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Structural, thermal and electrical properties of in situ synthesised poly (methyl methacrylate) / stannous (II) chloride

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ABSTRACT

Metal complexes of poly (methyl methacrylate) (PMMA)/ stannous chloride ($SnCl_2$) were synthesised by an in situ polymerization of methyl methacrylate with different molar concentrations of $SnCl_2$. The synthesized products were characterized by FTIR, UV, XRD, SEM and TGA. The FTIR and UV spectroscopic studies revealed that the $SnCl_2$ was coordinated to carbonyl oxygen and methoxy oxygen of methacrylate segments. The structure of polymer metal complexes studied by XRD revealed that the $SnCl_2$ particles were well inserted and orderly arranged in the polymeric system. The SEM photographs indicated that $SnCl_2$ particles were well dispersed into the polymer matrix. The incorporation of $SnCl_2$ in main chain of PMMA enhances excellent thermal resistance and the thermal stability of polymer complexes were increases with increase in concentration of $SnCl_2$. The AC conductivity of the polymer complexes was investigated in the frequency range of 10^2- 10^5 Hz at room temperature. The electrical properties (AC conductivity) of all polymer metal complexes were higher than pure PMMA and the conductivity increases with increase in molar concentration of $SnCl_2$.

KEY WORDS: Poly methacrylate, stannous II chloride, crystallinity, morphology, thermal stability, electrical conductivity.

1. INTRODUCTION

In the past decades much effort has been devoted to investigating metal-polymer system, by the attachment of inorganic components and the performance of polymer matrix will be greatly enhanced with respect to electrical, mechanical, thermal and especially optical properties (Singh and Gupta, 2011; Qiao, 2010; Ramesan, 2002). They have wide range of application in various sectors such as electronic devices, conductive composites, non-liner optical materials and so on (Ramesan, 2013). Poly (methyl methacrylate) (PMMA) is one of the important transparent polymeric materials and it is used in various applications as dielectric in organic thin films, opto-elctronic devices, optical lenses in cameras, optical fibers and advanced electronic devices (Lampe, 2001; Rusu, 2001).

Several researchers are focused on thermal and electrical properties of heterogeneous materials have gained momentum in recent years (Chae and Kim, 2005; Jayakrishnan and Ramesan, 2014). The properties of the polymeric materials used in plastic packaging play an important role in performance of devices. The electrical conductivity and relaxation behaviour of composites are affected by the interaction of metal/filler and polymer matrix. The surface area, surface conductivities, diameter and the dispersion of filler particles within the polymer influence the electrical conductivity of the resultant polymeric system (Ramesan, 2014 a). The conductivity in the filled macromolecules depends on time, temperature, frequency and strain.

In this work, a simple a simple in situ polymerization technique is used for the fabrication of PMMA/ stannous II chloride with different concentration of metal particles. The structure and morphology of the composite is ascertained by SEM and XRD. The interaction metal II chloride with the polar surface of the PMMA has been studied by UV and FTIR spectroscopy. The thermal stability of the fabricated polymeric system is studied by TGA measurements. This study is also concentrated on the influence of metal particles on electrical of PMMA/ stannous II chloride.

2. MATERIAL AND METHODS

Methyl methacrylate (MMA, analytical reagent grade), stannous (II) chloride (Sn II, analytical reagent grade), 2, 2′-azobisisobutyronitrile (AIBN) (analytical reagent grade), ethyl alcohol and acetone were all purchased from Nice Chemicals, Cochin, India.

2.1. Synthesis of PMMA/ Stannous II chloride complexes: 10 mL of freshly distilled methyl methacrylate (MMA) was mixed with different molar concentration of stannous II chloride (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°C for 6 hr in an inert atmosphere. The polymer was then precipitated from alcohol and dried to get a constant weight.

