DESIGN AND OPTIMIZATION OF CONSTITUENTS FOR CONDUCTIVE POLYMER NANOCOMPOSITE

By

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DECLARATION

This is to confirm that the work presented in this thesis is original. Outcome of accomplishment of the thesis on "Design and Optimization of Constituents for Conductive Polymer Nanocomposite" carried out by the student of Department of Materials and Metallurgical Engineering, BUET, Dhaka and it has not been submitted anywhere for any award, degree or diploma, nor it has been published in any technical journal.

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DEDICATION

Dedicated to my beloved parents.
ACKNOWLEDGEMENTS

First and foremost, thanks to Almighty Allah for giving me the strength and patience, for completing this thesis work.

It is actually a long journey from October 2014 to complete this work. During this journey, I always got encouragement and guidance from my respected supervisor, Professor Dr. Md. Aminul Islam. Every time he gave me a planned support towards the completion of the research work. I want to express my utmost gratitude to my supervisor for his dedicated and continuous support, invaluable advice and explanation related to the research work. Because of continuous motivation from my supervisor, I did not go back regarding this thesis work.

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ABSTRACT

In recent years, conductive polymer nanocomposites (CPNC) have attracted the considerable attention from worldwide researchers due to their wide range of applications. Presently, conducting polymer composites are being made with the high volume fraction of reinforcing fine particles as 12-30% [9-12]. In many cases, especially in fibre forming matrix, the highly concentrated conductive filler is resulting deterioration in mechanical properties because of their poor moldability and draw ability [7,13]. As a result, nowadays, a great challenge for the researchers in the field of conductive grade polymer nanocomposites is to minimize (possibly within 6%) the filler concentration with better conductivity.

Present study is designed to develop a conductive polymer nanocomposite of binary matrix of polypropylene (PP) and poly ethylene-co-vinyl acetate (EVA) to reduce the filling load with good thermal conductivity. Moreover, another target is to increase draw ability of the rigid polymer polypropylene (PP) without too much compromise of its tensile strength. The total work was done by taking one organic particle (activated carbon, AC) and one inorganic particle (alumina, Al) as reinforcement. For rigorous analysis, both microparticle and nanoparticle reinforced samples were made through melt compounding method by premixing and hot press. The samples were prepared by mixing individual particle as well as in various ratios of activated carbon and alumina with the PP/EVA matrix. For better understanding of thermal conductivity of the composite and optimize the constituent materials several analytical techniques as tensile, flexural, thermal conductivity, DSC and water absorption tests were conducted. In order to analyze and support the experimental results thus obtained SEM and FTIR were also used.

For all cases, tensile strength of binary matrix (PP/EVA) composite reinforced by binary particle (activated carbon/alumina) has been found higher than that of the binary (PP/EVA) matrix reinforced by single particle (activated carbon or alumina). From experimental result, it is revealed that the individual particle created a problem related to coagulation effect in the matrix, however, in the case of binary particle (activated carbon/alumina) better dispersibility of particle in the matrix has been observed and this has been thought one of the big challenge to achieve better functional properties in the particle reinforced polymer composites. Moreover, in all perspective, nanocomposites show better results than the microcomposites. The %elongation of the developed composite is decreased with the
increase in the alumina particles in the binary matrix and this phenomenon has also been found when the particles are used individually in the composite. Here it to be noted that PP/EVA matrix has been selected for composite design to improve the draw ability of the PP. This study found that whatever the particle content the % elongation is always greater than pure PP. Also in binary particle composite, the tensile as well as flexural strength and thermal conductivity increased with the increase in the relative proportion of alumina particle than carbon. The crucial finding in the present research is that the thermal conductivity shows a better result in a certain relative ratio of carbon and alumina, which is 1:4 in PP/EVA matrix. However, the composite containing binary reinforcing particle shows better thermal conductivity in both microcomposite and nanocomposite, where the thermal conductivity of nanocomposite is 23% higher than that of the microcomposite. Also the thermal conductivity of the developed nanocomposite is nearly 13 times higher than that of the pure PP and 10 times of that of the PP based microcomposite.
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<tr>
<td>CPNC</td>
<td>Conductive Polymer Nanocomposite</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>EVA</td>
<td>Poly(Ethylene-Co-Vinyl Acetate)</td>
</tr>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>AL</td>
<td>Alumina</td>
</tr>
<tr>
<td>IZ</td>
<td>Interfacial Zone</td>
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<td>TC</td>
<td>Thermal Conductivity</td>
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<td>IZ</td>
<td>Interfacial Zone</td>
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<tr>
<td>Wt%</td>
<td>Weight Percent</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>MMC</td>
<td>Metal Matrix Composites</td>
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<tr>
<td>CMC</td>
<td>Ceramic Matrix Composites</td>
</tr>
<tr>
<td>CCM</td>
<td>Carbon Carbon Composites</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetric</td>
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<tr>
<td>FM</td>
<td>Flexural Modulus</td>
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<td>WA</td>
<td>Water Absorption</td>
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<tr>
<td>Σ</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>N</td>
<td>Maximum load</td>
</tr>
<tr>
<td>A</td>
<td>Sample area</td>
</tr>
<tr>
<td>ε</td>
<td>Strain</td>
</tr>
<tr>
<td>ε_f</td>
<td>Straining of the Outer Fiber</td>
</tr>
<tr>
<td>D</td>
<td>Maximum Deflection of the center of the Beam</td>
</tr>
<tr>
<td>d</td>
<td>Depth of beam</td>
</tr>
<tr>
<td>b</td>
<td>Width of beam</td>
</tr>
<tr>
<td>L</td>
<td>Support span</td>
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<tr>
<td>σ</td>
<td>Stress</td>
</tr>
<tr>
<td>σ_f</td>
<td>Stress of the Outer Fiber</td>
</tr>
<tr>
<td>E_f</td>
<td>Modulus of Elasticity in Bending</td>
</tr>
<tr>
<td>h</td>
<td>Height of the measured sample</td>
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<tr>
<td>K</td>
<td>Thermal conductivity</td>
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<tr>
<td>R_s</td>
<td>The thermal resistance</td>
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<tr>
<td>Φ</td>
<td>Heat flow</td>
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<tr>
<td>φ_c</td>
<td>Critical volume fraction (percolation threshold)</td>
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<td>(dT/dt)</td>
<td>Slope of cooling curve</td>
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CHAPTER ONE
INTRODUCTION
INTRODUCTION

