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Research Article

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In situ synthesis of poly (methyl methacrylate)/ cobalt II nitrate: Structural, thermal and electrical conductivity

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ABSTRACT

In-situ polymerization of methyl methacrylate (MMA) was carried out in the presence of various concentrations of cobalt II nitrate ($Co(NO_3)_2$) to synthesize poly (methyl methacrylate) (PMMA)/ $Co(NO_3)_2$ complexes by a free radical polymerization method. The polymer metal complexes were characterized by employing UV–visible absorption and Fourier transform infrared spectroscopy. The surface morphology of the complexes was analysed with scanning electron microscopy. Thermal stability and glass transition temperature of the complexes was determined by thermal gravimetric analysis and differential thermal analysis respectively. AC conductivity behaviour was investigated in the frequency range of 100- 10^6 Hz at room temperature. The UV and FTIR spectra confirmed the co-ordination interaction between PMMA and $Co(NO_3)_2$. SEM images showed that the metal oxide particles were well dispersed in the macromolecular chain of PMMA. Thermal studies showed that the thermal stability and glass transition temperature of the samples were increased with increase in Co $(NO_3)_2$ concentration in PMMA. AC conductivity was significantly higher than pure PMMA and the conductivity increased with increase in Co $Co(NO_3)_2$ content and also with the increase in frequency.

Keywords: poly (methyl methacrylate), cobalt II nitrate, morphology, thermal stability, electrical conductivity.

INTRODUCTION

Interactions of inorganic materials with functional polymers are particularly interest for the fabrication of inorganic-organic structured material. Based on the level of interaction between the inorganic particles and macromolecular chain, one can develop a material that is mechanically superior and thermally stable. However, the interactions between the polymer and particles are poor due to the incompatibility which leads to agglomeration of particles in most cases and they are also difficult to disperse uniformly into the polymer chain[1, 2]. Several researchers are focused on thermal and electrical properties of heterogeneous materials in recent years [3, 4]. The electrical conductivity and relaxation behaviour of composites are depending upon the surface area, surface conductivities, diameter and the dispersion of filler particles within the polymer [5].

Poly (methyl methacrylate) (PMMA) is an important engineering material, used in various applications such as dielectric in organic thin films, opto-elctronic devices, optical lenses in cameras and advanced electronic devices [6, 7]. In this study, an attempt has been made to fabricate the PMMA/$Co(NO_3)_2$ complexes by a simple in situ polymerization of MMA with different molar concentration of cobalt II nitrate and performance of the complexes has been carried out by spectroscopic, morphological and thermal studies. The electrical conductivity of polymer metal complexes is compared with respect to corresponding properties obtained for unfilled PMMA.

EXPERIMENTAL SECTION

Methyl methacrylate (MMA, analytical reagent grade), cobalt (II) nitrate ($Co(NO_3)_2$), analytical reagent grade), 2, 2′-azobisisobutyronitrile (AIBN) (analytical reagent grade), ethyl alcohol and acetone were all purchased from Nice Chemicals, Cochin, India.

Synthesis of PMMA/ cobalt (II) nitrate complexes

Freshly distilled methyl methacrylate (MMA) was mixed (10 ml) with different molar concentration of Co $(NO_3)_2$ such as 1.6, 2.0, 2.4 and 2.8x 10^{-4} moles/liter in acetone and heated to reflux. After refluxing for 30 min, an appropriate amount of 2, 2′-azobisisobutyronitrile (AIBN) was added and the polymerization was carried out at 70 ^oC for 6 hr in an inert atmosphere. The synthesised polymer was then precipitated from ethyl alcohol and dried at 60 ^oC for 4h in a vacuum oven.

Characterization Techniques

The UV–visible absorption spectra of polymer solution in water were analysed using a JASCO V 550 spectrophotometer. The infrared (IR) spectra of the polymer metal complexes were recorded on a JASCO (model 4100) FTIR spectrophotometer in the region 400– 4000 cm^{-1}. The surface structure of the complexes was investigated by using field emission scanning electron microscopy (Hitachi, SU 6600 FESEM). TGA analysis was conducted by using Q 50 V2O 13 in a platinum pan with nitrogen flow rate of 60 ml per minute. The samples were heated at a rate of 10 ^oC/min in a temperature range of room temperature to 450 ^{0} C suitable for the given sample. The AC conductivity of PMMA and PMMA with different content of metal salt was measured over a frequency range 10^2-10^5 Hertz using a fully automatic Hewlett–Packard LCR Meter.

