Chapter 1

Introduction

Polymers are attracting increasing interest of scientific community, owing to their outstanding properties such as light weight, transparency, flexibility and ductility, resulting in their widespread potential applications [1-3] in diverse fields such as optics [4], electronics [5], optoelectronics [6] and biomedical [7]. However, polymers have certain inherent disadvantages such as inferior mechanical properties such as, young’s modulus, tensile strength, fatigue strength etc. Many research groups around the world are trying to modify the properties of polymers using different techniques such as ion implantation [8-10], gamma and electron beam irradiation [11-13] and encapsulating nanoparticles into the polymers [14-16] etc. It has been largely reported in the literature that the encapsulation of nanoparticles into polymers is an elegant way to improve the efficiency of polymer, through exploration of properties of nanoparticles such as large surface to volume ratio, quantum confinement effect without significant change in toughness and transparency [17-19] of the polymer. Thus synthesis and characterization of polymers encapsulated with nanoparticles is of fundamental interest as well as has scientific and technological importance.

Various techniques are reported in the literature for the synthesis of polymer based nanocomposites by incorporating nanoparticles. All these techniques are classified into two approaches: the first one is a physical approach such as physical vapor deposition (PVD) [20-21], laser ablation [22-23] etc. The second one is a chemical approach such as chemical reduction [24-25]. Further, chemical approach is employed by two routes: in-situ and ex-situ processes. The in-situ process is that where nanoparticles are grown within the polymer [26-27], whereas in the ex-situ process, externally pre-synthesized nanoparticles are incorporated into the polymer matrix [28-29].
In the present work, ex-situ chemical synthesis technique has been chosen to fabricate Ag-PMMA and Ag-PET nanocomposite films. This is because physical techniques require very high temperature and pressure condition; the growth time is large and is quite expensive. On the contrary, chemical techniques are quite simple, inexpensive, and relatively fast [30]. Through ex-situ chemical technique, pre-synthesized nanoparticles with controlled size and shape are incorporated in the polymer [31-32].

In the present work, variations in the optical, structural, electrical and dielectric behavior of Poly(methylmethacrylate) (PMMA) and Poly(ethylene terephthalate) (PET) after incorporation of silver (Ag) nanoparticles has been investigated. A brief outline about the concept of nanomaterials is discussed in section 1.1. The concept of nanocomposites, their classification, synthesis techniques and applications are described in section 1.2. Section 1.3 discusses the concept of polymer matrix nanocomposites along with their various synthesis techniques. Selection of host matrices with their basic structures is discussed in section 1.4. Section 1.5 contains the properties and applications of Ag nanoparticles as filler. Applications of Ag-PMMA and Ag-PET nanocomposites are discussed in section 1.6. Section 1.7 describes the modified properties of metal-polymer nanocomposite films and related literature. Justification and aim of the present work are described in the section 1.8. Finally, section 1.9 gives the brief layout of the chapters included in present thesis.

1.1 Nanoscience and Nanotechnology

A nanometer (nm) is one billionth of a meter, or \(10^{-9}\) m. One nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line. Nanoscience is the study of fundamental relationships between physical properties and phenomena and material dimensions in the nanometer scale [33]. The idea of nanotechnology was given by Richard Feynman in 1959 in a lecture entitled “there is plenty of room at the bottom” [34]. According to Drexler’s quote (1990) ‘nanotechnology is the principle of atom manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom by atom precision, yielding a variety of nanomachines’ [35]. Nanotechnology is a technology of design, fabrication and applications of nanostructured materials [36].
1.1.1 Nanomaterials

The materials having at least one dimension in nanometer scale are called nanomaterials [36]. Now-a-days nanomaterials are attracting increasing interest of the scientists around the world as these exhibit unique physical, optical, electrical, mechanical and magnetic properties often different from their bulk counterparts. These materials are of special concern because of their potential from mechanics to medicine [4-7]. The change in behavior of materials at nanoscale is mainly due to increase in surface to volume ratio (S/V) and quantum confinement effects [36]. For example, metallic nanoparticles are used as very active catalysts due to large S/V ratio. Quantum confinement effect alters the energy band structure and charge carrier density in nanomaterials as a result; electronic and optical properties of nanomaterials get modified [15].

There are two possible approaches for the synthesis of nanomaterials. The scheme of two approaches is depicted in figure 1.1 [36]:

![Figure 1.1: Scheme of Top-Down and Bottom-Up approach.](image)
(a) The “Top down” approach is the fabrications of nanomaterials from breaking up bulk materials. This approach involves mechanical milling [37], scanning probe lithography, nanoimprint lithography, block co-polymer lithography [38], chemical etching using acids or mechanical etching using ultraviolet light, X-rays, or electron beams [39] etc.

(b) The “bottom up” approach is related to the construction of multifunctional nanomaterials and devices by the self-assembly of atoms or molecules. This approach includes atomic layer deposition [40], sol-gel nanofabrication [41] and physical and chemical vapor phase deposition [42-43] etc.

### 1.1.2 Classification of nanomaterials

Developments in the field of nanoscience and nanotechnology have resulted in nanomaterials of various shapes and compositions. These include nanotubes, nanowires, nanofibres, nanoparticles etc. All these nanomaterials are categorized according to their dimensions which lie in nanometer range [33, 44].