Nanoparticle embedded nanocomposite a new grade of material will enable the circumvention of the classical material performance trade-offs by accessing new properties and exploiting unique synergism between materials that only occur when the length scale of morphology and the fundamental physics associated with a property coincide. Such material technologies are rapidly increasing, impacting many diverse areas of the commercial and military arena. Polymer nanocomposites, for example, have been a mainstay of high-performance aircraft for over a quarter century, offering a multitude of desirable properties, such as high strength and stiffness, and dimensional. Now this polymer nanocomposite technique will go from aircraft body to nano batteries. With the advent and application of nanotechnology, polymer nanocomposites could become even more attractive [1-3]. In that perspective particulate nanocomposite can be developed by nanoscale fillers. Nanocomposites exhibited superior mechanical performance and improved barrier properties at much lower loading levels of nanofiller compared to usual fillers. However, strong chemical bonding between the nanofillers and the polymeric matrix is compulsory in order to produce a nanocomposite with excellent mechanical properties [4].

Different particles are increasingly being used as additives to polymers to simultaneously enhance a variety of properties without sacrificing any qualities of the base polymer. Carbon black, activated carbon and alumina, for example, have very high potential in respect to thermal and electrical conductivities. As a consequence, these fillers can be used to convert thermally and electrically insulating plastics into conductive materials [5] and to increase their mechanical properties at the same time. Thermally conductive thermoplastics have many applications in the automobiles, aerospace, electronics, and battery industries [6]. They can be used as thermal interface materials or heat sinks to dispel heat from electronic devices such as computers, flat panel displays, and cell phones [7]. In principle, proper dispersion of particle in matrix is important to get desired thermal behavior, but it is not always easy to obtain such dispersion. In order to improve dispersion of nanofillers, there are at least two ways in practice. The first one is to treat the surface of nanofillers and the second one is to modify the surface of polymeric matrix [5,8]. The particle size and content in the composite determine the average interparticle distance [8,9], which is closely related to the thermal conductivity and mechanical properties. At the same particle content, smaller particle size leads to lower interparticle distance and more chances for the formation of thermal conductive „pathway“ [10,11].

Polymeric nanocomposites that possess increased stiffness and ductility with a reasonably low loading of nanofillers were reported [3]. The enhancements are normally established by a few factors, such as the inherent features of nanofillers and polymers, the interface and the interphase among the constituent components, and dispersion of nanofillers in the matrix [12,13]. Nanocomposites produced using either organic or inorganic nanofillers have been the main focus of numerous researches in current years as they generally not only dwell in the merged properties of organic polymers (e.g., elasticity, ductility, and dielectric constant) and inorganic materials (e.g., high thermal permanence, strength, hardness, and high refractive
index), but also they may obtain some particular or new properties. Besides their developed properties, another advantage of nanoscale reinforcements is recycling ability [13].

