Phase change induced by polypyrrole in iron-oxide polypyrrole nanocomposite

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Abstract. Nanocomposites of polypyrrole and iron oxide were prepared using simultaneous gelation and polymerization processes. Varied amounts of pyrrole monomer were added to a solution containing iron nitrate as precursor and 2-methoxy ethanol as solvent. The presence of oxide and polypyrrole was confirmed by using X-ray and FTIR techniques. Some of these nanocomposites exhibited magnetic behaviour. SEM studies of powders indicated presence of nanosized particles. Electrical conductivity studies of powders showed a slight variation in conductivity for lower concentration of pyrrole, with a sudden increase in conductivity at 15% of pyrrole concentration. A transition from a nonmagnetic to magnetic phase was also observed at the same concentration.

Keywords. Polypyrrole; iron oxide; nanocomposite; sol-gel.

1. Introduction

In the past few years nanocomposite materials have become one of the most extensively studied materials all over the world as they have shown to possess several applications such as effective quantum electronic devices, magnetic recording materials, sensors etc (Sinfelt 1977; Anderson *et al* 1980). Moreover, nanocomposite materials composed of oxides and conducting polymers have brought out more fields of applications such as smart windows, toners in photocopying, conductive paints, drug delivery, rechargeable batteries etc (Maeda and Armes 1994; Maeda *et al* 1994; Butterworth *et al* 1995; Jarjayes *et al* 1995).

Conducting polymers possess good tunable electrical conductivity and are organic electrochromic materials with chemically active surface (Skotheim 1986; MacDiarmid and Epstein 1989, 1993; Roth and Graupner 1993). But they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. On the other hand, nanomaterials show the presence of more sites for surface reactivity and are highly porous in sol form. Moreover, they possess good mechanical properties and are good dispersants too (Jewell *et al* 1991; Martin 1994).

Thus nanocomposites formed by combining conducting polymers and inorganic nanoparticles viz. oxides, possess all the good properties of both the constituents and an enhanced utility thereof. The properties of nanocomposite of such kind are strongly dependent on concentration of polymer. Polypyrrole, one of the conducting polymers, has received lot of attention in the preparation of nanocomposites due to its high stability in conducting oxidized form (Partch *et al* 1991; Huang and Matijevic 1995; Maeda and Armes 1995).

Nanocomposite materials based on nanosized magnetic materials have been of great interest to researchers due to their possible applications in refrigeration and high density information storage (Shull and Bennett 1992; Xiao *et al* 1993). These composites are often prepared by dispersing magnetic materials in a nonmagnetic matrix. In the present investigations, conducting polymer viz. polypyrrole, has been chosen to act as the nonmagnetic matrix. It is also a well known fact that solution containing ferric ion induces polymerization of pyrrole. In order to investigate the changes induced by pyrroles on the oxides formed during the gelation process, an attempt has been made to prepare these nanocomposites.

In this paper we report the preparation of nanocomposites of conducting polymer (polypyrrole) and iron oxide by a process of simultaneous gelation of oxide as well as polymerization of the monomer by taking different amounts of monomer in fixed concentration of oxide solution. The method has resulted in a magnetic phase. The earlier work carried out using gelation process resulted in formation of α-Fe_2O_3 phase which was further used in humidity sensors (Chauhan *et al* 1998, 1999).

In order to determine the composition, size, structural and thermal properties of the nanocomposite several structural investigations using X-ray, IR and SEM techniques were carried out and the results are presented here. The electrical properties of the nanocomposites are also discussed in this paper.

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2. Experimental

Nanocomposites of iron oxide and conducting polymer (polypyrrole) were prepared by sol gel process. In this process, oxide solution was prepared by using iron(III) nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$ as precursor and 2-methoxy ethanol as solvent (Chauhan *et al* 1998). To 20 ml of the above solution varied amounts of pyrrole monomer were added and the solution was heated initially at 60°C with continuous stirring to form the gel. The gel was further heated at 250°C to evaporate the solvent which resulted in powders or composites of iron oxide and polypyrrole. These powders were annealed at 350°C for further investigation of their properties. The powders were compressed using cylindrical dye and hydraulic press for further studies.