2.2. Characterization: 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 UV–visible absorption spectra of polymer were analysed using a JASCO V 550 spectrophotometer. X-ray diffraction measurements were carried

out by using a Bruker AXS D X-ray diffractometer using CuK_α radiation (λ= 1.5406 Å) with an accelerating voltage of 30 KV. The diffractogram was recorded in terms of 2 θ in the range of 20–80°. The surface structure of the composite 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°C/min in a temperature range of room temperature to 600^0 C suitable for the given sample. The AC conductivity (σ ac) was determined using Hewlett–Packard LCR Meter at a frequency range of 10^2-10^5 Hertz.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectra: FTIR spectra of PMMA and stannous II complexes of PMMA with different concentration are depicted in Figure 1. From the figure it is apparent that the synthesized polymer contains characteristic vibration bands of PMMA appear at 1728 cm^{-1} (C=O) and 1450 cm^{-1} (C–O). The bands at 3000 and 2900 cm^{-1} correspond to the C–H stretching of the methyl group (CH_3) while the bands at 1300 and 1450 cm^{-1} are associated with C–H symmetric and asymmetric stretching modes, respectively. The 1240 cm^{-1} band is assigned to torsion of the methylene group (CH_2) and the 1146 cm^{-1} band corresponds to vibration of the ester group C–O, while C–C stretching bands are at 1000 and 800 cm^{-1} (Ramesan and Pradyumnan 2011). However in the case of the stannous (II) complexes of PMMA, the stretching vibration of ester carbonyl group (C=O) present at 1724cm^{-1}, a shift in the frequency observed with respect to the synthesized PPMA which is attributed due to the interaction of metal complex with the methacrylate part of PMMA. It is also clear from the figure that a new peak is appeared at 1015cm^{-1} and it reveals that the chemical interaction is taking place in tin complexes with methacrylate unit leads to a shift in vibrational band shows that the coordination of metal may be takes place at oxygen atom of C-O group and C=O group of the adjacent monomer unit. Further, the intensity of vibrational bands also increases with increase in concentration of stannous (II) chloride.

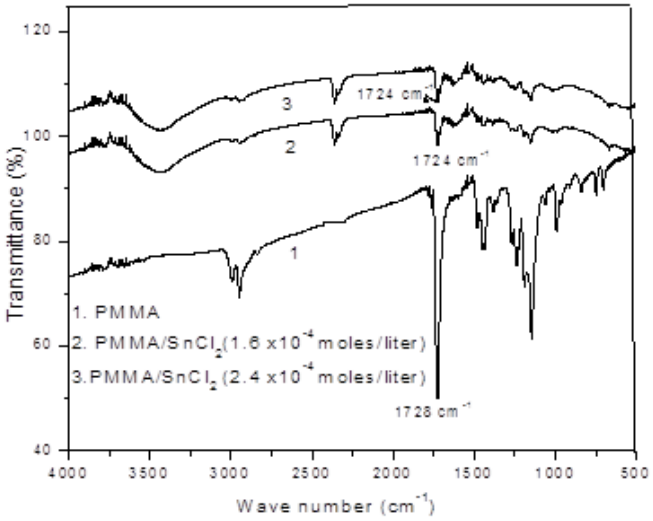

Figure.1.FTIR spectra of PMMA with various concentration of $SnCl_2$

3.2. UV spectroscopy: UV spectra of PMMA and stannous II complexes of PMMA with different concentration are illustrated in the Figure 2. In the UV spectrum of PMMA, the absorption peaks are appeared at 326nm and 212nm and this absorptions are corresponding to the n-π* and π- π* transitions respectively. It is interesting to observe that the absorbance of PMMA/ Sn II composite much higher than the pure PMMA. The higher absorption is due to the co-ordination interaction between the metal particles with the carbonyl groups of PMMA. As the concentration Sn II increases the intensity of absorption peaks increases and the absorbance peaks are shifted towards a higher wavelength region is due to the improved interaction between the polymer and Sn II system.

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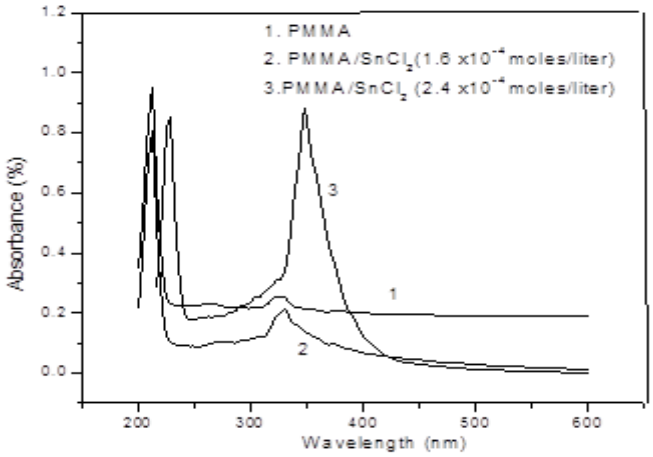

