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ORIGINAL PAPER

Solid state polymerization and intercalation of aniline in Fe rich montmorillonite

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Abstract Hybrid compounds formed by aniline as the organic phase and Fe rich montmorillonite have been prepared by conventional solution process and a novel solid state intercalation method reported recently in the literature. The structure of hybrids depends closely on the process of preparation. In fact, contrary to conventional solution intercalation method, solid solid reaction favours the intercalation of anilinium cations together with aniline chloride neutral species. In addition, aniline species intercalated by this method are able to polymerize in the interlayer space of clay after 9 weeks without the use of any initiator of polymerization, however, the structure of hybrid compounds prepared by conventional solution method did not change. The aging time is accompanied by the reduction of structural Fe(III) to Fe(II) for hybrids prepared by solid reaction. The structure and electrical properties of the obtained polyaniline/clay nanocomposites have been studied. It was shown that ac conduction shows a regime of constant dc conductivity at low frequencies and a crossover to a frequency-dependent regime of the type A ω^S at high frequencies.

Keywords Aniline · Montmorillonite · Solution intercalation · Solid-solid reaction · Polyaniline · Aging time

Introduction

The preparation of polymer-clay nanocomposite is an important target of modern materials research. The purpose behind such research is to develop functional materials. The smectite group, which includes montmorillonite, has enjoyed wide attention due to its interesting adsorptive/intercalation and cation-exchange properties. Organoclay and nanocomposites have received widespread attention in a number of industrial sectors including waste treatment catalysis, and corrosion protection [1–3]. The process often used for the preparation of organoclay is an intercalation into the clay in solution state. This route is based on a solvent system in which the guest is soluble and host is swellable. Hence, this system has limit because a compatible solvent system of guest and host is not always available. A process, which is not used very frequently and which allows the possibility of preparing of compounds which are not accessible from solutions [4], is the so-called solid-solid reaction. The latter is a mechanochemical adsorption that occurs between powders in the solid state [5]. Solid-state intercalation of organic guest species into layered vanadium phosphorus oxide [6], zeolites [7], and layered clay minerals [8–10] has been reported as a way of utilizing host structures. Solid-state intercalation can be split into two stages one is the diffusion of guest species from the outer surfaces of guest solids and the other is the penetration of the guest species into the interlayer spaces. In addition, we have reported [11, 12] the solid state intercalation of 2-mercaptopyridine into Na, Al and Co-montmorilonite. We have also demonstrated that the configuration and the structure adopted by these intercalated guest organic species in the interlayer of clay minerals differed from that obtained by conventional solution methods. This is assumed to be caused by the change of the clay structure under fine grinding. Moreover, we have studied [13] the effects of grinding on the physico-chemical of montmorillonite. Our study has shown that grinding could liberate metallic cations from octahedral layers of the clay mineral, especially Mg

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and Fe cations. We propose that these structural changes have an influence on the structure and the properties of organic species intercalated by solid-solid reaction. Moreover, as far as we know, these factors have been till now neglected and marginalized by all authors dealing with solid state intercalation method. In the present study, our primary attention was paid to study the effect of these factors on of the intercalation of aniline species and on its in situ polymerization.

Experimental

Synthesis and reagents

Natural montmorillonite (MMT) was obtained from Zaghouan region in Northeastern Tunisia. The < 2 μm fraction was separated by gravity sedimentation method. The < 2 μm material was sodium saturated by exchange with sodium chloride, centrifuged to remove excess NaCl, and dried. The presence of smectite was confirmed by the d_{001} spacing of the sample after air drying, calcination at 600°C for 2 h and glycol treatment. By means of lithium test it was found that it constitutes essentially of montmorillonite. The chemical composition of the montmorillonite was found to be as follows: 50.1 % SiO_2, 3.95% MgO, 17.4 % Al_2O_3, 0.2% K_2O, 0.08% CaO, 1.5 %Na_2O, 6.3 % Fe_2O_3 and 20.4 % loss on ignition. The cation-exchange capacity (CEC) of the clay is 90 meq per 100 g of dry clay. Aniline chloride (Ani-Cl) was purchased from Aldrich. The intercalation of Ani-Cl into MMT in solid state was achieved by grinding the host and the guest at room temperature for 12 min. The molar rate of Ani to the interlayer Na cations was varied from 1:1 to 5:1. Intercalation of aniline by conventional solution method has been done by dispersion montmorillonite in aqueous solution and subsequently aniline salt was added into the dispersed solution. The mixture was stirred vigorously for 2 h and then it was washed and filtrated. Hereafter, hybrid compounds prepared by solution method are denoted Ani/MMT_n(solut), and that by solid-solid reaction by Ani/MMT_n(solid) where n represents the molar rate of aniline to interlayer Na^+ cations

Instruments

Ani/MMT hybrid compounds were characterized via XRD, FTIR, TGA, and impedance spectroscopy. XRD patterns were obtained using Panalytical diffractometer using Cu radiation. Specific surface area was measured using an automatic adsorption instrument (Autosorb I). Thermogravimetry analysis was performed using a Setaram instrument at a heating rate of 10°C/min in an air atmosphere. The IR spectra were recorded in KBr pellets. The electrical conductivity of different samples were prepared as pellet form under a pressure of 10 Mg/cm^2 and coated on both sides with silver paint. Electrical conductivity measurements are carried were made using a Hewlett Packard model 4192A impedance analyser in the 0.01 kHz–10 MHz frequency range.

