CHAPTER 1

INTRODUCTION

1.1 General overview of the thesis

Materials with special combination of properties are the need of the hour. Many efforts have been made in the last few decades using novel nanoscience and nanotechnology to design such advanced materials [1-8]. Nanocomposites is an important class of such materials which are attracting increasing interest of researchers all around the world due to the exotic properties exhibited by them, resulting in their wide spread applications in diverse disciplines such as photovoltaics [9], optoelectronics [10], energy storage [11], super capacitors [12], flame retardants [13], sensors [14] etc. Thus nanocomposites are playing a vital role in the development of advanced materials with enhanced applications. Therefore, in depth studies related to nanocomposites may be of immense importance both from fundamental as well as application point of view.

In the present research work, an attempt has been made in this direction by synthesizing poly(vinylalcohol) (PVA) based nanocomposites using silicon carbide (SiC) nanoparticles and silver (Ag) nanoparticles and their various properties such as structural, optical, electrical, thermal and mechanical properties have been studied in detail.

A brief outline about the concept of nanomaterials, their classification, salient features, origin of the unique properties, various synthesis techniques have been described in section 1.2. Section 1.3 illustrates the concept of nanocomposites and their classification. An introduction to polymer nanocomposites alongwith their synthesis methods and unique properties has been discussed in section 1.4. PVA, host matrix has been discussed in section 1.5. Section 1.6 depicts the importance
and extraordinary properties of SiC and Ag nanoparticles used for making desired nanocomposites. Section 1.7 describes the modified properties of synthesized nanocomposites and related literature. Justification and aim of the present work has been presented in section 1.8. Finally, section 1.9 gives the brief layout of the chapters included in the present thesis.

1.2 Nanomaterials

1.2.1 Introduction to Nanomaterials

Over the last few decades, the science of nanomaterials has created great excitement and expectation in the scientific community due to the unique properties exhibited by these materials. One nanometer is defined as one billionth of a meter. Word ‘nano’ has a greek origin meaning dwarf and it denotes a factor of $10^{-9}$. Nanomaterials are those materials that have one or more dimensions in the range 1 to 100 nm. As an illustration, there are 25,400,000 nanometers in an inch or a human hair measures 75,000 nm. 3.5 atoms of gold or 8 hydrogen atoms lined up in a row make one nm [15-18]. Figure 1.1 gives the list of materials with their typical range of dimensions.

![Figure 1.1: Size comparison of some materials from micro to nano scale.](image)

1.2.2 Classification of Nanomaterials

Based on the number of dimensions which lie within the nanometer range, nanomaterials are usually classified into three classes [19, 20]:
(1) **1-Nano dimensional materials**: The materials having one dimension in nanoscale are called 1-Nano dimensional materials such as nanofilms, coatings etc.

(2) **2-Nano dimensional materials**: The materials having two dimensions in nanoscale are called 2-Nano dimensional materials such as nanorods, nanowires etc.

(3) **3-Nano dimensional materials**: The materials having all the three dimensions in nanoscale are called 3-Nano dimensional materials such as nanoparticles etc.

When materials are reduced to nano scale they exhibit distinctively different physical, chemical, optical, electrical, catalytic, magnetic properties from their bulk counterparts [19-23]. Some of the salient features of nanomaterials are highlighted as:

1) Nanomaterials are found to have significantly lower melting point as compared to their bulk forms. For example, the melting temperature of silver is 960°C, whereas the melting temperature of silver nanoparticles is below 200°C [24].

2) Physical characteristics of a material are highly dependent on its dimension. For example, the colour of metallic nanoparticles may change with size. Bulk gold is yellow, whereas gold nanoparticles are red or blue in colour depending on the size of the particle [19]. Reducing the size of silicon carbide particles makes it highly dense [25].

3) Mechanical properties of nanomaterials undergo a substantial change with decreasing size. For example, the hardness of palladium with 5-10 nm grains is 5 times higher than that of 100 µm grained sample [26].

