Available online at <u>www.pelagiaresearchlibrary.com</u>



Pelagia Research Library

Der Chemica Sinica, 2012, 3(2):521-526



Synthesis and Characterization of Inorganic Polymer Nano-Composites

Birendra Pratap Singh*, Jai Prakash Singh, Shruti Shukla and Shanti Sharma

Department of Chemistry, University Institute of Engineering & Technology, C. S. J. M. University, Kanpur, India

ABSTRACT

A polymer is a large molecule, composed of many smaller units bonded together by covalent bond. Polymeric material may be inorganic, organic, natural or synthetic. Polymer nano composite are those materials in which nanoscopic inorganic particles typically $10-100A^0$ in at least one dimension are dispersed in an organic polymer matrix. This type of materials has many important properties such as linear, optical, electronic and conducting. Polymer nano composite exhibits mechanical characteristics, heat resistance and chemical resistance. Nano composite are used as advance owner material and high quality colour copiers. The polymer nano composites $Ni_{0.3}Mn_{0.7}Fe_2O_4$ (1), $Ni_{0.6}Mn_{0.4}$ Fe_2O_4 (2), $Co_{0.3}Mn_{0.7}$ Fe_2O_4 (3) and $Co_{0.6}Mn_{0.4}$ Fe_2O_4 (4) were synthesized by the ferric chloride, target metal salts and acrylic acid aqueous solution in 2:1 molar ratio under with stirring. The above compounds were characterized by IR and XRD spectral techniques. The IR spectra of oxides 1, 2, 3 and 4 appeared in the range 438-628cm⁻¹ which shows the formation of a single phase spinal structure having two sub lattices, tetrahedral and octahedral sites. Besides that, the two peaks appear in the range of 1367 -1381 cm⁻¹ are due C-O stretching by anhydride group in the metal oxides, confirms the acrylic acid formed as polymer with spinal oxide. The XRD powder pattern of oxides 1, 2, 3 and 4 shows a cubic crystal with unit cell dimensions and crystalline sizes in the range of 8.299-8.33A⁰ and 15-21nm, respectively.

Key words: Polymer, Composites, Oxides, Nano materials, XRD.

INTRODUCTION

Nanotechnology can be broadly defined as the creation, processing, characterization and utilization of materials, devices and systems with dimensions on the order of 0.1-100 nm exhibiting novel and significantly enhanced physical, chemical and biological properties and processes due to their nano scale size [1]. Significant scientific and technological interest has been focused on composite materials [2] and nano composite materials over the last two decades, in particular using inorganic nano particles into polymer matrix to from the novel composite materials that can provide better performances in many industrial applications [3]. Polymer nano composite [4] is a polymer or a co-polymer having dispersed in its nano particles. The coordination polymers are also important for synthesizing the inorganic polymer nano composites [5-7]. Polymer nano composite exhibit superior mechanical characteristics, heat resistance and chemical resistance compared to the neat or traditionally filled resins. Researchers have successfully developed the new approaches for revealing the dispersion of nano particles in polymer nano composites. The assessment of polymer nano composites creates some major challenges. The particles are on the nano skill, similar to the semi crystalline morphology of the polymer. To asses the level of dispersion, it requires a large area to be

studied at a high magnifications. Polymer materials have been filled with several inorganic compounds in order to increase the properties like heat resistance, mechanical strength, impact resistance and to decrease other properties like electrical conductivity and dielectric constant their by increasing the permeability for gases like oxygen and water vapour. Polymer composites containing ferrites are increasingly replacing the conventional ceramic magnetic materials because of their mouldability and reduction in cast. The synthesis of polymer nano composites is an integral aspect of polymer nano technology by inserting the nano metric inorganic compounds [8]. The properties of polymer, improve enhance a lot of applications depending upon the inorganic material present in a polymer. Manganese, zinc ferrites is one of the ferrite having wide applications [9]. The single molecular precursor's methods have achieved great importance in synthesizing ferrite materials. The polymer pyrolysis method was thought to be simple and particularly suitable for preparation of mixed metal oxides. The nano crystalline, ZnCo₂O₄ oxides was synthesized by S. V. et al [10]. The highly homogeneous metal oxides cathode materials for lithium ion batteries were made by above methods [11]. The nano sized cobalt ferrites have been synthesized by polymer pyrolysis process [12]. An amphiphilic poly (styring-block-acrylamide) was synthesized by qu et al [13]. The functionalized copper nano composite/polymer composites can be copolymerized with other acrylic monomer [14] A series of binary composites based on high density polyethylene and nano inorganic particle were prepared by xin et al [15]. Polymer nano composites represent a new alternative to conventionally filled polymer because of their nano meter sizes. Polymers that contain transition metal complexes, either attach to or directly inserted in a pi conjugated back bone are an exciting and a promising class of modern materials. Inorganic polymer nano composites are materials comprising of nano meter sized [16]. Metals and metal alloys such as Fe or CoPt oxides such as ferric oxide and ferrites are used as inorganic nano fillers in the nano composite [17]-[22]. Xu et al [23] reported that the magnetic polyacrylamide particles using small molecular emulsifier (span 80) and magnetic polymeric particles can be attracted easily by magnet.

