

## **POLYBENZIDINE-MONTMORILLONITE NANOCOMPOSITES: SYNTHESIS VIA A MECHANOCHEMICAL INTERCALATION METHOD**

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### **1. Introduction**

In the last years, solid-solid reactions have attracted much attention owing to their ease of operation when compared to the liquid medium. In addition, this process offers the possibility to save time and to be a clean way to prepare solids not easy to get through the classical method using solutions [1-2]. Solid-solid reaction can be also applied to prepare different hybrid materials. In this field, it is well known that the smectite group of clay minerals constitutes a suitable host to shelter various organic molecules in their interlayer space [3–6]. Therefore, interactions that may occur between the clay and organic molecules are capable of generating new classes of hybrid materials [4–9].

The structure of the smectite group of clay minerals consists of octahedral sheets of  $\text{MO}_4(\text{OH})_2$  sandwiched between two tetrahedral sheets, giving then, a T:O:T layered crystalline mineral. The octahedral sites are usually occupied by Al, Mg or Fe, while the tetrahedral ones by Si. The partial substitution of  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  that can occur respectively in the tetrahedral layer and the octahedral one by less charged cations leads to an excess of the negative charge which is neutralized by the presence of exchangeable cations in the interlayer space.

A staining effect produced when diamines interact with the clays was extensively studied in the literature [3–7]. The characteristic blue colour produced when benzidine (BZ) is adsorbed and oxidized by the clay evidences this staining effect. These blue species were assigned to the semiquinone radical cation of benzidine ( $\text{BZ}^{\cdot+}$ ) formed through an electron transfer between BZ and  $\text{Fe}^{3+}$  ions occupying the octahedral sites of the clay mineral [6], or through a catalytic action of the atmospheric oxygen adsorbed on the aluminium atoms on the crystal edges [6, 9].

Polymerization of benzidine can occur in confined systems -in the nanospace of the clay interlayers [8] usually by the addition of an initiator, which gives raise to a hybrid polymer-clay nanocomposite. Interesting properties and applications for these materials could be obtained. In fact, the most important interest in the synthesis of new polymers lies essentially in the possibility of enhancing the conductivity of the bulk polymer. Polybenzidine-clay nanocomposites are usually prepared through a liquid medium by mixing a solution of benzidine and the polymerization initiator with the clay suspension. Our interest in this work is to explore the possibility of the preparation of benzidine-clay and polybenzidine-clay hybrid materials via a solid-solid reaction. The synthesized samples were characterized by XRD, UV-vis and DSC. Conductivity determination was also performed. To our knowledge, this work is the first attempt for preparing polybenzidine-clay nanocomposites with such a way using the mechanochemical intercalation method.

### **2. Experimental**

#### **2.1. Preparation of benzidine –Montmorillonite samples**

The clay used in the present work is a Tunisian smectite, having a cation exchange capacity (CEC) of 100 mEq /100 g of clay and a surface area of 80  $\text{m}^2/\text{g}$ . This montmorillonite was saturated with sodium. The intercalation of benzidine (Fluka) in the interlayer space of the clay was achieved via a solid-solid reaction, by grinding the clay with variable amounts of benzidine during 7 minutes. The amounts of benzidine ranged from 1 to 5 mmol/g of clay. The samples obtained were labelled as A-B a-b where A is the clay, B is Benzidine and a-b is the clay-benzidine ratio.

The sample A-B 1-0 corresponds to the purified clay and A-B 0-1 to benzidine.

#### **2.2. Preparation of the polybenzidine –Montmorillonite samples**

Polymerization of benzidine in the interlayer space of the clay was performed by grinding during 7 minutes, the clay, the adequate amount of benzidine to have 3 mmol/g of clay together with a polymerization

reagent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Fluka). The molar ratio benzidine to ammonium persulfate called R was fixed to 1. This sample was labelled as A-B 1-3I1.

As a reference and to synthesize polybenzidine via a solid-solid reaction, a sample using only ammonium persulfate and benzidine with a molar ratio  $R=1$  was prepared in the same way. The latter, was labeled I-B 1-1.

### 2.3. Characterization of the samples

XRD powder patterns were recorded on a PANalytical X'Pert High Score Plus equipment, using  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in the  $10\text{--}80^\circ$   $2\theta$  angle range.

The UV visible spectra were obtained using a Beckman Du<sup>®</sup> 530 instrument.

The differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC 821 equipment. The heating rate was  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

Conductivity determinations were performed using a HP 4192 A/LF impedance analyser in the 0.1 KHz-13 MHz frequency range. The sample was pressed into a pellet using a pressure of 5 tons with a 12.8 mm diameter and 1.2 mm thickness.

## 3. Results and discussion

### 3.1. Intercalation of BZ in the interlayer space of the clay

#### 3.1.1. XRD

The different samples obtained through mechanical grinding of the clay with the various amounts of benzidine showed an evolution of their colour with the grinding time. At the end of this step, blue mixtures were observed indicating the formation of  $\text{BZ}^+$  species and then the existence of an interaction between the clay layers and the benzidine molecule. This result corroborates with those reported in the literature [8] and is confirmed by the XRD study. In fact, Figure 1 illustrates the diffractogram patterns corresponding to the purified clay with those of the studied samples. As shown on this figure, for the purified clay the basal distance of the  $d_{001}$  is  $14.6 \text{ \AA}$ . This distance corresponds to a montmorillonite with two water layers adsorbed in the interlayer space of the clay. Nevertheless, when benzidine is introduced the value of the basal spacing changes compared to that of the purified clay. This result indicates the successful intercalation of benzidine between the clay layers-probably through water removal- proceeded via a mechanochemical method. In the literature [2], a similar procedure was reported for the intercalation of aniline within the clay layers and on the basis of the XRD data the authors have concluded that intercalation of aniline was successfully performed. Therefore, in our case, depending on the amount of benzidine introduced, the interlayer spacing recorded for the hybrid materials ranges between  $3.3$  and  $3.8 \text{ \AA}$ . These values were obtained by subtracting the thickness of an individual layer of montmorillonite ( $9.6 \text{ \AA}$ ) from the basal spacing. When compared to the purified clay, the decrease of this interlayer distance may suggest that benzidine molecules intercalate with a monolayer arrangement parallel to the plan of the clay layers. This hypothesis is in a good agreement with what was reported by Slade et al. [3], concerning the effect of the steric parameters in the establishment of interactions between benzidine and the silicate sheets of the montmorillonite clay. In such systems, it was concluded [3] that the C-N bonds of the organic cations are parallel to the surface of the silicate sheets and that the  $\text{NH}_2$  groups are located over oxygen ions. Such a conformation leads to a low basal spacing. Comparable 001 spacing to our values were also found by Lahav and Anderson [5], who explained that for low surface concentrations, the benzidine molecules lie in such a way to present their minimum thickness, in this case, the  $d_{001}$  spacing was  $12.5 \text{ \AA}$ .

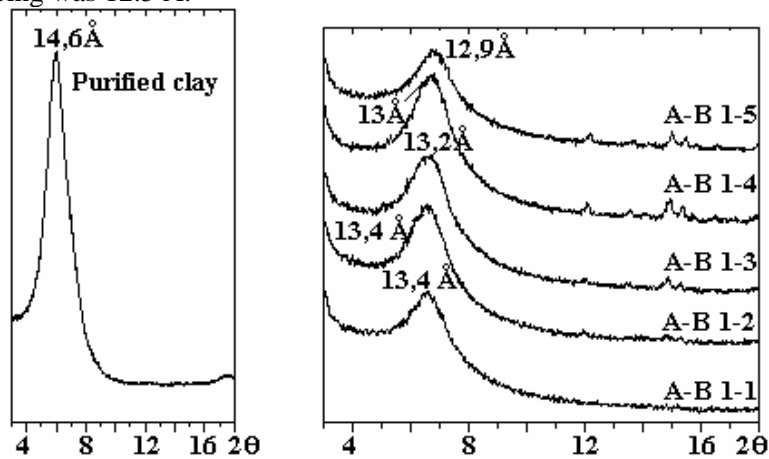


Fig. 1. XRD patterns of the purified clay and the studied hybrids

In our conditions and on the basis of literature data, it seems then, that this preparation method allowed the establishment of a reaction between the clay and the benzidine molecules.

### 3.1.2. UV vis

Figure 2 shows the UV-vis absorption spectra of the purified clay, benzidine and the hybrid samples. A weak absorption band at 600 nm is observed for the hybrid samples and is absent on the spectrum of pure benzidine. According to the literature [6] this band is assigned to the  $BZ^+$  species. This blue radical cation is formed through the oxidation of benzidine adsorbed on the clay surface [6-7] and was already evidenced by the blue colour observed by eye inspection during the grinding procedure. This result corroborates also with the XRD data and proves the existence of an interaction between the clay and benzidine occurring via a solid-solid reaction.