- **0D Nanomaterials** - The materials which are having all three dimensions within the nanoscale are known as 0D nanomaterials like nanoparticles, quantum dots etc.

- **1D Nanomaterials** - The materials which are having two dimensions within the nanoscale are known as 1D nanomaterials like nanotubes, nanowires etc.

- **2D nanomaterials** - The materials which are having one dimension within the nanoscale are known as 2D nanomaterials like nanoplates, thin films, layers, coating etc.

Figure 1.2 depicts the schematic diagram of classification of nanomaterials.

![Figure 1.2: Types of nanomaterials: 0D (nanoparticles, nanoclusters); 1D (nanotubes, nanowires); 2D (thin films); 3D (bulk material (polycrystals)).](image)
1.1.3 Properties at nanoscale

Nanomaterials exhibit distinct properties in comparison to their bulk material counterparts. Some of these unique properties are listed below:

❖ **Optical properties**
The scattering and absorption of light at nanoscale has many special features as compared to their corresponding macroscopic material. For example: metal nanoparticles show absorption peaks in the visible spectrum, which are absent in bulk metal. Metal nanoparticles show different colors with changing size and shape [44]. Due to these exceptional optical properties, metal nanoparticles have many applications such as in high sensitivity bio-molecular detection and diagnostics, refractive index sensors and spectroscopy etc [45-46].

❖ **Magnetic properties**
Magnetic properties of nanomaterials are associated with the discrete electronic states. Nanomaterials show size dependence magnetic susceptibility. For example: decrease in the size of Se nanoparticles leads to an increase in diamagnetism [47].

❖ **Structural and phase transformation**
Phase transformation occurs at nanoscale due to change in surface energy. For example: tantalum and tungsten have bcc lattice in the bulk state while they transformed to fcc or hcp structure at nanoscale [48]. For some elements such as Fe, Cr, Cd and Se, a decrease in particle size into nanoscale regime results in loss of crystal structure and appearance of amorphous structure [49-50].

❖ **Mechanical properties**
Mechanical properties such as hardness, strength, elasticity and plasticity etc also change with the reduction in particle size at nanoscale. Hardness of Ag, Cu, Pd, Fe and Ni increases when their size is reduced to nanoscale [51].

❖ **Electrical properties**
The changes in electronic structure at nanoscale result in change in electrical conductivity. The polycrystalline cobalt films having thickness in the nanometer range has higher resistivity than that of bulk cobalt [52].
1.1.4 What makes ‘nano’ special?

When materials are reduced to nanoscale they start behaving differently than their bulk forms. Their properties like optical, electrical, magnetic and mechanical become function of their size. These different behaviors of nanomaterial are related to different origins for example: (i) large fraction of surface atoms, (ii) large surface energy, (iii) Quantum confinement, and (iv) electronic structure [33, 53].

Surface to Volume (S/V) ratio

The reduction in the particle size results in increase in surface to volume ratio as depicted in figure 1.3. For a spherical nanoparticle, the surface area is given by $4\pi r^2$, and volume by $4/3\pi r^3$, then S/V becomes $3/r$ [54]. Therefore, S/V varies with the inverse of r. For a cube of volume 1 cm$^3$, the percentage of surface atoms will be only $10^{-5}\%$ and when the cube is divided into smaller cubes with an edge of 10 nm, the percentage of the surface atoms will increase to 10% [33].

![Figure 1.3: Surface/Volume ratio as a function of the particle size.](image)

However, the atoms in the interior of the material are more highly coordinated, form more bonds and are therefore more stable than those at the surface. For this reason, surface atoms exhibit the higher affinity to form bonds with adsorbate molecules, which ultimately results in higher catalytic activity [55-56]. The increase in S/V also results in increase of surface energy that causes greater chemical reactivity at nanoscale [57].
Quantum Confinement

When the particle size is reduced to nanoscale, then the particle behaves like in individual atoms due to the formation of discrete energy levels rather than the continuum in the energy levels [54, 58]. Figure 1.4 depicts the continuous energy levels in bulk material (3D), which changes into discrete energy levels as dimension of material reduces from 3D to 0D.

![Figure 1.4: Formation of 0D nanomaterials from 3D materials with continuing the discretization of the energy states.](image)

Quantum confinement influences metal nanoparticle by two ways. Firstly energy gap between conduction band and valence band becomes larger with decreasing size. Secondly discrete energy levels arise at both the conduction band and valence band. These two size-dependent effects on electronic structure are schematically depicted in figure 1.5 [59-60]. A reduction in the particle size at nanoscale results in change of electronic structure, leading to widening and discrete band gap.

This flexibility of changing the band structure at nanoscale has impact on a number of technologies, and opens up interesting application possibilities such as low-threshold lasers, light-emitting diodes, photovoltaic devices, fast optical switches, Infrared detectors, fast access memories and spintronic devices etc [61].
Figure 1.5: Energy level diagrams of (a) bulk metal (b) large metal cluster and (c) small metal cluster.

