

Preparation, morphology, and thermal and optical properties of thin films of ferric chloride/polyethylene oxide composites

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Pure poly (ethylene oxide) (PEO) films and PEO-FeCl₃ films of various concentration were prepared and studied for thermal and optical properties. Various analytical techniques like XRD, EDX, SEM, TGA, and UV were used to examine the structural properties of PEO and PEO-FeCl₃ systems. X-ray scans (XRD) revealed the existence of some crystalline part in the PEO matrix. The concentration of FeCl₃ has a great effect on the crystallinity of PEO. Thermogravimetric analysis (TGA) data established that accumulation of FeCl₃ to PEO films enhanced the thermal stability of PEO. The optical properties of these systems were also studied in the UV-Visible region as a function of FeCl₃ concentration at room temperature. The obtained data were analyzed in terms of absorption formula for non-crystalline materials. From the measured absorption data optical energy gaps (E_{opt}) were determined. The optical energy gap was found to decrease with the increase in FeCl₃ concentration, which indicates that FeCl₃ concentration had a significant influence on optical energy band gap. The absorption coefficient increased sharply at concentration of FeCl₃ (5%) wt as compared with the pure PEO.

Key Words: Poly (ethylene oxide), FeCl₃, XRD, optical properties, TGA, SEM, EDX

Introduction

Polymer composites made by addition of metals have wide applications and are being studied vigorously for their structure property relationship. The measurement of optical properties of polymers has been vigorously pursued due to their wide application in optical devices. These optical properties can be customized by the

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addition of some filler, which depends upon its reactivity with the host polymer matrix. The addition of metal chlorides to a polymer is also pursued because transparent films can be produced from them. The addition of conductive fillers/metal fillers can also improve the thermal behavior remarkably.¹ These transparent films can be used as optical filters, polarizers, total reflectors, narrow pass-bands, etc.² Optical absorption spectrum is very important in terms of optical characterization of the materials. The absorption spectrum is usually studied by ultraviolet (UV) absorption method. UV absorption is generally thought to be associated with electron (or anion) transitions from the top of the valence band to the bottom of the conduction band.^{3,4} These transitions can be direct or indirect depending on wave vector. Davis and Shalliday⁵ reported that near the fundamental band edge both direct and indirect transitions occur and can be observed by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of energy ($h\nu$). Many studies on poly (ethylene oxide) (PEO)-salt composites have been reported; they are mainly based on electrical and thermal properties.² Peng Su and co-workers reported that the addition of an appropriate amount of FeCl_3 results in a beneficial effect on defect-free electrospun chitosan/PEO blend nanofibers.⁶ PEO is a unique polymer because it is soluble both in aqueous and organic solvent and is a useful polymer available in a variety of molecular weights. PEO forms yellow complexes with FeCl_3 , showing photochromic effect under UV irradiation. FeCl_3 is known to be one of the most efficient oxidants in several polymeric polymerizations (especially poly pyrrole) leaving chloride ion and hence making it conducting. The Fe^{3+} ions are bound by the coordinating oxygen atoms of the PEO chain. This will suppress crystallization of PEO and ensure homogeneous distribution of FeCl_3 along the PEO. In the Fe^{3+} ions, d-electron shells are not filled as Fe^{3+} ions have d^5 configuration. Modification in physical properties of the polymer doped with transition metals of partially filled d-electron shells can be expected in general and in optical properties in particular. There are Fe(III) atoms are loaded in the studies. Particular, in the synthesis of conducting polymers, Fe(III) ion is used. Much experimental work is needed to be done in this direction. Keeping in mind the importance of PEO as a unique polymer and the utility of metal chlorides' incorporation to produce transparent films, the present work is undertaken on the system of PEO- FeCl_3 .

Experimental

Materials

Research grade PEO (MW 600,000 g/mol) was obtained from Acros chemicals. Research grade FeCl_3 was obtained from Sharlu chemicals. The polymers and salt were used as such without further purification. Triply distilled water was used as a solvent. Water is a good solvent for the PEO and salt, used as reinforcement material in our study.

