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Synthesis, characterization and ac-conductivity measurements of polyaniline based composites with fly-ash and clinker

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Abstract

We report the synthesis, characterization and ac-conductivity (σ_{ac}) results of some polyaniline (PAni) based composites. These materials were synthesized through incorporation of various fractions (20 to 60% by weight) of insulating fly-ash (FA) or clinker (Ck) in semiconducting PAni host. The synthesis was carried out for two different polymerization times (t_p) of 8 and 14 h, at 5 °C through oxidative polymerization, using ammonium-persulfate as initiator. Characterization of samples was done using x-ray diffraction (XRD), electron microscopy (SEM), and infrared spectroscopy (FTIR). Electrical conductivity analysis showed that synthesis for longer t_p produced more conducting samples because it allowed the formation of longer and thicker polymer chains. In general, σ_{ac} of the composites further increased with the fraction of FA or Ck, at least up to their maximum concentration studied in this work. Uniformly dispersed particles of FA or Ck apparently occupied the vacant spaces within the intertwined bundles of several polymer chains in such a way that continuity of the latter was not broken. Consequently, their presence pushed the bundles, and thus the individual chains, closer to each other, making the polymer parts more compact. The increased compactness of these conductive parts facilitated better mobility of charge carriers and therefore, the electrical conductivity increased.

Keywords: Polyaniline, Fly-ash, Composites, Electrical conductivity

1. Introduction

In the last couple of decades, CP based composites and blends have emerged as a new class of interesting materials because of their exceptional physical properties. Many of these can be utilized in technical as well as in industrial applications and therefore, a number of investigators all around the world are working on

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various aspects of these materials. Electrical conductivity is potentially the most useful of all the properties of CPs that can be easily translated into practical applications. Moreover, through the incorporation of various agents, the conductivity of CPs can be altered to suit specific requirements [1,2].

Polyaniline (PAni) is one of the most common CPs, which is environmentally stable and can be synthesized through simple and relatively cheaper methods. Room temperature dc-conductivity (σ_{dc}) of pure emeraldine salt (ES-I) form of PAni ranges within 10^{-1} to 10^{2} S.cm^{-1} [1-4], and it can be modified by several orders of magnitude through appropriate doping or incorporation of other materials [5-8]. The frequency dependent ac-conductivity (σ_{ac}) of PAni based composites have also been studied in great detail and reported by many authors [4,9-17]. Conductivity measurements provide a suitable experimental method, not just to evaluate the electrical properties of these disordered systems, but also to understand their microscopic structure. In the view of possible technological applications, often both of these features play significant roles.

Fly-ash (FA) and clinkers (Ck), on the other hand, are the by-products of combustion of coal, which are generally treated as waste materials. Several hundred million tons of FA is globally produced each year, primarily in the thermoelectric power plants. Similarly, Ck is generated by natural combustion in mining complexes. Disposal of these wastes is still believed to be a worldwide problem. However, with the increasing number of applications, recognized and realized in the past few decades, FA does not seem to be a waste material any longer and it is gradually proving to be one of the most cost-effective and environment friendly resources. Both FA and Ck are generally composed of aluminosilicates, and thus they can be used as structure fills, in soil amendments, for the production of new materials, as well as in various environmental applications [18]. More recently, materials scientists and engineers have suggested and devised various methods to use these waste products for the synthesis of some useful composites [6,9,18].

In this paper, we report about the synthesis, characterization and the results of ac-conductivity (σ_{ac}) measurements for two types of PAni based composites; one with various concentrations of FA (PAni/FA composites) and the other with that of Ck (PAni/Ck composites).

2. Experimental

2.1 Materials synthesis

The chemical reagents and solvents used in the present work were supplied by Merck KGaA and were used as-received without any additional purification. All chemicals were of analytical grade. FA was obtained from Termozipa Power Station, and Ck was collected from Cerrejón Mining Complex, in Colombia.

The composites were synthesized by the method of oxidative polymerization, as reported earlier by some of us [6]. A 0.1 mol of aniline was dissolved in 1 L of 2 M HCl and subsequently 20%, 40% and 60% by weight of Ck or FA were added under vigorous stirring. Finally, a 0.1 mol solution of ammonium-persulfate $[(NH_4)_2S_2O_8]$ was added. The synthesis was conducted at 5 °C for two different polymerization times of 8 and 14 h. The reaction products thus obtained were washed with distilled water and acetone, and then left to dry at room temperature for 26 h.

In this paper, we have named the samples according to the following scheme: A letter (F for FA and C for Ck) is used to indicate the type of material introduced into PAni matrix, followed by four digits. The first two digits after the letter represent the concentration (x) of the added constituents in terms of their respective weight percentage (%wt), and the last two digits indicate the polymerization time (t_p) in hours. Thus, the name F2008 represents PAni/FA composite with 20% FA by weight, prepared through 8 h of polymerization, and so on. Moreover, the pure PAni samples have been given the names PAni08 and PAni14 according to the polymerization time of 8 h and 14 h, respectively.

2.2 Measurements

All the samples were characterized by Fourier transform infra-red spectroscopy (FT-IR), x-ray diffraction (XRD), and scanning electron microscopy (SEM). Functional groups in the composites were identified through FT-IR using a Bruker Tensor-27 infrared spectrometer. The pellets of the samples for FT-IR were prepared with KBr. XRD data were collected on a Rigaku D/MAX IIIB, using CuK$_\alpha$ (λ= 1.5406 Å) radiation at 40 kV and 20 mA settings with 2θ ranging from 2 to 70º. The morphology of the samples was examined using a LEO 430 scanning electron microscope up to the magnification of 1000×.