The crystal structure of the powders was examined by a Rigaku Rotaflex diffractometer using CuK*a* ($l = 1 \cdot 5418$ Å) at 40 keV. The surface morphology was analysed by a JEOL (JSM 840) scanning electron microscope (SEM). The Fourier transform infra-red spectra was recorded using the Nicolet 510 P FTIR spectrophotometer. The conductivity studies were performed by a four-probe technique using Keithley 614 electrometer.

3. Results and discussion

The powders prepared by simultaneous gelation and polymerization process are reported in the present work. These were found to be magnetic on being tested with simple magnet. This probably is due to the formation of magnetic phases of the oxide. In order to investigate the various phases the following studies were carried out.

3.1 *X-ray diffraction*

Figures 1a–e show XRD pattern of powders having 5%, 10%, 15%, 20% and 25% of pyrrole monomer, respectively. In figure 1a for the powder formed with 5% of monomer (pyrrole) peaks at $2q = 24 \cdot 4°$, $33 \cdot 2°$, $41°$ and $49 \cdot 67°$ were observed corresponding to *a*-Fe_2O_3 with *hkl* values (012), (104), (113) and (024). Additional peaks at $2q = 35 \cdot 2°$, $44 \cdot 54°$, $54 \cdot 8°$, $64 \cdot 86°$ and $74 \cdot 4°$ with *hkl* values (311), (400), (511), (531) and (533) corresponding to cubic Fe_3O_4 phase were also present. It can be seen from figure 1b (10% concentration of pyrrole) that only peaks at $2q = 33 \cdot 2°$ and $49 \cdot 67°$ belonging to *a*-Fe_2O_3 phase with *hkl* values (104) and (113) are observed, whereas rest of the peaks at $2q = 35 \cdot 2°$, $44 \cdot 54°$, $54 \cdot 8°$, $64 \cdot 86°$ and $74 \cdot 4°$ with *hkl* values (311), (400), (511), (531) and (533) correspond to Fe_3O_4 phase.

As the concentration of monomer is increased to 15% in the mixture, the peaks at $2q = 35 \cdot 2°$, $38 \cdot 2°$, $44 \cdot 54°$, $54 \cdot 8°$, $64 \cdot 86°$ and $74 \cdot 4°$ with *hkl* values (311), (222), (400), (511), (531) and (533) corresponding to only Fe_3O_4

phase are observed as shown in figure 1c. For the composites having higher concentration of pyrrole viz. 20% and 25% of monomer respectively, figures 1d and e show the formation of single phase *a*-Fe_2O_3 as seen from peaks at $2q = 24 \cdot 4°$, $33 \cdot 2°$, $35 \cdot 4°$, $41°$, $49 \cdot 67°$, $54 \cdot 1°$, $64 \cdot 2°$. The X-ray diffraction peaks were found to be broadened and was possibly due to the formation of nanosized oxide particles. The particle size obtained using the full width at half maximum in the Scherrer's formula yielded a value of ~ 10–20 nm.

Thus it is observed that for lower concentrations of pyrrole (i.e. 5% and 10%) both the *a*-Fe_2O_3 and Fe_3O_4 phases are present. Whereas, as the concentration of pyrrole is increased to 15% only the peaks corresponding to cubic Fe_3O_4 phase are present and the lattice constant was estimated to be $a = 8 \cdot 42$ Å. For the concentrations higher than 15% the hexagonal *a*-Fe_2O_3 phase is predominant and the lattice constant was calculated to be $a = 4 \cdot 98$ Å and $c = 13 \cdot 65$ Å. The values of the lattice constants obtained above compares well with the literature values (Dhara *et al* 1992).

3.2 *Scanning electron microscopy*

Figures 2a–d show SEM pictures of the powders obtained for different pyrrole concentrations viz. 5%, 10%, 15% and 25%, respectively.

