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Characterization by Tga and Uv-visible of New Pigment Materials Containing Mica, P4VP and D&C Red 6 Dye

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The pigments and dyes industry must constantly develop new products with more innovative visual effects. Various industrial sectors such as cosmetics, textile fibers, painted paper and ceramics…etc, need new optical effects for their commercial products. The field of study of these pigments is vast and the market is in full expansion. Among the desired optical effects, manufacturers try to imitate nature by creating the appearance of increasingly sophisticated products: for example interferential compounds changing color and aspect under the effect of the light and according to angle. These effects can be achieved through the existence of highly ordered structures defined and organized within compounds to be developed. In our work, we succeeded in formulating new pigmentary materials by adsorption of polymer on mica particles and fixation of D&C Red 6 dyes on polymer. These new pigmentary materials can either differ by their colors, or to present interferential effects.

1. Introduction

Recently polymer-based inorganic/organic composites have been given more attention. For example, the study of polymer-silicate systems is a very active field of research in polymer and material science. (Heinz 2003).

The development of such materials aimed generally to improve the properties of polymers (Pinnavaia, 1994), such as mechanical behavior, thermal stability, and flame retardancy (Messersmith 1994), with or without exfoliation of silicate by polymers (Wang 2002).

The general purpose of the work presented here is the development of new organic/inorganic composites that are able to exhibit special visual aspects. Indeed, the control of color plays an important role in the conception of products and objects of daily life (cosmetics, tissues, painted papers, ceramics, etc.).

In this field, incorporation of dyes in a variety of materials has been already investigated in various systems such as membrane filters (Kost 1992), inorganic particles (Mansri 2009), clay and DNA (Sheppard 1943, Bunting 1989).

The visual aspect of materials is not simply limited to the classical effects of light absorption and reflection. The origin of such appearances is the existence of highly ordered structures in materials.

Industries are now looking for more sophisticated appearances to improve the impact of their products which may include iridescence or color changes with external factors such as temperature and moisture.

Basically, the pigments used in industrial applications can be divided into three groups according to their interaction with light: traditional pigments, metallic pigments, and pearlescent and interference pigments. Synthetic pearlescent pigments are either transparent or light-absorbing platelet shaped crystals.

They can be in multilayered structures in which the layers have different refractive indices and light absorption properties.

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 a chemically inert alumino-silicate mineral. Its

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crystalline structure consists of preliminary negatively charged 2:1 layers whose charges are compensated by interlayer cations [monovalent (Na^+, K^+, etc.) or divalent (Ca^{2+}, Mg^{2+}, etc.)]. (Brinks 2009)
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 (Parvole 2002 and 2003).
One of the important features of mica flakes is that they conserve their lamellar structure under different conditions. The elaboration of a multilayered composite by adsorption of the polymer from the mica surface, more precisely, adsorption of the P4VP on the Mica surface with different ratios (R) between Mica and P4VP (R=0.2 and R=0.5).
This composite material has been characterized by TGA, IRTF, ESEM, DSC and the stability of these materials were studied by conductimetry and potentimetry are presented in previous paper (Mansri 2012).
After formulation and characterization of this hybrid material, we succeeded in formulating new pigmentary materials by fixation of D&C Red 6 dyes on polymer.
These new pigmentary materials [P4VP/Mica/R=0.2/Red6] and [P4VP/Mica/R=0.5/ Red6] can either differ by their colors, or to present interferential effects. The latter step is presented in figure 1.
This paper describes the various methods used in each of the previously listed steps as well as the chemical characterization of the composites obtained using complementary techniques [Thermogravimetric analysis (TGA), UV-Visible]. The amount of D&C Red 6 dye fixed on the hybrid materials [P4VP/Mica] is determined by TGA. The presence and the shape of the dye fixed on hybrid materials [P4VP/Mica] are determined by UV-VISIBLE.

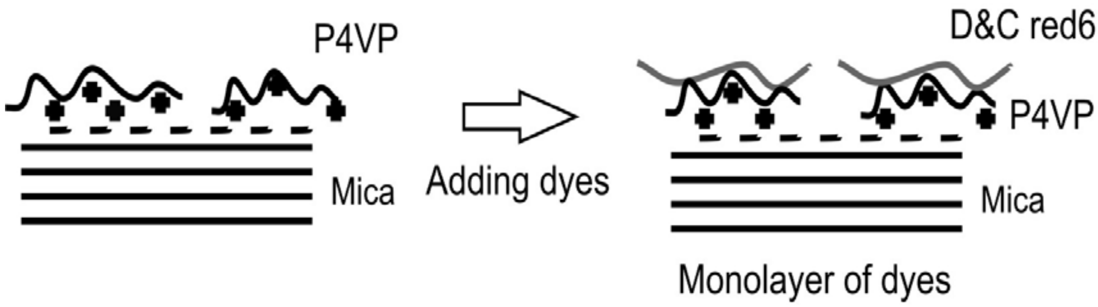

Figure 1: Concept of fixation of D&C Red6 dye on hybrid material [P4VP/Mica]