1.1.5 Applications of nanomaterials

Nanomaterials offer an extremely broad range of potential applications from electronics, optical communications and biological systems to new devices [62-64]. The utilization of nanomaterials is based on their physical and chemical properties. Several researchers have proposed various scientific and technical applications of nanomaterials in different areas, some are listed below:

- Mesoporous materials containing metal nanoparticles such as Ag, Au are used as catalyst as well as miniaturize electronic and optical devices [65].
- Metal nanoparticles paste is used for circuit pattern formation of a printed wired board in the electronic industry [66].
- Nanofibrils of perylene based fluorophores act as nanosensors indicate fish and meat spoilage by detecting gaseous amines [67] and therefore, are used for packaging.
- Quantum dots are used for thin film solar cells due to their high absorption cross-section [68].
- Due to antimicrobial action, Ag nanoparticles are used in packaging material [69].
- Nanocrystals are used to make cutting and drilling tools extra hard and wear-resistant [70].
- Sun-screen lotions containing nano-TiO$_2$ enhance sun protection factor (SPF) while eliminating stickiness [71].
Porphyrin-modified Fe$_3$O$_4$ nanoparticles are used in multifunctional nanomedicine and for magnetic resonance imaging [72].

Single-walled carbon nanotubes are intensively used for nanoelectronics devices such as single-electron field effect transistor, transistors, and sensors etc. for its semiconducting behavior [33].

The conventional form of amorphous silica nanoparticles, called as food additive E551, are used as anti-caking agent to maintain the flow properties in powder products (e.g. instant soups) and to thicken pastes [73].

The as-synthesized nanomaterials have limited applications because of their instability due to very high surface to volume ratio which leads to their agglomeration, easily oxidizing nature and contamination by impurities besides the problems associated in their handling because of their small size. These complexities can be taken care of by embedding the nanomaterials into suitable dielectric matrix. The resulting new class of materials is known as nanocomposites. Development of nanocomposites is a rapidly evolving area of composites research. Fabrication of nanocomposites is a unique approach of harnessing the benefits of different constituents. They are often superior as compared to conventional microscale composites and can be synthesized using simple and inexpensive techniques. The study of nanocomposite materials requires a multidisciplinary approach with impressive technological promise, involving novel synthesis techniques and an understanding of physics and surface science. Hence, it is necessary to understand fundamental concepts of nanocomposites.

1.2 Nanocomposite

Nanocomposite is the combination of a matrix and filler, where filler has at least one dimension at nanoscale. Matrix phase is a continuous phase or the primary phase. It can be metals, ceramics or polymers. Dispersed (reinforcing) phase is the second phase (or phases) which is incorporated into the matrix. It can be fiber or particles in nano regime [44].

The association of nanofiller with a matrix offers significant features beyond the advantages of a single material. Several researchers conducted studies on nanocomposites and reported improvement in the optical, thermal, mechanical, electrical, magnetic and flammability properties of matrix materials [14-19].
Chapter-1 Introduction

1.2.1 Properties and applications of nanocomposites

Properties of nanocomposites are different from those of corresponding composites with larger particles because their physical constants and structure are different. The following properties of nanocomposites are different from their bulk counterparts [33].

- Mechanical properties (strength, modulus and tensile strength)
- Optical properties (Optical transparency, UV absorption, Refractive index, dichroism etc)
- Electrical conductivity
- Thermal stability
- Surface appearance (Colour)
- Chemical resistance

Due to the large variations in properties of nanocomposites they have wide spread applications. Some of these are listed below.

- Nanocomposites are frequently transparent (or translucent) while corresponding composites with larger particles are opaque. High transparency in nanocomposites is useful in optical applications, photocatalysis and photoconductivity [44].

- The colour of the nanoparticles depends upon the particle size, so the composites containing nanoparticles can be used as translucent colour filters. For example colour filters consisting of poly-vinylpyrrolidone and Ag particles appeared translucent yellow or red depending on the diameter of the Ag particles which ranged between 6 and 12 nm [61].

- ZnO and TiO₂ absorb UV radiation over a broad wavelength range but are transparent to visible light. Accordingly, Nanocomposites with ZnO and TiO₂ are transparent to visible light but absorb UV light to a high extent. Therefore, such nanocomposites may be used in the protection of UV sensitive materials [33].

- The refractive index of organic polymers is in the range 1.3-1.7 while inorganic materials have refractive indices in the range less than 1(for gold) or above 3 (e.g. PbS or
silicon). Hence introduction of inorganic nanoparticle into polymer matrices can result in polymeric materials with controlled variation of refractive index [33].

- Major disadvantage of polymers as compared to inorganic materials is their tendency to burn at high temperatures. The flame retardance of polymers is improved by addition of nanoparticles of Al(OH)$_3$ [17].

- The high specific surface area in nanocomposites is also relevant in applications where adsorption processes at inorganic particles are of importance, for example in gas sensors [68].

- Improvement in mechanical properties makes them a very potential candidate for industrial applications [19].