Film preparation

PEO/ FeCl_3 films were prepared by dissolving PEO in water at 30 °C in solution 1, while an appropriate amount of FeCl_3 was dissolved in water in solution 2 at the same temperature. Finally these 2 solutions were mixed together with continuous stirring for 24 h and then cast on a petri dish at room temperature. After solvent evaporation thin films of the composites were separated from the petri dish and were kept in a desiccator. The

amount of FeCl_3 in the prepared films was 0%, 5%, 10%, 15%, and 20% wt. The thickness of the film was measured by micrometer.

Instrumentation

Absorption spectra of the films were recorded in the UV/Vis wavelength region of 200-800 nm using a PerkinElmer UV/VIS spectrometer. A Rigaku (Japan) FX Geiger Series RAD-B system was used for X-ray diffraction measurements. Polymeric samples were cut into pieces 2.5 cm^2 each and then put into the standard glass sample holder. Then the sample holder along with the sample was placed into the X-ray generating chamber under accelerating voltage of 350 kV and current of 20 mA. Scanning electron microscopy was done by Micro analyzer Model JSM 5910. The thin films were cut smoothly with a sharp blade. Special holders were made for SEM analysis to hold the film perpendicularly upright. The surfaces of the film were made conducting by coating with gold (Au). The samples were viewed through the microscope, and were then analyzed using computer software. The elemental analyses were conducted by energy dispersive X-ray analyzer (EDX) (Inca, Oxford Instruments, Abingdon, UK). A suitable magnification was chosen for obtaining micrographs. Thermal analysis was used to measure the degradation temperature as a function of actual amount of FeCl_3 present in the resulting composite, and the rate of weight loss of composite material with temperature. Thermal analysis was carried out in the temperature range of $0 \text{ }^\circ\text{C}$ to $650 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ using a thermal gravimetric analyzer (TGA), Perkin Elmer Model 6300.

Results and discussion

Optical absorption

The optical absorption measurements were conducted over the specified wavelength for 6 different compositions and are shown in Figure 1.

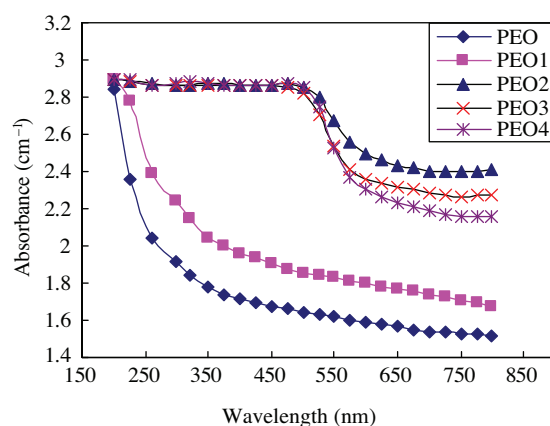


Figure 1. Optical absorption of pure PEO polymer and PEO- FeCl_3 systems (PEO-1 = 5% wt, PEO-2 = 10% wt, PEO-3 = 15% wt, and PEO-4 = 20% wt) and PEO- MnCl_2 (PEOM) composites.

This figure clearly indicates that these specimens are of amorphous character. X-ray diffraction patterns of our samples also support this behavior.

The absorption coefficient (α) was calculated from absorbance (A), after correction for reflection, using the following relation:

$$I = I_0 \exp(-\alpha x). \quad (1)$$

Hence

$$\alpha = 2.303/x \log \left(\frac{I}{I_0} \right) = \left(\frac{2.303}{x} \right) A, \quad (2)$$

where (I_0) is the incident intensity and (I) is the transmitted intensity, while x is sample thickness.