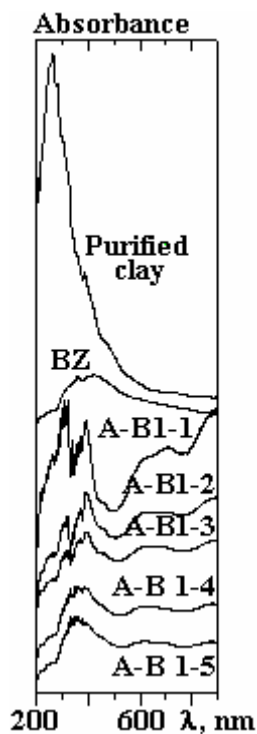


Fig. 2. UVvis spectra of the purified clay, benzidine and the studied hybrids

### 3.1.3. Differential Scanning Calorimetry (DSC)

The results of the DSC measurements recorded for the purified clay, pure benzidine and the hybrid solids are shown on Figure 3. An endothermic event centred on 100 °C and corresponding to the removal of adsorbed water is observed for the purified clay. This event does not exist on the thermograms of the hybrid solids. It seems then, that the intercalation of benzidine in the interlayer spacing of the clay occurs simultaneously with the water departure, which is in a good agreement with the hypothesis expressed above.

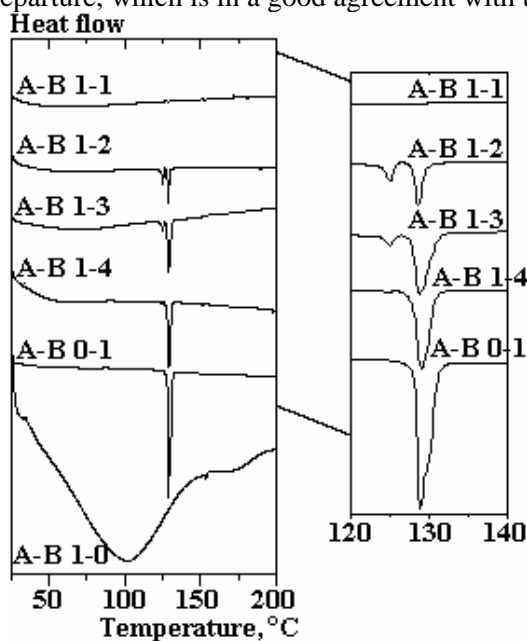


Fig. 3. DSC thermograms of the hybrid solids, benzidine and the purified clay

When the amount of benzidine increases from 2 to 4 for the hybrid solids, an endothermic pick is observed at around 129 °C. This temperature corresponds to the melting point of benzidine. However, for the solid A-B 1-1, no significant pick was observed, which could be explained by the low amount of benzidine. Furthermore, another endothermic pick centred at 125 °C is observed for the hybrid solids. The intensity of this pick decreases when the amount of benzidine increases, simultaneously, to the appearance of a shoulder at 130 °C for sample A-B 1-3. It seems then, that the amount of benzidine and the presence of the clay affect deeply the melting point of benzidine and favours the formation of a new crystallographic phase having a melting point of 125 °C. In the literature, several works were investigated concerning the crystal chemistry of benzidine. In fact, Rafilovich et al. [10] reported the existence of more than one melting point for benzidine, which were attributed by the authors to the different crystallographic forms of benzidine.

### 3.2. Polymerization of BZ in the interlayer space of the clay

In the literature, polymerization of benzidine has been studied by Kumar et al. [11] who presented three different types of polymers obtained for benzidine. Other works [6, 8] investigated the polymerization of benzidine in the interlayer space of the clay. These authors characterized the obtained polymers using Raman spectroscopy and XANES to propose the type of coupling reactions favoured to synthesize free and confined polybenzidine.

In the present work and as mentioned in the experimental section, polymerization of benzidine between the clay layers was studied for the sample obtained through a solid-solid reaction and prepared with 3 mmol of benzidine/g of clay, by addition of a polymerization reagent. It is worth noting, that for this ratio, three crystallographic phases of benzidine exist simultaneously and were already evidenced by the DSC study.