### 1.2.2 Classification of nanocomposites

On the basis of the nature of the matrix, nanocomposites are classified into three major categories [74-75]:

(a) **Ceramic matrix nanocomposites**

In this class of nanocomposites, the host matrix is a ceramic and second component can be metal nanoparticles, carbon nanotubes or some ceramic nanopowder etc. Ceramics have high strength and stiffness but are brittle. Its strain fracture toughness gets enhanced by adding suitable nanoparticulates into it. The resulting nanocomposites possess low density, high melting point, high mechanical properties and chemical stability etc. Ceramic matrix nanocomposites are widely used for space and aeronautical applications etc [75-76].

(b) **Metal matrix nanocomposites**

In this class of nanocomposites, the host matrix is a metal while the filler can be metal nanoparticles or ceramic nanoparticles etc. Metal matrix nanocomposites exhibit high strength, stiffness, electrical conductivity, thermal conductivity, radiation survivability (laser, UV, nuclear, etc). These nanocomposites have diverse applications in aerospace, transportation (automotive and railway), superconducting magnets, power conduction materials etc [77-78].
(c) Polymer matrix nanocomposites

In this class of nanocomposites, the host matrix is a polymer and filler can be ceramic nanoparticles or metal nanoparticles etc. By appropriately adding nanoparticulates to a polymer matrix, its optical, electrical and mechanical properties like stiffness, toughness and creep resistance etc. can be enhanced. Polymer matrix based nanocomposites have numerous applications such as in optical displays, catalysis, photovoltaic, gas sensors, electrical devices, photoconductors, superconductor, transport, aerospace etc [17-19].

In the present work, polymer matrix based nanocomposites have been synthesized by adding metal nanoparticles into the polymer matrix. The properties of polymer nanocomposites depend on type of incorporated nanoparticles, their size, shape, concentration and interaction with polymer matrix.

1.3 Polymer matrix nanocomposites

Polymer nanocomposites are the mixtures of polymer and nanometer length scale fillers, whereas, conventional polymer composites contain micrometer scale particles. The advantages of nanocomposites over macrocomposites include reduced filler amount and better properties than obtained from the conventional composites.

1.3.1 Classification of polymers

Polymers can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymer can be classified in different ways. The broad classification of polymers is described below.

Linear chain polymers

These are polymers in which monomeric units are linked to form linear chains. These linear polymers are well packed and therefore have high densities, high tensile strength and high melting points. For example, polythene, nylon and polyesters are linear chain polymers.
Branched chain polymers

These are polymers in which monomers are joined to form long chains with branches of different lengths. These branched chain polymers irregularly packed and therefore, they have low tensile strength and melting points than linear polymers. For example, low density polyethene, glycogens etc.

Cross-linked polymers

These are polymers in which monomer units are cross-linked together to form a three-dimensional network. These polymers are hard, rigid and brittle because of network structure. For example melamine formaldehyde resin bakelite etc.

1.3.2 Synthesis of metal-polymer nanocomposites

In the large field of nanotechnology, polymer based nanocomposites have become a prominent area of current research and development due to their potential optical, electrical and magnetic applications. The integration of metal nanoparticles into the polymers allows both properties from metal nanoparticles and polymers to be combined/enhanced and thus advanced new functional materials with exceptional properties can be generated.
Several researchers reported different techniques for the synthesis of metal polymer nanocomposites such as electron beam resist [79], ion implantation method [80], physical vapor deposition [81], photolysis [82] and chemical reduction [83-90] etc. Some of the techniques are described below:

*Electron beam Resist*

The resist is prepared by blending a saturated solution of the metal precursor with polymer. This blend is spin-coated on clean substrate such as Si. Electron (e⁻) beam lithography (EBL) is performed on the blend film coated on a Si substrate. e⁻-beam exposures convert the resist blend into patterns containing metal nanoparticles. Bhuvana et al. [79] have reported growth of Ag-PS (polystyrene) nanocomposites using e⁻ beam resist technique.

*Ion implantation*

In this technique, an energetic metal ion such as Ag⁺ ion strikes the polymer and penetrates at varying depths depending on its ion energy. The incoming ions lose their energy through inelastic or elastic collisions with electrons and target atoms. The implantation depth distribution depends on the energy, fluence and type of ions as well as on the nature of target material. When the dosage is high of order of $10^{16}$ ions cm⁻², the equilibrium solubility of metallic implants in insulators (in particular, polymers) is usually increased, causing the nucleation and growth of metal nanoparticles. The dose threshold value depends on the type of polymer and implant amount. Osesa et al. [80] have reported synthesis of Ag-PMMA nanocomposites using ion implantation technique.

*Physical vapor deposition (PVD)*

PVD technique is based on co-evaporation of metal and polymer from two independent sources. In co-evaporation processes polymer films are produced by evaporation of the monomers and polycondensation on the substrate and isolated metal particles impinge simultaneously on the substrates. The formation and growth of metal nanoparticles and simultaneously growing polymer is affected by the sticking coefficient of metal atoms during deposition. Takele et al. [81] have reported the synthesis of Ag-PMMA nanocomposites using PVD technique.
Photolysis

In this technique, a saturated solution of metal salt and polymer is prepared. The resulting solution undergoes photolysis using a UV lamp, which reduces Ag salt into Ag nanoparticles immersed into polymeric solution. Khanna et al. [82] have reported synthesis of Ag/polyaniline nanocomposites using photolysis.