These expressions can be applied to both direct and indirect transitions and are helpful in the determination of the band structure of the materials. When a direct band gap exists, the absorption coefficient has the following dependence on the incident photon:⁷⁻⁹

$$\alpha(\omega)h = \beta(h\omega - E_{opt})^r \text{ for } h\omega > E_{opt}, \quad (3)$$

$$\alpha(\omega)h = \beta(h\omega - E_{opt})^r = 0 \text{ for } h\omega < E_{opt},$$

where β is a constant equal to $(4\alpha_0/nc\Delta E)$, α_0 is the extrapolated dc conductivity and ΔE is a measure of the extent of band tailing, and r is an exponent that can assume values of 1, 2, 3, 0.5, and 3/2. For allowed direct transitions r takes the value of 0.5 and in some materials quantum selection rules forbid direct transition; in such cases r will take the value of 3/2. The absorption study of PEO composite with MnCl_2 was also carried out during the course of this investigation for comparison. It is noted that the addition of 15% wt MnCl_2 to PEO resin reduces the absorption of PEO at the UV region, especially at 260 nm, while it shows enhancement at 320 nm, although the variation is not as sharp as already been reported for 5% wt by Zihlif et al.² Figure 1 shows the plot of absorption coefficient vs. wavelength for pure PEO and FeCl_3 -PEO composites. It was found that the addition of 5% wt FeCl_3 to PEO shows almost the same spectrum as pure PEO, but for higher concentration composites the trend is different. Absorbance is high at 260 nm and remains almost the same up to approx. 550 nm and then it decreases, which is opposite to the trend observed in the case of the PEO- MnCl_2 system reported by Zihlif et al.² The direct band gaps were evaluated from $(\alpha h\omega)^2$ vs. $h\omega$ (photon energy) plots and the allowed direct transition energies were determined by extrapolating the linear portion of the curve to zero absorption. The direct band gaps, as given in the Table, lie at 4.75 eV for pure PEO while for 5%, 10%, 15%, and 20% wt FeCl_3 -PEO polymer films, the values were shown to be decreasing.

Table. Optical energy band gap (E_{opt}) vs. salt concentration.

Sample	E_{opt} (eV)
PEO	4.75
5% FeCl_3 /PEO	3.80
10% FeCl_3 /PEO	2.80
15% FeCl_3 /PEO	2.61
20% FeCl_3 /PEO	2.51

The indirect band gap values were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (photon energy). From these graphs we found that for pure PEO polymer the indirect band gap lies at 5.1 eV, while for 5%, 10%, 15%, and 20% wt FeCl₃-PEO polymer composites film systems, the values of indirect band gap showed a decrease with the increase in the concentration of FeCl₃.

From the Table and Figure 2, it is clear that the direct optical energy band gap (E_{opt}) values showed a decreasing trend on complexing with FeCl₃. This may be due to the fact that added FeCl₃ forms some kind of complex with the polymer lattice. These may be charge transfer complexes. The presence of high absorption regions from 200 to 480 nm in the doped samples (see Figure 1) shows that these kinds of complexes have been formed and are contributing ionically. The increase in electrolyte concentration also plays a role in this. This type of behavior has also been reported on different polymer films.^{10,11} The best straight line obtained for pure PEO polymer was when $r = 0.5$, which is indicative of the fact that the electron transition for pure PEO polymer is direct transition in k space.

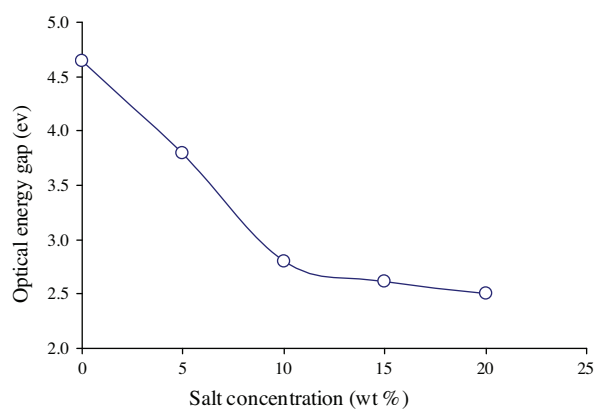


Figure 2. Optical energy gap (E_{opt}) vs. salt concentration.