Results and discussion

The effect of grinding on structure of montmorillonite and a mixture of montmorillonite with Ani-Cl

We have studied in our previous work the effect of the manually grinding on the structure of 250 mg of clay [13]. We have demonstrated that for a period of treatment below 10 min, the grinding process has for effect the amelioration of adsorption properties of the clay and it did not significantly alter the chemical structure of MMT. However for a period above 10 min, particles are stuck one to another which reduce the cation exchange capacity and the surface area. As can be seen from Table 1. The cation exchange capacity (CEC) and the specific surface area increased respectively from 90 meq/100 g of clay and 80 m^2/g to 103 meq/100 g of clay and 190 m^2/g after 10 min of grinding, after that, the surface area and the CEC decreased.

Simultaneously, a decrease and broadening of the XRD spectrum peaks were also detected, indicating a reduction of crystallinity. In addition, the intensity of the $AlFe_3^+OH$ band localised at 917 cm^{-1} decreased, which proves that deformation mainly disrupted the octahedral sheet and preferentially destroyed those sites occupied by Fe cations. To see if these effects are even pronounced in the presence of Ani-Cl we have studied by XRD the crystalline structure of MMT grinded alone and in mixture with aniline chloride with a molar rate of aniline to interlayer Na cations corresponding to 3. We have presented the (001) and (060) peaks in Fig. 1a, b and c. It can be seen a significant broadening and decrease of (001) and (060) peaks with increasing grinding time of montmorillonite indicating a progressive reduction of structural order.

The loss of intensity of the (001) peak indicates that the stacking of the layers gets disrupted. After 20 min grinding of it was impossible to calculate the d_{001} and d_{060} values as complete destruction of montmorillonite layers occurred. This observation supports previous works [14, 15]. Comparing the (060) peak of montmorillonite grinded with aniline chloride to that treated alone, it can be established that both treatment induce decrease and broadening of the intensity of (060) peak. These results show that crystallinity of montmorillonite is affected by the same way in the presence or not of aniline chloride.

Table 1 Cation exchange capacity of MMT grinded at different periods

Period of grinding (min)	0	2	5	7	10	15	20
CEC (meq/100 g)	90	92	98	100	103	95	85
Surface area (m^2/g)	80	123.8	135	150	190	90	50

Consequently, the destruction of the clay structure is commonly followed by chemical analysis. To determine the proportion of Fe species liberated from MMT and its mixture with Ani-Cl under grinding treatment we have immersed the grinded materials in distilled water and we have kept stirring for 72 h and then detected the iron content of the centrifugal residual liquid by Atomic Absorption (AAS VARIO). Figure 2 shows the mass percentage of the amounts of Fe^{3+} released from grinded montmorillonite and its mixture with Ani-Cl. It can be observed that Fe ions are more extracted from octahedral layers of grinded MMT than from MMT grinded with Ani-Cl compound. After 10 min of grinding the percentage of released Fe ions attains respectively 7% for MMT and 2% for a mixture of MMT with Ani-Cl.

Characterization of Ani/MMT hybrid compound after synthesis

Figure 3 shows the XRD patterns of Ani/MMT hybrid compounds prepared by solid-solid reaction for n within 1 to 5 together with that prepared by solution method for n corresponding to 4. It can be seen that from all samples the d_{001} basal spacing has shifted toward higher value after adding of Ani-Cl which proved the successful intercalation of aniline within the clay layers. However, the basal spacing d_{001} has changed its position depending on the molar rate of aniline chloride to interlayer sodium and depending on the process of intercalation. For hybrids prepared by conventional solution method, we have observed a d_{001} basal spacing varying from 14 to 14.6 Å and it did not exceeding these values even after a molar rate of Ani to interlayer cations corresponding to 5. Taking into account the thickness of the silicate layer (about 9.6 Å), an expansion of clay interlayer varying from 4.4 to 5.4 Å was obtained for these hybrid materials. These values correspond to intercalated species that exist in the interlayer spaces with their aromatic rings perpendicular or inclined to the silicate sheet [16]. The same expansion is observed for Ani/MMT_1 and Ani/MMT_2 hybrid compounds prepared by solid-solid reaction. However, with the increasing of Ani cations. The basal spacing of the product greatly increased to attain 25 Å which corresponding to an interlayer expansion of 15.4 Å. Thus larger quantity of aniline species has been intercalated in the interlayer spaces of MMT. This observation has been already reported by Yoshimoto and co-workers [17] for aniline sulphate. The authors suggested the existence of two species; neutral species (aniline sulphate) and anilinium cations. Thus we propose the following configuration of aniline species in the clay interlayer and which is represented in Fig. 4.

Figure 5 presented the FTIR spectra of Ani/MMT hybrid material together with that of MMT and Table 2 summarized their frequencies and assignment of vibration modes. The identification of vibration modes of aniline has been assigned referring to the literature [18].