After characterization, the electrical response of samples was analysed at room temperature in the frequency range 0.1 to 1 × 10^6 Hz on an impedance spectroscope EIS model PC4 (Gamry FrameWork). The powder samples of the pure PAni as well as of the composites were pressed into pellets of 12 mm diameter and 0.2 – 0.3 mm thickness, and placed between the stainless steel electrodes. The software used for data acquisition and analysis was also supplied by Gamry Instruments. In order to minimize the effects of noise, the whole experimental set-up was placed inside a Faraday cage.

3. Results and discussion

3.1 Infrared spectroscopy

Figure 1 shows the FTIR spectra for PAni/FA composites with 20, 40 and 60 %wt of FA, as well as for similar compositions of PAni/Ck composites. A characteristic broad band at 3422 cm^{-1} in the spectra of the

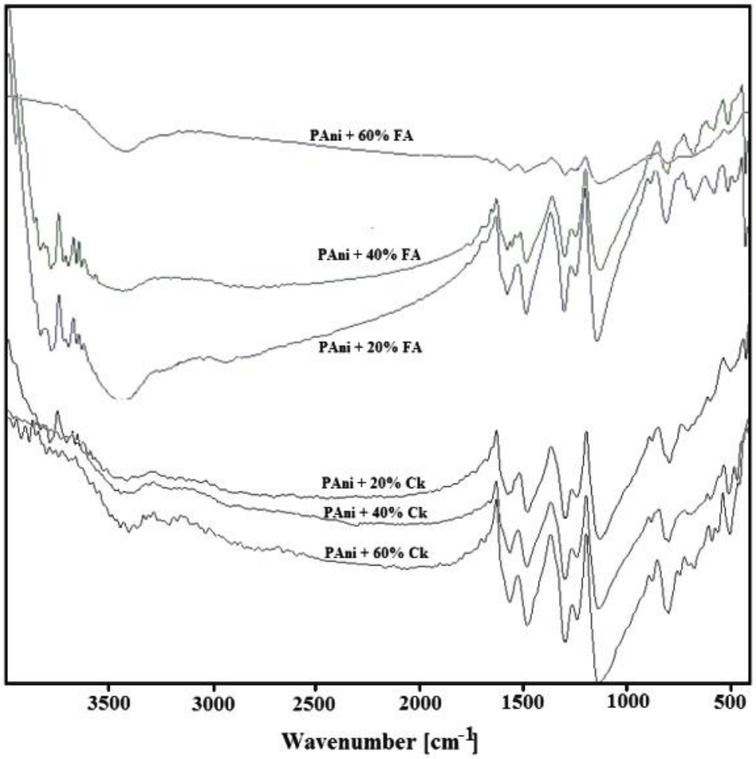


Fig. 1 FTIR spectra of the PAni/FA and PAni/Ck composites.

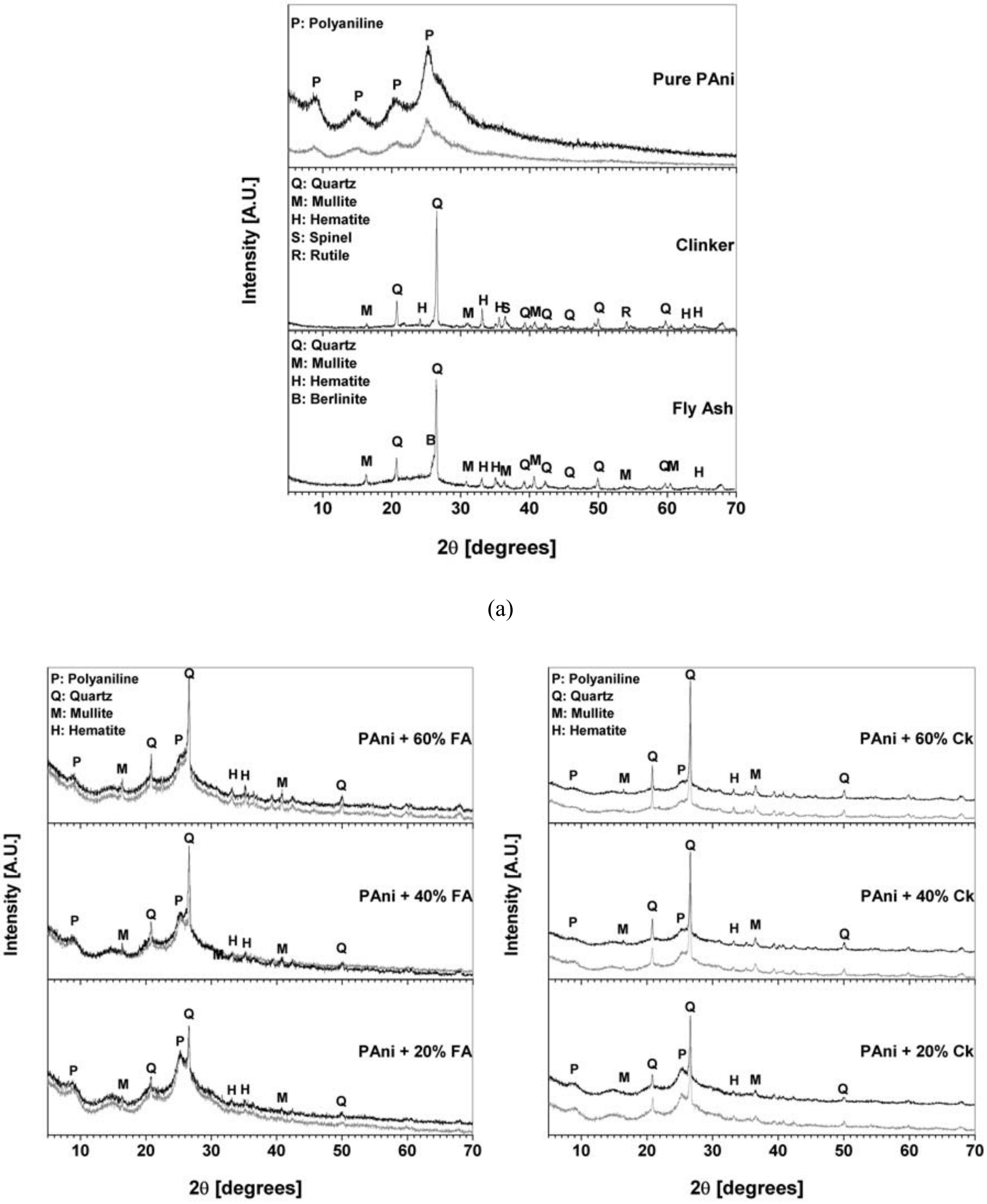
composites is due to N-H stretching of aniline. The absorption peak near 1630 corresponds to quinoid, and the one between 1542 to 1490 cm^{-1}, to the benzenoid rings. Another peak around 890 cm^{-1} shows the presence of benzoquinone in the polymer. These are characteristic of the emeraldine salt (ES-I) form of PAni. Several absorption peaks are observed in the range from 1400 to 1300 cm^{-1}, which corresponds to various metal oxides present in the FA or Ck. Absorptions at 1297.49 ± 10, 1139.71 ± 10, 1089.48 ± 10 and 794.81 ± 20 cm^{-1} correspond to FA constituents in PAni/FA; and those at 1300.94 ± 10, 1105.70 ± 10, 1039.66 ± 10, 889.37 ± 10 and 420.58 ± 10 cm^{-1}, to Ck contents in PAni/Ck composites. Moreover, the FTIR results for the composites do not apparently show any signs of new chemical bonds forming between PAni and FA or Ck.

