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Chemistry

SPONTANEOUS POLYMERIZATION OF 4-VINYLPYRIDINE MONOMER ON MICRON-SIZED MICA PLATELETS

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Abstract. In this study, we reported the spontaneous polymerization of two composite materials based on P4VP and mica at two different ratios, 4VP/mica/R=5 and 4VP/mica/R=10, noted as P4VP5@mica and P4VP10@mica, respectively. The obtained composites were characterized using thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The polymerized P4VP on the inorganic surface has potential interest for the modification of the interfacial properties of the mica.

Keywords: mica, 4-vinylpyridine (4VP), spontaneous polymerization, composite.

1. Introduction

In the past few years, a great number of organic/inorganic composites have been developed using many synthesis procedures described in the literature.[1-6] In fact, these developed composites have multiple technological and fundamental applications. They have been also based on both the physicochemical and polymerization methods. The most effective means of the synthesis of these hybrid materials are based on the specific interactions at the interface between the two organic and inorganic phases. The deposited polymers on the inorganic surface have a potential interest for the modification of its interfacial properties and the preparation of composite materials. Thus, a certain inorganic number of hybrids and organic nanocomposites were cited in the literature.[4-10] The matter is intended for a large variety of fields of application such as adhesives, chromatography, protein immobilization, colloidal stabilization, medicine, dentistry, and beauty products.

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 various clays (montmorillonite, silica, talc, mica, *etc.*), mica was chosen for the application. Mica is frequently used as a 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,[7] and mica 'platelets' show promise for permeation barriers in polymer composites.[11] 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 which 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. As well it can be found in the form of small platelets, which have for a long time particularly attracted attention for use in cosmetic products. The adsorption or coating of neutral polymers onto mineral supports (silica gel, alumina, *etc.*) was largely studied.[5,7] Comparatively, the modification of mica using organic polymers is relatively new.

In particular, the spontaneous polymerization of 4-vinylpyridine (4VP) on the mica surface has not been studied at all. In a previous paper, we succeeded in synthesizing for the first time two hybrid composite materials [P4VP/mica] containing mica, as a mineral material and poly(4-vinylpyridine) [P4VP] polymer, with respective ratios R=0.2 and R=0.5 obtained by adsorption of the polymer on the mica surface.[12] In this paper, we present the synthesis and characterization of hybrid materials obtained by spontaneous polymerization of 4-vinylpyridine on the mica surface with the P4VP@mica ratios of R=5 and R=10; illustrated in Fig. 1.

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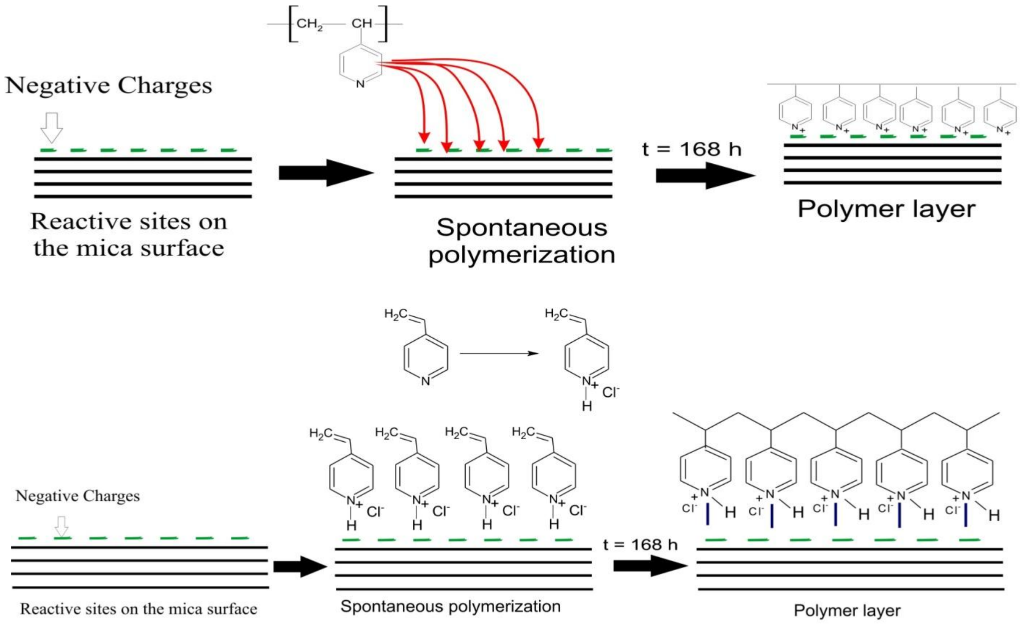


Fig. 1. Spontaneous polymerization of 4-inylpyridine on the mica surface

2. Experimental

2.1. Materials

Mica Software® was supplied by "Le Comptoire des Minéraux et des Matières Premières" in France and its characteristics are presented in Table 1. 4-Vinylpyridine 4VP was purified by distillation under reduced pressure (35-40 °C/0.01 mm Hg), using 100 ppm hydroquinone.