The SEM photograph of powder obtained for 5% pyrrole monomer shows clusters of spherical shaped particles (figure 2a). As the concentration of pyrrole is
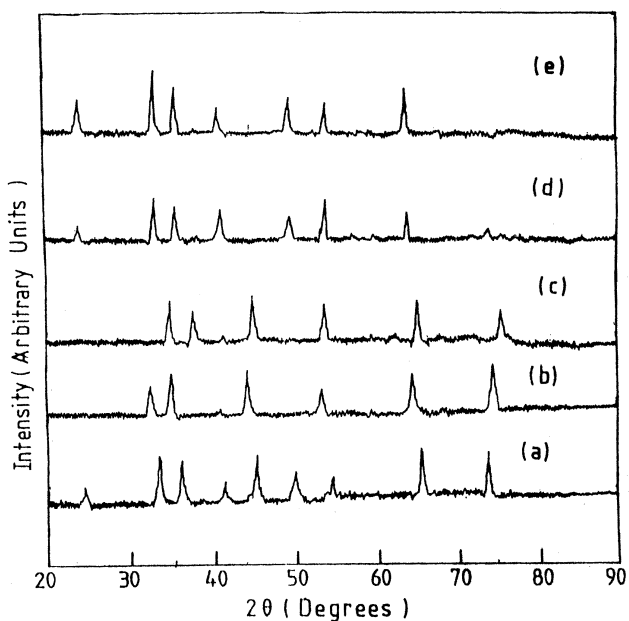

Figure 1. X-ray diffraction pattern of nanocomposite powders obtained from varied amounts of pyrrole monomer: (a) 5%, (b) 10%, (c) 15%, (d) 20% and (e) 25%.
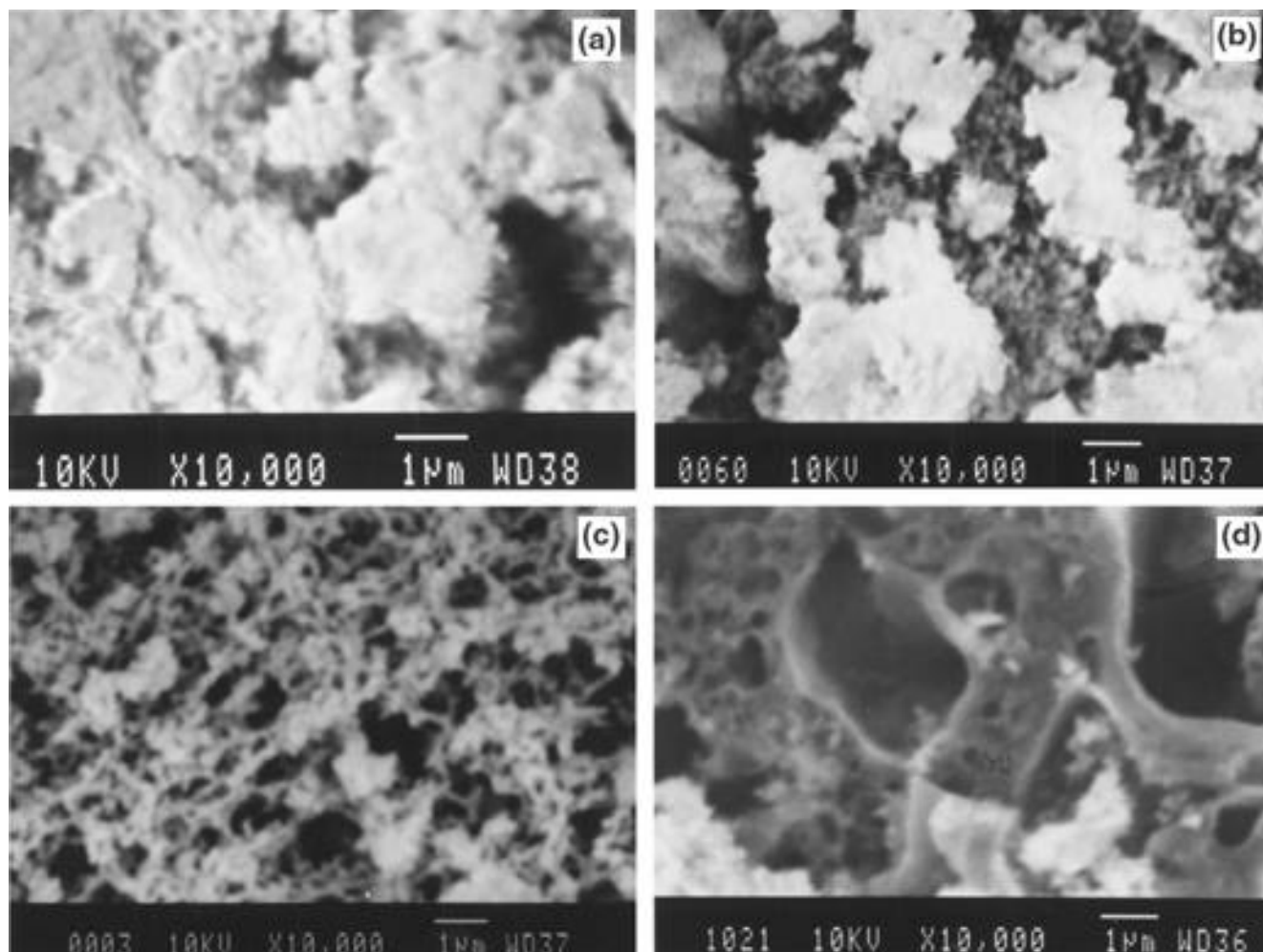
Figure 2. SEM photographs of nanocomposite powders obtained from varied amounts of pyrrole monomer: (a) 5%, (b) 10%, (c) 15% and (d) 25%.