3.2 X-ray diffraction

XRD results are depicted in Fig. 2 for pure PAni, as received FA and Ck; and the composites. Diffraction pattern for pure PAni [Fig. 2 (a)] shows large amorphous material contents with a characteristic broad peak at $2\theta = 25.21^\circ$ and some other peaks with lesser intensity at $2\theta = 8.73^\circ$, 14.80° and 20.85°. Mineralogical characterization by XRD shows many common phases in FA and Ck as shown in Fig. 2 (a). Both of these materials contain significant amount of amorphous phases. However, Ck (with about 22% amorphous parts) was found to be more crystalline than FA (nearly 76% amorphous).

The most important crystalline part in FA was identified as Quartz (SiO_2) with reflection peaks at $2\theta =$ 20.75°, 26.53°, 50.05° and 59.85°. Some other constituents detected in FA through XRD were Mullite [$Al(Al_{0.83}Si_{1.08}O_{4.85})$] with peaks at $2\theta = 26.20^\circ$, 16.34° and 40.78°; Berlinite ($AlPO_4$) at $2\theta = 26.41^\circ$; Magnetite (Fe_3O_4) at $2\theta = 35.52^\circ$; Hematite (Fe_2O_3) at $2\theta = 33.14^\circ$; Rutile (TiO_2) at 27.08° and Anatase (TiO_2) at 25.71°. In the analysis of the diffraction data for Ck, following crystalline phases were identified: Quartz (SiO_2) with reflections at $2\theta = 20.84^\circ$, 26.60°, 50.06° and 59.88°; Mullite [$Al(Al_{1.27}Si_{0.73}O_{4.9})$] at $2\theta =$ 16.37°, 35.08° and 36.89°; Cristobalite (SiO_2) $2\theta = 21.65^\circ$; Spinel $(Mg_{0.75}Al_{0.25})(Al_{0.875}Mg_{0.125})_2O_4$ at $2\theta =$ 36.63°; Hematite (Fe_2O_3) at $2\theta = 33.22^\circ$; Rutile (TiO_2) at $2\theta = 27.48^\circ$, Calcite [$Ca(CO_3)$] at $2\theta = 29.42^\circ$; and Cordierite [$Mg_2(Al_4Si_5O_{18})$] at $2\theta = 10.40^\circ$.

From the diffraction profiles for composites, the PAni/Ck samples [Fig. 2 (c)] look more crystalline than their PAni/FA counterparts [Fig. 2 (b)], as evidenced by the broadened peaks of the latter. This may essentially be attributed to the crystallographic nature of the original FA or Ck. The increasing heights of some prominent peaks with FA and Ck %wt correspond to the increasing fractions of the constituents of FA or Ck in the composites. It may also be noted from these plots that the more intense PAni band has shifted to a higher $2\theta = 25.36^\circ$ in the PAni/FA composites. Similar shifts were also found in the position of the peaks of FA constituents, for example, the mullite peak at $2\theta = 16.34^\circ$ shifted to $2\theta = 16.44^\circ$. Similarly, the incorporation of PAni with Ck also resulted in shifts of many characteristics peaks of the latter. For example, the most intense peak corresponding to quartz appeared at $2\theta = 26.60^\circ$. Also the peak for pure PANI appeared at $2\theta = 26.66^\circ$ in the composite with $x = 20$ %wt of Ck, whereas in the composites with $x =$ 40 and 60 %wt of Ck, it was seen at $2\theta = 26.61^\circ$. Usually, such peak-shifts are associated with the small modifications of lattice structure in crystalline materials due to doping of impurities, when phase transformation is not expected. However, in the present case, the host PAni (ES-I form) is partly crystalline, which is also evident from Fig. 2 (a). As a result, the components of FA or Ck can move into the PAni matrix in two possible ways. First, the lattice sites and interstitials of the crystalline parts can be occupied by the atomic constituents of FA or Ck, leading to small lattice distortions. The above mentioned peak-shifts in the XRD profiles of the composites clearly point out to small lattice distortions of the crystalline parts of host PAni. Secondly, the FA or Ck can also move into the vacant spaces between the polymer chains, as larger particles. This has been conclusively observed in the SEM pictures, as mentioned in the following section.