4) Reduction in size shows a considerable effect on the chemical reactivities of material. For example, gold is chemically inert and is one of the most stable metals in the group 8 elements and it is resistant to oxidation. However, gold in the nanoparticle form possesses some catalytic ability [27].

5) The special structure of nanomaterials affects their thermal properties also. For example, carbon nanotubes have extremely high thermal conductivity as compared to their bulk form [28].

With improved properties, nanomaterials find diverse applications in semiconductor electronics [29, 30], sensors [14, 31], solar cells [8], optoelectronic devices [9], catalysis
[32], recording media [33] etc. The origin of unique physico-chemical properties of nanomaterials, that are neither similar to bulk nor to individual atoms or molecules, arise as a consequence of the confinement of the electron wave function and due to extremely high proportion of surface atoms – both these factors are directly dependent on the size of the nanomaterial [19, 34-36].

1.2.3 Surface to Volume ratio

The physical and chemical properties of bulk as well as nanomaterials are governed by their surface. At the nanoscale, there is an increase in the surface-to-volume ratio of a material as significant proportion of the atoms are the surface atoms, therefore the extent of any phenomenon or chemical reaction that occurs on the surface will increase. As the material becomes smaller the percentage of atoms at the surface increases relative to the number of atoms in its bulk form [19, 34] as depicted in figure 1.2.

![Figure 1.2: Particle size versus % of atoms on surface.](image)

When a bulk material is subdivided into nano dimension the total volume of the material remains the same whereas the collective surface area increases. As can be discerned from figure 1.3, each time a cube is divided into smaller cubes, the total volume of all the cubes remains constant while the total surface area increases
dramatically, which leads to higher surface energy resulting in their increased reactivity in comparison to corresponding bulk material. The specific surface area and thus, the total surface energy are negligible when material is large, but become significant for very small particles. The huge increase in surface area available from nanoscale materials can be exploited for potential applications in catalysis and specialized filters [37].

**Figure 1.3:** Schematic diagram showing how surface to volume ratio increases as size decreases.

**1.2.4 Quantum confinement effect**

Unique properties of nanomaterials may arise due to the discrete energy levels formed because of the confinement of the electronic wave function within the physical dimensions of the particles. This phenomenon is called quantum confinement. When the size of the nanomaterial is smaller than the de-broglie wavelength, then the electrons and holes are spatially confined resulting in the formation of discrete energy levels similar to a particle in a box [38]. The energy separation between adjacent levels increases with decreasing dimensions. Figure 1.4 schematically illustrates discrete electronic configurations for bulk, nanofilm, nanowire and nanoparticle. The electronic configurations of nanomaterials are significantly different from their bulk counterparts. As a result of changes arising due to systematic transformation of density of states as the function of the size, a
strong variation in the optical and electrical properties of nanomaterials with size is observed [19].

![Figure 1.4: Schematic illustration of discrete electronic configurations for bulk, nanofilm, nanowire and nanoparticle.](image)

Some peculiar properties of nanomaterials are known but there are a lot more yet to be discovered. Many such properties are size dependent, in other words, they can be tuned considerably, simply by adjusting the size, shape or extent of agglomeration. Thus controlled synthesis of nanomaterials with desired tunable properties is a subject of great interest among the research communities and efforts are being continuously made to develop new methods for the production of such nanomaterials.

### 1.2.5 Synthesis of Nanomaterials

Due to increasing interest in nanomaterials, numerous methods for their synthesis have been reported. The two main approaches routinely being used to produce nanomaterials are top down approach and bottom up approach [Figure 1.5] [19].
1.1 Top down method

According to this approach, formation of nanomaterials involves breaking, or cutting down larger pieces of a material to the nano-size regime by bombardment with high energy electrons, etching or milling. Some techniques that employ the top down approach include wet/dry grinding, reactive grinding, etc [19]. The top-down approach often uses the traditional workshop or microfabrication methods where externally controlled tools are used to cut, mill and shape materials into the desired shape and order.