The IR spectrum of MMT showed the following bands; ν_{OH} of H_2O ~ 3,446 cm^{-1} ; and δ_{OH} at 1,643 cm^{-1}). The bands at 1,038 cm^{-1} is assigned to Si-O stretching vibration

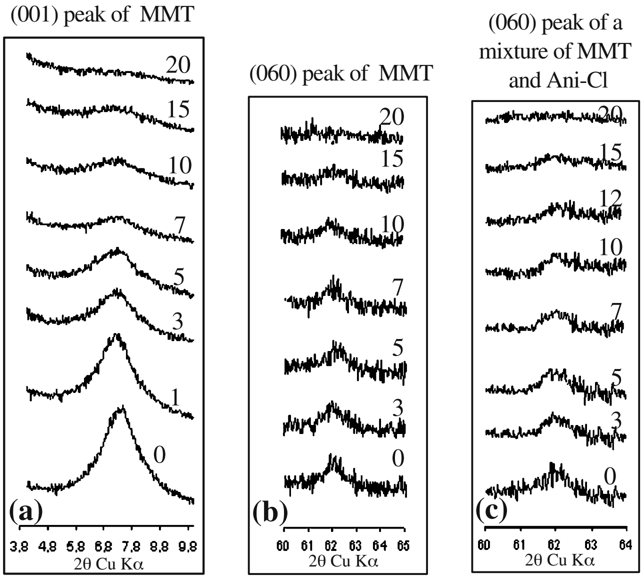

Fig. 1 Comparison between XRD spectra before and after grinding treatment (3–20 min) of: **a** (001) basal peak of MMT, **b** (060) peak of MMT **c** (060) peak of a mixture of MMT with Ani-Cl

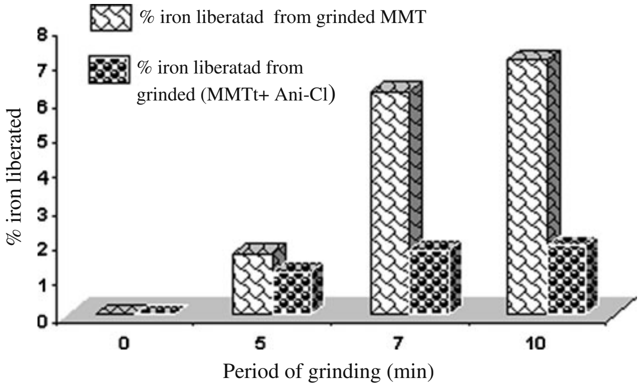

Fig. 2 Mass percentage of released iron from grinded MMT and its mixture with Ani-Cl

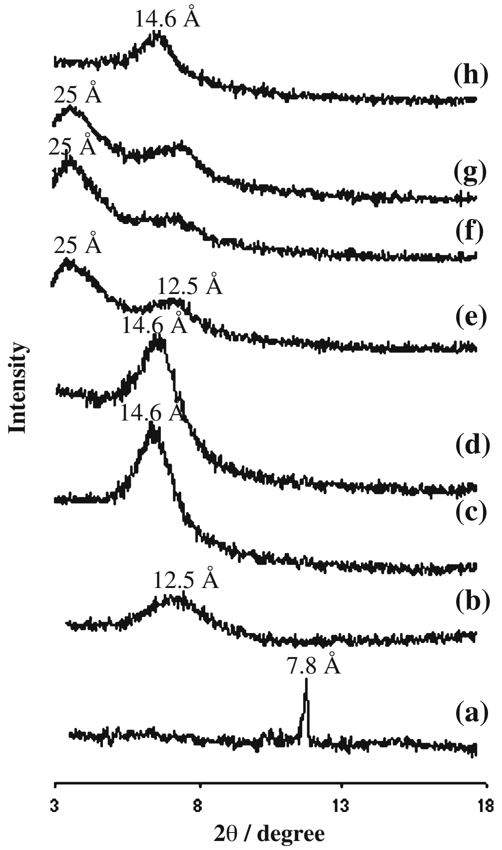

Fig. 3 X-ray diffraction patterns of **a** Ani-Cl **b** Pure clay; **c** Ani/MMT$_1$(*solid*); **d** Ani/MMT$_2$ (*solid*), **e** Ani/MMT$_3$(*solid*), f) Ani/MMT$_4$(*solid*), **g** Ani/MMT$_5$(*solid*) and **h** Ani/MMT$_4$(*solut*)