In the present work, the polymer nano composites $Ni_{0.3}Mn_{0.7}Fe_2O_4(1)$, $Ni_{0.6}Mn_{0.4}Fe_2O_4(2)$, $Co_{0.3}Mn_{0.7}Fe_2O_4(3)$ and $Co_{0.6}Mn_{0.4}Fe_2O_4(4)$ were synthesized by polymer pyrolysis roots. The structures were characterized by IR and XRD spectral techniques.

MATERIALS AND METHODS

Materials and measurements

The chemical reagents, FeCl₃.6H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O, MnCl₂.4H₂O, (NH₄)₂S₂O₈, acrylic acid and NaOH were used as obtained. All reagents are analytical grade and were used without further purifications. The infra red spectra were recorded on FT-IR spectrophotometer, brucker (vertex 70) using KBr pallets in a range of 4000-400cm⁻¹. X-ray powder diffraction patterns of compounds were recorded on an X-ray differactometer (ISODEBYE. FLEX-2002) using Cu-k\alpha as radiation source (λ =1.54181A°)

Preparation of standard solution

Aqueous solution of acrylic acid (acrylic acid: water :: 70:30) and 5% ammonium per sulphate solution were prepared for experiment. The sample solution was prepared by dissolving stoichiometric amounts of the metal salts in distilled water. The NaOH solution was standardized against a solution of primary standard such as oxalic acid and oxalic acid was titrated as dibasic acid. 25ml of oxalic acid was taken into a flask and added 8-10 drops of phenolphthalein. The above solution was titrated with the NaOH solution, when all the acid neutralized, a more stable pink color was appeared. The end of the titration was taken as the point at which the color persists for about 30 seconds in the solution stirred after addition of the last drop of NaOH.

Synthesis of complexes

Ferric chloride salt and target metal chlorides were dissolved in 10 ml of acrylic acid aqueous solution (acrylic acid: water :: 70:30) under with stirring. Above solution added into 5% $(NH_4)_2S_2O_8$ solution at 70-90°C for two hours. The mixed solution were dried to form the distributed poly acrylic salt. The poly acrylic salt were dried at 90-100°C for 24 hours and the salts were heated at 170°C about four hours to obtained the amorphous nature of salt. The above salts were sintered at 400°C about four hours in air. Then the final products were obtained after being slowly cooled at room temperature.



Scheme-I

RESULTS AND DISCUSSION

Infra-red spectroscopy

The IR spectra (Fig.1) of compounds 1, 2, 3 and 4 showed the v(OH) group was confirmed due to the appearance of peaks at 3422 cm⁻¹, 3414 cm⁻¹, 3413cm⁻¹ and 3387cm⁻¹, respectively. The appearance of peaks in the range of 1367-1381cm⁻¹ due to C-C and C-O stretching, respectively, confirmed the anhydric group of acrylic acid present in compounds 1- 4 as polymeric form (Table 1). The absorption bands in the region 438-628 cm⁻¹ indicated the formation of single phase spinal structures.

	Wave numbers of absorption band v(cm ⁻¹)				
Compounds	v_1	v_2	v_3	v_4	v_5
	(OH)	(C-O)	(C-C)	single phase s	oinal structure
Ni0.3Mn0.7Fe2O4	3422	1381	1466	611	464
Ni _{0.6} Mn _{0.4} Fe ₂ O ₄	3414	1382	1481	615	438
Co _{0.3} Mn _{0.7} Fe ₂ O ₄	3413	1367	1531	596	463
Co _{0.6} Mn _{0.4} Fe ₂ O ₄	3387	1367	1480	628	603

Table 1. Infrared spectra of compounds

X-ray diffraction pattern

The XRD pattern of compounds 1, 2, 3 and 4 are shown in Fig.2. X-ray diffraction powder pattern of compounds 1, 2, 3 and 4 showed that these oxides crystallizes in a cubic crystal with the unit cell dimensions of $8.298-8.338A^{\circ}$ and the crystallite size (S,15-21nm). The diffraction pattern and lattice parameters of all diffraction peaks match well those of JCPDS card (10-0319) for all oxides. All the oxides showed spinal structures in the XRD patterns. The crystalline dimensions can be calculated from XRD patterns using the "Scherer's Equation". The trends of decrease of lattice parameters are shown in Table 2.