(a)

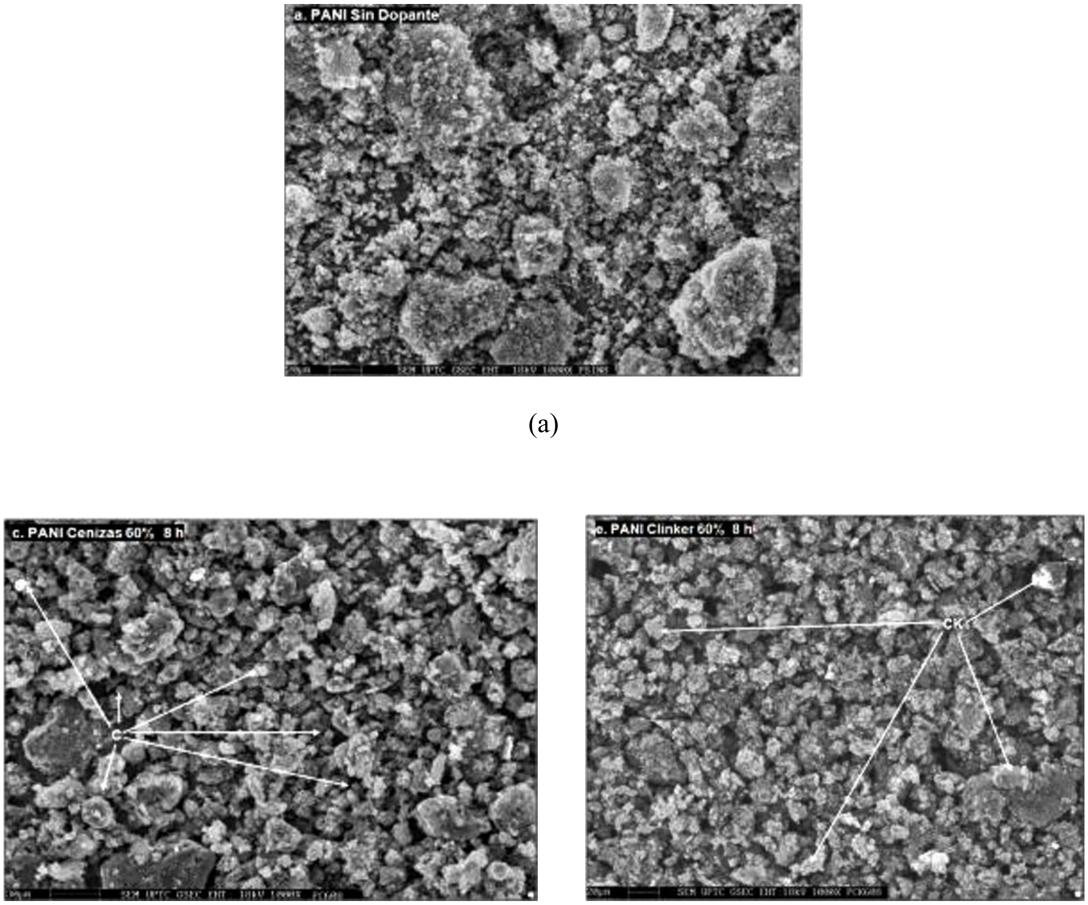
(b)

(c)

Fig. 2 XRD results for (a) Pure PAni, and as-received FA and Ck; (b) PAni/FA composites, and (c) PAni/Ck composites. Gray line denotes 8 h, and black, 14 h polymerization time.

3.3 Scanning electron microscopy

Figure 3 (a) shows SEM picture of pure PAni, which appears to be quite homogeneous. Figure 3 (b) and (c) show the SEM pictures of PAni/FA and PAni/Ck composites, with 60 %wt (maximum) of FA or Ck, respectively. White cenospheres of FA of varying size are clearly visible in Fig. 3 (b), whereas, in Fig. 3 (c), particles of Ck appear in irregular shapes of different sizes with flat faces.



(a)

(b) (c)

Fig. 3 Typical SEM pictures of (a) Pure PAni, (b) PAni + 60% FA, and (c) PAni + 60% Ck. Magnification in all pictures is 1000×.

The most important observation in all SEM images is that the grain connectivity doesn't seem to be deteriorating with the increasing amount of either FA or Ck. Moreover, the particles of FA or Ck are seen as uniformly distributed in the PAni host and located at large distances from one another. This implies that the presence of these particles does not seem to interfere with the continuity of polymer chains, at least up to x = 60 %wt of their concentration studied in this present work. However, the possibility of a changed scenario cannot be ruled out at higher fractions of FA or Ck in the composites.

3.4 Electrical conductivity

Figures 4 and 5 show the conductivity σ_{ac} as a function of frequency ω (= $2\pi f$), for various PAni/FA and PAni/Ck composites, respectively. The data for pure PAni have also been plotted alongside to facilitate good comparison. As mentioned earlier, these samples were prepared under two different polymerization times (t_p) of 8 h and 14 h. It may be noted immediately that a longer t_p produces better overall conductivity in pure PAni, as well as in the composites, as expected [19]. The observed improvement is nearly 30 times in pure PAni, around 2 to 7 times in the PAni/FA, and more than 25 times in PAni/Ck composites. These observations may be attributed to the fact that prolonged polymerization leads to formation of longer and thicker polymer chains that can support electrical conduction.

