CHAPTER 1

INTRODUCTION

1.1 Prologue

A lot of interest has grown recently in the development and study of thermo-physical properties of the metal compound polymer composite as their synthesis is comparably easier for mass production as well as a small amount of metal in polymer brings drastic changes in the properties. This also presents an opportunity for development of material with specific properties for specific applications [1-8]. The variation that crops out in the properties of the metal polymer composite depends largely on the chemical behaviors of the inserted metal and its interaction with the host polymer [9-14]. Poly-methylmethacrylate (PMMA) is one such polymeric material utilized in a number of applications as mentioned in a vast amount of research papers [4,11,15-38] due to its interesting characteristics of being light weight, transparent, miscible with most metals and their oxides and possessing interesting electrical properties. Apart from these properties, due to its being economically variable for us we choose it to be our host polymeric material.

In this work we have prepared two different sets of its (PMMA) composite films doped with different concentration of (i) potassium per magnate ($KMnO_4$) and (ii) potassium chromate (K_2CrO_4) using solution cast technique. Then these prepared films were characterized for their structural, electromagnetic interference shielding behaviour, optical and electrical properties. Complexion and particle size were determined by XRD, FTIR and SEM analysis. For the study of electromagnetic shielding behaviour we developed $KMnO_4$ – PMMA and K_2CrO_4-PMMA composite films in both forms -layered structure form and bulk form. Our study suggests our prepared samples to be promising material for EMI shielding purpose. For this purpose the study on the optical and electrical behaviour of the samples has also been carried out. The absorbance spectra obtained using double beam spectrophotometer is used to obtain information on energy band structure and type of optical transitional within the material. In the work, presented in this thesis the variation of significant optical parameters like optical band gap, refractive index, extinction coefficient and variation of dielectric parameters like real and imaginary part of dielectric constant, loss tangent and conductivity with frequency and composition have been calculated.

Before preparing the above mentioned samples, to estimate whether these will serve as good shielding material or not, we had initially prepared the samples of same concentration of filler but of different thickness and tested these prepared samples using the gauss probe and variable electromagnetic system (RF source) at room temperature. It was found that the prepared films were quite effective in shielding the magnetic field, as magnetic field decreases with increase in the film and for the film of 450 μm thickness the magnetic field was reduced to half the value of original field. These samples were also rigorously tested for their electric properties in microwave region for their compatibility to electro-magnetic shielding. In this the a.c. conductivity (σ), dielectric constant (ε_r), loss tangent (tan δ), dielectric loss (ε_i), relaxation time (τ),absorption index (K) and refractive index (η) of pure and doped composites were investigated at microwave frequency equal to 8.92 GHz and at room temperature (33°C) to understand the action of doped $KMnO_4$ and K_2CrO_4 on the dielectric parameters of PMMA. From this study we find that the dielectric losses in doped films are higher in composite films than that in pristine PMMA films as the doped material creates additional hopping sites for the charge carrier in the sample thereby increasing the a.c. conductivity.

1.2 Overview of the research work

Recently a lot of attention has been focused on development of metal oxide polymer composites. The introduction of inorganic small dimensional metal particles into a polymer yields in high performance novel materials having improved performance in varied industrial applications [39-43]. Although, with the advancements in the research field of manufacturing and designing, inorganic materials have been synthesized with significant cooperative physical phenomena, yet they suffer from typical limitations of having high manufacturing cost, difficulties of making them in desired shapes and sizes and their being difficult or rather impossible for further processing. On the other hand, the polymeric materials are not only light weighted, flexible, inexpensive materials but they are amenable to easy processing and mass production. Further they can be molded in various shapes and sizes and can be even synthesized as thin film (in micro range) by various techniques like solution casting, dip coating, printing, spin coating etc. These materials are presently being used in versatile applications [7, 44-50]. Thus limitations of inorganic metal oxides small dimensionally-structured materials or the large molecular structured polymers can be trounced by embedding a very small amount of metal oxide in polymer. It is expected that the inclusion of metal or metal oxide fillers into the polymer makes properties of both the inorganic metal particles and the polymer to combine or even enhance, resulting in desired advanced new functions and applications.