Birendra Pratap Singh et al





Compounds	Dimensions(A ⁰)	Particle size(nm)
$Ni_{0.3}Mn_{0.7}Fe_2O_4$	8.336	15
Ni _{0.6} Mn _{0.4} Fe ₂ O ₄	8.305	17
Co _{0.3} Mn _{0.7} Fe ₂ O ₄	8.300	18
$Co_{0.6}Mn_{0.4}Fe_2O_4$	8.298	18



Fig. 2. XRD powder patterns of compound 1,2,3 and 4 at 400°C.

CONCLUSION

The nano crystalline compounds were prepared by the reaction of ferric chloride, target metal salts and acrylic acid. IR analysis showed that the acrylic acid polymerizes at a low temperature and to form spinal ferrite. The study of XRD analysis indicated that the decrease in lattice parameter can be explain on the basis of differences in the ionic radii of $Mn^{+2} > Co^{+2} > Ni^{+2}$. The trend of ionic radii showed, decrease in lattice parameter on addition of Mn^{+2} and Co^{+2} , stoichiometrically. The oxides sintered at 400°C have good crystallinity with spinal structure and uniformly distributed in size of 15- 20 nm.

Acknowledgements

Authors are thankful to the Director, University Institute of Engineering & Technology, C.S.J.M. University, Kanpur for providing laboratory facilities.

REFERENCES

[1] American Ceramic Society, 2004.
[2] R. Kumar, S. Obrai, A. Sharma, *Der Chemica Sinica*, 2011, 2(4), 219.

- [3] S. Li, M. Lin, M. Toprak, D. K. Kim, M. Muhammed, Nano. Rev., 2010, 1, 5214.
- [4] C. Kiyoshi, Purasuchikkusu., 1995, 46(9), 20.
- [5] A. D. Patel, N. K. Prajapati, S. P. Patel, G. R. Patel, Der Chemica Sinica, 2011, 2(2), 130.
- [6] Y. S. Patel, H. S. Patel, Der Chemica Sinica, 2011, 2(6) 58.
- [7] S. M. Shah, F. B. Bux, V. Parmar, A. Singh, Der Chemica Sinica, 2011, 2(6), 304.
- [8] L. N. Larikov, Metallofizika(kiev)., 1992, 14(7), 3.
- [9] K. Raj, R. Moskowitz, J. Magn. Magn. Mater., 1990, 85, 233.
- [10] S. V. Bangale, S. M. Khetre, S. R. Bamane, Der Chemica Sinica, 2011, 2(4), 303.
- [11] L. H. Yu, Y. L. Cao, H. X. Yang, X. P. Ai, Y. Y. Ren, Mater. Chem. Phys., 2004, 88, 353.
- [12] L. H. Yu, H. X. Yang, X. P. Ai, Y. L. Cao, J. Phys. Chem., 2005, B109, 1148.
- [13] Y. Z. Qu, Z. S. Sun, Y. N. Su, Shivoy. Xuebao. Shivoy. Jigang., 2007, 23(5), 55.
- [14] K. C. Anuyaogu, A. V. Fedorov, D. C. Nackers, Langmuir., 2008, 24(8), 4340.
- [15] D. Xin, Q. Shang, Q. Jia, S. Li, Y. Xia, Poly. Engg. & Sci., 2010, 50, 894.
- [16] S. Li, M. Toprak, Y. Jo, J. Dobsan, K. D. Kim, M. Muhammed, Adv. Mater., 2007, 19, 4347.
- [17] L.J. Wilson, P. Poddar, A. N. Frey, H. Srikanth, K. Mohomed, P. J. Harmon, S. Kotha, J. Wachsmuth, J. Appl. Phys., 2004, 95,1439.
- [18] D. A. N. Burke, H. D. Stover, P. F. Dawson, Chem. Mater., 2002, 14, 4752.
- [19] J. Fang, D. L. Tung, L. K. Stokes, J. He, D. Caruntu, L. W. Zhou, J. C. O'connor, J. Appl. Phys., 2002, 91,8816.
- [20] R. Gangopadhyay, A. De, Eur. Poly. J., 1999, 35, 1985.
- [21] J.Gass, P. Poddar, J. Almond, S. Srinath, H. Srikanth, Adv. Funct. Mater., 2006, 16, 71.
- [22] T. Prabhakaran, J. Hemalatha, J. Poly. Sci. B. Poly. Phys., 2008, 46, 2418.
- [23] Z. Z. Xu, C. C. Wang, W. L. Yang, Y. H. Dang, S. K. Fu, J. Jmmm., 2003, 277, 36.