We have further observed that the inclusion of FA or Ck into PAni leads to an increase of ac-conductivity. This improvement of σ_{ac} is more pronounced in PAni/FA composites than in PAni/Ck materials. As compared to pure PAni, the increase is as much as two orders of magnitude (t_p = 8 h) and nearly by a factor of 20 (t_p = 14 h) in the composites with 60 %wt of FA. In the case of 60 %wt Ck composites, this increase is nearly 7.5 times (t_p = 8 h). For the composites with 40 %wt of Ck also, an increase in σ_{ac} of approximately 7 times (t_p = 8 h), and 2.5 times (t_p = 14 h) were observed. These are

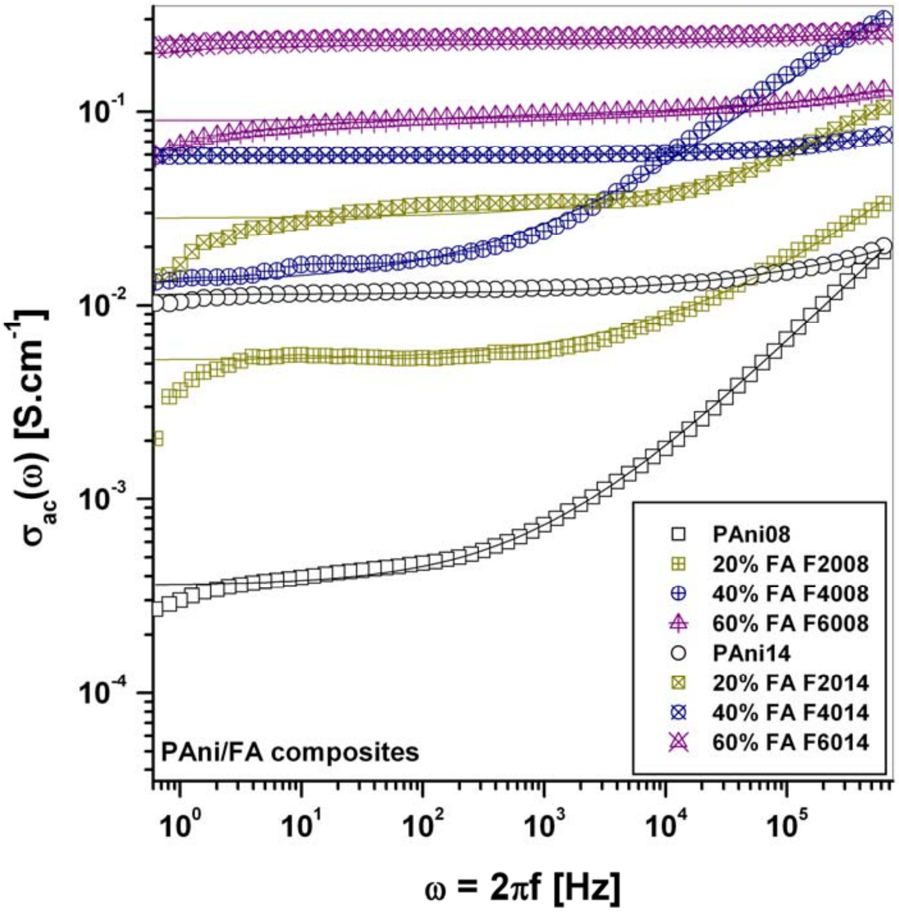


Fig. 4 AC Conductivity behaviour of PAni/FA composites. The solid lines represent the best fitted curves according to Eq. (1), using the parameters given in Table 1.

interesting results but not unusual. Many authors have reported similar increase of σ_{ac} in some PAni/insulator [4,10,13], as well as in other CP/insulator [20-22] composites, and they have attributed the observations to an increased orderness and compactness, and to the changed molecular orientations of the composites.

Various mechanisms responsible for, and influencing, the frequency dependent conductivity of these highly disordered materials have been suggested. However, it is well established that the total ac-conductivity (σ_{ac}) at a given temperature, can be expressed as the following relationship [10-12, 19, 21]:

$$\sigma_{ac}(\omega) = \sigma_0 + \sigma_\omega \qquad (1)$$

where, σ_0 is the frequency independent part of the conductivity as observed in the low ω regime. In the higher ω regime, however, the frequency dependent part, σ_ω takes over, which generally follows a characteristic power law of the type,