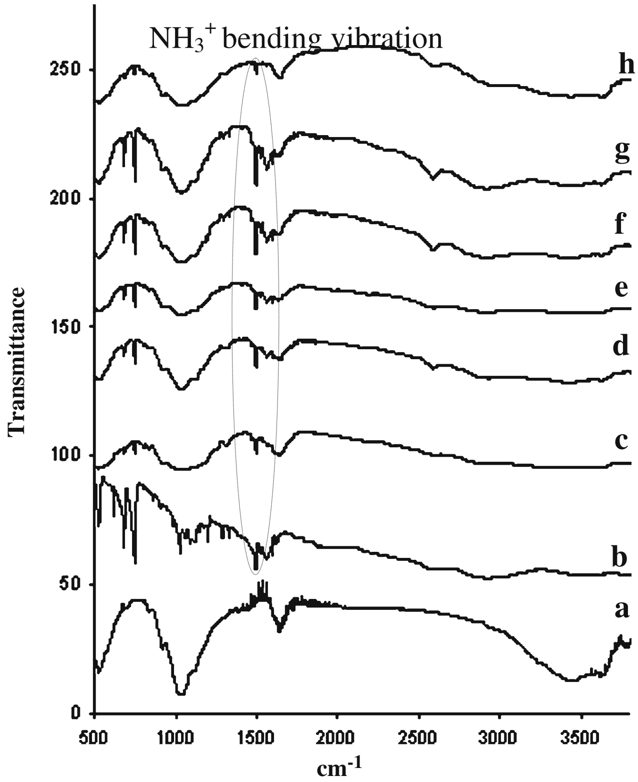

Fig. 5 FTIR spectra of **a** MMT, **b** Ani, **c** Ani/MMT$_1$(*solid*); **d** Ani/MMT$_2$ (*solid*); **e** Ani/MMT$_3$(*solid*); **f** Ani/MMT$_4$(*solid*); **g** Ani/MMT$_5$(*solid*) and **h** Ani/MMT$_4$(*solut*)

[19]. The presence of NH_3^+ bending (at 2,609–2,940 cm^{-1} and 1,519–2,616 cm^{-1}) in the IR spectra of different intercalated compounds indicates that the mechanochemical intercalation also occurs by a cation-exchange reaction similar to a conventional solution method. In order to evaluate the mode of interaction with the clay, it is interesting to study the modification Si-O stretching of the clay. The position of vibration is gradually shifted toward higher frequency, this is suggested to be due to the Coulomb interaction between the positive nitrogen of the anilinium layer and the partially negatively charged surface of the clay.

Figure 6 showed the TG curves of Ani/MMT$_4$(solid) and Ani/MMT$_4$(solut) hybrid materials together with that of MMT. In general, the decomposition of pristine montmorillonite (Fig. 6a) shows two-step weight loss process, i) the

Fig. 4 The configuration adopted by aniline species in the clay interlayer after intercalation

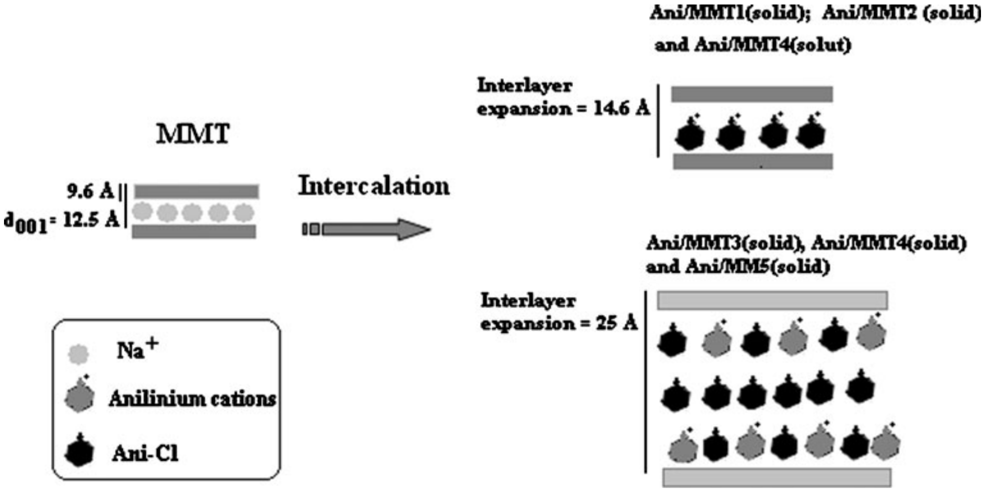

Table 2 Frequencies (cm^{-1}) and assignment of vibrational modes in IR spectra of Ani/MMT hybrid materials

Attribution Sample	ν $_{\text{Si-O}}$	νNH$_3^+$	νNH$_3^+$	δNH$_3^+$	δNH$_3^+$	δNH$_3^+$	δC-N
Ani-Cl	–	2,940	2,616	1,600	1,564	1,519	1,294
MMT	1,038	–	–	–	–	–	–
Ani/MMT$_1$(solid)	1,056	2,950	2,626	1,610	1,564	1,525	1,255
Ani/MMT$_2$(solid)	1,064	2,950	2,616	1,602	1,564	1,521	1,266
Ani/MMT$_3$(solid)	1,064	2,950	2,616	1,600	1,560	1,521	1,300
Ani/MMT$_4$(solid)	1,056	2,950	2,616	1,600	1,564	1,519	1,294
Ani/MMT$_5$(solid)	1,056	2,950	2,609	1,600	1,560	1,520	1,294
Ani/MMT$_4$(solut)	1,064	2,950	2,626	–	1,560	1,525	–