increased to 10% the particles become slightly elongated and at the critical concentration of 15% of pyrrole a complete chain pattern is observed, with the chains connecting the nanosized oxide particles (figures 2b and c respectively). Figure 2d shows that as the concentration of pyrrole is increased further above the critical concentration, the chain pattern becomes less and less visible and clusters are observed. It is probable that at lower concentrations the oxide is encapsulating the polymer and with increasing monomer concentration, more and more polymerization give rise to chain pattern as observed in figure 2c. A further increase in the pyrrole concentration does not result in chain formation but rather a clustered growth.

3.3 *Fourier transform infrared spectroscopy*

The FTIR transmission spectra of the powders having KBr pellets obtained using 5%, 10%, 15%, 20% and 25% of pyrrole monomer was recorded in the range 400–
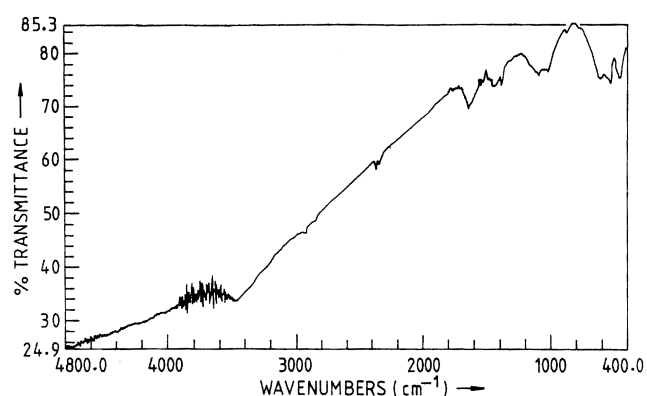

Figure 3. FT-IR spectra of nanocomposite powder for 15% pyrrole concentration.

4000 cm^{-1} to confirm polymerization of pyrrole. The spectra (figure 3) for all the samples showed peaks at 780 cm^{-1}, 1090 cm^{-1} and 3400 cm^{-1} indicating the presence of polypyrrole. The intensity of these peaks was

Table 1. Values of s for different concentrations of pyrrole in the nanocomposite powders.

Concentration of pyrrole	5%	10%	15%	20%	25%
s (s/cm)	$1 \cdot 05 \times 10^{-1}$	$4 \cdot 3 \times 10^{-1}$	$1 \cdot 13 \times 10^{1}$	$2 \cdot 3 \times 10^{-1}$	$1 \cdot 4 \times 10^{-1}$
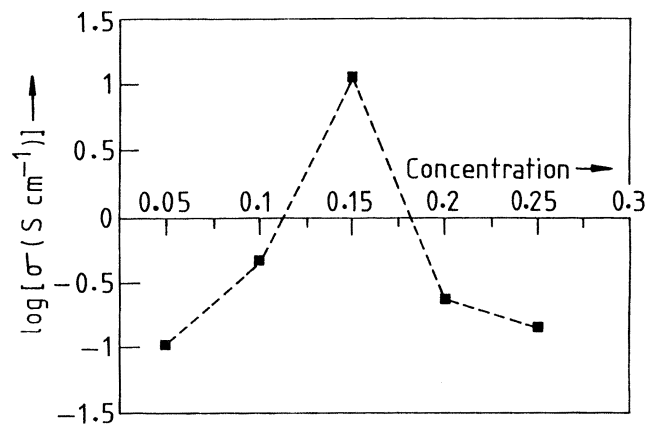
Figure 4. Variation of conductivity with concentration of polypyrrole.

found to increase with increase in the concentration of pyrrole.