Among different types of polymers used to produce nanocomposite, polypropylene is a semicrystalline thermoplastic that is characterized by light weight, low cost, easy processing, high mechanical strength, excellent chemical stability, and electrical properties [14,15]. This polymer not only use in polymer industry but also it is a bulk market as a fibre in textile industry. The nanocomposite technique convert it to smart fiber than normal one, which has a potential application such as t-shirt like garment that looks like and feels like soft ribbed cotton knit, intimate apparel like socks, sport vest, smart fabrics and interactive textiles.

Nanocomposite based on polypropylene can be made as conductive fibers which have drawn considerable attention due to use it in smart fabric [16-20]. Conductive polymers are playing an important role as conductive fibers, which are able to sense electrical, thermal, chemical, magnetic or other stimuli from the environment and adapt or respond to them, using functionalities integrated into the textile structure. Conducting polymeric materials also have a big potential in antistatic coatings, electromagnetic shielding materials, biomaterials, neural tissue design, engineering materials, semiconductors and batteries [1,17,20].

In the field of conducting polymeric composites, one great challenge is to minimize the filler concentration because high-concentration of the conductive filler could lead to deterioration of mechanical properties, mold ability and draw ability of textile fiber of the composite. To overcome these challenges several research works were done by blending two or more immiscible polymers. A good example of the former is the incorporation of elastomeric polymer in a glassy [21–23].

This study was targeted to minimize the filler concentration with no loss of mechanical property of base matrix. But at the same time increase the thermal conductivity of the developed composite. That”s why throughout the study binary matrix system of polypropylene (PP) / poly ethylene-co-vinyl acetate (EVA) was used with a constant filling load. Moreover, only the relative particle ratio of carbon and alumina in the developed composite was vary in the constant filling load of 6 wt %. PP/EVA blend was reinforced by single particle (carbon or alumina) and binary particle (carbon: alumina).The basic background of the work, as PP/EVA combination is non polar and polar, so they create a co-continuous network in the matrix [24]. This co-continuous network helps to produce uniform dispersion and entanglement of particle in interfacial area of PP/EVA, which may leads to give better thermal conductivity with minimum filler concentration. The composite was made by melt mixing and hot press technique. After development, the conductive nanocomposites were characterized for thermal conductivity, thermal properties (DSC), tensile strength, young”s modulus, flexural strength; modulus and hardness. SEM analysis of tensile fracture surfaces of all types of composites were carried out accordingly. FTIR spectroscopy of both pure and developed composites was also performed.

This report was chronologically written from the background information to final findings of the present study. However, this chapter contains some concise information about related
research of this study and a specific target of this research. After that, next chapter contains some basic characteristics about the materials used in this study. Also the same chapter bears a broad research review related to this study. Here after the chapter carries the sampling plan and characterization technique following the materials information of this study. Then the subsequent charter explain the result found by characterization of the develop sample. Subsequently the conclusion chapter carries some concise findings from the whole study. Finally the report ends up by narrating some future work and related reference.
CHAPTER TWO
LITERATURE REVIEW
In this chapter, research works on the relevant field and outcomes have been discussed. This chapter also covers theory behind characterization, application of nanocomposites.

2.1 Composite Materials

Composite materials are made from two or more constituent materials with significantly different properties, which remain separate and distinct on a macroscopic level within the structure. Polymer composites are mixtures of polymers with inorganic or organic fillers having various geometries (fibers, flakes, spheres, particulates). They consist of two or more components and two or more phases. Figure 2.1 shows different types of composite used in aircraft industry which clearly indicate more than 60% of body material are made by composite.

Figure 2.1: Composite in aircraft [23].

They comprise of synthetic or natural inorganic and organic compounds, such as powered, fibrillar, or fabric one [25]. Firstly, powdered fillers, being finely or coarsely dispersed, may be divided into two groups: inorganic compounds, such as oxides, metals, carbonates, phosphates, sulphates, talc, clays, mica, blacks, graphite, etc, and organic compounds - polystyrene, rubber, wood particles, etc. Secondly, a rich variety of fibrillar fillers are employed, inorganic fibers, such as glass, carbon, and basalt fibers, and organic fibers - polyamide, aramid, and viscose fibers. Finally glass and textile fabrics are used as fillers [26]. Filler introduction not only yields a decrease in the polymer cost, but decreased material contraction and tendency to destruction and ageing [25].