1.2 Bottom-up method

In this approach, constituents of the material are arranged into more complex assemblies atom–by–atom or molecule–by molecule till the desired dimensions of the material are achieved. This approach generally provides nanostructures with better homogeneity in chemical composition and precise control on their size and shape. Some of the bottom-up methods of nanomaterials synthesis include chemical vapour deposition, laser ablation deposition, sputtering techniques, hydrothermal synthesis, sol-gel process etc [19].

![Figure 1.5: Schematic representation of Top down and Bottom up approaches.](image_url)
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 areas of composites research [39, 40]. 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.

1.3 Nanocomposites

Nanocomposites are composites in which at least one of the phases have dimensions in the nanometer range or nanocomposites are the materials that are synthesized by introducing nanoparticulates (often referred to as filler) into a host material (often referred to as the matrix) as depicted in figure 1.6 [19, 39-41].

![Figure 1.6: Illustration of nanocomposite.](image)

After adding nanoparticulates to the matrix material, the resulting nanocomposite may exhibit drastically enhanced properties. For example, nanocomposite formed by noble metal nanoparticles embedded in a dielectric matrix show extraordinary physical
properties [42-44] which are interesting for many fields including opto-electronics, high voltage applications, sensors, textile applications, wound healing etc [45-50]. Addition of carbon nanotubes tends to drastically enhance the mechanical and thermal properties of host material [51]. Nanoparticulates of silicon carbide, cerium oxide and zinc oxide are used as reinforcement for nanocomposites as they exhibit high stiffness and strength [52-54]. Hence, depending on the nanoparticles, types and shapes, nanocomposites can have different properties.

Depending on the nature of the host material, nanocomposites are generally classified into three categories viz ceramic matrix nanocomposites, metal matrix nanocomposites and polymer matrix nanocomposites [55].

Among these matrices, polymers are particularly gathering interest as a host matrix for nanomaterials because they exhibit interesting properties as will be discussed in section 1.4. Hence, in the present work, polymer has been chosen as a host matrix for the preparation of nanocomposites.

1.4 Polymer nanocomposites

Polymer nanocomposites are fabricated by embedding inorganic filler having at least one dimension in nanoscale in a polymer host matrix [56]. Polymers are interesting as an embedding phase because they have variety of inherent characteristics such as

- Low fabrication cost, light weight, good mechanical strength, good flexibility, easy workability etc.
- They can be electrical and thermal insulator or conductor
- Can have hydrophobic or hydrophilic nature
- Resistance to corrosion effects
- Resistance to chemicals

Thus, polymers are the most indispensable engineering materials. The exceptional properties of polymeric materials make them widely used materials which are fastly replacing metals in most of the applications.
The large surface area of the embedded nanofiller even at very low concentration can markedly change the macroscopic properties of the polymer and contribute many new characteristics to the polymer. Thus, polymer nanocomposites is a unique way of having the advantages of both polymers as well as nanomaterials [57-59]. The incorporation of nanofillers in the polymer matrix produces composites with properties and performance superior to polymer and nanoparticles alone. Thus, polymer nanocomposites are an exciting emerging area of research and have been gaining wide attention of many researchers [60-63].

1.4.1 Methods of synthesis

Scientists around the world are conducting research to develop novel methods for the synthesis of nanocomposites, with the aim to have a better control over the particle size, distribution, morphology, purity, quantity and quality by employing environment friendly economical processes. As enhanced properties and performance displayed by nanocomposites are governed by these factors.

Basically there are three methods to prepare such nanocomposites:

(a) Solution casting

(b) Melt blending

(c) In-situ polymerization

In solution casting, a polymer, a solvent and the nanomaterial are combined and thoroughly mixed by ultrasonication and the solvent is allowed to evaporate leaving behind the nanocomposite, typically as a thin film [64].

In the case of melt blending, extruder or an internal mixer is used. Polymer and nanomaterial are added in the extruder and subjected to intensive mixing for some time which results in the formation of a nanocomposite. In this method, polymer mobility simply comes from thermal energy [65].