Table 1. Physicochemical characteristics of the mica

Physical properties	
Density (g/cm^3)	2.80
pH (in H_2O)	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
Residues	3,5

2.2. Techniques

Thermal stability of P4VP-adsorbed mica particles noted P4VP@mica hybrid has been studied in the temperature range between 20 and 850 °C under air by thermogravimetric analysis performed using the TA instrument "TGA Q50" apparatus.

The FTIR analysis of KBr pellets form is performed using the apparatus Magna IR 560 spectrometer Nicolet.

SEM-EDX analyses are conducted using the apparatus MINI-SEM TM-1000 HITACHI. The EDX will enable us to measure the average weight percentage of the component present on the mica surface.

2.3. Spontaneous Polymerization of 4VP on the Mica Surface

Mica distilled 4VP with different ratios R=5 and R=10 was placed in a 100 mL sealed tube with a magnetic stirrer; we add 100 mL of acid chloride HCl (1M). The quantities and volumes of materials used in the reactions are summarized in Table 2. The mixture was stirred for 168 hours at 50 °C until a complete reaction was reached. Hybrid materials were separated by centrifugation and dried at 65 °C for 24 hours in a drying oven.[13]

Table 2. Conditions of the spontaneous polymerization

	P4VP5@mica	**P4VP10@mica**
Volume of 4VP (g)	48.75	97.5
Weight of mica (g)	10	10
Volume of HCl (1M) (mL)	100	100
Time (h)	168	168

3. Results and Discussion

3.1. Thermogravimetric "TGA" Weight Loss Measurements

The thermal stability of P4VP polymers polymerized on the mica surface has been studied in the temperature range between 20 and 850 °C under air, using the TA instrument apparatus "TGA Q50". The thermogravimetric curves obtained for mica and composite materials are represented in Fig. 2.

The results of the thermogravimetric analyses show that the most visible losses of mass are observed for the samples of P4VP@mica composite material R=10. The maximum achieved percentage was 0.42% out of P4VP polymer, as shown in Fig. 2. The lost organic matter corresponds to the adsorbed polymer, as confirmed by FTIR analysis. The sample of P4VP@mica composite material R=5 shows a weight loss which is 0.31% out of organic matter, as shown in Fig. 2 as well. In the previous article,[14] we succeeded at the adsorption of the poly(4-vinylpyridine) on the mica surface with the following [P4VP/mica] ratios R=0.2 and R=0.5. Thermogravimetric measurements show that the P4VP copolymer is more visible in the sample [P4VP/mica] composite material R=0.5 with 0.60% than for the sample [P4VP/mica] composite material R=0.2 which shows 0.48% of P4VP copolymer.

Thermogravimetric measurements show that the P4VP polymer is more visible in the sample [4VP/mica] composite material R=10 than for the samples P4VP@mica composite material R=5 which shows an amount of 0.31% in P4VP polymer. The results obtained by TGA (heating weight loss) for various tests are reported in Table 3.

The weight loss between the composite material obtained by adsorption of poly(4-vinylpyridine) on the mica surface and the composite material obtained by spontaneous polymerization of the 4-vinylpyridine on the mica surface showed the same temperature of degradation near 300 °C.

The weight loss has relied on the fast dequaternisation phenomenon resulting from the secession of C-N$^+$ bonds. Claret *et al.*,[15] showed that near 300 °C, the fundamental stage of degradation consists of an electron transfer from the halogen X- to the π* orbital of the aromatic ring. A complex with a charge transfer is formed with the simultaneous hemolytic secession of C-N$^+$ bond.[16]