Chemical reduction and solution casting

This is one of the most successful methods adopted for the synthesis of metal-polymer nanocomposites. In this method, metal salt is chemically reduced using suitable reducing agent and simultaneously synthesized metal nanoparticles are protected using some capping agent. A variety of reducing agents have been used by various research groups [83-88]. Some researchers have also used tea leaf or plant extracts [89-90] for the synthesis of metal nanoparticles. The synthesis of metal nanoparticles can be performed by either in-situ (i.e. inside the polymer) or ex-situ (i.e. outside the polymeric solution). The resulting solutions are casted into petri dish to obtain nanocomposites.

1.4 Selection of host matrix

In the present work, Poly (methyl methacrylate) (PMMA) and Poly (ethylene terephthalate) (PET) are used as host matrix for the synthesis of metal-polymer nanocomposites. Both these polymers are hydrophobic in nature.

1.4.1 Poly(methyl methacrylate) (PMMA)

PMMA is an acrylic polymer. The monomer structure of PMMA is depicted in figure 1.6. It is available in form of white granules and easily grown into thin films. It is highly transparent (92% transmission). It is having poor mechanical properties such as tensile strength of 48-76 MPa, fracture toughness of 1.21 MPam^{1/2} in air, tensile modulus of 3100-2700 and Poisson’s ratio of 0.35. It is soluble in chloroform while insoluble in water. The value of refractive index for PMMA is 1.49. Its density is 1.18 g/cm^3 [91-93].

PMMA is selected as the host matrix for its distinct properties such as high transmission of visible light, environmental stability and durability are used in various industrial applications; some are listed below [93-95]:

- Hard contact lenses
- Enclosures for swimming pools, shopping malls and restaurants
Instrument panels
Nameplates
Medical Science such as bone cement, dentistry
Aircraft window
Luminous ceilings
Shields

Although PMMA has distinct properties but it has some drawbacks such as low tensile strength, low absorption of visible light, low electrical conductivity and small positive temperature coefficient of resistance (~ 1 to 3 orders magnitude change in resistivity) [6], which limits their use as temperature sensors and in other industrial applications. These properties are improved by encapsulating nanofillers into the PMMA matrix [17-19].

![Monomer structure of PMMA.](image)

**Figure 1.6:** Monomer structure of PMMA.

### 1.4.2 Poly(ethylene terephthalate) (PET)

PET is aromatic polyester. The monomer structure of PET is depicted in figure 1.7. It is a clear amorphous material. It is available in form of white granules and can be easily grown into thin films. It is having molecular weight \((192)_n\). It is having good mechanical properties such as high strength, rigidity, stiffness and toughness; low creep etc. It is having tensile modulus of 1700 MPa, flexural modulus of 2000 MPa, hardness of R105. Its dielectric constant at \(10^6\) Hz is 3.2 and volume resistivity is \(10^{15}\) ohm cm [91].
PET is widely used in various industrial applications; some are listed below [96-98]:

- Fiber
- Blow-molded bottles for carbonated soft drinks
- Magnetic tape, X-ray and photographic films
- Food packaging applications such as boil-in-bag food pouches
- Automobile applications such as window and door hardware, speedometer frames and gears, servo pistons, and automobile ignition system components
- Commercial applications such as handles, and housings for small appliances (toasters, cookers, fryers and irons)
- Consumer products like buckles, clips, buttons, and zippers.

In spite of the exceptional properties of PET, its performance is often limited due to its high gas permeability, transparency and the quite low electrical conductivity. Therefore, nanofillers are incorporated into the PET matrix to enhance its optical, electrical as well as gas permeability [99-100].

### 1.5 Choice of nanofiller: Silver (Ag) nanoparticles

Metallic nanoparticles such as Ag, Cu and Au exhibit significantly different physical and chemical properties in comparison to their bulk counterparts. Among them, Ag nanoparticles are more interesting in nanotechnology due to their excellent optical, electronic and chemical properties [41].

The optical behavior of Ag nanoparticles such as the occurrence of surface plasmon resonance (SPR) is an interesting feature for the researchers working in many interdisciplinary areas involving photonics, electronics, mechanics, chemistry, biology, nanofabrication, condensed matter, quantum physics, and many others.

Ag nanoparticles exhibit many potential applications, some are listed are listed below:
Optical Sensors

Dielectric properties of the surroundings shift the LSPR (localized surface plasmon resonance) in Ag nanoparticles. This behavior of Ag nanoparticles is used for optical sensing [101].

Electronic devices

Ag nanoparticles are used in conductive inks and integrated into composites to enhance thermal and electrical conductivity [102]

Drug delivery

Because of their small sizes, Ag nanoparticles are taken by cells where large particles are excluded or cleared from the body [103].

Anti-bacterial agents

As anti-bacterial agents, Ag nanoparticles are applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment. Ag nanoparticles are used in the health industry, food storage, textile coatings and a number of environmental applications [104-105].

Optoelectronic devices

Efficiency of photovoltaic cell is improved using Ag nanoparticles. These absorb solar radiation and concentrate the light on photovoltaic cell [106-107].