In case of in-situ polymerization, dispersion of nanomaterials takes place in a solvent in which a monomer is also dissolved. The subsequent polymerization of monomer leads to uniform dispersion of polymer around the nanomaterial. In many instances the generated polymer can also be chemically grafted to the surface of nanomaterial [66, 67].
Not all nanomaterials can form stable nanocomposite with polymers. The compatibility and interfacial properties between polymer matrix and nanomaterials significantly influence the essential characteristics of nanocomposite. Synthesis of nanocomposites to have a better control over the particle size, distribution, morphology, purity, quantity and quality by employing environment friendly economical processes has always been a challenge for the researchers. In the present work, the solution casting method has been used for synthesizing nanocomposites.

### 1.4.2 Unique properties of polymer nanocomposites

Polymers act as the excellent host materials for metal as well as semiconductor nanoparticles by immobilizing the nanoparticles and also protect them against aggregation. Nano scale metals or semiconductor materials encapsulated in polymer matrices exhibit enhanced properties such as improved stiffness, strength, toughness, electrical or thermal properties over those of conventional polymers [68-72] and hence have lot of potential applications depending upon the inorganic material present in the polymers.

The unique physical and chemical properties of polymer nanocomposites are [62, 73-82]:

- Surface appearance (colour)
- Fluorescence
- Linear and nonlinear optical behaviour
- Electrical conductivity
- Mechanical properties such as stiffness, strength, hardness
- Corrosion resistance
- Fire retardency
- Thermal stability
- Better abrasion resistance
- Improved barrier properties etc.

Based on these distinctive properties, polymer nanocomposites have a huge range of potential scientific applications in optical data storage media, optical waveguides, optical switches, solid-state lasers, sensors, display devices, photovoltaics, aerospace applications, automobiles, for decorative purposes, textiles etc [58, 83-91]. Performance
and properties of nanocomposites in all these applications is determined by the size, shape, number density and distribution of the nanomaterials in the host matrix.

1.5 Selection of host Matrix: Poly(vinylalcohol) (PVA)

PVA is a hydrophilic, nontoxic and biodegradable polymer, which is an excellent host for the nanofillers and thus has numerous technological applications [92, 93]. It has good solubility in water due to the formation of strong hydrogen bond (H-bond) between the functional group of polymer and the water molecules. The aqueous solutions of PVA form complexes with the additives, which make it technologically important as a binding material [72, 92-95]. Furthermore, it has good film forming ability when the films are prepared by solution casting technique [96, 97]. The films of the PVA are highly optically transparent, which makes it suitable for surface coating of the solid state optoelectronic devices and other multifunctional materials [91, 98-100]. The monomer structure of PVA is shown in figure 1.7. It is generally available in the form of white granules or powder with specific gravity of 1.25 ~ 1.32, bulk density of about 0.4 ~ 0.7, glass transition temperature (T_g) = 85°C and melting point in the range of 210 ~ 230°C [101]. It is soluble in water and is resistant to animal oil, plant oil and grease oil.

![Monomer structure of PVA](image)

Figure 1.7: Monomer structure of PVA.

The main drawback of this hydrophilic polymer is its poor mechanical and thermal stability. For the improvement in these performance properties and in order to increase applications of PVA in various fields, researchers are using emergent field of nanotechnology by incorporating nanoparticles into PVA matrix to produce novel materials [91, 100, 102, 103].
1.6 Selection of nanofillers

1.6.1 Silicon carbide (SiC) nanoparticles

SiC nanoparticles based polymer nanocomposites has captivated the attention of many research groups [add]. SiC is an important wide band-gap semiconductor, and a well known ceramic material with more than 250 polytypes [104, 105]. It is an excellent candidate for nanocomposite synthesis because of its excellent physical and chemical properties such as high chemical stability, excellent thermal conductivity, smaller thermal expansion coefficient, better abrasion resistance, high-electron mobility, high break down field strength, superior mechanical properties etc [106-110]. SiC nanoparticles are commercially used in optoelectronic devices, such as photodiodes and light-emitting diodes which emit throughout the visible spectrum into the ultraviolet region [111]. Hence, they can be good candidates for labels of biological molecules. The applications of SiC nanoparticles also cover the area of high-temperature sensors [109], high-power devices [112] and microwave devices [113]. Its peculiar electronic properties make it a promising material for next-generation electronic devices.