2. Experimental Section

2.1 Materials

Mica Software® was supplied by "*Le Comptoire des Minéraux et des Matières Premières*" and its characteristics are presented on Table 1.
Poly(4-vinylpyridine) were supplied by Aldrich Company. The choice of this polymer was established considering the following conditions:
- The P4VP molecular weight is chosen to facilitate polymer thin layer adsorption on the mica surface.
- The P4VP with its nitrogen groups is able to act with the Mica surface. The P4VP can undergo quaternization reaction and thus, it can theoretically fix on the surface of the mica.
- The P4VP is a polymer which can be transformed easily and it is very much used in many applications (Brinks 2009, Parvole 2002 and 2003). Thus, we try to formulate new composites by combining the P4VP and mica properties.

The dye chosen for this study is D&C red6 because it has a great application in cosmetics.

3. Results and discussion

3.1 Thermogravimetric "TGA" weight loss measurements

Thermal stability of D&C Red6 dye fixed on the [P4VP/Mica] materials has been studied in the temperature range between 20 and 850 °C under air.
A thermogravimetric analysis is made using the apparatus TA instrument "TGA Q50". The thermogravimetric curves obtained for D&C Red6 dye are represented in figure 2.
The results of the thermogravimetric analyses show that the most important losses of mass are observed for the samples of [P4VP/mica/Red6] composite material R=0.5.

The maximum reached is 8 % out of D&C Red6 dye fixed dye, as shown in the figure 2.
The sample of [P4VP/mica/Red6] composite material R=0.2 shows a weight loss which is 2.80% out of dye, as shown in figure 2.
Thermogravimetric measurements show that the D&C Red6 dye is more visible in the sample [P4VP/mica] composite material R=0.5 than for the sample [P4VP/mica] composite material R=0.2 which shows an amount of 8 % in D&C Red6 dye. The results obtained by TGA (heating weight loss) for the various tests are reported in table 2.

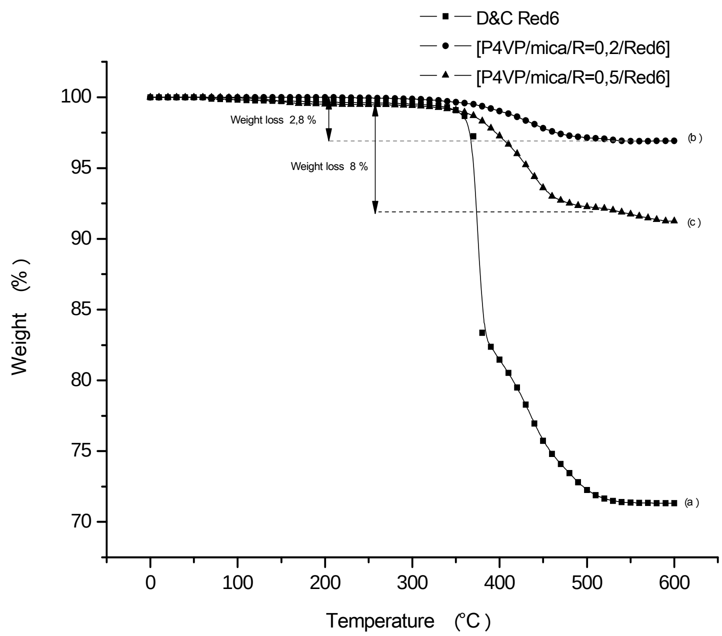

Figure 2: Thermograms: (a) D&C Red6, (b) [P4VP/Mica/R=0.2/Red6], (c) [P4VP/Mica/R=0.5/Red6]

Table 1: Physicochemical characteristics of the mica

Physical properties	heading 2
Density (g/cm^3)	2,80
pH (in water)	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 %

Table 2: Results of the thermogravimetric analysis

	[P4VP/Mica/R=0.2/Red6]	[P4VP/Mica/R=0.5/Red6]
Weight loss (%)	2.80%	8.00 %

3.2 UV-vis Spectroscopy characterization

The presence and the shape of the D&C Red 6 dye fixed on hybrid materials [P4VP/Mica] are determined by UV-VISIBLE measurements. UV-visible spectra were recorded using a Shimadzu UV-2101 PC spectrometer.