RESULT AND DISCUSSION

FTIR characterization

FTIR spectra of PMMA and PMMA with various molar concentrations of cobalt II complexes are given in Figure 1. It is clear that the characteristic vibration bands of synthesized PMMA appears at 1728 cm^{-1} (C=O) and 1450 cm^{-1} (C–O). The absorption bands observed at 3000 and 2900 cm^{-1} are associated with the C–H stretching of the methyl group (CH_3) while the bands obtained at 1300 and 1450 cm^{-1} are related to the C–H symmetric and asymmetric stretching modes, respectively [8]. The ester and methylene group of PMMA is appeared at 1240 cm^{-1} and 1146 cm^{-1} respectively.

In the case of Cobalt (II) complexes of PMMA, the stretching vibration of ester carbonyl group (C=O) of sample is appeared at 1724cm^{-1}, a shift in the frequency observed with respect to the synthesized PMMA which is attributed due to the co-ordination interaction of metal complex with the methacrylate part of PMMA. The vibration of ester group (C-O) is not seen at the range of 1146 cm^{-1}, but the introduction of Co $(NO_3)_2$ induces a new absorption band at 1018 cm^{-1}. From these observations, it can be predicted that the cobalt (II) nitrate is coordinated to C=O group of methacrylate unit and C-O group of the adjacent methacrylate unit make a bonded with the metal atom.

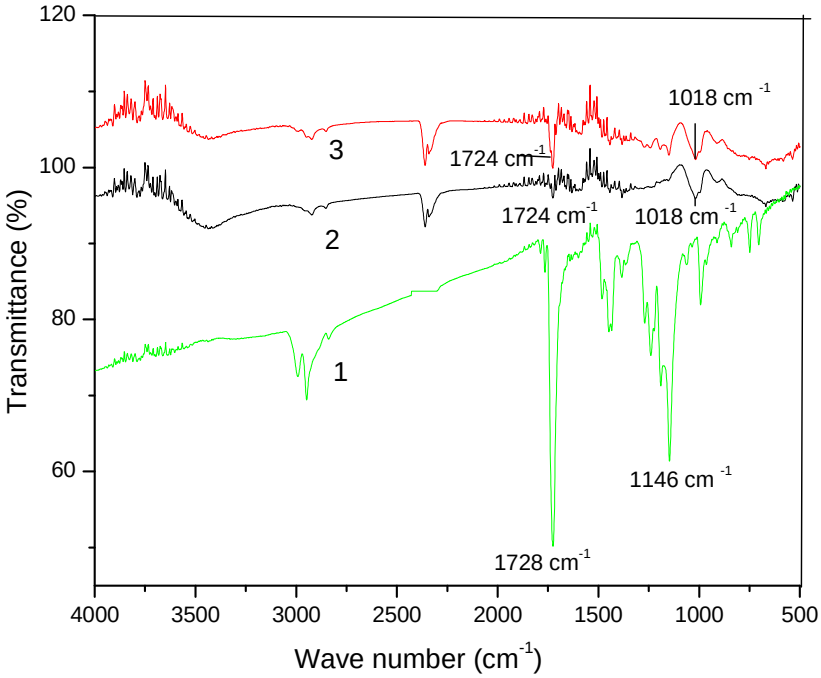

Figure 1. FTIR spectra of (1) PMMA (2) low and
(3) higher concentrations of Co II complexes of PMMA