1.6.2 Silver (Ag) nanoparticles

Ag nanoparticles play a significant role in nanomaterials science and technology due to many peculiarities. One of the main characteristic of Ag nanoparticles is the occurrence of surface plasmon resonance (SPR) due to the collective oscillation of free electrons in resonance with the illuminating light and has $10^5$-$10^6$ times larger extinction cross section than ordinary material chromophores [114-116]. The SPR can be tuned to any wavelength in the visible spectrum by changing the shape, size or concentration of nanoparticles [15]. Its higher efficiency to plasmon excitation leads to enhanced properties including catalysis, electrical conductivity, antimicrobial activity, surface enhanced raman scattering etc [117-119]. These extraordinary features make it a potential candidate in numerous applications such as biosensors [1], photonics [120], colour filter technology [121], photovoltaic applications [91] etc.
1.7 Modified properties of SiC-PVA and Ag-PVA nanocomposites and related literature

Polymer nanocomposite technology is one of the driving forces in stimulating and promoting nanotechnological developments. Intense research in the field of synthesis and study of composite materials containing metal as well as semiconducting nanoparticles is motivated by the remarkable properties exhibited by such composites leading to their various potential applications in diverse disciplines of science and technology. Currently PVA based nanocomposites with metallic, semiconducting, ceramic nanofiller embedded into it are attracting increasing attention due to their widespread applications. Wu et al. [71] have fabricated nanohybrid membranes using Ag-PVA/polyethyleneimine blend that act against simulants of chemical and biological weapons while retaining their ability to transmit moisture vapor. Improvement in the thermal resistance of PVA/silica nanocomposite compared to PVA has been highlighted by Peng et al. [122]. Wang et al. [123] fabricated nanocomposites of poly(vinylidene fluoride) by incorporating, PVA modified rGO using solution cast method and characterized their dielectric properties to obtain high performance flexible dielectric materials. Zhang et al. [124] synthesized PVA composite films using well dispersed single wall carbon nanotubes (SWCNT) and the formed nanocomposite exhibited significant improvement in tensile strength and modulus. Mbhele et al. [125] formed Ag-PVA nanocomposites and studied the improvement in thermal and mechanical properties. Kumar et al. [126] have prepared copper oxide-PVA nanocomposite which serves as a seed for the crystal growth of copper oxide.

SiC nanoparticles are an important semiconducting material having numerous unique properties for reinforcing polymer matrices. Extensive research is being carried out to achieve stable and uniform dispersion of SiC nanoparticles in polymer matrix. Cao et. al. have improved the interfacial adhesion between polymer matrix and SiC nanoparticles by coating SiC nanoparticles surface with polystyrene [127]. Iijima et. al. have modified the surface of SiC nanoparticles by using azo radical initiators such as 2,2’-azobisisobutyronitrile and 2,2’-azobis (2-methylpropionamidine) dihydrochloride [128]. Che et. al. have improved the dispersion of SiC nanoparticles in non aqueous medium by grafting polyacetals via inorganic-organic coating [129]. Kassiba et. al. have synthesized
PANI-SiC core-shell nanocomposites by functionalizing SiC nanoparticles using aniline [130].

There are quite few reports highlighting the effect of addition of SiC nanoparticles on PVA matrix. Vivekchand et al. [131] have reported an increase in the elastic modulus of PVA with addition of 0.8 volume% SiC nanowires. Zhang et al. [132] have studied the influence of PVA as a binder on the zeta potential and rheological properties of SiC slurries. There are hardly any reports in literature describing the structural, thermal, electrical and mechanical characterization of SiC-PVA nanocomposites.