2.2 History of Composites

The first man made composites based upon polymers appeared in about 5000 B.C. in the Middle East where pitch was used as a binder for reeds in boat-building. The three key steps leading to modern composites were,
1. The commercial availability of fiberglass filaments in 1935. The development of strong aramid, glass, and carbon fibers in the late 1960’s and early 1970’s, which are parallel to the development of resins dating back to 1968 (phenolics) and 1937 (epoxies),

2. The promulgation of analytical methods for structures made from those fibers [25].

2.3 The Reason for Consumption of Composites

The increases in consumption of composite materials were primarily due to the need for nonconductive electrical components and noncorrosive storage containers and transfer lines, and sporting goods. Designers of structures have been quick to capitalize on the high strength-to-weight or modulus-to-weight ratios of composites. The use of composite always having enormous advantages like below:

1. Weight reduction (high strength- or stiffness-to-weight ratio)
2. Tailorable properties (strength or stiffness can be tailored to be in the load direction)
3. Redundant load paths (fiber to fiber)
4. Longer life (no corrosion)
5. Lower manufacturing costs because of lower part count
6. Inherent damping
7. Increased (or decreased) thermal or electric conductivity
8. The ease of formability

Also it has some disadvantages which can be recovered by the manufacturing process; listed below:

1. Cost of raw materials and fabrication
2. Possible weakness of transverse properties
3. Weak matrix and low toughness
4. Environmental degradation of matrix
5. Difficulty in attaching
6. Difficulty with analysis

Composites provide the designer, fabricator, equipment manufacturer, and consumer with sufficient flexibility to meet the demands presented by different environments (e.g. heat or high humidity) as well as any other special requirements. Proper design and material selection can avoid many of the disadvantages [27,28].

2.4 Basic Concepts of Composites

The combination of dissimilar materials can have unique and very advantageous properties if the materials have appropriate characteristics, and result in a material that is better in certain key properties than either of the materials alone. The reinforcements and the matrix are usually very distinct types of materials with widely different properties [28].

It is probably true to say that all polymers contain some form of additives ranging from small fractions of catalyst residue to large-scale incorporation of mineral filler. The most important
additives are these introduced for some specific purpose and would therefore include fillers, plasticisers, colorants, reinforcing fibers, blowing agents, stabilizers, flame retardants, processing aids, and final group of miscellaneous additives. Because of low specific gravities, the strength-to-weight and the modulus-to-weight ratios, and also fatigue strength-to-weight ratios of these materials are superior to those of metallic materials [27]. Most low-density material would be weak, but in the case of composites, the reinforcement provides the structural attributes [28].

In general, the properties of a fiber-reinforced composite depend strongly on the direction of measurement, whereas the traditional structural materials have weaker dependence.

1. **Heterogeneous nature** of composites provides mechanisms for high-energy absorption on a microscopic scale comparable to the yield process, exhibiting gradual deterioration in properties, but they do not usually fail in catastrophic manner.

2. **Coefficients of thermal expansion (CTE)** for many fiber-reinforced composites are much lower than that of metals, exhibiting a better dimensional stability over a wide temperature range.

3. **High internal damping** leads to better vibrational energy absorption within the composite material, resulting in reduced transmission of noise and vibrations to neighboring structures [28].

### 2.5 Reinforcement-Matrix Interface

The load acting on the matrix has to be transferred to the reinforcement via the interface. Thus reinforcements must be strongly bonded to the matrix. The fracture behavior is also dependent on the strength of the interface. A weak interface results in low stiffness and strength, but high resistance to fracture, whereas a strong interface produces high stiffness and strength but often a low resistance to fracture, i.e., brittle behavior. The exact role of interface may differ with the type of reinforcement. The interface can be viewed as a planar region of only a few atoms in thickness across in which there is a change in properties from those of the matrix to those of the reinforcement. Thus, the interface is usually a discontinuity in chemical nature, crystal and molecular structure, mechanical and other properties [28,29].

### 2.6 Wettability

Interfacial bonding is due to adhesion between the reinforcement and the matrix and mechanical keying. For adhesion to occur during the manufacture of a composite, the reinforcement and the matrix must be brought into intimate contact [28]. Wettability defines the extent to which a liquid will spread over a solid surface (for melting proper mixing). Covering every bump and dip of the rough surface of the reinforcement and displacing with air carries out good wettability [29].

### 2.7 Interfacial Bonding

Once the matrix has wet the reinforcement, therefore there will be contact between them and bonding will occur. For a given system more than one bonding mechanism may be operative at the same time.
2.7.1 Reaction or inter diffusion bonding

The atoms or molecules of two components of the composite may inter diffuse at the interface to give this type of bonding, Figure 2.2, considered as due to the intertwining of molecules.