Thermogravimetric analysis

The major weight losses are shown in the temperature range of 250 to 500 °C for PEO with and without salt (FeCl₃). For pure PEO the initial weight loss starts at 250 °C. A decrease in sample weight was observed from 350 to 500 °C, indicating thermal stability for PEO up to 350 °C. This weight loss can be due to burning of organic phase and the thermal dehydration of inorganic particles. No major weight change was observed after 500 °C. The total weight loss at 500 °C for composites was lower than that of pure PEO, indicating that inorganic particles dispersed into the PEO matrix. It is clear from the Figure 3 that the thermal decomposition of PEO-salt films shifts unsystematically for various filler compositions. For a composition of FeCl₃ (5% wt) there is a shift towards higher temperature than that of pure PEO, which means that there is enhanced thermal stability of intercalated polymer as also reported elsewhere.¹² The absorbance vs. wavelength spectra (Figure 1) also show that both pure and FeCl₃ (5% wt) composite behavior is the same, while for the rest of composites it is different. This means that 5% wt addition of salt is not making any complex, while further increases in the weight of salt promote complex formation. The composites with complexes are less thermally stable. Moreover, 10% and FeCl₃ (15% wt) addition somewhat reduced the thermal stability. The case of FeCl₃ (20% wt) is still different, which shows initial decomposition earlier up to 150 °C; after this it becomes stable up to 380 °C and

finally decomposes. There is nonuniformity in thermal behavior of all the composites with salt concentration. This means that amount of filler addition plays a role. For enhancing thermal stability 5% wt addition is ideal, while further increase in filler composition is not suitable. If we see thermal stability in terms of weight of residue left, then all the composites show less weight loss as compared to the pure PEO; this means that the addition of stabilizer (salt) affected the weight loss in the composite.

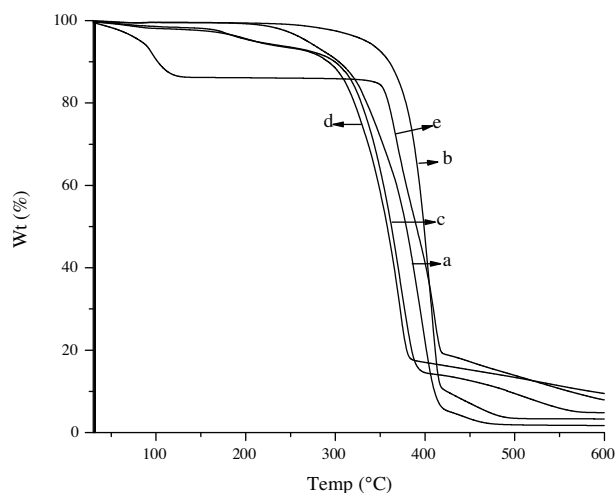


Figure 3. TGA of pure PEO (a) polymer and [5(b), 10(c), 15(d), and 20(e)% wt] FeCl₃.

Scanning electron microscopic (SEM) and energy dispersive X-ray (EDX) analysis

EDX (spectra given in Figures 4b and 5b) results confirm the presence of iron particles in the polymer matrix. The presence of some signals in the EDX spectra can be ignored as they arise from the analytical technique. Moreover, the SEM micrograph also depicts that FeCl₃ is randomly distributed within the PEO, having no surface contact between them but with good interfacial bonding.

