lamellar silicate or clay the superposition of two layers of organic compounds. In this paper, as in the case of inorganic compounds among the various clays (montmorillonite, silica, talc, mica, etc.), mica was chosen for the application. Mica is frequently used as filler in polymeric materials. For example, mica 'paper' confers excellent electrical properties to polymer composites for high-voltage insulators, mica 'powders' are used as fillers to increase the stiffness of thermoplastic polymers, especially polypropylene, and mica 'platelets' show promise for permeation barriers in polymer composites. [20] In order to get more information about the roles of these charges in a polymer matrix, it is very important to characterize the polymer/filler interactions and establish the dimensions of the macromolecular chains grafted or adsorbed on the surface. Mica is a chemically inert alumino-silicate mineral. Its crystalline structure consists of preliminary negatively charged 2:1 layers whose charges are compensated by interlayer cations [monovalent cations (Na^+, K^+, etc.) or divalent cations (Ca^{2+}, Mg^{2+}, etc.)] [1], each 2:1 layer consists of two tetrahedral sheets sandwiching one octahedral sheet. Because of its lamellar structure, mica has been extensively studied. It can as well be found under the form of small platelets which have for a long time attracted attention for use in cosmetic products, in particular. The adsorption or coating of neutral polymers onto mineral supports (silica gel, alumine, etc.) was largely studied [1, 7, 8, 9, 12]. Comparatively, the modification of mica using organic polymers is relatively new. In particular, the adsorption of poly(4-vinylpyridine) (P4VP) on the mica surface has not been studied at all. One of the important features of mica flakes is that they conserve their lamellar structure under different conditions. It was very important to control the nature and the thickness of the polymer layer, and so a low vitreous transition temperature Tg [P4VP] polymer has been observed. In previous paper, we have synthesized hybrid materials containing Mica and P4VP with the following P4VP@Mica ratios R=0.2 and R=0.5; according to the following figure 1. These materials were characterized in previous article using, Thermogravimetric analysis (TGA), Fourier transformed infrared (IRTF) and Scanning Electron Microscopy coupled with Energy dispersive X-Ray Spectroscopy (SEM-EDX). In this article we study a stability of the poly(4-vinylprydine) on the mica surface by potentiometry and conductimetry.

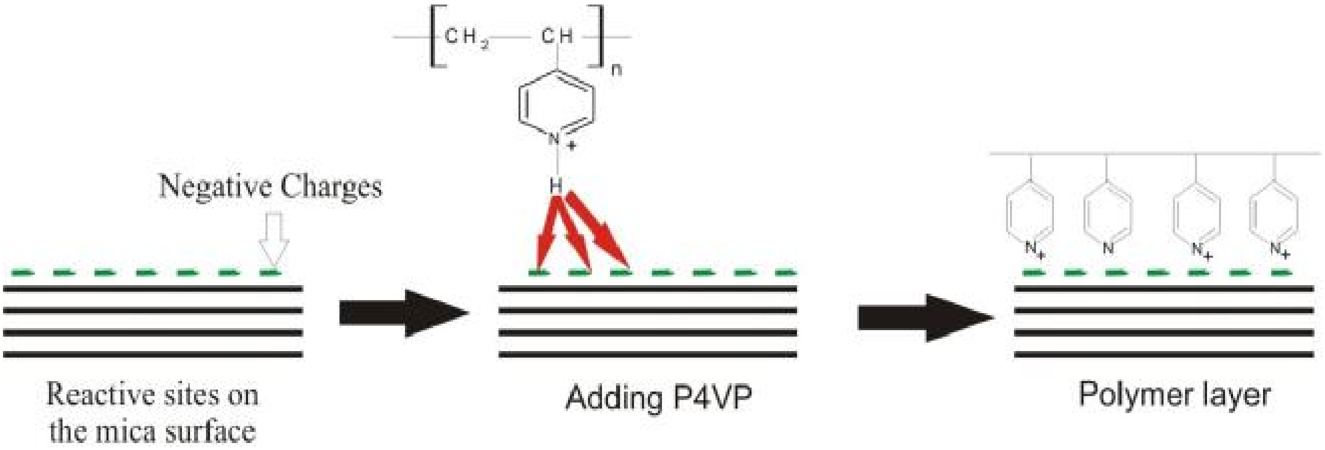

Figure 1: Concept of formation of the polymer layer on the mica surface

2. Materials and methods

2.1. Materials

Poly (4-vinylpyridine) $6*10^4$ g/mol were supplied by Aldrich Company. Mica Software® was supplied by “Le Comptoire des Minéraux et des Matières Premières” and its characteristics are presented in Table 1.

