MICROSTRCTURAL CHANGES AND OPTICAL BEHAVIOR OF $FeCl_3$ DOPED PMMA THINN FILMS

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ABSTRAC:
Pure Ferric Chloride ($FeCl_3$) doped with PMMA Poly(methyl methacrylate) of different concentration films were prepared by solution casting method. The chemical composition and its influence on the optical properties of these films for different $FeCl_3$ concentration studied.. Optical absorption increases along with a peak centroid shift towards lower wavelength region (blue shift) with increasing concentration. The taucs plot of UV-Visible spectra shows three different optical band edges, which corresponds to three optical band gaps and activation energies. Shows existence of defect levels and disorder in the films. The microstructure and hence the optical properties of a polymer films along with magnetic properties can be tailored by doping. for the applications in the sensors, storage devices, LEDs and dielectric constants.

INTRODUCTION
It is well known that the physical and chemical properties of a polymer needed for specific application may be obtained by adding or doping metal like salts, which has significant effect on their optical, thermal and electrical properties [1]. This induces structural defects within the material and is responsible for change in the optical, electrical, mechanical and chemical properties of a polymeric material. Optical properties justify importance in fabrication of optical sensors, LEDs, antireflective coatings etc. The systematic analysis of the optical absorption spectra is one of the most productive tools for understanding the energy band diagram of both crystalline and amorphous materials. Among the optical polymers, PMMA is one of the important polymers used for different applications due to its high transparency and low birefringence [2-3].

EXPERIMENTAL
PMMA ($CH_2CH_3CCOOCH_3$) was obtained from M/s. Sigma-Aldrich Inc. USA. Anhydrous $FeCl_3$ was procured from M/s Loba Chemie Pvt. Ltd. Mumbai, India. PMMA films with 0, 0.5, 0.75, 1.0, 1.5 wt% of $FeCl_3$ dopant were prepared by solution casting method.. The doped polymer samples were subjected to spectral studies using Shimadzu UV-Visible Spectrophotometer (UV-1601) in the wavelength range 195–700 nm.

RESULTS AND DISCUSSION
. The figure Fig 1 shows three absorption peaks at 236 nm, 315 nm and 363 nm for unirradiated sample The peak is attributed to $n \rightarrow \pi^*$ transitions occurring as a result of double bond formation between carbon and oxygen with lone pair of electrons present in oxygen. Another peak at 363 nm shows an increase in absorbance without shift in the wavelength attributed to the $\pi \rightarrow \pi^*$ transition [6]. In addition, the above figure shows a broadening accompanied by a continuous blue shift at the lower wavelength region, which increases with electron dose. These variations in the absorption peaks suggest the presence of defects such as anions, cat ions, radicals, organic species etc. within the polymer created by doping. Such defects may result in the formation of new energy levels within the polymer [7].

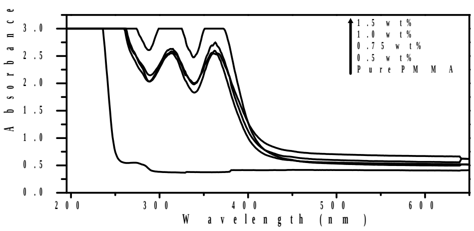

Fig 1: Optical absorption spectra for $FeCl_3$ doped PMMA for doping concentration.

The optical energy band gap is determined by translating the UV–visible spectra into Tauc's plot using the frequency dependent absorption coefficient $\alpha(\nu)$ by Mott and Davis

$$\alpha(\nu)h\nu = \beta(h\nu - E_g)^r \qquad (1)$$

where, $\alpha(\nu) = 2.303A/d$ (A is the absorbance and d is the film thickness), h is Planck's constant, ν is the frequency of the incident photons, β is a constant, E_g optical energy band gap and $r = 2$ is empirical index, valid for indirect allowed transitions. A plot of $(\alpha h\nu)^{1/2}$ verses $h\nu$ shows a linear behavior, which can be considered as an evidence for indirect allowed transition. Extrapolation of this linear portion of the curve to zero absorption gives the optical energy band gap E_g for the pure and $FeCl_3$ doped PMMA

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The activation energy is can be determined using the Urbach rule

$$\alpha = \alpha_o \exp(h\nu / E_a) \qquad (2)$$

Where α_o is a constant and E_a is the activation energy. The values of the activation energy were calculated by taking the reciprocal of the slopes of the linear portion of these curves.

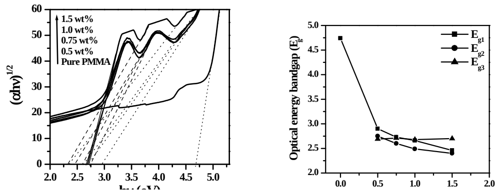

Fig 2: a) Plots of $(\alpha h\nu)^{1/2}$ verses $(h\nu)$ and b) variation of band gap with dopant concentration for $FeCl_3$ doped PMMA films.

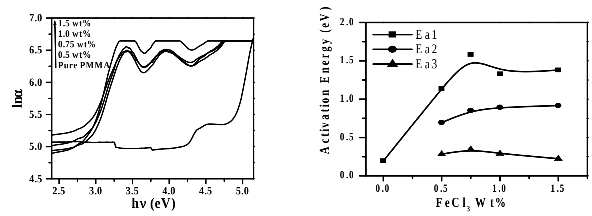

Fig 3: a) Plots of ln(α) verses photon energy (hν) and b) variation of activation energy with dopant concentration for $FeCl_3$ doped PMMA films.

The increase in E_a upon doping concentration indicates an increase in disorder in the $FeCl_3$ doped PMMA films. The disorder in amorphous materials leads to a redistribution of states from band to tail. As a result, two effects occur: a narrowing of the optical band gap and a broadening of the absorption peaks.

CONCLUSIONS

This study shows doping concentration modifies the chemical and optical properties of $FeCl_3$ doped PMMA. The shift in the wave numbers and change in the peak intensities indicates the deformation of the polymer structure under doping concentration Due to this change, two band gaps E_{g1} & E_{g2} decreases and E_{g3} remains constant where as the activation energy increases with concentration dose These variations in the band gap and activation energy invoking the existence of defect levels and disorder within the $FeCl_3$ doped PMMA films.

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