Catalyst

Catalytic activities of Ag nanoparticles are due to large S/V ratio. The bleaching of the organic dyes by application of potassium peroxodisulphate is enhanced strongly by addition of Ag nanoparticles [108-109].

SERS

Surface enhanced Raman scattering (SERS) of organic molecules adsorbed on Ag nanoparticles substrates is used for detecting minimal quantities of biomolecules and single molecule detection [110-111].
**Plasmonic waveguide**

Coupling between adjacent closely spaced metal nanoparticles such as Ag sets up coupled plasmon modes that give rise to coherent propagation of energy along the array and therefore, work as Plasmon Waveguide [112].

**Surface Plasmon Resonance and Coloring**

Surface plasmon resonance is the coherent excitation of conduction (free) electrons stimulated by external electromagnetic radiation. When the size of a metal nanoparticle is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated. Figure 1.8 depicts the schematic of surface plasmon oscillation of a metal nanoparticle, indicating displacement of the conduction electron cloud relative to the nuclei [113-114]. The electric field of an incoming electromagnetic radiation induces a polarization of the free electrons relative to the positive nuclei. Therefore, a dipolar oscillation of electrons is created with a certain frequency.

![Figure 1.8: Schematics of plasma oscillation for spherical metal nanoparticles.](image)

The explanation of interaction of incident light with small metal nanoparticles was given by Mie in 1908. According to Mie’s Theory, for a spherical metal nanoparticle having size much smaller than the wavelength of incident light ($2r << \lambda$), optical extinction cross-section ($\sigma_{ext}$) can be given by following equation:

$$\sigma_{abs}(\omega) = \frac{9\omega\varepsilon_m(\omega)^{3/2}V\varepsilon_2(\omega)}{C[\varepsilon_1(\omega) + 2\varepsilon_m(\omega)]^2 + \varepsilon_2^2}$$
where $V$ is the particle volume, $\omega$ is the angular frequency of incident light, $c$ is the velocity of light. $\varepsilon_m$ is the dielectric constant of the surrounding medium which depends on frequency. $\varepsilon (\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the dielectric constant of metal nanoparticle, which is complex and is a function of energy. In the presence of electric field of incident light, metal nanoparticle get polarize and behave as a dipole. When $\varepsilon_1 = -2\varepsilon_m$, maximum absorption of energy by metal nanoparticle will take place and plasmon resonance occur [33].

The energy of the surface plasmon resonance depends on both the free electron density and the dielectric medium surrounding the nanoparticle. Variation in these parameters alters the position as well as the intensity of surface plasmon resonance band. SPR of metal nanoparticles has wide range of applications in medical such as cellular imaging, molecular diagnosis etc. as well as in electronics and optics [4-5, 115].

In the present work Ag-PMMA and Ag-PET nanocomposites are fabricated by embedding Ag nanoparticles due to the interesting properties exhibited by Ag nanoparticles.

### 1.6 Applications of Ag-PMMA and Ag-PET nanocomposites

Ag nanoparticles embedded into PMMA and PET provides high-performance novel materials that find applications in modern nanotechnology. Some applications are listed below:

- **Antibacterial packaging**

  Due to antimicrobial activity of Ag nanoparticles against bacteria, viruses, and fungi, Ag-PET nanocomposites are used as antibacterial packaging material [116-117].

- **Optoelectronic devices**

  Due to plasmonic action of Ag nanoparticles, Ag-PMMA nanocomposites are used for various optoelectronic devices such as plasmonic waveguides, plasmonic photocrystals, and sensors etc [118].
Electronic devices

Doping of Ag nanoparticles modulate the electrical property of Ag-PMMA and Ag-PET nanocomposites, which make them suitable candidate for fabricating small electronic devices such as Schottky junction, sensors, batteries etc [119-120].

Medical science

Ag-PMMA and Ag-PET nanocomposites are used as cosmetic skin care mask for treatment of skin healing, skin cleansing. High surface area of Ag nanoparticles will facilitate greater utilization and faster rate of transfer of additives to the skin [121-122].

Gas sensor

Gas sensors have a broad range of applications such as industrial production, food processing, environmental monitoring, health care, etc. Ag-PMMA and Ag-PET nanocomposites are good candidates for gas sensors because of their large surface areas and interaction with the gas analyte, the electrical conductivity of nanocomposites change drastically [123].

1.7 Modified properties of Ag-PMMA and Ag-PET nanocomposites and related literature

The encapsulation of Ag nanoparticles in polymer host matrix like PMMA and PET has opened up many new and exciting possibilities to tailor the optical, electrical and dielectric properties of these matrices by controlling the size and shape of Ag nanoparticles rather than by altering the composition. The simplicity and affordability of synthesis of Ag-PMMA and Ag-PET nanocomposites render them one of the most exceptional and market-competitive materials for applications in photovoltaics, light emitting diodes (LED), photodetectors, lasers, sensors and more. Many research groups from all over the world have reported modification of some properties of PMMA and PET using different dopants. Although very few reports are available on the synthesis and characterization Ag-PMMA and Ag-PET nanocomposites. Systematic studies of optical properties such as band gap, refractive index, Urbach’s energy, dispersion coefficients, photoluminescence (PL) etc. of Ag-PMMA and Ag-PET nanocomposites have rarely been discussed in literature. A brief description of related literature is presented here.