first weight loss starting from 50 to 120°C is attributed to free (absorbed) water residing between montmorillonite crystallites and interlayer water residing between the aluminosilicate layers and comprising the hydration spheres of the cations and ii) the region between 450°C and 1,000°C constitutes the dehydroxylation of the aluminosilicate lattice [20, 21]. The observation of TG curves of Ani/MMT$_4$(solid) and Ani/MMT$_4$(solut) showed the appearance of third weight loss region which starts at 180°C for composite prepared by solid-solid reaction and at 210°C for that prepared in solution. The weight loss from 180 to 210°C for Ani/MMT$_4$(solid) is ascribed to the vaporization of Ani-Cl which is localized in the interlayer space. However, that beyond 210°C for Ani/MMT$_4$(solut) is assigned to anilinium cations. From TG curves, we can observe that the amount of intercalated aniline for Ani/MMT(solid) cation is about four time greater than that prepared by a liquid reaction. This result is in agreement with XRD analysis.

Characterization of Ani/MMT hybrid compounds after 10 weeks

The initial colour of Ani/MMT(solid) materials is pale green as shown in Fig. 7. However with time, we have noticed that the colour has gradually changed to dark green after 10 weeks of aging. Interestingly, this change occurs only for hybrid compounds prepared by solid-solid reaction. This result proves that mechanism of intercalation in solid state is different from that in aqueous solution. It is well known the dark green colour is characteristic of the protonated emeradine form of polyaniline. Thus, by observing just the colour, we can estimate at this stage that for these composites, aniline species have been polymerized into protonated emeraldine salt forming thus polyaniline-montmorillonite nanocomposite.

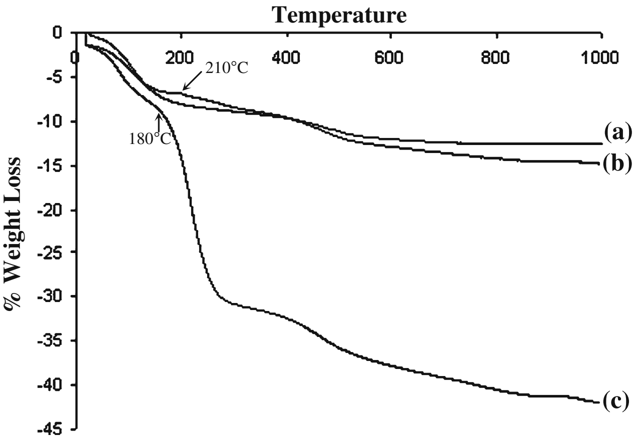

Fig. 6 TG curves of: **a** MMT; **b** Ani/MMT$_4$(*solut*) and **c** Ani/MMT$_4$(*solid*)

Evidence for the polymerization of aniline is provided by FTIR spectroscopy. Figure 8 shows the IR spectra of Ani/MMT$_n$(solid) for n varying from 1 to 5 and Ani/MMT$_4$(solut) after 10 weeks of synthesis. One can be seen that the spectrum of Ani/MMT$_4$(solut) did change, it still presents the characteristics bands of NH$_3^+$ localized at 1,525, 1,653, 2,626 and 2,950 cm^{-1}.

On the other hand, the spectra of Ani/MMT hybrid compounds prepared by solid-solid reaction showed the appearance of five characteristic peaks at 1,567–1,575 cm^{-1}, 1,490–1,498 cm^{-1}, 1,313–1,328 cm^{-1}, 1,260–1,282 cm^{-1}, 1,122–1,132 cm^{-1} and 742–746 cm^{-1}, which agree well with the bands of polyaniline reported in the literature [22, 23].

The characteristic bands at 1,575–1,577 cm^{-1} arises mainly from both C=N and C=C stretching of the quinoid diimine unit, while the band near 1,480 cm^{-1} is attributed to the C–C aromatic ring stretching of the benzenoid diamine unit. The band around 1,300 cm^{-1} bands can be assigned to C–N stretching of the secondary aromatic amine and an aromatic C–H out-of-plane bending vibration, respectively [23, 24]. The FTIR spectrum of Ani/MMT$_3$(solid) shows a broad absorption band at wavenumbers higher than 2,000 cm^{-1} which is typical of the conducting form of PANI. This band is due to free-charge carrier absorption in the conductive polymer.

It is interesting to observe that the bands of aniline cations at 1,618 and 1,621 cm^{-1} still persist in the spectra of Ani/MMT hybrid compounds for n corresponding to 1 and 2 which proves that the polymerizations is not completely

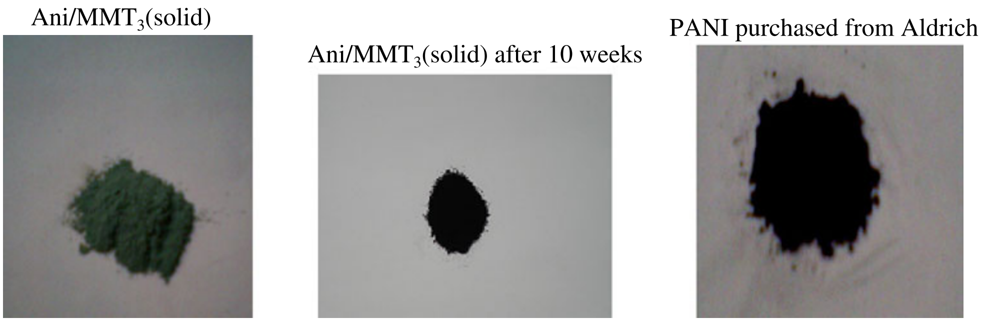

Fig. 7 Colour change of Ani/MMT hybrid compounds just after synthesis and after 10 weeks

achieved. Thus, from FTIR characterization we have proven that aniline intercalated in MMT by solid solid reaction could be polymerized without the use of an external oxidant forming thus polyaniline/clay nanocomposite.