Table 3. Results of the thermogravimetric analysis

	P4VP5@mica	**P4VP10@mica**
Weight loss (%)	0.31	0.42

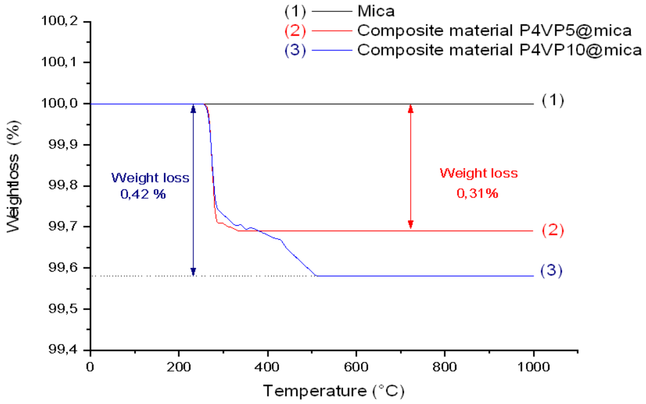
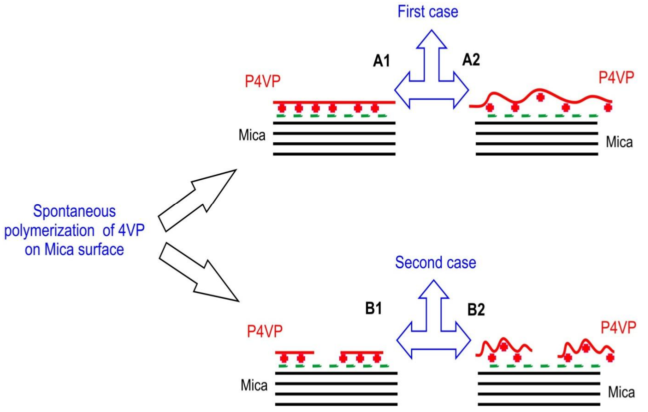


Fig. 2. TGA Thermograms: (1) mica, (2) composite material P4VP5@mica, (3) composite material P4VP10@mica

We will be able to schematize different possibilities of the formation of the P4VP polymer on the mica surface. Scheme 1 summarizes different possible cases:



Scheme 1. Different propositions of spontaneous polymerization of the 4-vinylpyridine on the mica surface

First, the polymer covers the totality of the mica surface, without or with free polymer segments respectively ([**A1**] and [**A2**]). Both possibilities indicate that in the [P4VP@mica/R=10] hybrid material, the "theoretically" covered surface of the mica by the P4VP is probably completely covered. The second case shows the adsorption of the P4VP which does not cover the totality of the mica surface ([**B1**] and [**B2**]). This adsorption can be done according to two possibilities described previously. Both possibilities indicate that in the P4VP@mica [R=5] hybrid material, the covered surface of the mica by the polymer leads to an incomplete covering. In fact, these two hybrid materials P4VP@mica [R=0.2] and P4VP@mica [R=0.5] present a similar visual aspect since they were prepared under the same experimental conditions.