Several researchers have reported synthesis and modification of metal-polymer nanocomposites. But most of the work has performed by adding Ag nanoparticles as filler...
in different polymer host matrix such as polyvinylalcohol (PVA), polyethylene (PE), polymethacrylic acid (PMAA) and polystyrene (PS) etc. Some reports are also available on the synthesis of nanocomposites using PMMA as host matrix but different fillers such as Au, Al etc.

Singh et al. [124] have fabricated Ag-PMMA nanocomposite films by reducing silver nitrate (AgNO₃) using N, N-dimethylformamide (DMF) and reported enhancement in thermal stability of PMMA on incorporating Ag nanoparticles. Xiong et al. [125] have synthesized Ag-PMMA nanocomposite films by adding AgNO₃ into DMF/PMMA solution with PVP as stabilizer and investigated the growth and shape of Ag nanoparticles in PMMA using UV-Visible spectroscopy and TEM. Vodnik et al. [126] have reduced AgNO₃ via sodium borohydride (NaBH₄) and mixed hydrophilic Ag nanoparticle with hydrophobic PMMA with the help of oleylamine as transfer agent and reported enhancement in thermo-oxidative stability of PMMA upon incorporation of Ag nanoparticles. Chen et al. [127] have also fabricated Ag-PMMA nanocomposite films by reducing silver nitrate (AgNO₃) using N, N-dimethylformamide (DMF) and reported improvement in electrical conductivity of PMMA by incorporating Ag nanoparticles. Tuzuner et al. [128] have prepared Ag-PMMA-polystyrene (PS) nanocomposite films by reduction of AgNO₃ via NaBH₄ using cetyltrimmonium bromide (CTAB) as capping agent and investigated the role of CTAB on the formation of Ag-PMMA-PS nanocomposite. Chatterjee et al. [129] have prepared Au-Ag-PMMA nanocomposite films by reduction of HAuCl₄.3H₂O and AgNO₃ using NaBH₄ and the resulting nanoparticles were incorporated in PMMA. Gadomsky et al. [130] have synthesized Ag-PMMA nanocomposites and have investigated the optical reflection and transmission behavior of Ag-PMMA nanocomposites and have reported modification in the value of refractive index of PMMA on adding Ag nanoparticles. Basak et al. [131] have incorporated Ag nanoparticles into PMMA to improve electrical conductivity which have potential applications in fabrication of different electronics as well as nanoelectronics devices. Altunin et al. [132] have investigated the change in refractive index of PMMA on incorporation of Ag nanoparticles. Kim et al. [133] have studied electrical properties of Ag-PMMA nanocomposites. Pour et al. [134] have investigated conduction mechanism in Ag-PMMA nanocomposites.

In the literature, reports on Ag-PET nanocomposites are very few. Prosycėvas et al. [135] have reported synthesis of Ag-PET nanocomposites using electron beam
evaporation followed by annealing. There is no report available in the literature on the synthesis of Ag-PET nanocomposites using chemical route. Optical constants like band gap, Urbach’s energy, refractive index, electrical conductivity and dielectric constants have rarely been studied for PET based nanocomposites.

Solomon et al. [136] have prepared Ag-PMAA nanocomposite films by reducing AgNO\textsubscript{3} using green approach and characterized the anticorrosion performance of the Ag-PMAA nanocomposite films by gravimetric, electrochemical analysis. Sadeghnejad et al. [137] have reported synthesis of Ag/Low density polyethylene (LDPE) nanocomposites by immersing corona air plasma treated LDPE in colloidal solution of AgNO\textsubscript{3} in fructose. Shamy et al. [138] have investigated indirect band gap values for Ag doped PVA nanocomposites and reported decrease in the band gap due to increase in the defect levels in the band gap on increasing the concentration of Ag nanoparticles. Mahmoud [139] has studied indirect band gap in Ag-PVA nanocomposites and reported decrease in band gap of PVA from 4.8 eV to 4.45 eV on incorporating Ag nanoparticles. Abdelghany [140] have investigated the change in the indirect band gap of polyvinyl pyrrolidone (PVP) on incorporating Ag-Au nanoparticles. Karthikeyan [141] has observed emission peak at 540 nm in Ag-PVA nanocomposite films with excitation wavelength 375 nm. Tripathy [142] has reported increase in photoluminescence intensity of PVA on incorporating Ag nanoparticles. Lee et al. [143] have investigated effect of polyaniline on electrical conductivity of Ag-PMMA nanocomposites. Saini et al. [144] have discussed the threshold values of Ag nanoparticles in PVA below which the insulating properties of PVA are enhanced and above the threshold value the conductivity of PVA has increased. Feng [145] have discussed electrical properties in Ag-PVA nanocomposites and reported increase in electrical resistivity of PVA on increasing the size of Ag nanoparticles. Xu et al. [146] have improved electrical conductivity of PMMA on encapsulating graphite nanoplatelets. Feng et al. [147] have reported change in dielectric properties PVA on doping with Ag nanoparticles. Singh et al. [148] have reported increase in the values of dielectric constant and dissipation factor of PMMA on incorporating Al nanoparticles due to increase in the interfacial polarization after doping with Al nanoparticles. Uddin et al. [149] have reported increase in dielectric constant of PVA after doping with Ag nanoparticles.
1.8 Justification and aim of the present work

It has been clearly revealed from the existing literature [116-135] that Ag-PMMA and Ag-PET nanocomposite films has advanced technological applications in the fabrication of photonic devices, data storage systems, biosensors, waveguides, solar cells, aerospace, microelectronic devices etc.