To elucidate the origin of this phenomena and to visualize better the role of iron in aniline polymerization we have presented in Fig. 9 the spectra of Ani/MMT$_3$(solid), Ani/MMT$_4$(solut) hybrid materials just after synthesis and after aging time together with that of MMT in the 600–950 cm^{-1}range.

Evidence of the ferruginous character of MMT is given from the vibration bands localized at 835, 781, and 672

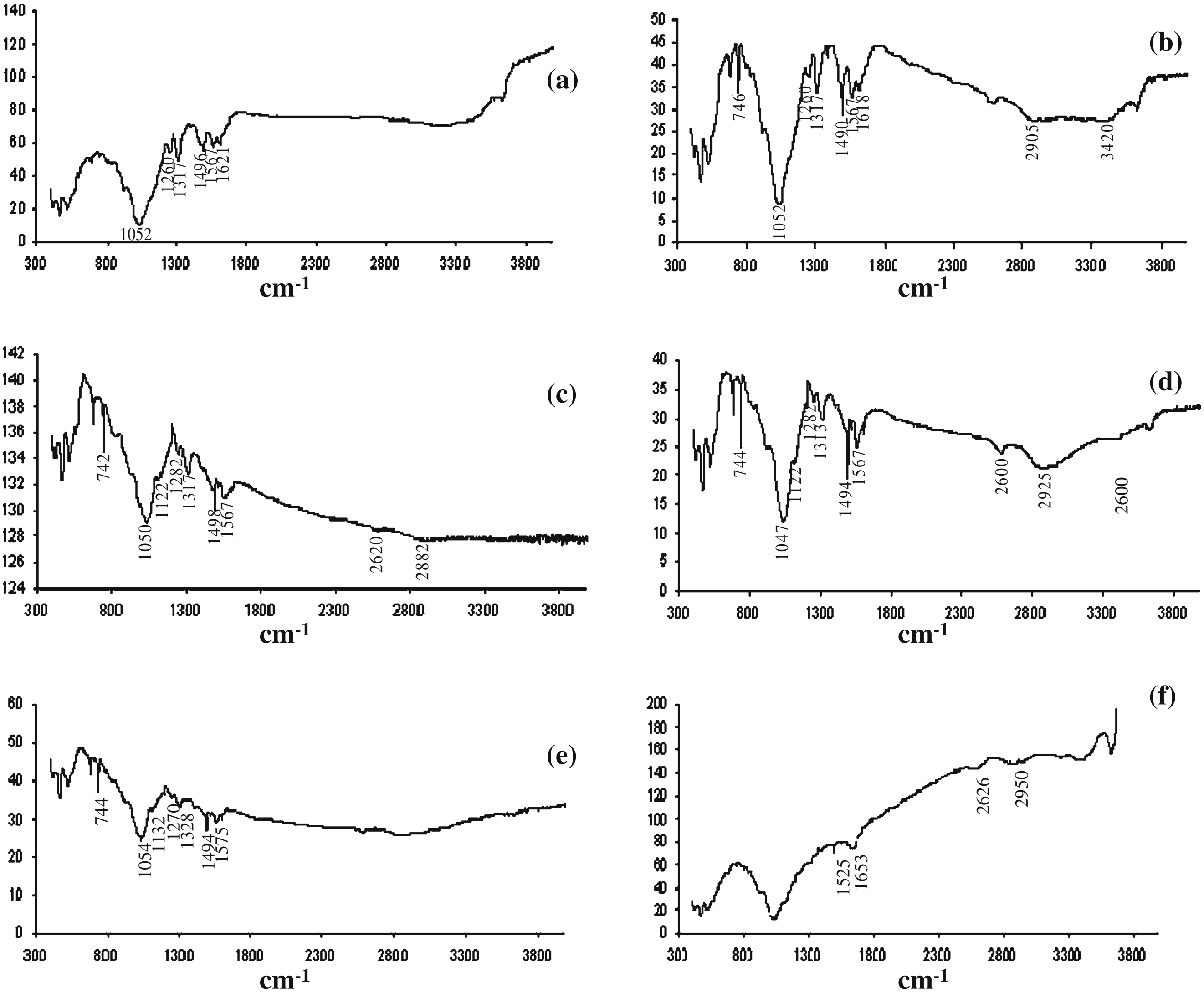

Fig. 8 FTIR spectra of different hybrid materials after 10 weeks **a** Ani/MMT$_1$(*solid*); **b** Ani/MMT$_2$ (*solid*); **c** Ani/MMT$_3$(*solid*); **d** Ani/MMT$_4$(*solid*); **e** Ani/MM$_5$(*solid*) and **f** Ani/MMT$_4$(*solut*)