Thus the metal oxide polymer nano-composites are those composite materials which comprise of inorganic metal particles dispersed uniformly into a polymer matrix. Since these metal oxide particles act as an additive that boost the performance of the polymer so they are normally referred as fillers or inclusion of fillers [31]. Inorganic fillers of micron size were used as additives within polymeric materials either by making blends or copolymers of them to exhibit unusual thermo-physical properties. With the advent of technology and rapid development of composite materials, a lot of fillers to be incorporated in polymers have been reported with reports on novel applications. These have been listed in the Table1 below:

Table 1.1: Fillers in Polymers

Class of Inorganic fillers	**Examples**
Metals and Metal alloys	Au, Ag, Cu, Ge, Pt, Fe, Co, Pt
Semiconductors	PbS, CdS, CdSe, CdTe, ZnO
Clay minerals	Montmorillonite, Vermiculite, Hectorite, $CaCO_3$"
Oxides	SiO_2, TiO_2, ZnO, SnO_2, Fe_2O_3, $KMnO_4$, $BaTiO_3$
Carbon-based materials	Carbon nanotube (CNT), graphene, carbon nanofiber

The choice of host polymer is also manifold and is taken as per the type of application involved. This is listed in the Table below:

Table 1.2: Class of Polymers

Class of polymer	**Examples**
industrial plastics	Nylon 6, nylon MXD6, polyimide, polypropylene
conducting polymers	Polypyrrole, polyaniline PANI
transparent polymers	Polymethylmethacrylate(PMMA),polystyrene (PS)

The metal oxide polymer composites are popularly used for varied optical, magnetic, mechanical, catalysis, electrochemical, electrical, thermal and biomedical applications. In sensor, the catalytic and electrochemical based applications, metals like Cu, Zn, Fe, Cr, Co and metal oxides like SiO_2, TiO_2, ZnO, SnO_2 etc have been reported to be used as fillers [7, 44-46, 53-54]. From a decade the carbon containing materials like CNTs, grapheme and carbon nano fibers are vastly used to enhance the electrical conductivity of the host polymer matrix [23, 55-56]. Earlier the gold and iron oxide metal particles were generally used in biomedical field, now their polymeric composites are also recently been exploited for intelligent therapeutic system and as bio-imaging agents [14]. The recently reported class of polymer metal-oxide composites are the characteristic type of composites consisting of a polymer matrix with 'transparent fillers' which make the material transparent as well as conducting one [32,35]. In this research work too, we have focused on the two important aspects of these metal oxide polymer composite the optical properties and the electric properties related to shielding. For optical applications, metal oxides such as TiO_2, ZnO, K_2CrO_4 or SiO_2 have been commonly reported as optically effective additives, and polymers such as PMMA, PVA, PS, PES, and PC have been reported as host polymer [9, 15-38, 57-59]. For electrical applications, metals (Fe, Zn, Pb etc.) and metal alloys (ZnS, $FeCl_3$, CoPt, etc), oxides ($KMnO_4$, Fe_2O_3, MnO_2) and ferrite have been reported [60-62].

1.2.1 *Electromagnetic interference and shielding as its solution*

The e.m. radiation comprises from large wavelength and low energy radio waves to too small wavelength but higher energy gamma rays and are generated by all communication and broad casting device at varying frequencies.

Problem of Electro-magnetic Interference:

When the emitted e. m. wave of one device interferes with the working of device, creating disruptions in its functioning, the problem is referred as electromagnetic interference. The effects can be seen even in day to day life. Here I list certain examples of it:

- ❖ Momentary disturbance in TV and radio reception due to operation of mixer-grinder electric shavers/a passing vehicles etc.
- ❖ Malfunctioning of flight controlling system due to use of laptop by passenger.
- ❖ Failure of pace maker implemented in a patient due to a walkie talkie.
- ❖ It can lead to change of setting of status of control equipments and reset the computers leading to loss of data.
- ❖ Environment & living systems are also affected

Thus apart from disturbing the proper functioning of electronic devices, it may even result into loss of revenue, energy, time, or even precious human life serving as a threat as a special kind of environmental pollution. The easy accessibility of electronic gadgets enables rapid inflation of electromagnetic noise in the atmosphere. The human body gets affected when exposed to such an atmosphere. The e.m. radiations are transmitted and most of the radiations get absorbed by the body, thus causing ailment like skin rashes, muscle soreness and sometimes leading to infertility.

The advancements in the electronic industry and tremendous urge for use of electronic devices in various applications; and as technology evolves to make devices more lighter, faster and smaller, the problem of electromagnetic interference (EMI) have magnified and become severe. With the advances of wireless electronic devices, the electromagnetic radiations have covered the entire environment and are now are posing a serious threat. Due to escalating EMI issues, the attention of scientific community has gone to develop materials and methods as a blocking mechanism to control it.

Shielding as a solution to EMI problem:

The case of EMI can be either of the two:-

1) EMI due to conducted radiation by cables and circuits. This is solved by designing devices for filtering the e.m. radiations.

2) EMI due to radiated emission that penetrate into susceptible components. These are checked by encasing the device by an e.m. shielding or absorbing material.