In the literature, lots of researchers have reported fabrication and characterization of Ag-PVA nanocomposites due to compatibility between hydrophilic nature of PVA and surface of Ag nanoparticles. Very few reports are available on Ag-PMMA and Ag-PET nanocomposites due to hydrophobic nature of PMMA and PET. Moreover, synthesis of Ag-PMMA nanocomposites using ex situ chemical technique has rarely been discussed and there is no report on the synthesis of Ag-PET nanocomposites by encapsulation of nanoparticles in PET. Thus the synthesis of Ag-PMMA and Ag-PET nanocomposites having uniform distribution of Ag nanoparticles without much agglomeration of Ag nanoparticles in host matrix is highly challenging. In the literature, few reports are available on investigation of optical and electrical properties of Ag-PMMA nanocomposites. But possible conduction mechanism and dielectric properties are rarely studied for Ag-PMMA nanocomposites. There are no reports available on optical, electrical and dielectric properties of Ag-PET nanocomposites.

Although numerous reports are available on optical, structural, electrical and dielectric characterization of polymer nanocomposites, but most of these studies have been carried out in different contexts and in random manner. Therefore, there is still a need to make a systematic study of optical, electrical, and dielectric response of polymers on incorporation of nanoparticles, which are the basis for functionality of any device. These properties are significantly influenced by size, type and quantity of incorporated nanoparticles in host matrix. Hence, for proper understanding of variation in optical, electrical and dielectric properties of polymer with change in the quantity of nanofillers in a systematic manner is required.

Keeping above facts and prospects in consideration an effort has been made in the present research work to synthesize Ag-PMMA and Ag-PET nanocomposite films using ex-situ chemical route and to investigate their optical, electrical and dielectric properties. Here PMMA and PET have been chosen as a host matrix due to wide spread industrial applications. Ag metal as nano filler have been taken into consideration as they display
surface plasmon resonance in the visible region besides their high conductivity and easy availability. The resulting nanocomposite films show surface plasmon resonance (SPR) band of Ag nanoparticles. The position of SPR band gets tuned upon changing the concentration of Ag nanoparticles in PMMA and PET matrix. Tuning of SPR band is useful in various optical phenomena like optical filters and surface enhanced fluorescence.

In the present work, the effect of increasing concentration of Ag nanoparticles on absorption, band gap, Urbach’s energy, reflection, refractive index, dispersion coefficient, transmission, luminescence intensity, electrical, dielectric behavior of PMMA and PET has been studied. The structural characterizations of prepared nanocomposite films have been studied using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD). These studies will definitely open up several new avenues for efficient and flexible nanofabrication with unique and varying combinations of properties and having high potential for successful commercial development.

1.9 Layouts of chapters

In addition to chapter 1(Introduction) the rest of the thesis is divided into following chapters:

**Chapter 2: Materials and Experimental techniques**

This chapter gives a brief description of the experimental methods which have been used in the synthesis and characterizations of Ag-PMMA and Ag-PET nanocomposites. In this chapter, description of procedure used for the synthesis of Ag-PMMA and Ag-PET nanocomposite films has been discussed. Also the description of characterization techniques such as UV-Visible Spectroscopy, Photoluminescence Spectroscopy (PL), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), I-V studies and Dielectric studies have been included to get information regarding optical, structural, electrical and dielectric properties of resulting nanocomposites.
Chapter 3: Results and Discussions

This chapter presents the results and discussion of the research work that has been carried out. It describes the studies related to the characterization of Ag-PMMA and Ag-PET nanocomposite films. The synthesized nanocomposite films were characterized by various techniques such as UV-Visible Spectroscopy, Photoluminescence Spectroscopy, Transmission electron microscopy and Scanning electron microscopy. Various optical parameters like absorption, band gap, Urbach’s energy, and transmission, reflection, refractive index, and dispersion coefficient, real and imaginary part of dielectric constant have been calculated and the results are presented in details. These synthesized nanocomposites were structurally characterized by various techniques such as TEM, SEM, FTIR and XRD. Electrical conductivity and possible conduction mechanism for synthesized nanocomposites have been studied and presented in detail. Variations of dielectric constant and dielectric loss with frequency and also with change in concentration of Ag nanoparticles in polymers have been studied and the results are presented in detail. A comparative study of Ag-PMMA and Ag-PET nanocomposites is also presented in this chapter.

Chapter 4: Summary, conclusions and scope of the future work

This chapter presents an extract of the study undertaken which includes the brief summary, important conclusions of the present investigations and future projections of present work in the exciting area of research.
References


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Chapter-1 Introduction

Chapter 1 Introduction