$$\sigma_\omega = A\omega^s \qquad \text{(with } 0 < s < 1\text{)}, \qquad (2)$$

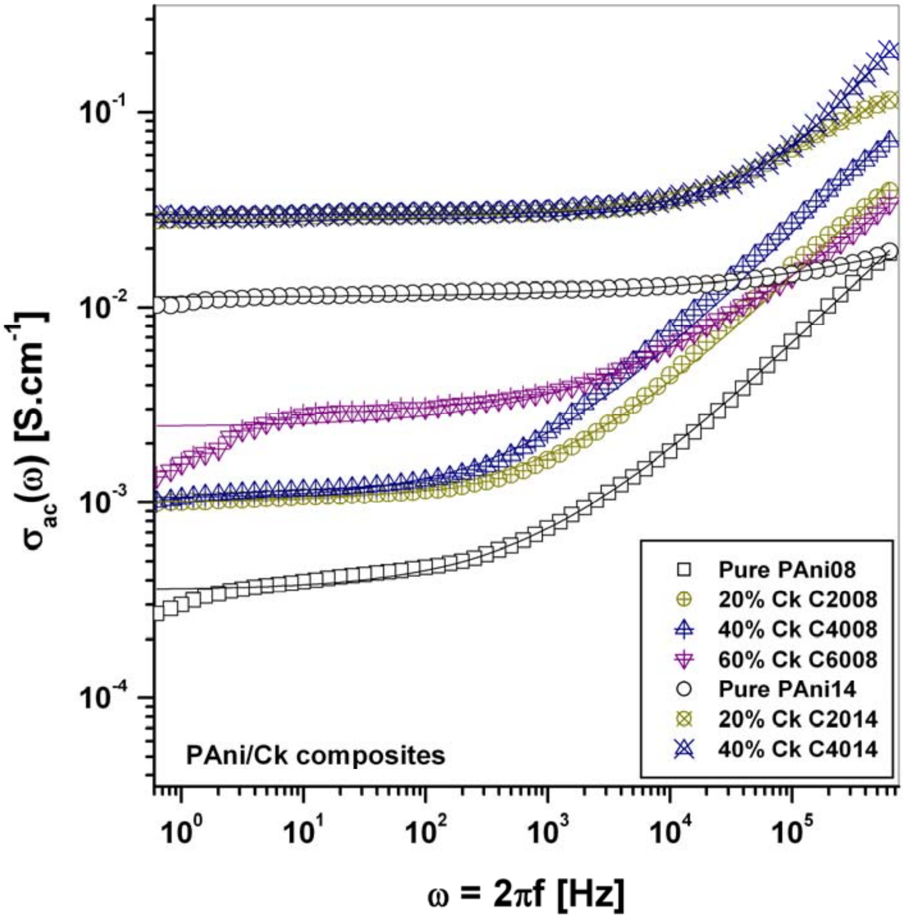


Fig. 5 AC Conductivity behaviour of PANI/Ck composites. The solid lines represent the best fitted curves according to Eq. (1), using the parameters given in Table 1.

for hopping conduction between localized states in disordered materials [10-16, 19]. Here, A is a temperature dependent constant [15]. We have fitted our experimental data using Eq. (1) in the full range of frequency investigated. The values of parameters σ_0, A and s, corresponding to the best fitting curves have been collected in Table 1, and their variations with FA or Ck fractions in the respective composites is depicted in Fig. 6.

In disordered systems, the microscopic conduction is governed primarily by two processes: the classical hopping and the quantum mechanical tunnelling (QMT) of the charge carriers over a potential barrier between two energetically favourable randomly distributed centres. A true picture of the mechanism responsible for charge transport in these systems is given by the nature of temperature dependence of the frequency exponent s in Eq. (2) [12,15]. Moreover, a frequency independent s suggests that correlated barrier hopping (CBH) may be the responsible mechanism for conductivity. In the present study, we note that each data set can be nicely fitted with a curve generated by a single value of s for almost the full range of ω under consideration. Therefore, for a given sample, s can be treated as independent of frequency, and hence the CBH seems to be responsible for conduction in these materials [4]. This argument is supported by the fact that CBH has been suggested as the process responsible for conduction in similar systems [4,12,15,16,19]. Nevertheless, temperature dependent data are required to consolidate these observations.

Extrapolated values of σ_{ac} of the individual curves in Figs. 4 and 5, as $f \rightarrow 0$ give the frequency independent part σ_0 for the corresponding sample [13]. Since most of the experimental curves showed a slow increase of σ_{ac} with ω in extremely low ω regions (< 10 Hz), we selected the most flat parts of the curves (within 10 Hz < ω < 500 Hz for most of the curves) to obtain σ_0 from the experimental data. The σ_0 thus obtained for pure PAni are 4.21×10^{-4} S.cm^{-1} (PAni08) and 1.22×10^{-2} S.cm^{-1} (PAni14), which are in good agreement with the reported values [4,9,15]. However, better dc-conductivity in the range of 10^{-1} to

Table 1 Fitting parameters

Sample	σ_0 (Expt) [S.cm^{-1}]	σ_0 (Best-fit) [S.cm^{-1}]	A [S.cm^{-1}]	s
Polymerization time (t_p) = 8 h				
Pure PAni08	4.21×10^{-4}	3.20×10^{-4}	5.7×10^{-6}	0.61
PAni + 20% FA F2008	5.32×10^{-3}	5.21×10^{-3}	4.0×10^{-5}	0.50
PAni + 40% FA F4008	1.62×10^{-2}	1.28×10^{-2}	4.7×10^{-4}	0.49
PAni + 60% FA F6008	9.18×10^{-2}	8.98×10^{-2}	4.0×10^{-4}	0.35
PAni + 20% Ck C2008	1.10×10^{-3}	1.00×10^{-3}	1.0×10^{-5}	0.63
PAni + 40% Ck C4008	1.14×10^{-3}	1.05×10^{-3}	1.5×10^{-5}	0.64
PAni + 60% Ck C6008	2.92×10^{-3}	2.44×10^{-3}	3.0×10^{-5}	0.51
Polymerization time (t_p) = 14 h				
Pure PAni14	1.22×10^{-2}	1.13×10^{-2}	6.0×10^{-5}	0.36
PAni + 20% FA F2014	3.35×10^{-2}	2.82×10^{-2}	1.2×10^{-4}	0.48
PAni + 40% FA F4014	6.05×10^{-2}	5.95×10^{-2}	1.0×10^{-5}	0.55
PAni + 60% FA F6014	2.43×10^{-1}	2.35×10^{-1}	2.3×10^{-6}	0.71
PAni + 20% Ck C2014	2.99×10^{-2}	2.82×10^{-2}	6.0×10^{-5}	0.55
PAni + 40% Ck C4014	3.10×10^{-2}	2.99×10^{-2}	2.6×10^{-6}	0.83

10^2 S.cm^{-1} [1-4,6] have also been obtained for pure PAni samples, which are associated with the formation of denser polymer chains during polymerization. Therefore, we may attribute our observed smaller σ_0 to relatively less compact packing of the polymer chains. This is also in agreement with the fact that longer polymerization time produces higher conductivity in pure PAni as it allows the formation of thicker chains, which eventually bundle up more tightly as compared to the samples prepared through shorter period. The same argument holds for the composites also. Experimental values of σ_0 are also listed in Table 1, which are very close to those estimated from the best-fitted curves for obvious reasons. Fig. 6 shows that σ_0 increases with FA or Ck concentrations in the composites, which is clearly a reflection of the overall improvement of σ_{ac}.