Figure.2.UV spectra of PMMA and PMMA with different molar concentration of $SnCl_2$

3.3. X-ray diffraction studies (XRD): The X-ray diffractograms of PMMA and PMMA with stannous II chloride matrix is shown in Figure 3. It is obvious that the X-ray pattern of synthesized PMMA shows a strong broad band at 2θ =14.2 ° and two peaks at 2θ = 30.2 °, 2θ and 42.3° shows the good agreement with the JCPDS card no. 13-0835 (Sathish and Shekar, 2014). The X-ray peaks obtained for PMMA indicates the amorphous nature of the polymer. The XRD pattern of PMMA/ $SnCl_2$ shows two sharp peaks around 2θ = 14.3° and 30.7° and this means that the metal particles are well inserted into the polymer chain. It is also evident from the figure that the broad peak of the PMMA is decreased due to the attachment of $SnCl_2$ in the main chain of PMMA.

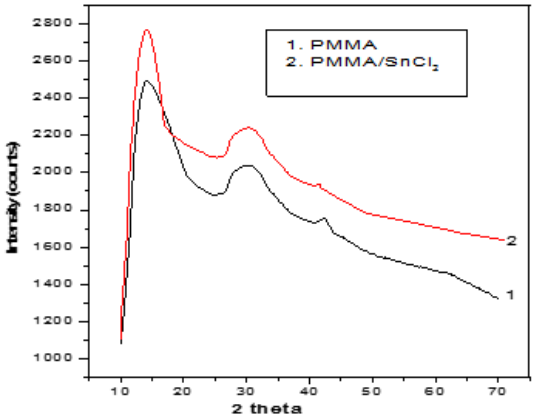

Figure.3.XRD patterns of PMMA and PMMA/$SnCl_2$

3.4. Scanning Electron microscopy (SEM):SEM photographs of pure PMMA and PMMA with 2.0 x 10^{-4} moles/liter of Sn II is given in Figure 4. The SEM image of PMMA (Fig. 4 (a)) reveals a porous structure having some apparent holes in the fracture surface of polymer. However the metal complex linked PMMA (Fig. 4(b)) shows the uniform structure and the metal particles are dispersed well in the polymer indicating stronger co-ordination interaction between the tin and methacrylate unit of PMMA.

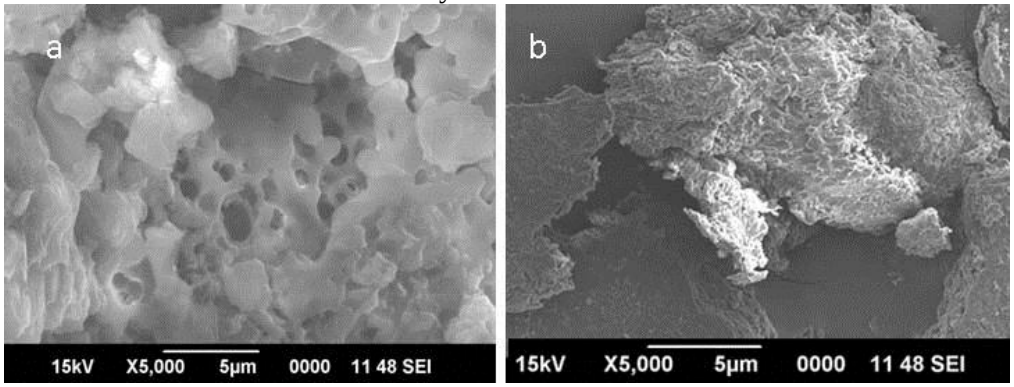

Figure.4.SEM photographs of (a) PMMA (b) PMMA with 2x10^{-4} mol/L $SnCl_2$

3.5. Thermogravimetric analysis: The TG curves of the PMMA and tin II complexes of PMMA with different concentrations are reproduced in Figures 5. The degradation of PMMA starts at 242°C and goes up to 385 °C with 99.85 % of the sample disappearing as a result of the complete degradation. In the case of tin II complexes it is interesting to see that as the concentration of metal complexes increases, the thermal stability of the PMMA is found to be increasing. The thermal degradation starts at 262 °C and goes up to 420 °C for lower concentrations of metal whereas at higher concentrations the degradation stars from 270 °C and goes up to 445 °C. This deviation from the regular structure may be due to the incorporation of small amount of metal unit in the polymer chain. Then attachment of metal complexes in the polymer chain may be interfering in depropagation as well as stabilizing at least part of the polymer (Ramesan, 2014).