#### 3.2.1. UV-vis

Figure 4 shows the UV-vis absorption spectra of the purified clay, benzidine and the hybrid samples A-B 1-3 and A-B 1-3I1. The presence of the polymerization initiator (sample A-B 1-3I1) induces an increase of the intensity of the band at 600 nm attributed to the  $BZ^+$  radical cation, when compared to the same sample prepared without initiator A-B 1-3. In fact, during the preparation of A-B 1-3I1, an intensification of the blue colour was also observed when the reagents were ground. The enhancement of this band could be explained by an increase of the amount of  $BZ^+$  species which could facilitate polymerization. In fact, using *in situ* resonance Raman spectroscopy do Nascimento et al. [6] found that the increase of the  $BZ^+$  coloured species makes easier the polymerization process.

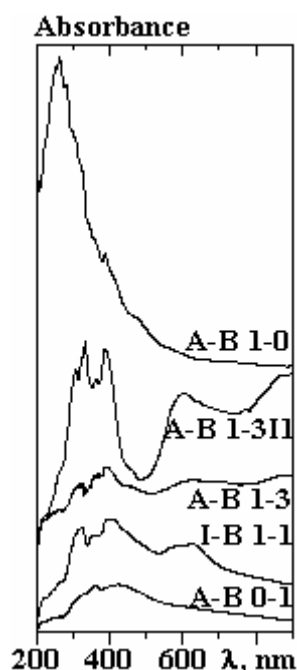


Fig. 4. UV-vis spectra of the purified clay, benzidine and the studied hybrids

#### 3.2.2. DRX

As shown on Figure 5, the basal distance of the  $d_{001}$  for sample A-B 1-3I1 is 15 Å. This means that considering a layer clay thickness of 9.6 Å, the interlayer space height's will be of 5.4 Å, while those of the purified clay and A-B 1-3 were 5 and 3.8 Å, respectively. These results indicate the intercalation between the

layers of the clay -for sample A-B 1-3I1- of new species, different from those observed in the case of A-B 1-3. These species correspond probably to polybenzidine formed between the clay layers. It seems then, that when a polymerization reagent is used a reaction has occurred in a solid state owing to the grinding step. This result is in a good agreement with what was found earlier using the UV-vis technique. In fact, an important amount of the  $BZ^+$  radical cations implies the formation of polybenzidine species and proves that the corresponding reaction is possible through a mechanochemical process.

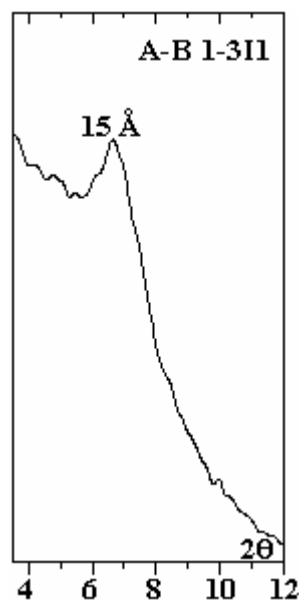


Fig. 5. XRD patterns of sample A-B 1-3I1

### 3.2.3. Differential Scanning Calorimetry (DSC)

The DSC thermograms of samples A-B 1-3I1 and I-B 1-1 are plotted on Figure 6. Details in the region 210-250 °C are displayed on the right. For the latter sample, many thermic events are observed indicating the presence of more than one polymer or different crystalline and amorphous phases within the sample. For this sample (I-B 1-1), an exothermic pick centred around 200 °C and an endothermic one at 230 °C are observed. These picks may correspond respectively to the crystallization and the melting point of a first type of polymer (P1) contained in the sample. A shoulder observed at 300 °C could be attributed to a glass transition of an amorphous polymer (P2). However, the endothermic event at 340 °C could be assigned to the melting point of a third polymer (P3). Therefore, as the melting point of pure benzidine is situated between 125 and 129 °C and on the basis of the different thermic events obtained above, polymerization of benzidine is confirmed.