The comparison of ultraviolet-visible (UV-vis) absorption spectra of D&C Red 6 dye, [P4VP/Mica/Red6] pigment with two ratios R=0.2 and R=0.5, represented in figure 3, shows that the absorption band at 436 nm and 540 nm.

Moreover, in these partially conjugated systems, we are most likely to observe the changes that arise from the modification of the whole extended electronic system and not merely from localized changes. This demonstrates qualitatively that modification was successfully made.

The comparison of ultraviolet-visible (UV-vis) absorption spectra of D&C Red 6 dye between the solid form represented in figure 3 and the liquid form represented in figure 4, shows that the absorption band at 310 nm and 480 nm (liquid form) shifts to 436 nm and 540 nm.

The form of D&C Red 6 dye fixed on the [P4VP/Mica] surface is different from the form present in solution; therefore there is an interaction which exists between the forms D&C Red 6 dye and [P4VP/Mica] composite materials.

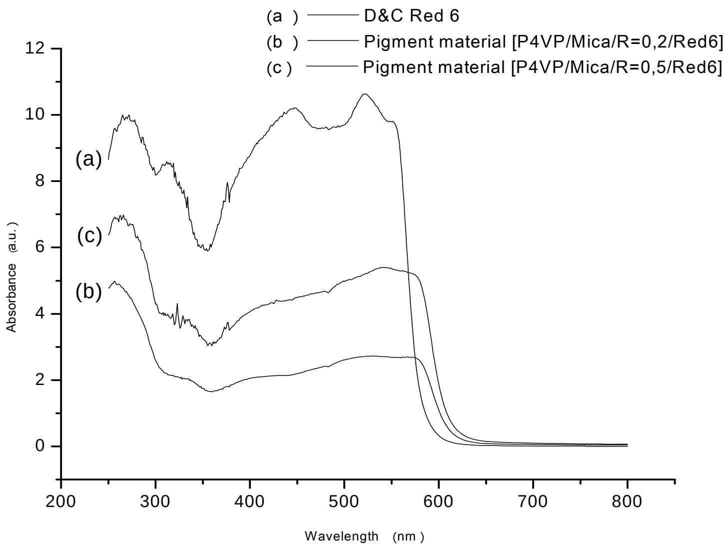

Figure 3: UV-vis spectra of: (a) D&C Red6, (b) [P4VP/Mica/R=0.2/Red6], (c) [P4VP/Mica/R=0.5/Red6]

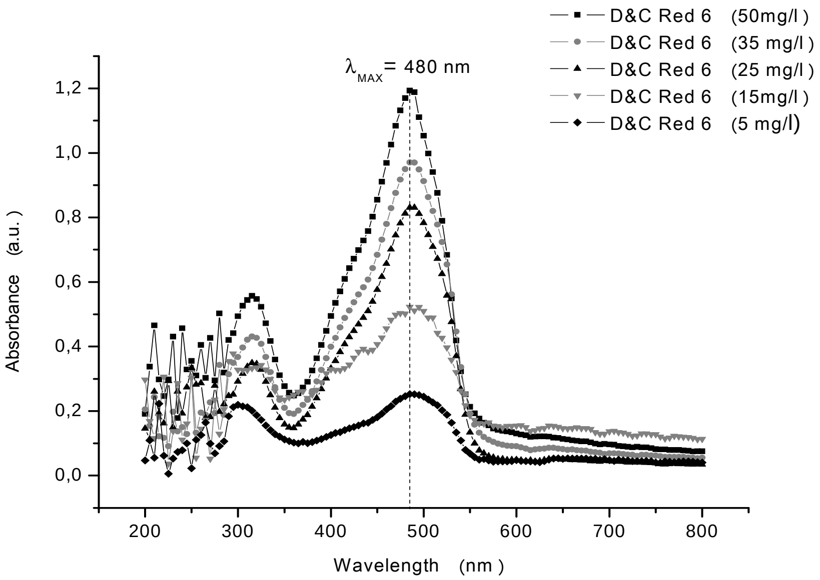

Figure 4: UV-vis spectra of D&C Red6 solution at different concentrations

Conclusion

This paper describes a relatively simple method for characterization of new pigmentary materials containing Mica, poly(4-vinylpyridine) and D&C Red 6 dye.
We show that the color of mica is changed upon polymer adsorption, and when one of the copolymer sequences includes a dye, its color is influenced by the chemical properties of the mica surface.
However, these new pigment types do not exhibit, at least visually, interferential effects. Neither the choice of the polymer nor the thickness of each sequence was optimized to produce such effects.
From the general pathways described in this paper, it may be possible to obtain a monitoring of the visual aspect of these pigments via selected experimental conditions.

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