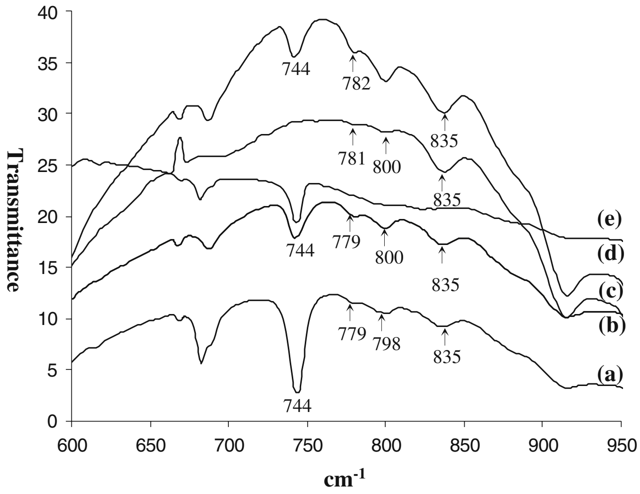

Fig. 9 IR spectra in 600–950 cm^{-1} region of **a** Ani/MMT$_3$(*solid*), **b** Ani/MMT$_4$(*solut*), **c** MMT, **d** Ani/MMT$_4$(*solute*) after aging and e) Ani/MMT$_3$(*solid*) after aging

which are attributed respectively to [Fe(III)]$_2$OH , Fe (III)MgOH deformations and Fe-O out-of-plane vibration [24, 25]. In addition, referring to Frost et al [26], the term iron-rich (ferruginous) smectitesis used for dioctahedral smectites when Fe^{3+}>3% which in accordance with our result.

The band attributed to [Fe(III)]$_2$OH vibration which is localized initially in MMT at 835 cm^{-1} remained almost stationary for Ani/MMT$_3$(solid) just after synthesis and for Ani/MMT$_4$(solut) after aging. However, it totally disappeared for Ani/MMT$_3$(solid) after aging. The same thing is observed for the band attributed to Fe(III)MgOH vibration. The decrease in intensity and the disappearance of the [Fe (III)]$_2$OH and Fe(III)MgOH vibration after aging time and which reflects the progressive loss of OH groups had been observed in several studies [27–30] after reduction of structural Fe in ferruginous smectite and nontronites. The changes in the absorptivity of [Fe(III)]$_2$OH and Fe(III) MgOH vibrations after aging for Ani/MMT$_3$(solid) can be related to the reduction of iron cations (Fe(III) → Fe(II)). It has been explained in terme of change in the OH dipole orientation due to different electric field environments as a result of changes in Fe oxidation state and/or Fe rearrangement within the octahedral sheet [27–30]. In fact, the reduction of Fe(III) to Fe(II) induces a deficit of charge on the apical oxygen (O) of the nearest tetrahedron which enhances attraction between O and the proton of the OH dipole, resulting in a change in the orientation of the OH dipole and the weakening and disappearance of the O-H bond. This result proves that after aging time structural Fe (III) cations localized in Ani/MMT hybrid compounds synthesized by solid solid reaction have been reduced to Fe(II). In addition, we have demonstrated that grinding of smectite is accompanied with a weakness and liberation of structural Fe cations. We suggest, hence, that polymerisation of intercalated aniline by solid-solid reaction is induced by Fe(III) cations liberated under grinding.

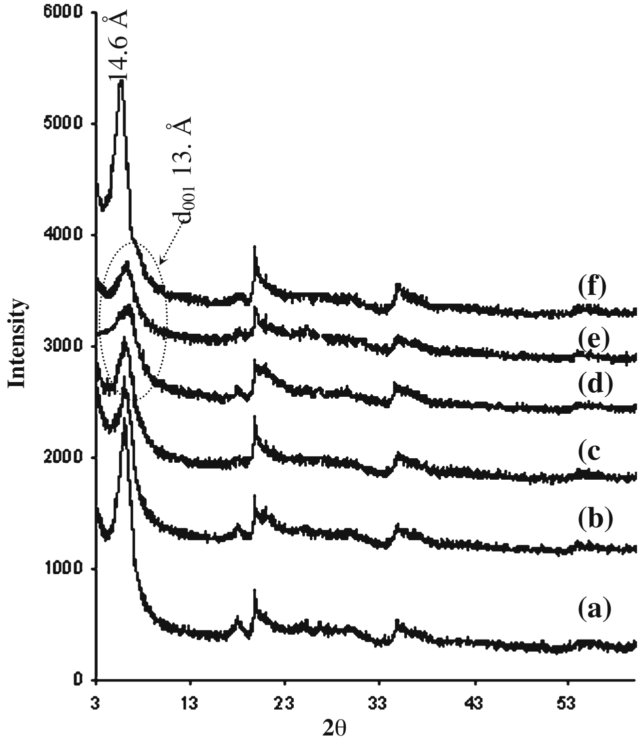

Fig. 10 The X-ray diffraction patterns after 10 weeks for **a** Ani/MMT$_1$(*solid*); **b** Ani/MMT$_2$ (*solid*); **c** Ani/MMT$_3$(*solid*); **d** Ani/MMT$_4$(*solid*); **e** Ani/MM$_5$(*solid*) and **f** Ani/MMT$_4$(*solut*)