UV spectroscopy

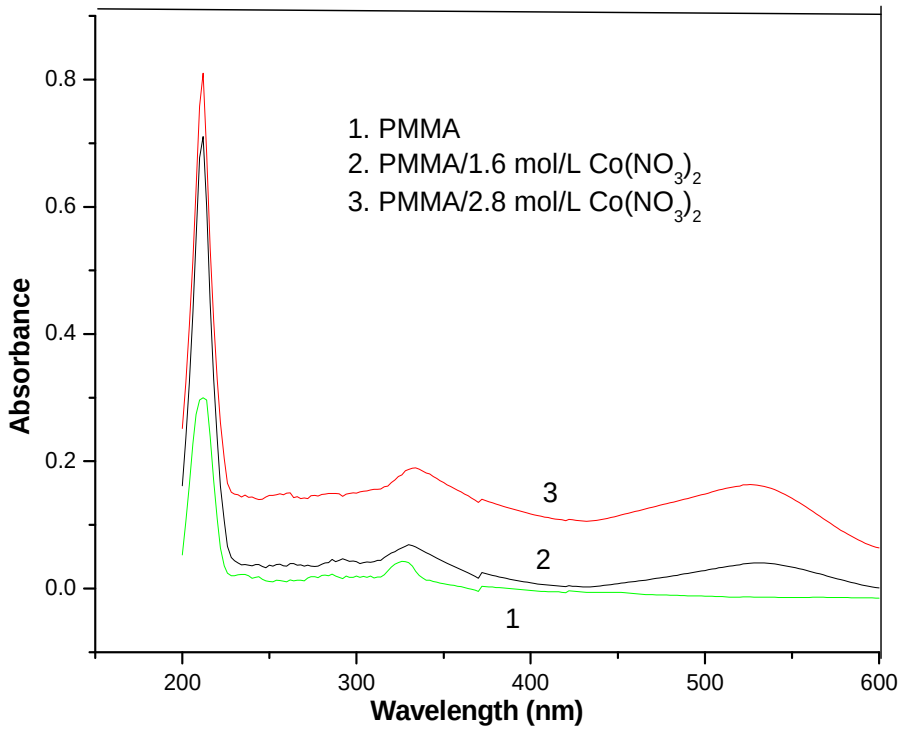

Figure 2. UV spectra of PMMA with differnt concentrations of Co II

Figure 2 shows the UV spectra of PMMA and PMMA with different molar concentration of Co $(NO_{3)2}$. In the UV spectrum of PMMA, the absorption peaks shown at the range of wavelength of 326 nm and 212 nm. This absorptions are corresponding to the n-π* and π- π* transitions. In the case of cobalt (II) nitrate complex, nitrate ion is a chromophore, so hypsochromic effect takes place, which is the shift of absorption to shorter wavelength and nitrate ion act as an electron acceptor as well as donor. The electron density of cobalt is less due to the transfer of electron from cobalt to ligand [9]. Due to this, cobalt (II) coordinated to lone pair of oxygen more strongly and the intensity of absorption increases with increase in molar concentration of Co $(NO_{3)2}$.

Scanning Electron microscopy (SEM)

Figure 3 shows the SEM images of PMMA and PMMA with 2.0 x 10^{-4} moles/liter of Co $(NO_3)_2$. The SEM image of PMMA (Fig. 3 (a)) shows the porous structure with few apparent holes in the fracture surface of polymer. However the metal complex linked PMMA (Fig. 3b)) reveals the uniform structure and the metal particles are well inserted into the macromolecular chain of PMMA, which indicates the stronger co-ordination interaction between the cobalt II nitrate and methacrylate unit of PMMA.

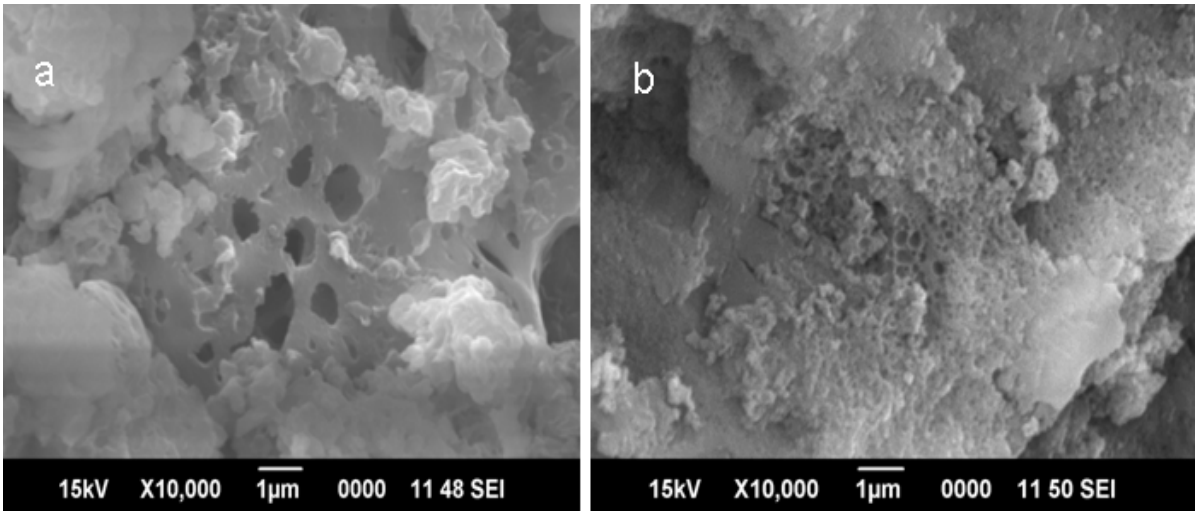

Figure 3. SEM images of pure PMMA and PMMA with 2.0 x 10^{-4} moles/liter of Co $(NO_{3)2}$