Nanocomposites prepared from metallic nanoparticles, especially noble metals like Ag has been an area of intensive research. Many research groups have discussed various insitu and exsitu techniques for the fabrication of Ag based nanocomposites. For example, Devi et al. [133] synthesized AgNO₃ doped PVA composite films by solution growth technique. Khanna et al. [134] have made Ag-PVA nanocomposites by reduction of AgNO₃ using hydrazine hydrate. Karthikeyan [135] has fabricated Ag-PVA nanocomposites by reducing AgNO₃ with PVA. Badr et al. [136] have reduced AgNO₃ using sodium citrate and resulting Ag nanoparticles were dispersed in PVA. Krkljes et al. [137] have reported the synthesis of Ag-PVA nanocomposites using 2-propanol. Sadjadi et al. [138] have reduced AgNO₃ using N-N’-dimethyl formamide (DMF) for obtaining Ag-PVA nanocomposites. Mbhele et al. [125] used NaBH₄ for reducing Ag₂SO₄ and resulting Ag nanoparticles were dispersed in PVA to obtain nanocomposites. Many attempts have been made to optically, structurally and electrically characterize these nanocomposites. Many such reports, in general, have highlighted the changes observed in structural, optical, thermal, electrical properties as function of concentration of Ag nanoparticles. However, there is still an on-going discussion about threshold values of Ag nanoparticle content above or below which the polymers show varying properties.

1.7.1 Optical Properties

Study of optical properties of nanocomposites is of immense importance due to their applications in various sectors such as optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, etc [139]. Optical characterization helps to determine various parameters such as optical energy gap, Urbach’s energy, refractive index, dielectric constant etc [140]. The optical
properties of nanocomposites depend on several parameters such as size, shape, surface characteristics, concentration of nanofillers and their interaction with the surrounding matrix [15, 64, 141].

Literature contains reports on tuning of optical properties of polymer matrices by using various types of nanofillers. *Sun et al.* [142] have studied the absorption properties of PVA embedded with gold nanoparticles. *Jabbar et al.* [143] have calculated various optical constants like optical energy gap, refractive index of PVA by adding Ag nanoparticles. *Khanna et al.* [134] have made Ag-PVA nanocomposites by reduction of AgNO₃ using hydrazine hydrate and characterized the nanocomposite using UV-Visible spectroscopy. *Anthony et al.* [144] have fabricated Ag-PVA nanocomposite films and have highlighted that such films are promising candidates for optical limiting devices. *Saikia et al.* [91] have fabricated CdS(PVA)-CdTe thin film solar cell and showed that doping of Ag into this nanocomposite thin film has improved the conversion efficiency from 4.92% to 5.63%. However, there is no literature available on optical characterization of SiC-PVA nanocomposites.

### 1.7.2 Electrical Conductivity Behavior

Electrical conduction refers to the phenomenon of charge transport through the nanocomposites. The electrical properties of the nanocomposites are strongly influenced by the changes occurring in the microstructure as a result of addition of nanofiller. Critical concentration of nanofiller must be incorporated into the host matrix to transfer the nanocomposite from the insulating state into the conducting state [145,146]. A detailed analysis of current-voltage characteristic is significant in order to understand the exact conduction mechanism such as ohm’s law, variable range hopping, Schottky emission, Poole-Frenkel emission, space charge-limited conduction (SCLC) mechanism responsible for charge transport in polymer nanocomposites [147-149].

Very few reports are available in literature that have studied the electrical conductivity of SiC nanoparticles in a polymer matrix. *Tkaczyk* [150] has observed a substantial increase in current with addition of 5 wt% SiC nanoparticles in Polybutadiene matrix and have concluded that hopping and Poole-Frenkel conduction mechanisms are chiefly responsible for increased conductivity of
Polybutadiene. There exist reports in literature which show an increase in conductivity of PVA after incorporation of Ag nanoparticles. For example, Devi et al. [133] have synthesized Ag-PVA nanocomposites by solution growth technique and observed enhanced conductivity of the resultant nanocomposite and concluded that the Schottky mechanism was responsible for increased conductivity. Gautam et al. [151] have shown that Ag-PVA nanocomposite follows ohm’s law with increasing concentration of Ag nanoparticles.