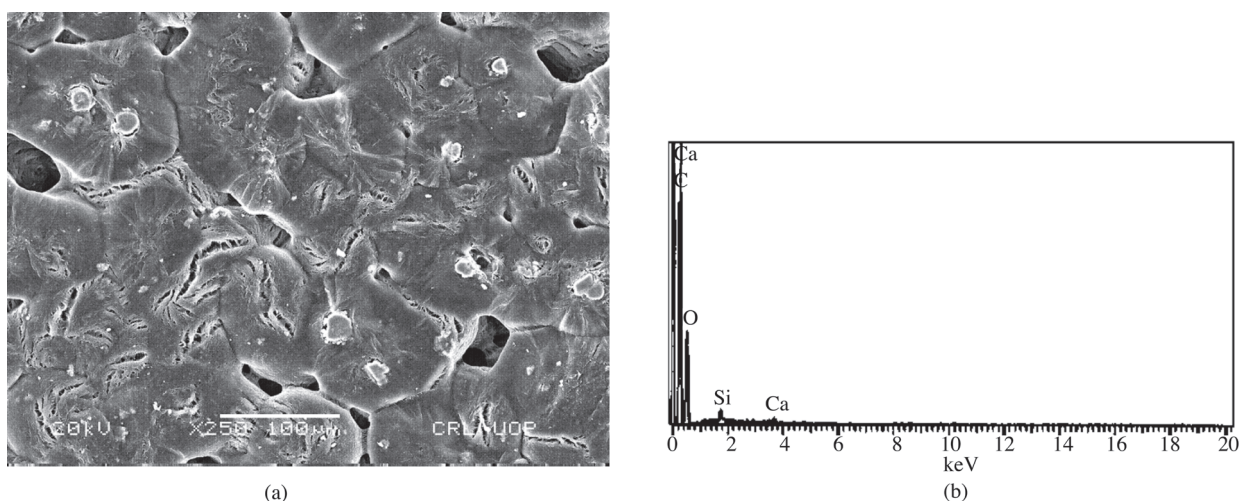


Figure 4. a) SEM micrograph for pure PEO; b) EDX micrograph for pure PEO.

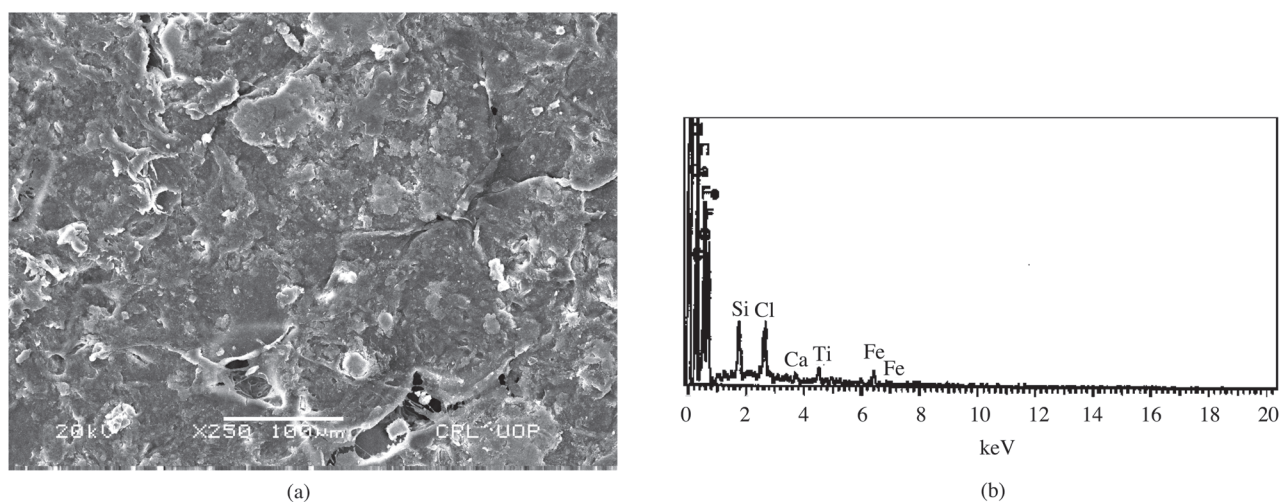


Figure 5. a) SEM micrograph for 5% wt of FeCl_3 ; b) EDX micrograph for 5% wt of FeCl_3 .