Thermal Analysis

Differential thermal analysis (DTA) of PMMA, different concentrations of Co $(NO_3)_2$ is given in Figure 4. DTA detects the release or absorption of heat, which is associated with chemical and physical changes in materials as they are heated. From the DTA data it is observed that there are two exothermic peak one at 137 ^oC, which is its glass transition temperature and other at a higher temperature around 380 ^oC for PMMA. In addition to this there are two endothermic peaks one appear around 230-312 °C and another around 313-361 ^oC. In Co II of PMMA, an exothermic peak is appeared at 141 ^oC for lower concentration of metal whereas at higher concentration it increases to 145 ^oC. This shift in glass transition temperature indicates that the formation of bonds between the metal and the methacrylate groups in the polymerization process, which in turn make the polymer chain to enhances the processability [10]. The second exothermic peak occurs at a higher temperature around 388 ^oC. Unlike PMMA it has only one endothermic peak appear around 260-355 ^oC.

The TGA curves of PMMA and PMMA with different content of Co $(NO_3)_2$ are presented in Figure 5. It can be seen from the figure that all the compounds exhibit a major stage of decomposition with minor weight losses at the initial stage. The initial stages of weight losses are attributed to the decomposition of oligomers and unreacted monomers present in PMMA. The thermal decomposition temperature of PMMA/Co $(NO_3)_2$ is much greater than that of pure PMMA and the thermal stability of the complexes is found to be increases with increase in molar concentration of cobalt II. The increased thermal stability of the complexes is due to the strong co-ordination interaction between the polar segment of PMMA with the Co $(NO_3)_2$.