1.7.3 Thermal Properties

Thermogravimetric analysis (TGA) is a widely used technique to study the thermal stability of nanocomposites [152]. Several reports are available on the study of thermal stability and degradation of polymer nanocomposites by TGA. Decomposition of polymer nanocomposites significantly depends on the nature of nanofillers and on their dispersion in the host matrix. Alamari et al. have depicted that after the addition of 3 and 5 wt % n-SiC in epoxy resulted in increase in char residue from 13.1 to 13.2% and 14.0%, respectively [153]. Rodgers has incorporated SiC nanoparticles in SC-15 epoxy resin and the results indicate that 1 wt % loading of SiC nanoparticles leads to maximum improvement in thermal properties of epoxy [110]. Mbhele et al. have synthesized PVA nanocomposites by incorporating Ag nanoparticles and showed that the thermal decomposition temperature of PVA is increased by about 40°C [125]. Krkljes et al. have shown that Ag nanoparticles increase the onset of thermal degradation of PVA [137]. Khanna et al. prepared Ag-PVA nanocomposites and reported that the thermal decomposition has been shifted to higher temperatures after embedding Ag nanoparticles in PVA [134].

1.7.4 Mechanical Properties

Hardness of a nanocomposite is defined as its ability to resist permanent deformation. Polymers are widely used in various technical applications because of their unique advantages such as ease of production and light weight. However they have certain inherent disadvantages such as low hardness and low tensile strength. For polymers, mechanical properties, namely its hardness, can be significantly improved by embedding nanofillers.
A hard material is generally defined as one which is not easily indented by a rigid body or as one which is difficult to scratch. The greater the hardness of a material, greater is its resistance towards deformation. The microhardness measurement of materials is usually carried out with the help of Vickers or Knoop microhardness tests [154-157].

There are quite a few reports in literature which have highlighted the improvement of hardness of polymers by incorporating nanoparticles. Khaled has measured the Vicker’s microhardness of PVA doped with copper chloride and chromium chloride and the nanocomposites showed enhanced microhardness with increased chromium chloride concentration [158]. Bakr et al. have shown increased microhardness of PVA with increasing PbCl₂ concentration [159]. Lan et al. have reported the improvement of about 75% in microhardness of SiC nanoparticles reinforced magnesium composites [160]. Gazawi et al. performed Vicker’s microhardness tests on Al-4wt.% Cu-(2.5-10) vol. % SiC nanocomposites and has shown the high effectiveness of SiC nanoparticles in strengthening the material [161]. In literature to the best of our knowledge there are no reports available on the studies of Knoop microhardness of SiC-PVA and Ag-PVA nanocomposites.

1.8 Justification and aim of the present research work

It has been clearly revealed from the existing literature, that the dedicated research and development activities in the field of synthesis of polymer based nanocomposites have increased tremendously because it is a unique mode of harnessing the advantage of distinctive properties of nanofillers as well as of polymers. Such materials often result in lightweight structures having high stiffness and tailored properties for specific applications. Several reports have depicted that the addition of small amount of nanofiller in a host matrix have led to remarkable changes in various properties of the nanocomposites [56-59, 64-67]. As a result their usage has increased for a variety of applications, particularly in the fabrication of photovoltaics, energy storage devices, switches, sensors, supercapacitors, fire retardents, optical waveguides etc [72-74, 85-91, 162, 163].

SiC nanoparticles are very attractive semiconducting material that can be used as filler in different polymer matrices due to the numerous unique properties they exhibit as
discussed in section 1.6.1. However, because of the presence of strong van der waals interactions among SiC nanoparticles, their dispersion in a polymer matrix is not homogeneous. Thus uniform dispersion of SiC nanoparticles in polymers is still a challenge. As a result, despite the fact that SiC nanoparticles possess many extraordinary properties, their potential as reinforcing filler for the improvement of mechanical, thermal or electrical properties of polymers has not been fully harnessed. An effective approach to prevent aggregation is the modification of the surface of SiC nanoparticles, which aids in dispersing and stabilizing SiC nanoparticles within a polymer matrix. There are many reports in literature which discusses the synthesis of Ag-PVA nanocomposites using various stabilizers. However, reports highlighting the synthesis of Ag-PVA nanocomposites without any external stabilizing agent are rare. Moreover, systematic studies reporting the changes occurring in structural, optical, electrical, thermal and mechanical properties of Ag-PVA nanocomposites films are hardly available.