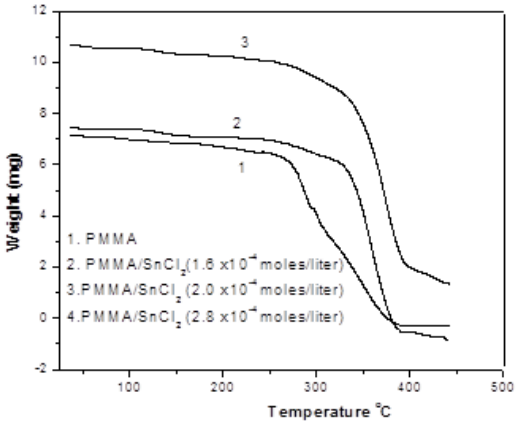

Figure.5.TGA curves of PMMA and PMMA with various contents of SnCl

3.6. Conductivity studies: The AC electrical conductivity of PMMA and various concentrations of Sn (II) complexes incorporated PMMA at different frequencies is given in Figure 6. It is observed from figure that the conductivity of all samples is increases with increase in frequency. The magnitude of conductivity of all the sample is higher at higher frequencies is due to the formation of excess charge carriers developed in the polymer matrix (Ramesan, 2014 b). The conductivity of PMMA/Sn II complex is much higher than the pure PMMA and the conductivity is found to be increases with increase in molar concentrations of stannous chloride in the polymeric system. The higher conductivity of PMMA/ $SnCl_2$ is due to the uniform dispersion and the spatial arrangement of metal particles within the polymer matrix and this result is in good agreement with the SEM and XRD studies.

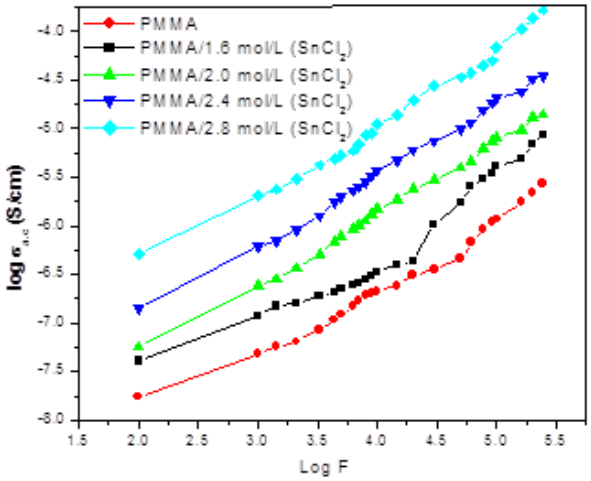

Figure.6. AC conductivity of PMMA with various contents of $SnCl_2$

4. CONCLUSIONS

PMMA with different molar concentration of stannous chloride (0, 1.6, 2.0, 2.4 and 2.8x 10^{-4} moles/liter) was successfully synthesized through an in situ free radical polymerization method. The FTIR spectrum confirms the presence of metal particles through the co-ordination interaction between the particles and methacrylate unit. The UV-visible studies showed the charge transfer complexes between tin and the polar groups of PMMA chain. XRD studies showed that the broad amorphous nature of the pure PMMA is reduced by the attachment of $SnCl_2$

into the polymer matrix. SEM images confirmed the presence of tin which was uniformly distributed throughout the macromolecular chain of PMMA. The thermal stability of PMMA/ $SnCl_2$ was higher than the pure PMMA and the thermal decomposition temperature were found to be increases with the increase in molar concentration of tin chloride. The AC electrical conductivity was studied as a function of frequency of the applied filed at room temperature. The increase in conductivity with the increase in loading of metal is due to the increase in volume of interfaces where the particle to particle distance is too small

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