Further, one can easily notice that the high ω regime onsets earlier in the pure PAni samples as compared to the composites. Another important inference may be drawn from a comparison between the plots corresponding to 8 h and 14 h polymerization (Figs. 4 and 5). Apparently, longer polymerization time not only improves the overall conductivity of all the samples, but it also weakens the dependence of σ_{ac} on ω, which is revealed by the increased flatness of the curves. In terms of the fitting parameters, the flatness of curves corresponds to smaller values of A. One can observe from Fig. 6 that A increases in the t_p = 8 h composites, but in the case of t_p = 14 h composites, it increases only up to x = 20 %wt and then decreases. The latter explains the increased flatness of the curves observed with samples prepared through longer polymerization time. Since the parameter A is temperature dependent, there seems to be a possibility that it is linked with the number and mobility of the charge carriers, and therefore the flatness of the σ_{ac} curves may be associated with some kind of saturation behaviour.

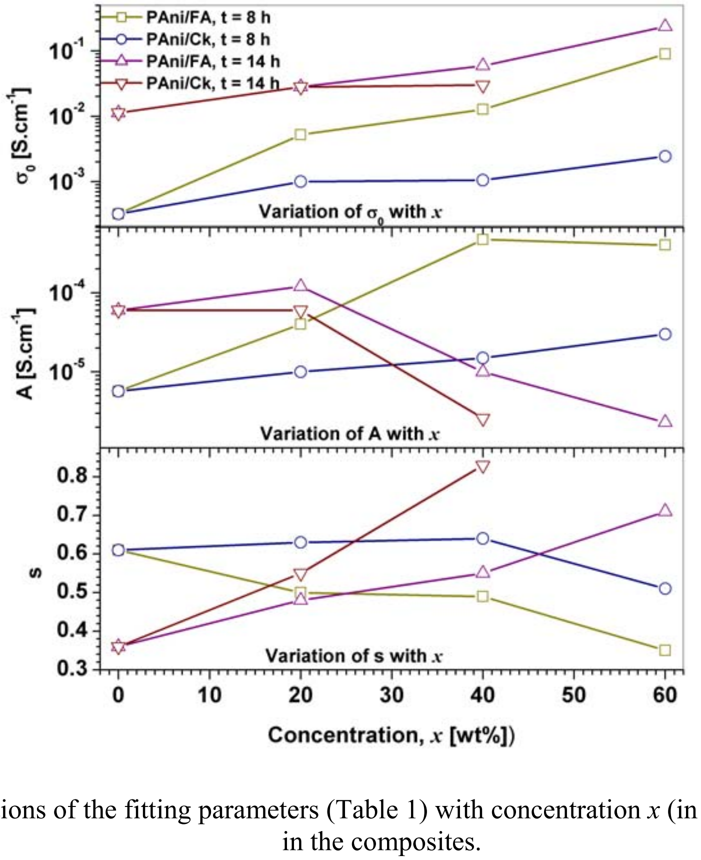


Fig. 6 Variations of the fitting parameters (Table 1) with concentration x (in %wt) of FA or Ck in the composites.

In the macroscopic scales, as mentioned above, the increasing fraction of FA or Ck does not seem to break the continuity of polymer chains even in the composites with maximum concentrations of the latter. This is evident from the SEM pictures (Fig. 3), which show increased connectivity of grains in the composites (even up to $x = 60$ %wt) as compared to that in pure PAni. These pictures also show that the FA or Ck particles are uniformly dispersed in the host, presumably occupying the vacant spaces within the intertwined bundles of several polymer chains. As a consequence, their presence supposedly brings the individual chains closer, thus making the polymer parts more compact. The increased compactness of these conductive parts, which is visible as better grain connectivity in the SEM pictures, facilitates better mobility of the charge carriers and thus the electrical conductivity increases. In this regard, the loose packing of the polymer chains, as noticed earlier from the σ_0 values as well as from the SEM picture for pure PAni, apparently favours their compression into denser bundles. This argument is supported by the observation that the increase of σ_{ac} in $t_p = 8$ h composite was very large (nearly 5 times) as compared to the $t_p = 14$ h composite with similar FA concentration (of $x = 60$ %wt). In the case of composites with $x = 40$ %wt Ck also, $t_p = 14$ h produced an increase of σ_{ac} slightly under 3 times than that with $t_p = 8$ h sample. Clearly, the loosely packed polymer chains (e.g., those formed during shorter polymerization time) get more compact after the introduction of FA or Ck and eventually lead to higher increase in conductivity. On the other hand, longer duration of polymerization already produces tighter bundles of chains and thus, further increase in compactness due to FA or Ck incorporation is not as much significant as in the previous case. This discussion reasonably explains the observed trend of σ_{ac} in the composites.