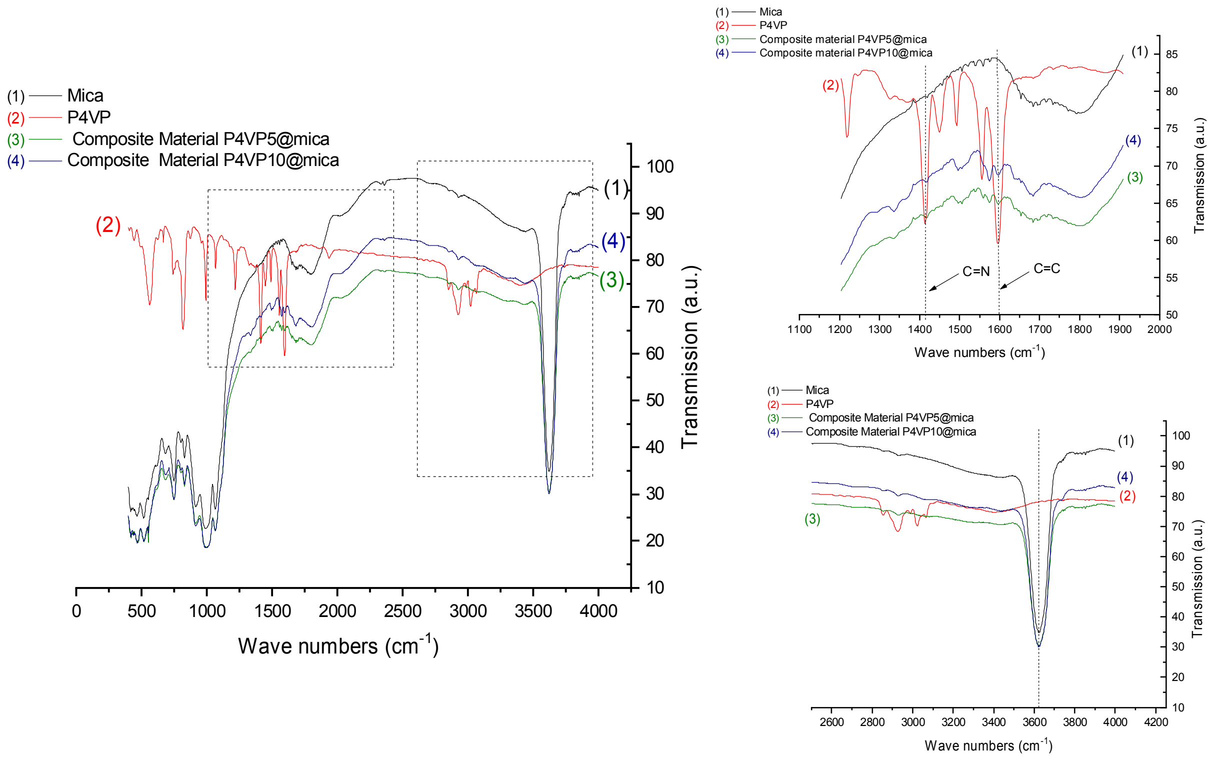


Fig. 3. FTIR spectra of: (1) mica, (2) P4VP, (3) composite material P4VP5@mica, and (4) composite material P4VP5@mica

3.2. FTIR Characterizations

The FTIR analysis was conducted using the Magna IR 560 spectrometer Nicolet apparatus. The obtained FTIR curves for composite materials are represented in Figs. 3–5.In order to confirm the thermogravimetric results, we have characterized these composite materials using FTIR technique. In the FTIR spectrum of P4VP5@mica and of P4VP5@mica (containing 0.31% and 0.41% of P4VP respectively) (Fig. 3), the presence of polymerized P4VP on the mica surface is detected and is attested by the band with the wavelength of 1600 cm^{-1} corresponding to stretching vibration of C=C in the aromatic ring (see Figs. 4–6), a slight peak at 1420 cm^{-1} corresponding to stretching vibration of C=N in the aromatic ring and a slight peak shoulder at 3300-3500 cm^{-1} and 2850-3080 cm^{-1} correspondent with the aromatic connections of elongation of CH. We observe in the present FTIR spectra the siloxane transmittance bands characteristic of the mica material. In fact, the silicon, when it is bound to oxygen atom Si-O, gives three types of vibrations corresponding to Si-O stretching (1080 cm^{-1}), Si-O bending (805 cm^{-1}), SiO rocking (450 cm^{-1}), and the SiOH band at 3500–3650 cm^{-1}.[17]

3.3. Morphology and Composition of the Hybrid Micron-Sized Particles

Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDX) characterizations were performed. The SEM-EDX observation obtained for raw mica and both different composite materials are represented in Figs. 4–6.

The SEM-EDX results of the raw mica show that the aluminum percentage is 24%. The silicon and potassium border 44% and 33%, respectively (Fig. 4).

These results correspond to the described chemical analysis of mica (Table 1) and have been obtained from different zones. The SEM-EDX results of P4VP5@mica composite material are represented in Fig. 7.

In the corresponding EDX, a significant reduction of the silicium weight percent from 44% to 39% is observed. This observation enables us to say that the 4VP polymerization on the mica by SiO$^-$/4VP$^+$ occurs due to electrostatic interactions. The diminution of the silicon weight percent is a consequence of the 4VP polymerization on the mica surface. The polymer cannot be detected by the EDX because the nitrogen, carbon, and hydrogen atom cannot be detected due to their low number of electrons (light atoms). For comparison, the SEM-EDX results of P4VP10@mica composite materials are also reported in Fig. 5.