The P4VP molecular weight is choice to facilitate polymer thin layer adsorption on the mica surface. Indeed, the P4VP is a polymer bearing aromatic groups with nitrogen atoms which are able to act with the positively charged Mica surface, after quaternization reaction.

The P4VP is a polymer which can be transformed easily and it is very much used in many applications [5, 18, 19, 20, 21, 22, 23]. Thus, new composites were formulated in aqueous media by combining the positive P4VP and negatively charged mica particles.

Table 1: Physicochemical characteristics of the mica

Physical properties	
Density [g/cm^3]	2.80
pH (dans l’eau)	9
Size average particles [µm]	45-150
Specific surface [m^2/g]	5.9

Chemical analyses [%]	
SiO_2	49.2%
Al_2O_3	28.3%
K_2O	9.8%
Fe_2O_3	6.9%
Na_2O	0.8%
CaO	1%
H_2O	0.2%

2.2. Instruments

Our conductimetric measurements were taken using a CDM 210 conductimeter (Radiometer, Meter Lab). The studied solutions are contained in a cell out of glass with double thermostatic wall with (25 ± 0.1) °C using a circulation thermostat**.**
We used a cell with glass holder comprising two platinum plates of type CDC641T, its constant K = 0.805 cm^{-1}.The value posted directly on the apparatus is either that of the resistivity (R) or that of the conductivity (σ) of the solution.

Our potentiometric measurements were taken using a potentiometer Denver instrument model 225 (pH +ISE meter). The studied solutions are contained in a cell out of glass with double thermostated wall with (25 ± 0.1) °C using a circulation thermostat.

3. Results and discussion

3.1. Stability study by conductimetry and potentiometry

The variation of the conductivity and the potentiometry of the mica according to time in experimental conditions show two parts. A reduction of the pH is observed for the first 70 minutes, this reduction can be allotted to the swelling phenomenon of the mica in aqueous media. Interfoliar space of mica increase when water penetrates. That causes the release of cations, mainly K^+ cations.

We can explain that by the structure of the mica (figure 4), the tetrahedrons ZO_4 (Z = Al or Si) give layers with $[AlSi_3O_{10}]_n$ composition by binding three of their respective tops. The "Basal" oxygen atoms implied in these connections form a hexagonal assembly. The other oxygen atoms, localized at the tops of the nondependent tetrahedrons are known as "apical". Two tetrahedral layers are superimposed, the tops (still free) of the tetrahedrons pointing towards the interior. They thus determine octahedral gaps filled to two thirds by aluminium atoms in co-ordination number six. For this reason, mica is a "dioctaedric" [24, 25]. Groupings hydroxyls, placed at the center of the hexagons formed by apical oxygen, are related exclusively to the octahedral aluminum atoms and form double-layered strongly dependent. Each potassium atom is placed in a large cavity formed with two basal oxygen hexagons. Potassium is in co-ordination number twelve. The K-O connection weak and is easily broken. So, mica can be cleaved very easily in the plan (001), it is this facility to break the connection K-O which allows K^+ to be released [24- 26]. In the second part, we observe a stability of the pH in time. The evolution of conductivity, confirms what we observed by potentiometry. In the first 70 minutes, the conductivity increase confirming the release of the loads K^+. After, we have a stabilization of conductivity in time [26].

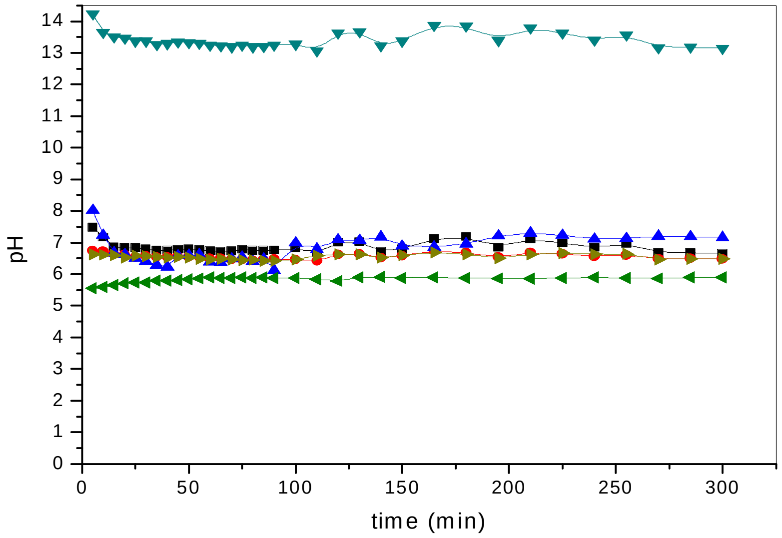

Figure 2: Variation of the pH according to time of: (■) mica suspension, (●) P4VP suspension, (▲) Physical mixtures [P4VP+mica], (▼) Addition of Mica and P4VP values, (◀) Composite material P4VP@Mica [R=0.2] and (▶) Composite material P4VP@Mica [R=0.5]. (T= 21°C, pH $_{\text{bi-distilled water}}$ = 6.50)