XRD

The XRD scans are illustrated in Figure 6.

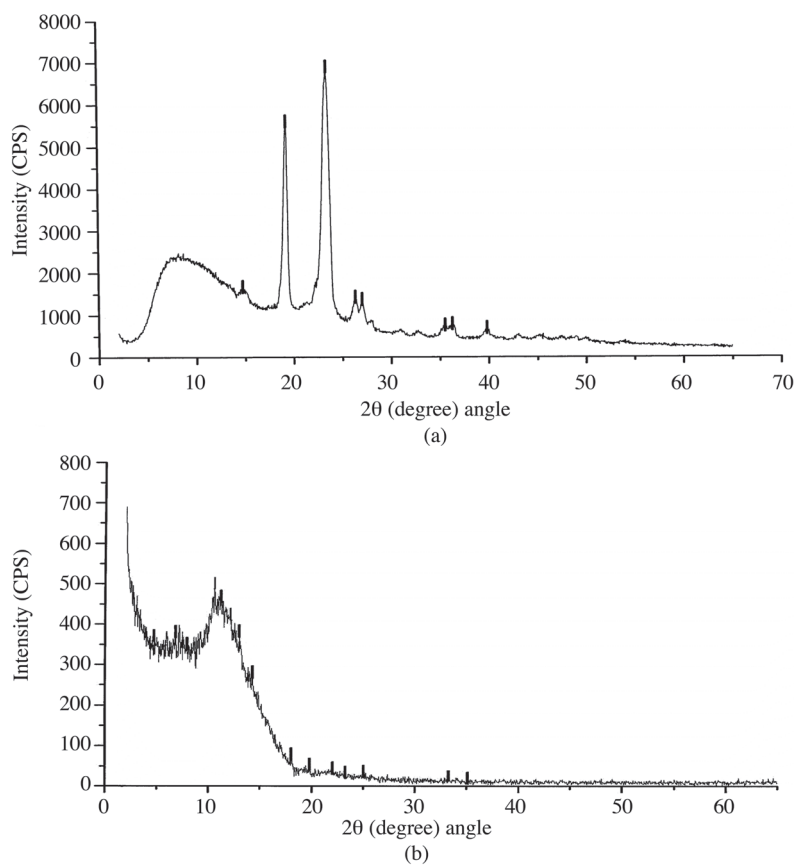


Figure 6. X-ray diffraction scans of pure PEO film (a) and with 5% wt of FeCl_3 (b).

The X-ray scans of the synthesized composite showed no significant change due to FeCl₃ filling. The spectrum of PEO films containing FeCl₃ showed a sharp peak at $2\theta = 18.5^\circ$ for $W \geq 10\%$ wt. This result indicates that the addition of FeCl₃ at $W = 10\%$ wt can bring about more structural disparity in the polymeric network.¹³ The location of the sharp peak at $2\theta = 18.5^\circ$ coincided with the peak at $2\theta = 18.5^\circ$ in the X-ray scan of pure FeCl₃. This result confirms the presence of FeCl₃ crystallites within the polymeric structure. The present findings are consistent with the results reported in the literature.¹⁴

Conclusion

Pure PEO and PEO-FeCl₃ films were prepared by solvent cast method and the effects of FeCl₃ salt on the optical and thermal properties were studied by means of different spectroscopic techniques. The FeCl₃ influence on the degree of crystallinity of PEO was ascertained by X-ray scans. The adding of FeCl₃ to PEO films affected thermal stability in an unsystematic manner. It was also observed from TGA spectra that the weight loss for the PEO-FeCl₃ system was different from the weight loss values for pure PEO, which shows that the addition of salt affects the decomposition behavior of pure polymers. The optical energy gap (E_{opt}) values were found to decrease with the rising salt concentration. It was found that absorption coefficient increases with increasing salt concentration in the case of PEO doped with FeCl₃ composites.

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