3.4 *Conductivity*

The surface conductivity of compressed pellets of these powders was studied using four-probe method. The pellets of samples obtained for 5%, 10%, 15%, 20% and 25% of pyrrole monomer were used for conductivity studies. The values of s found for samples having different amounts of pyrrole monomer are shown in table 1.

Figure 4 shows the variation of conductivity with concentration of pyrrole. The conductivity (s) values showed a slight change for composites having low concentration of pyrrole. A sudden increase in s value is found for a particular concentration of pyrrole (i.e. 15%). This is the critical concentration for which electrical conductivity has maximum value and on further increasing the concentration we find a decrease in s value. This sudden increase in conductivity could possibly be explained on the basis of percolation theory (Tanioka *et al* 1982; Stauffer 1985), which predicts that at a certain amount of concentration of conducting polymer a full conducting path is formed for the flow of current. The conductivity remains almost negligible for lower concentrations and quite suddenly for some concentration a continuous path is set-up and conductivity rises. This has also been confirmed from SEM which shows the formation of chain pattern at a particular critical concentration viz. 15%, providing an increased conducting path and conductivity consequently.

4. Conclusions

The nanocomposites of polypyrrole and iron oxide were prepared using iron nitrate and 2-methoxy ethanol by simultaneous gelation of the oxide and the polymer viz. polypyrrole. The particles were found to be nano-crystalline. However, the composites exhibited mixed phase, belonging to both the corrundum a-Fe_2O_3 (non-magnetic) and the cubic phase, Fe_3O_4, which is ferri-magnetic. The presence of both the phases is clearly seen from the XRD studies. The existence of the Fe_3O_4 phase is the cause for the magnetic behaviour of the composites. The conductivity values did not show much change for lower concentrations of pyrrole. A marked increase in the conductivity is observed for a critical concentration, which needs further investigation. It can be observed that appropriate concentration of pyrrole can result in either a single magnetic phase or a nonmagnetic phase.

References

Anderson A, Hunderi O and Granqvist C G 1980 *J. Appl. Phys.* **57** 757
Butterworth M D, Corradi R, Johal J, Lascelles S F, Maeda S and Armes S P 1995 *J. Colloid Interface Sci.* **174** 510
Chauhan P, Annapoorni S and Trikha S K 1998 *Bull. Mater. Sci.* **21** 381
Chauhan P, Annapoorni S and Trikha S K 1999 *Thin Solid Films* **346** 266
Dhara S, Kotnala R K and Rastogi A C 1992 *Jpn J. Appl. Phys.* **31** 38
Huang C L and Matijevic E 1995 *J. Mater. Res.* **10** 1327
Jarjayes O, Fries P H and Bidan G 1995 *Synthetic Metals* **69** 343
Jewell J L, Harbison J P and Scherrer A 1991 *Sci. Am.* **5** 265
MacDiarmid A G and Epstein A J 1989 *Faraday Discuss. Chem. Soc.* **88** 333
MacDiarmid A G and Epstein A J 1993 *Conducting polymers,*

science and technology, Second Brazilian polymer conference (Brazil: Plenum Publishing Corp.)

Maeda S and Armes S P 1994 *Mater. Chem.* **4** 935

Maeda S and Armes S P 1995 *Chem. Mater.* **7** 171

Maeda S, Gill M and Armes S P 1994 *Polym. Mater. Sci. Eng.* **70** 352

Martin C R 1994 *Science* **266** 1961

Partch R, Gangolli S G, Matijevic E, Cal W and Arajs S 1991 *J. Colloid Interface Sci.* **144** 27

Roth S and Graupner W 1993 *Synthetic Metals* **57** 3623

Shull R D and Bennett L H 1992 *Nanostructured Matls.* **1** 83

Sinfelt J H 1977 *Science* **195** 641

Skotheim T (ed.) 1986 *Handbook of conducting polymers* (New York: Dekker) **1**

Stauffer D 1985 *Introduction to percolation theory* (London: Taylor and Francis)

Tanioka A, Oobayashi A, Kageyama Y, Miyasaka K and Ishikawa K 1982 *J. Polym. Sci. Polym. Phys. Ed.* **20** 2197

Xiao T D, Zhang Y D, Strutt P R, Budrick J I, Mohan K and Gonsalves K E 1993 *Nanostructured Matls.* **2** 285