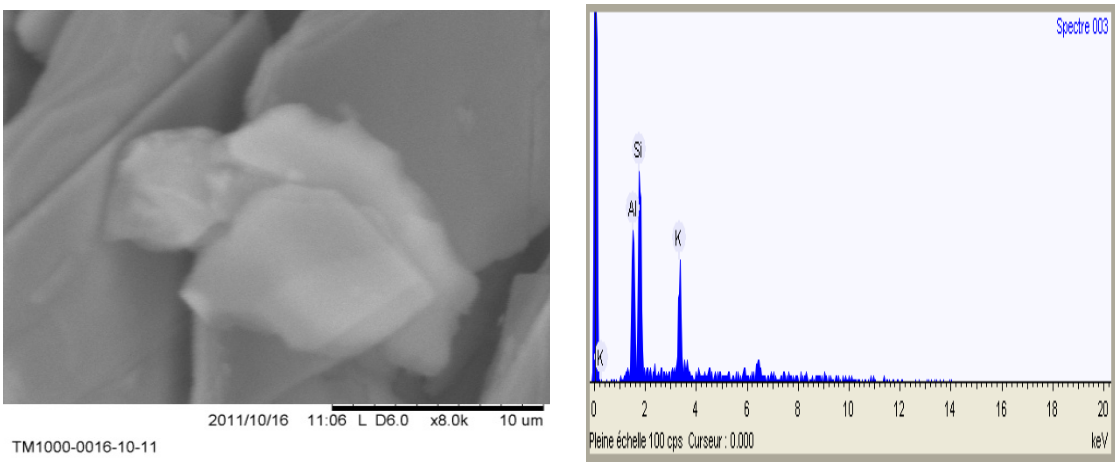


Fig. 4. SEM observations (left, scale bare = 10 μm) and EDX spectrum (right) of raw mica

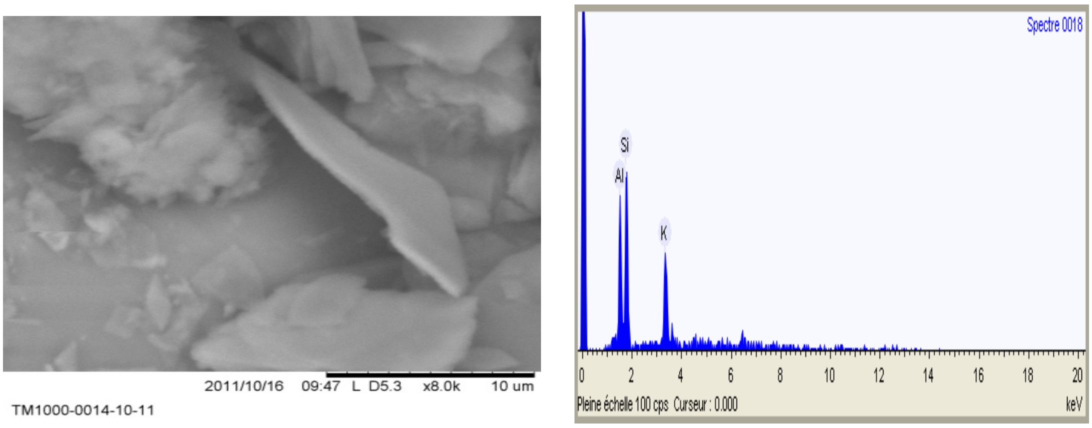


Fig.5. SEM observations (left, scale bare = 10 μm) and EDX spectrum (right) of P4VP5@mica

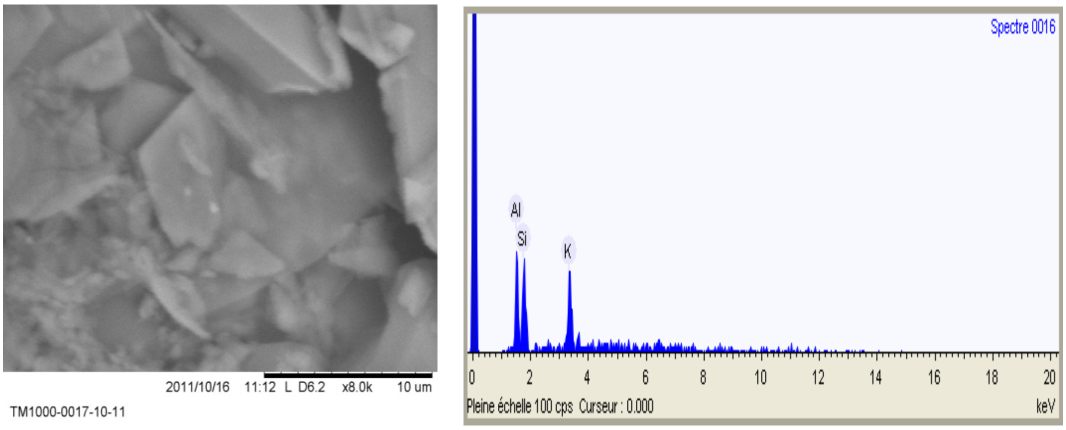
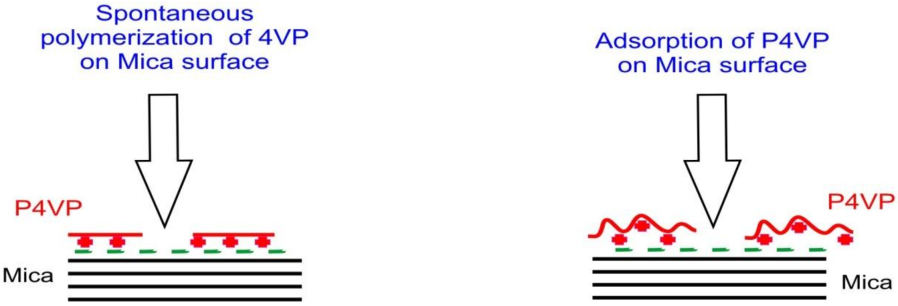