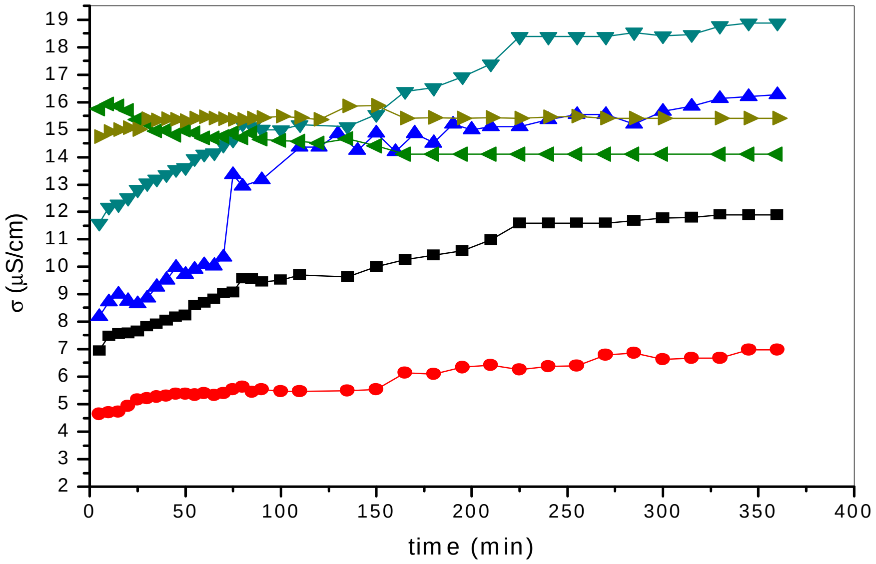

Figure 3: Variation of the conductivity according to time of: (■) mica suspension, (●) P4VP suspension, (▲) Physical mixtures [P4VP+mica], (▼) Addition of Mica and P4VP values, (◀) Composite material P4VP@Mica [R=0.2] and (▶) Composite material P4VP@Mica [R=0.5]. (T= 21°C, pH $_{\text{bi-distilled water}}$ = 6.50)

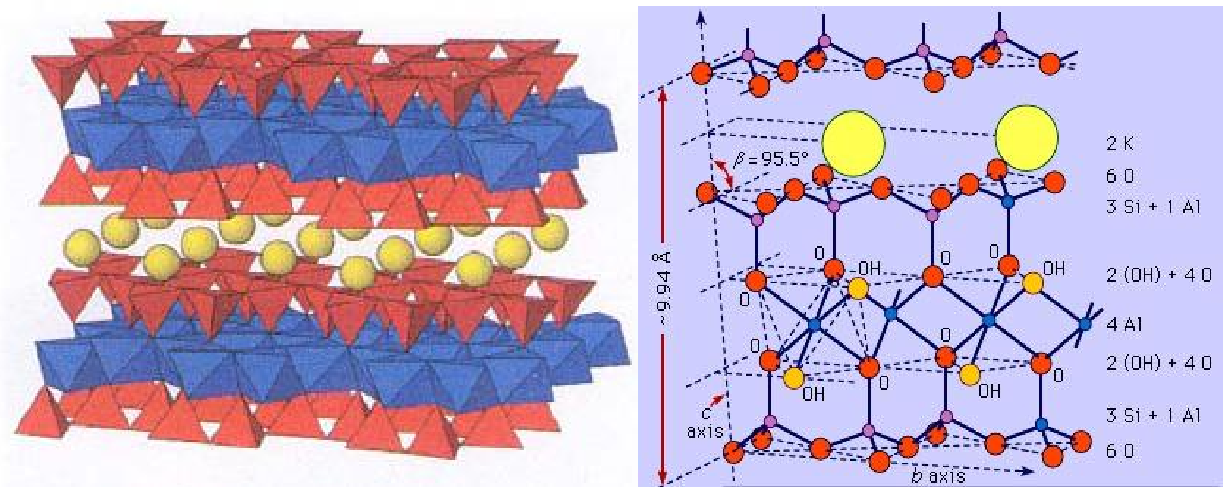

Figure 4: Mica layer

The study of the P4VP by potentiometry and conductimetry shows a stability of polymer in water. The values of conductivity and pH correspond to species OH^- released by the reaction between P4VP and water, it corresponds to the partial quaternisation of the P4VP and a release of ions OH^- (figure 5 [1]).