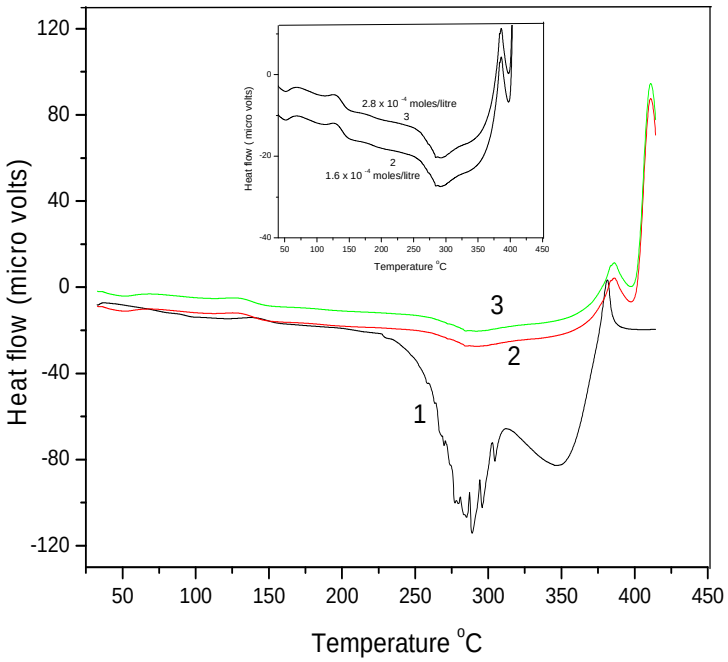

Figure 4. DTA curve of (1) PMMA (2) 1.6 mole (3) 2.8 mole of Co II - PMMA

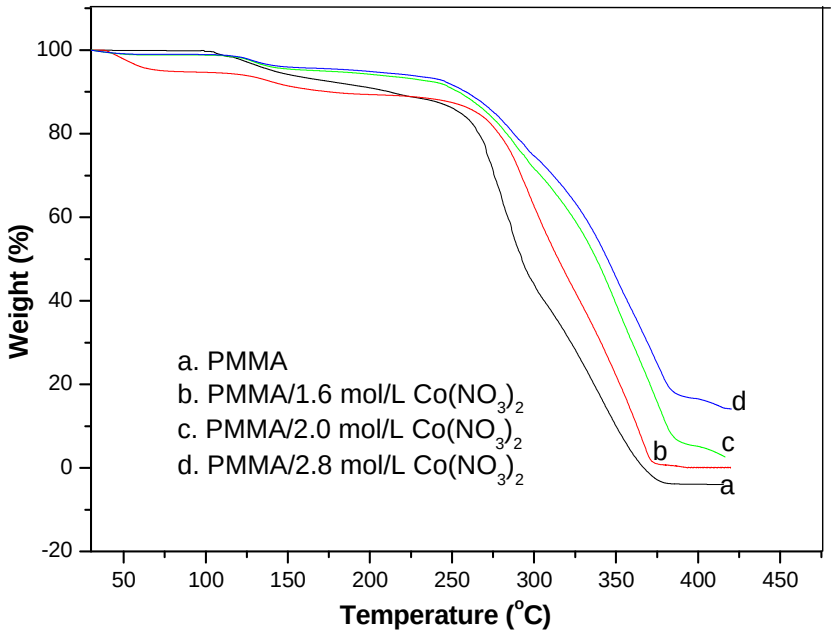

Figure 5. TGA of PMMA with diffrent concentration of Co $(NO_3)_2$

Conductivity studies

The AC electrical conductivity of PMMA and various concentration of Co (II) incorporated PMMA has been computed for different frequencies at atmospheric temperature are given in Figures 6. It is observed from the figure that the conductivity of all sample increases with increase in frequencies and the conductivity of PMMA is poor as compared to its metal complexes. Also the conductivity of metal complex is found to increases with increase in molar concentration of metal nitrate. This may be attributed to the tendency of dipoles in polymeric samples to orient themselves in the direction of the applied field [11, 12]. However at the high frequency range, the increasing trend seems to be sharp as compared for lower frequency region. This trend is observed for all graphs for different concentration of metals

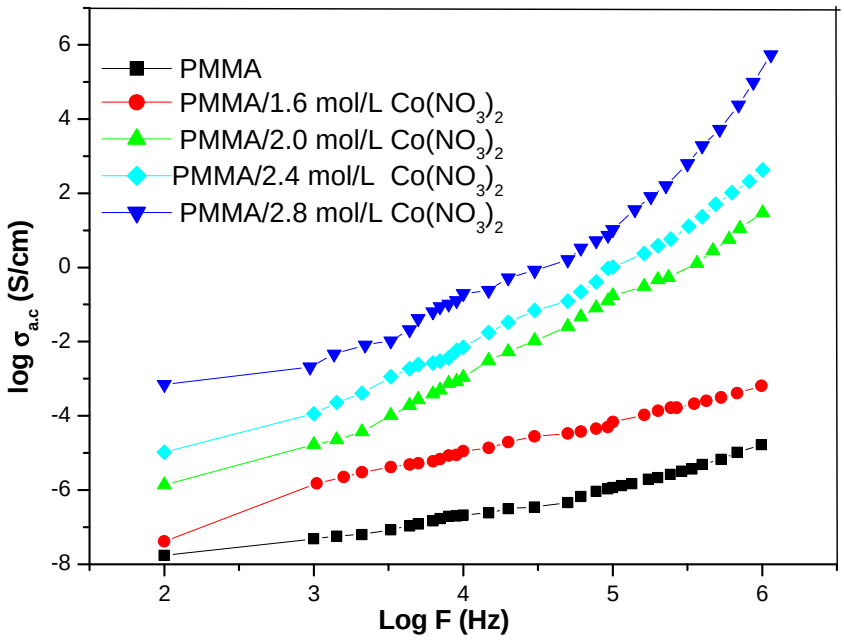

Figure 6. AC conductivity of PMMA with various contents of $Co(NO_3)_2$

CONCLUSION

PMMA with various molar concentration of cobalt II nitrate were successfully synthesized by free radical polymerization technique. The optical properties studied by UV spectra proved that the absorption of PMMA/ metal complexes increased with increase in molar concentration of Co $(NO_{3)2}$. FTIR spectra indicated the appearance of a new frequency and the shifting of absorption frequency in the complexes which is attributed to the strong co-ordination interaction between Co $(NO_3)_2$ and the polar part of polymer chains. The morphological observations revealed the dispersion of metal nitrate particles in the polymer. The basic decomposition pattern and thermal stability of the complexes were carried out using TGA/DTA. TGA results showed that the PMMA/ Co $(NO_3)_2$ complexes had better thermal stability than that of PMMA, due to the interaction between the carboxyl group of PMMA and the metal oxide moieties. DTA studies revealed that the glass transition temperature of PMMA was much improved by the introduction of metal complexes in PMMA. The AC conductivity values of metal complexes incorporated PMMA were higher than that of the pure PMMA and the conductivity of complexes were increased with increase in concentration of cobalt II nitrate.

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