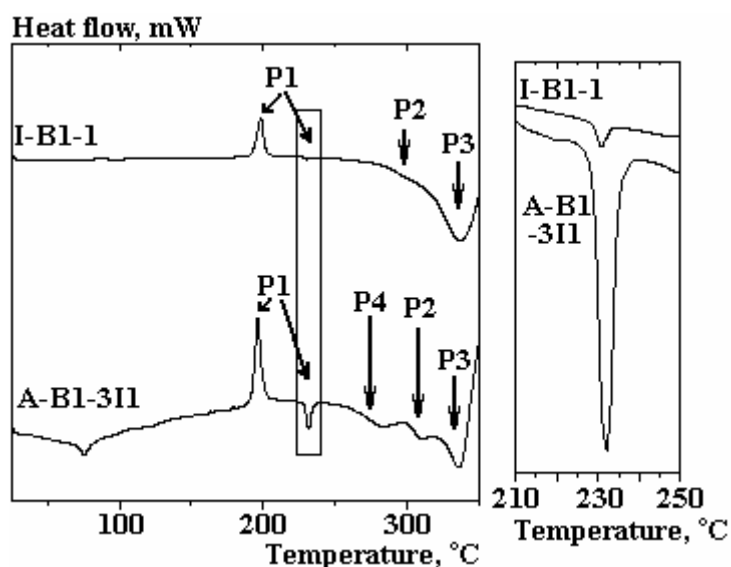


Fig. 6. DSC thermograms of samples A-B 1-3I1 and I-B 1-1

The same peaks are observed on the thermogram of A-B 1-3I1, indicating the formation of the same polymers (P1, P2 and P3). In addition to these ones, another event at 270 °C is also observed corresponding to a glass transition phase of another type of polymer (P4). These findings show that, firstly, polymerization of benzidine has occurred in the presence of the clay, via a solid-solid reaction. Moreover, on the basis of the XRD data, one can conclude, that the polymerization reaction took place in the interlayer space of the clay. On the other hand, the clay seems to favour the formation of a new type of polymer (P4) which does not exist in the clay-free polybenzidine sample.

#### 3.2.4. Electrical conductivity

The conductivity values recorded at room temperature for I-B 1-1 and A-B1-3I1 are  $5.5 \times 10^{-8} \text{ S.cm}^{-1}$  and  $1.6 \times 10^{-6} \text{ S.cm}^{-1}$ , respectively. Then, it is clearly seen that, when polybenzidine is formed in a confined environment, its conductivity is enhanced which could be related to the formation of the polymer P4, absent in the sample I-B 1-1. Even if this value of the conductivity reported here for A-B 1-3I1 remains lower than those reported in the literature [8] for polybenzidine ( $10^{-4} \text{ S.cm}^{-1}$ ) prepared through a liquid medium, these results suggest that this preparation method of the polybenzidine-montmorillonite hybrid materials is as promising as the conventional synthesis. Furthermore, the improvement of the control of the formed polymers, through the optimization of the preparation parameters, could offer the opportunity to increase the conductivity of these solids. Consequently, the mechanochemical intercalation process might be more interesting, in this case, than the classical method using solutions.

#### 4. Conclusion

Benzidine-clay and polybenzidine-clay hybrid samples were synthesized via a solid-solid reaction. The amount of benzidine was varied to study the effect of this parameter on the intercalation process. The XRD technique confirmed the incorporation of BZ in the nanospace of the clay and showed that BZ molecules intercalate with a monolayer arrangement parallel to the plan of the clay layers. The presence of the clay induces the formation of, at least, three crystallographic phases of benzidine evidenced by their different melting points in the DSC measurement. The UV-vis results revealed the increase of the amount of  $\text{BZ}^+$  species formed through the oxidation of benzidine adsorbed on the clay layers, which could facilitate polymerization. The XRD study confirmed that polymerization of benzidine in the interlayer space occurred by the mechanochemical method. The DSC study showed that when polymerization took place in a confined environment, the formation of a new type of polymer which does not exist in the clay-free polybenzidine sample seems to be favoured. This one, is probably responsible for the enhancement of the electrical conductivity. The mechanochemical process used for the synthesis of polybenzidine-montmorillonite samples is as promising as the conventional method.

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*Received 10.03.10*

### **Summary**

A new and clean preparation method of Polybenzidine-montmorillonite conducting nanocomposites is reported in this paper. Solid-solid reaction was successfully used to synthesize these hybrid materials by grinding mixtures of various amounts of benzidine (BZ) and sodium montmorillonite. The characterization techniques confirmed the incorporation of BZ in the nanospace of the clay and showed that BZ molecules intercalate with a monolayer arrangement parallel to the plan of the clay layers. The amount of BZ and the presence of the clay affect deeply the melting point of benzidine and favour the formation of new crystallographic phases. Polymerization of benzidine between the clay layers was performed using the same method by adding ammonium peroxodisulfate. The formation of four types of polymers in the interlayer space of the clay was pointed out. One of them is probably responsible for the enhancement of the conductivity when compared to the clay-free polybenzidine sample.

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