The XRD patterns along with basal spacing (d$_{001}$) data of the different composites after 10 weeks are presented in Fig. 10. It reveals that d$_{001}$ is about 14.6 Å for Ani/MMT$_4$(solut) sample and it did change with aging time. This

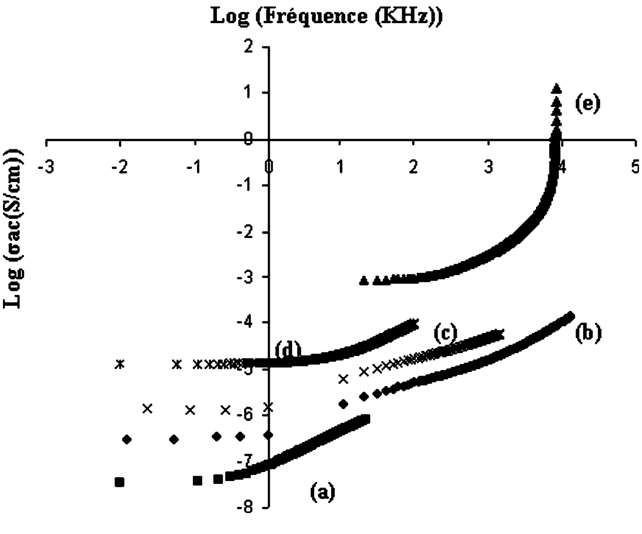

Fig. 11 AC conductivity versus frequency of **a** Ani/MMT$_5$(*solid*), **b** Ani/MMT$_1$(*solid*), **c** Ani/MMT$_4$(*solid*), **d** Ani/MMT$_2$(*solid*) et **e** Ani/MMT$_3$(*solid*) after 10 weeks of synthesis

result is supported by FTIR analysis. However, the d_{001} of hybrid compounds synthesized by solid-solid reaction has been shifted from 25 to 13.9 Å which corresponds to an expansion of about 4.3 Å, the basal spacing is similar to that reported by Zeng et al [31] for polyaniline/montmorillonite nanocomposite.

Thus these results prove that after an aging time of 10 weeks aniline species have been polymerized in the clay interlayer. To study electrical properties of these materials, we have presented in Fig. 11 the frequency-dependent conductivity σ(ω) of Ani/MMT hybrid materials after aging. It is well known that none of clay or aniline/clay hybrid compounds presented electrical conductivity. However, the electrical behaviour of Ani/MMT hybrid materials presented the universal behaviour of organic semiconductor. In fact, the characteristic property of σ(ω) is independent of frequency at low-frequency regions and almost equal to the direct-current (dc) conductivity. Then, the ac conductivity starts to increase. This trend in conductivity is similar to common electrical behaviour of disordered materials. It is well known that for disordered semi-conductive, the real part of the ac conductivity can be represented by the following forms [32]:

$$\begin{array}{lll} \sigma(\omega) & = \sigma_{dc} & (\omega < \omega_c) \\ \sigma_{ac}(\omega) & = A\omega^s & (\omega > \omega_c) \end{array} \tag{1}$$

At low frequencies, σ is a constant corresponding to dc conductivity σ(0). At higher frequencies, $\sigma_{ac}(\omega)$ increases with the frequency. The high-frequency domain can be approximated by a power-law behaviour with exponent $0 < s < 1$. The transition from one regime to the other is marked by a frequency $\omega_{c.}$ and A is a constant dependent on temperature [33].

The low conductivity of different samples ranged from 4 10^{-8} S/cm for Ani/MT_5(solid) to 10^{-3} S/cm for Ani/MT_3(solid). These values are comparable to polyaniline/montmorillonite nanocomposite prepared using an external oxidant and superior to that reported by Celik et al [34] for polyaniline/montmorillonite synthesized using benzoyl peroxide as oxidant.

Conclusion

In this study, we have demonstrated that polyaniline/montmorillonite nanocomposite could be prepared without the use of an external oxidant. The process involves the grinding of a rich Fe montmorillonite with aniline chloride and let hybrid material for a period of 10 weeks of aging to stimulate polymerization reaction. What is interesting is the fact that for hybrid prepared by conventional solution method, the structure remained the same. The polymerization of aniline is accompanied by reduction of octahedral Fe(III) to Fe(II), in addition grinding has for effect the weakness and the liberation of Fe species from the octahedral layers of the clay. This permits a closer contact between aniline species and these oxidizing metal cations which induced the polymerization and the formation thus of polyaniline/clay nanocomposite. Based on the characterization results, especially the FTIR spectra, we have proved the conductive emeraldine salt has been obtained. The dc conductivity of different nanocomposites is comparable to polyaniline/montmorillonite nanocomposite prepared using an ammonium persulfate as oxidant and is ranged from 4 10^{-8} S/cm for Ani/MT_5(solid) to 10^{-3} S/cm for Ani/MT_3(solid).

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