Although numerous reports are available on optical, electrical, thermal and mechanical characterization of polymer nanocomposites, but before the fabrication of functional devices with optimized performance, a lot of work still needs to be done in a systematic manner on the evaluation of optical properties, electrical conductivity behavior, thermal stability, mechanical properties, which forms the basis of operation of any device. These properties keep on evolving depending on size, type and concentration of nanoparticles in the host matrix. Hence, for proper understanding of variation in optical, electrical, thermal and mechanical properties with increasing concentration of nanofillers, a systematic and detailed investigation is required as it has special importance for the development of functional devices.

Keeping above facts in mind, an effort has been made in this endeavor to carry out a systematic study on the nanocomposites fabricated by embedding SiC and Ag nanoparticles in PVA matrix. PVA has been chosen as a host matrix due to its variety of applications in diverse fields, transparency and ability to behave as an excellent matrix for nanofillers. SiC nanoparticles as nanofiller have been taken into consideration due to its excellent thermal, mechanical, electrical properties as discussed in section 1.6.1. Ag nanoparticles were selected as they display surface plasmon resonance in the visible region besides their high conductivity.
In the present work the effect of increasing concentration of SiC nanoparticles and Ag nanoparticles on structural, optical: optical energy gap, Urbach’s energy, refractive index, dielectric constant etc., electrical conductivity behaviour, thermal properties and mechanical properties: microhardness of PVA have been studied using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) Spectroscopy, Raman Spectroscopy, UV-Visible spectroscopy, I-V measurements, Thermogravimetric Analysis (TGA) technique and Knoop Microhardness technique.

1.9 Layout of chapters

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

Chapter 2: Experimental Techniques

This chapter of thesis deals with the description of experimental method and various characterization techniques used in the course of this study. It comprises of the description of chemical routes utilized for the synthesis of SiC-PVA and Ag-PVA nanocomposites. Various characterization techniques such as XRD, TEM, SEM, FTIR spectroscopy, Raman spectroscopy, UV-Visible spectroscopy, I-V measurements, TGA, knoop microhardness technique utilized to ascertain the structural, optical, electrical, thermal and mechanical properties of SiC-PVA and Ag-PVA nanocomposites has been discussed in this chapter.

Chapter 3: Results and Discussion

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 SiC-PVA nanocomposites (synthesized using as received SiC nanoparticles, surface treated SiC nanoparticles and PVA grafted SiC nanoparticles) and Ag-PVA nanocomposites. These synthesized nanocomposites were structurally characterized by various techniques such as XRD, TEM, SEM, FTIR and Raman spectroscopy. Various optical parameters such as optical energy gap ($E_g$), Urbach’s energy ($E_u$) refractive index ($n$) and dielectric constant have been calculated using UV-Visible spectroscopy and the results are presented in detail. This chapter describes the
dispersion of refractive index analyzed using Wemple-DiDomenico single oscillator model and presents the values of various dispersion parameters. I-V characteristics of SiC-PVA and Ag-PVA nanocomposites were studied in detail and the exact charge transport mechanism responsible for increased conductivities in the synthesized nanocomposites has been discussed in this chapter. It also presents the discussion related to the changes occurring in the thermal stability curves of the resulting nanocomposites using TGA and the modifications induced in surface hardness of the nanocomposites studied using Knoop microhardness measurements.

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

This chapter includes the brief summary, innovative outcomes of the present investigations and conclusions along with suggestions for future scope of present work in this exciting area of research.
Chapter 1 Introduction

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