Shields are used to isolate a region, to prevent interference from outside sources and to avoid the leakage of unwanted radiation due to internal sources. These are highly desired to protect the workspace and environment from deepening radiation from computers and telecommunication equipment as well as for protection of sensitive circuits. Shielding can be done by placing the device in an enclosure which will reflect all the electromagnetic wave thus protecting the device from external electromagnetic interference or it could be done by placing material on the device which will absorb the electromagnetic wave incident on it.

The Faraday's cage principle states that within an enclosed conductor no electrical field is present and no e.m. field escapes it. So any conducting material seems to be the best candidate for shielding by reflection as it has good availability of mobile charge carriers. These mobile charge carriers generate an impedance mismatch between free space wave impedance and essential impedance of shield so that a large part of incident field is affected. Therefore a simple and easy way of shielding is to put metal shield or wire mesh of a conductive metal like copper or aluminum, or a coating of metallic ink around encasing the interior of devices with a shroud or cage. While this is effective, but adequate shielding can be achieved only by using thick metal sheets which not only adds weight to the device but have the issue of rigidity and corrodibility and is considered a restriction on how small the device can be designed. With technology advancing so fast, we expect smart devices to have more capabilities and become smaller every day. This means packing more electronic parts in one device and more devices surrounding each other and also us. To have all these electronic components working without interfering with each other, we need shields that are thin, light and easy to apply to devices of different shapes and sizes. So use of thick metal sheets is restricted by issues related to size, weight, shape and hindrances offered during manufacturing process.

Another way is using the metal as foil cover but this when is put over apertures act as a transmitting slot antenna, enhancing the problem of interface more. Conducting polymers too enable shielding behaviors. General polymers are highly insulating in nature but as they are flexible, lightweight, corrosion free, cost-effective, easily process able for mass production and process able in thin form in various shapes seems to be a promising solution. We have also seen that there is an increased use of plastic housing for electronic devices. This makes EMI shielding more significant as most the present day housing polymers are insulators, so em waves can pass through them freely and conductive barriers must be applied as shields to block the waves. To provide shielding, the plastic housing can be coated with a conductive layer or the housing itself should be made conducting. The findings suggest that nano materials as fillers in polymer matrix can be more effective at blocking and containing electromagnetic interference, with the added benefit of being extremely thin and easily applied on any surface.

Another aspect to shield these EMI are e.m. wave absorber materials having ability to shield by absorbing the unwanted e.m. signals. Recently the materials that shield e.m. by absorbing the radiations have also attracted much attention. The e.m. absorber material is required to be light weight, having wide absorption frequency and high thermal stability. These desired properties can be tailor made by incursion of filler materials (such as inorganic magnetic particles, metal oxide nanoparticles or carbon nano tubes) in polymeric materials [30, 55-56, 69-74]. Now a days lot of efforts are focused on development of metal oxide filled polymers as they posses the properties of traditional composition and also further unique thermo physical properties. The uniqueness of property is highly dependent on the type of filler (metal oxide) inserted. The metal oxide lays the foundation of conduction mechanism within the polymer and therefore we have focused our attention towards this.

Apart from the type of filler the quantity and structural topography of the inserted filler too also has effect on the absorption of e.m. radiation. Literature review suggests that a lot of work has been reported with CNTs, iron and zinc oxide etc.., but as the attenuation mechanism is primarily based on losses whether electric loss or magnetic, these parameters must be studied meticulously [30, 55, 70-71,73]. At very high frequency as the permeability of materials tend to be near one. Thus to make an effective e.m. radiation absorber material, we need a proper understanding of the constants of the materials like permittivity, dissipation factor, skin depth, extinction coefficient etc. We need to increase these constants of the material so as to design it for proper impedance matching. So we generally look for filler materials that are electrically conductive to make polymeric composite capable of shielding and absorbing e.m. waves. Thus to design and develop such materials we need to first study the electric and optical properties of these materials so as to assess the values of dielectric constants, ac conductivity and optical constants.

EMI shielding in the range of 8.2 to 12.4 GHz (the X band) is quite important for military and other commercial purposes as all significant applications like Doppler, weather radar, TV picture transmission and telephone microwave relay systems lie in X band. The potential use of metal oxide as additive for polymers as EMI shielding materials is emerging as a major application area [60, 61, 73, 81]. The increase in filler loading increases the shielding effectiveness of such composites. But there is a limit to loading of the filler within the polymer and that at higher loading of filler the composite system suffers from poor mechanical properties [70]. Studies also show that the thickness of such filler loaded polymer composites is at least 1 mm thick to provide reasonable shielding effectiveness [73, 81]. Certain researchers have tried to obtain good shielding effectiveness by stacking thin films of composites in layers. They have compared the effectiveness of their stacked layer composites with that for bulk composites of same thickness and have concluded that the composite stacking process is a better fabrication method for this purpose [28, 30, 91]. Adopting their idea we too decided to stack layer our prepared composite thin films for achieving considerable EMI SE. The theoretical consideration for EMI Shielding effectiveness has been explained in chapter 3 and results obtained for our samples have been discussed in chapter 4.