We studied the stability of physical mixture of [mica+P4VP] by potentiometry and conductimetry. We observed two fields of variations. The first corresponds exactly to the increase observed for the mica alone for the first 70 minutes. Therefore, it is always due to the phenomena of swelling already observed previously and the release of the loads K^+. The increase of the pH and the conductivity reduction after 70 minutes, are allotted to the reaction between water and the P4VP which led to a partial quaternisation of the P4VP by water (figure 5 [2]). This reaction is very slow and gives a material close to the hybrid material which remains stable in time. This reaction shows that the P4VP and the mica have a very great affinity between us. In the other hand, the simple mixture between mica and P4VP does not make it possible to control the percentage of quaternisation of the P4VP and fixation of polymer on the mica surface.

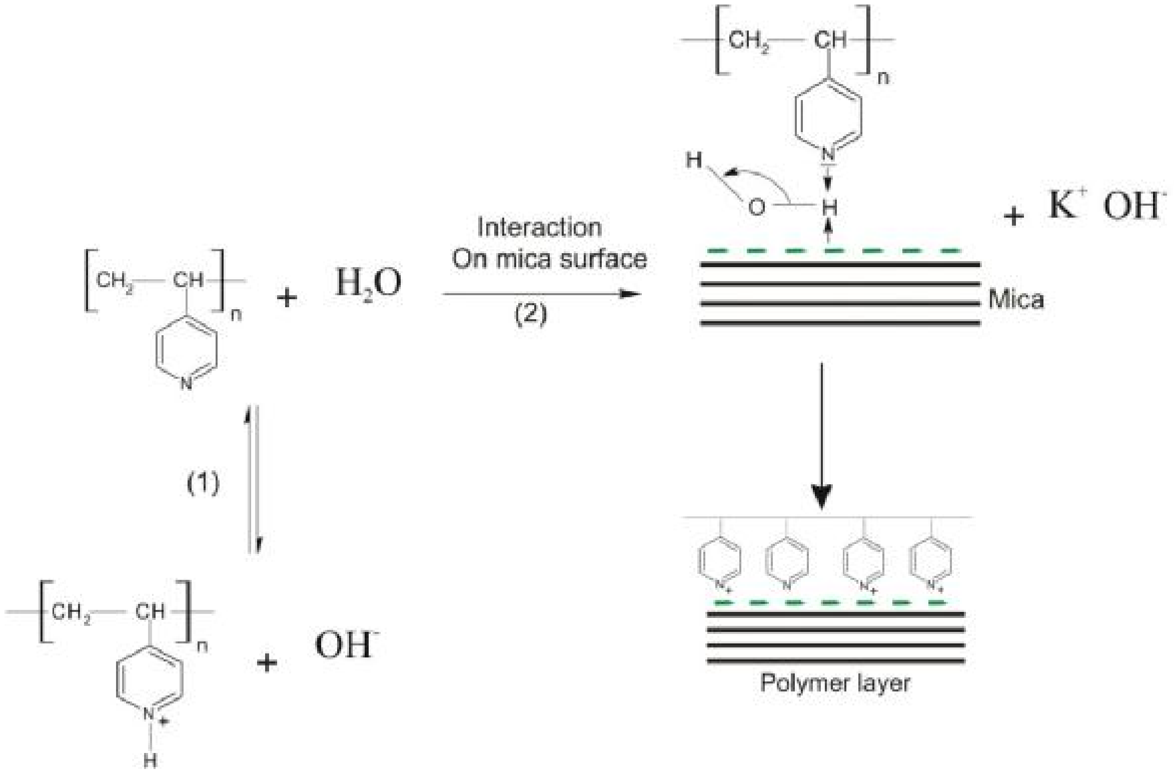

Figure 5: Mechanism of formation of the polymer layer from a simple mixture between the P4VP and mica in water

Conclusion

The study of the composite materials P4VP@mica [R=0.2] and P4VP@mica [R=0.5] by conductimetry and poteniometry shows a very great stability. So, P4VP is a good candidate for adsorption on the mica surface. Hybrid materials of mica having a well defined layer of poly(4-vinylpyridine) were prepared with two different ratios [P4VP@mica/R=0.2] and [P4VP@mica/R=0.5].

A physical mixture [P4VP+mica] does not give the same graph as the addition of the mica and P4VP values. These results are different from hybrid materials P4VP@mica [R=0.2] and P4VP@mica [R=0.5].We can thus establish the following conclusions:

1) The mixture of the P4VP with the mica is not a simple addition of the values of each one of these two last alone. This result confirms the interactions which exist between the mica and the P4VP.

2) The composite materials P4VP@mica [R=0.2] and P4VP@mica [R=0.5] give not the same graph for the physical mixture graphs or for the addition graphs. Therefore, this confirms that we obtained new stable composite materials under the experimental conditions.

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