Fig. 6. SEM observations (left, scale bare = 10 μm) and EDX spectrum (right) of P4VP@Mica [R=10]

On the EDX spectra (Fig. 6 right) a significant and higher reduction of the silicon weight percent from 44% to 30% is observed. This observation enables us to say that the 4VP polymerization on the mica occurs due to SiOH bonds. The diminution of the silicium weight percent in this zone is a consequence of the polymerization on the mica surface. This observation enables us to conclude that the polyelectrolyte polymer is adsorbed on the mica surface by SiO^-

interactions. The higher decrease of the silicon weight percent is a consequence and evidence of the high coverage of the mica surface. Indeed, the final polymerized amount for P4VP10@mica is much higher than for the composite material [R=5], from 39 to 30% respectively, which confirms the TGA results as we previously claimed.

The comparison of the results obtained by FTIR and SEM-EDX, enables us to know the way in which polymerization surfaces occurred and of being able to compare it with the adsorption of polymer on mica surface. Scheme 2 summarizes the different possible cases:



Scheme 2. Spontaneous polymerization of the 4-vinylpyridine on the mica surface and the adsorption of the poly(4-vinyl pyridine) on the mica surface

4. Conclusions

In this study, we developed a spontaneous polymerization of 4-vinylpyridine on the mica surface. Hybrid materials of mica having a well-defined layer of poly(4-vinylpyridine) were prepared with two different ratios P4VP5@mica and P4VP10@mica.

The thermogravimetric analyses (TGA) enabled us to successfully determine the quantity of polymer adsorbed on the mica surface. The spontaneous polymerization of 4-vinylpyridine on the mica surface under precise conditions shows that the most visible losses of mass were observed for the samples of [4VP/mica] composite material R=10. The maximum achieved percentage of 0.42% out of P4VP polymer is very low and unsatisfactory, compared to the composite material obtained by adsorption of poly(4-vinylpyridine) on the mica surface, which showed a maximum of 0.6% for the composite material [P4VP/mica/R=0.5].

The FTIRSEM-EDX analyses confirm the presence of the polymer P4VP and the manner of its adsorption on the mica surface. We could decide between several possibilities.

The determination of the adsorption way of the polymer is very important for the aspect of the pigment materials and the fixing of the dyes. Quantitative and qualitative results demonstrate that it is possible to polymerize the 4-vinylpyridine by spontaneous polymerization on the mica surface. The next step will consist of the synthesis of a new pigment from the [4VP/Mica] composite material and will be presented in a forthcoming paper.

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СПОНТАННА ПОЛІМЕРИЗАЦІЯ МОНОМЕРУ 4-ВІНІЛПІРИДИНУ НА ПЛИСТАХ СЛЮДИ МІКРОННОГО РОЗМІРУ

Анотація. *У цій роботі повідомляється про спонтанну полімеризацію двох композитних матеріалів на основі P4VP і слюди у двох різних співвідношеннях: 4VP/ слюда/R=5 і 4VP/слюда/R=10, позначених як P4VP5@mica і P4VP10@mica відповідно. Отримані композити були охарактеризовані за допомогою термогравіметричного аналізу (TGA), інфрачервоної спектроскопії з перетворенням Фур'є (FTIR) і сканувальної електронної мікроскопії (SEM). Полімеризований P4VP на неорганічній поверхні має потенційний інтерес для модифікації міжфазних властивостей слюди.*

Ключові слова: *слюда, 4-вінілпіридин (4VP), спонтанна полімеризація, композит.*