Finally, the higher values of σ_{ac} and its large improvements with x in the PAni/FA composites as compared to PAni/Ck materials may be attributed only to the properties of FA or Ck, respectively. Although most of the constituents of FA and Ck are quite similar, they are essentially different in terms of electrical conductivity and crystallinity. Both FA and Ck are practically insulators with extremely low dc-conductivity (σ_{dc}). However, FA ($\sigma_{dc} = 2.71 \times 10^{-6}$ S.cm^{-1}) is more conducting than Ck ($\sigma_{dc} = 3.37 \times 10^{-8}$ S.cm^{-1}) by as much as two orders of magnitude. This explains why PAni/FA composites were more conducting than the PAni/Ck composites. Moreover, XRD results showed that the FA used in this investigation contained about 76% amorphous phases, whereas Ck, only about 22%. Similar trend was observed in the XRD patterns of composites also [Fig. 2 (b) and (c)]. Combined with the σ_{dc} values, it indicates that the amorphous phases present in FA were probably more conducting than those in Ck. The amorphous, but more conducting nature of FA apparently also supported the large improvements of σ_{ac} with x in the PAni/FA composites, since it is possible that FA islands in host PAni acted as bridges in the process of hopping conduction [13].

Conclusions

Composites synthesized with the incorporation of various concentrations (20 to 60 %wt) of insulating FA or Ck into PAni, through two different polymerization times, showed some interesting ac-conductivity results. Longer polymerization time during synthesis produced more conducting samples, obviously because it allowed the formation of longer and thicker polymer chains. Interestingly, the σ_{ac} further increased with the amount of FA or Ck in the composites, even though these are insulating materials. The SEM micrographs showed that even up to the maximum concentration of added constituents (of $x = 60$ %wt), homogeneity and continuity of the grains were not broken. It was also observed that the particles of FA or Ck were evenly dispersed in the host PAni apparently occupying the empty spaces within the intertwined bundles of several polymer chains. As a consequence, their presence brought the individual bundles and chains closer to each other making the polymer parts more compact. Better mobility of the charge carriers was facilitated due to this increased compactness of the conductive parts, and thus the electrical conductivity increased.

Nevertheless, it should be noted that increasing the fraction of added constituents further may break the continuity of the polymer chains, which may deteriorate the observed electrical conductivity.

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References

1. A.B. Kaiser, Rep. Prog. Phys. 64 (2001) 1.
2. A.B. Kaiser, Adv. Mater. 13 (2001) 927.
3. J. Stejskal and R.G. Gilbert, Pure Appl. Chem. 74 (2002) 857.
4. C. Basavaraja, Na Ri Kim, Eun Ae Jo, R. Pierson, and Do Sung Huh, Bull. Korean Chem. Soc. 30 (2009) 1543.
5. D. Lee, K. Char, S.W. Lee and Y.W. Park, J. Mater. Chem. 13 (2003) 2942.
6. H. Narayan, H.M. Alemu and E. Iwuoha, Phys. Stat. Sol. (a) 203 (2006) 3665.
7. H.C. Pant, M.K. Patra, S.C. Negi, A. Bhatia, S.R. Vadera and N. Kumar, Bull. Mater. Sci. 29 (2006) 379.
8. H.L. Frisch, B. Xi, Y. Qin, M. Rafailovich, Nan-Loh Yang and I. Yan, High Perform. Polym. 12 (2000) 543.
9. S.C. Raghavendra, S. Khasim, M. Revanasiddappa, M.V.N. Ambika Prasad and A.B. Kulkarni, Bull. Mater. Sci. 26 (2003) 733.
10. D. Hui, R. Alexandrescua, M. Chipara, I. Morjana, Gh. Aldica, M.D. Chipara, K.T. Lau, J. Optoelectronics Adv. Mater. 6 (2004) 817.
11. P. Dutta, S. Biswas and S.K. De, J. Phys.: Condens. Matter 13 (2001) 9187.
12. S. Ebrahim, High Perform. Polym. 21 (2009) 468.
13. A. Fattoum, M. Arous, F. Gmati, W. Dhaoui and A. Belhadj Mohamed, J. Phys. D: Appl. Phys. 40 (2007) 4347.
14. F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein, Phys. Rev. B 39 (1989) 3570.
15. A. Dey, S. De, A. De and S.K. De, Nanotechnology 15 (2004) 1277.
16. K. Dutta, S. De and S.K. De, J. Appl. Phys. 101 (2007) 093711.
17. J.M.G. Neto, G.F. Leal Ferreira, J. Ribeiro Santos Jr., H.N. da Cunha, I.F. Dantas, and R.F. Bianchi, Brazilian J. Phys. 33 (2003) 371.
18. H. Narayan, H.M. Alemu, V.S. Somerset, E.I. Iwuoha, M.L. Hernández, J.A. Hernández, A.M. Montaño and J.A. Henao, Chapter 5 In: *Fly Ash: Reuse, Environmental Problems and Related Issues* Ed: Peter H. Talone, Nova Science Publishers, Inc. (New York), (2009) pp 111-136.
19. S. Bhattacharyya, S.K. Saha, M. Chakravorty, B.M. Mandal, D. Chakravorty, K. Goswami, J. Polym. Sci. (B): Polym. Phys. 39 (2001) 1935.
20. M.V. Murugendrappa, S. Khasim and M.V.N. Ambika Prasad, Bull. Mater. Sci. 28 (2005) 565.
21. T.K. Vishnuvardhan, V.R. Kulkarni, C. Basavaraja and S.C. Raghavendra, Bull. Mater. Sci. 29 (2006) 77.
22. C. Basavaraja, Y. Min Choi, H. Tae Park, D. Sung Huh, J. Wook Lee, M. Revanasiddappa, S.C. Raghavendra, S. Khasim, and T.K. Vishnuvardhan, Bull. Korean Chem. Soc. 28 (2007) 1104.

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