1.2.2 *Dielectric properties*

The electrical properties of the composites developed by dispersing a conductive phase in an insulating matrix significantly depends on the type and concentration of the filler added. For small concentration of filler particles, as the average distance between the filler particles is generally more than their size the electrical conductivity of the composite material is more likely to that of the pure insulating matrix [36, 75]. On an addition of adequate amount of filler, a percolation path of is formed connecting the filler particles which allows charge transport through its surface leading to a change in the charge storage capacity [10, 11, 53]. Thus, the determination of dielectric parameters offers an understanding of the electrical characteristics of the material in two ways:

(i) The capacitive behavior indicates the ability of material in charge storage and

(ii) The conductive behavior indicates the ability of electronic charge transfer.

The variation of dielectric parameters (ε', ε'', tanδ, σ) with frequency and composition is therefore required to be studied. The values of impedance parameters *viz* . .resistance, capacitance, inductance, dissipation factor (tan δ), phase angles and impedance are measured using impedance analyzer and from the data obtained the dielectric parameters *viz.*, the real part ε' and imaginary part ε'' of dielectric constant and ac conductivity are calculated in the given frequency range at room temperature. The theoretical framework for the study of these properties is described in Chapter 3 and the results and analysis has been done in chapter 4.

1.2.3 *Optical properties*

From the very beginning of the development of metal oxide polymer composites, the optical properties and applications have attracted the scientists and technocrats. These have an advantage over the optical properties of those materials which are difficult to be grown in single crystal structure or are affected by environmental aspects and also are being provided the ease of processing. This can be understood as if the host polymer is there just to hold the metal oxide particles together to provide the processibility while the properties achieved are similar to those of metal oxides. The optical properties of PMMA based polymer metal composites, in particular, have been found to have dopant-dependent properties [1, 5, 8-9, 12, 14-15, 57, 59, 63-65]. So in our research work we have also explored the ability of metal oxide particles to serve as optically effective additive to the polymer composite. Although this study of optical behaviour in this wavelength region does not aids to the understanding of the shielding behaviour yet it serves to understand the behavioral aspect of our synthesized material. Also a meticulous carried out literature survey also showed that although a great deal of work has been reported in literature to the optical properties of filler doped PMMA composite films, not a single report is there on optical properties of $KMnO_4$ doped PMMA or K_2CrO_4 doped PMMA films [4,11,15-32,66-67]. So it seemed meaningful to us to study and analyze the optical properties of these prepared samples and report them here. The research would be significant as knowledge of optical constants like optical band gap, refractive index, and extinction coefficient would aid in examining their potential to be used in optoelectronic devices and for e.m. shielding purpose. The theoretical framework for study of optical constants of such composites has been described in chapter 3 and the discussion of obtained results has been presented in chapter 4.

1.3 Objective of the research work

The electromagnetic radiations have become quite ubiquitous (pervasive) with the advances and augmentation of modern electronic devices. Radio and television were the traditional circuit devices for emitting e.m. radiations but the advent of wireless devices has preheated this to generate a congested environment of such radiations. The spur in the speed, frequencies and operations of these equipments will further make this congested environment almost saturate. This lays the foundation for need of e.m. shielding and absorbing devices with the possessing reduced size, weight and cost, versatile performance ability and the amenability for molding into various desirable shapes, it appears that polymer are promising potential materials to develop things of desired properties. However, polymeric materials are inapt in providing shielding from absorbance of e.m. radiation fortunate enough, that the advent of a wide range of fillers within a polymers precise modification have become achievable.

The aim of this research work is to develop such polymer metal oxide composites so as to shield or absorb e.m. radiation and can be used by the electronic industry for designing and producing equipment and devices preventing e.m. interference. We would ensure that process of development and characterization of these materials is such that they could further be reproduced (giving same result) to be used commercially. This research work has been taken with the aim of developing solid thin composite material and to examine its potential role as suitable shielding solution.

The key areas of our research work are:

- Synthesis of $KMnO_4$ – PMMA and K_2CrO_4-PMMA composite films made by dispersing the metal oxides in different concentrations in PMMA separately.
- Investigation of dielectric properties of these synthesized composites. The primary objective for this is to identify the composite with optimum values of electric constants that can serve as good shielding material. This identified composite shall be further developed in stacked layer and bulk form.
- A suitable test for electromagnetic shielding effectiveness of these.
- Study of structural and optical properties of these composites so as to satiate the curiosity to understand the structure-property correlation for these composites.