![Figure 2.2: Inter diffusion bonding [23].](image)

The strength of this type of bonding depends on the distance over which the molecules have entwined the extent of the entanglement of the molecules and the number of molecules per unit area of interface [29].

2.7.2 Electrostatic bonding

Bonding occurs between the matrix and the reinforcement when one surface is positively charged and the other negatively charged, Figure 2.3, leading to an electrostatic attraction between the components of the composite depending on the difference in charge on their surfaces. Electrostatic interactions are short range and are only effective over small distances.

![Figure 2.3: Electrostatic bonding [23].](image)

2.7.3 Chemical bonding

Chemical bonding is the bond formed between chemical groups on the reinforcement surface, marked (B) in Figure 2.4 and the compatible groups (A) in the matrix. Strength depends on the type of bond and the number of bonds.

![Figure 2.4: Chemical bonding [23].](image)

2.7.4 Mechanical bonding

A mechanical interlocking or keying of two surfaces can lead to a reasonable bond. The rougher the
2.8 Basic Resin Concepts

Resins are of the general class of materials called polymers. The length of the chain determines a basic polymer property known as the molecular weight. As the chains get larger, the mechanical properties (such as tensile strength and toughness) improve. Figure 2.5, shows some basic resin which can use to develop compotes. The improvement in properties is thought to result from inter chain forces, including entanglements of chains. Therefore, the entanglement of nearby polymer chains is a key characteristic in determining the nature of polymeric materials. Both polymer molecular weight and crystallinity affect mechanical and thermal properties like another key feature of polymers; this is stiffness of the polymer chain. As a chain stiffened, both mechanical and thermal properties increase [28].

2.8.1 Thermoplastic resin properties

2.8.1.1 Chemical structures
The matrix in a particle-reinforced resin-matrix composite has several functions. It transfers the imposed loads to the particulate, so it must have a good adhesion with the reinforcing agents. It gives the shape to the part, so must be readily formable, and it must retain that shape and mechanical properties throughout the temperature range of use. In order to protect the reinforcing agents from environmental damage, the matrix should have toughness and impact resistance [28].

2.8.1.2 Mechanical properties
The discussion of mechanical properties of resins used for matrix materials in composites must consider the effect of reinforcement material. Domination of composite properties by the reinforcement is true for many properties such as tensile strength, flexural strength, and thermal properties [30].
2.8.1.3 Thermal properties

As the temperature of the composite is increased, more and more energy is imparted to the polymer, converting into molecular motion. At lower temperatures, the motion is largely vibrational which relatively unrestricted motion. When temperatures become higher, the molecules gain sufficient energy to flex and rotate and at even higher temperatures they begin to translate. Figure 2.6 shows to improve the thermal properties of composite via graphene inclusion.

![Figure 2.6: Increase Thermal conductivity by graphene inclusion.](image)

In highly crystalline polymers the crystal lattice energies are strong resulting in tightly held molecules with very little rotation and almost no translation till the imposed energy is to overcome the lattice energies. This phenomenon is called the crystalline melting point for the polymer. In totally amorphous polymers there is no crystalline structure and therefore no crystal lattice energy. The transition from solid to melt is more gradual with only small indications of the increased mobility of the molecules. The temperature at which this transition occurs is called the glass transition temperature, \( T_g \), for the polymer. The \( T_g \), crystalline melting point, \( T_m \), and the heat distortion temperature, HDT, the maximum use temperature for the polymer for continuous service, define general thermal characteristics of a given polymer to be used [30-32].

2.8.1.4 Environmental resistance

Mostly related with their structures, the high performance thermoplastics have an excellent solvent resistance (to water and organic solvents), that is better than the common thermoset matrix materials. The engineering thermoplastics are generally much more sensitive to solvent attack performing roughly the same resistance level as the common thermoset materials. Another environmental consideration namely the flame resistance of the polymers is important in composite uses. Highly aromatic polymers (including most of the high performance thermoplastics) are inherently flame retardant because of their tendency to form char [28].
2.9 Polymer Matrix Composites

The major classes of structural composites exist today are defined by the types of their matrices, namely polymer, metal, ceramic, carbon-carbon, intermetallic matrix composites. Polymer matrix composites are the most developed class of composite materials, fabricated into large, complex shapes, and have been accepted in a variety of aerospace and commercial applications [27].

2.10 Polypropylene (PP)

Polypropylene (PP) is one of the most widely used commercial polyolefins. All polyolefins provide an excellent combination of mechanical and chemical properties, low cost, superior processability, and recyclability. PP is a thermoplastic material that is produced by polymerizing propylene molecules, which are the monomer units, into very long polymer molecules or chains [33]. PP is saturated hydrocarbon polymer, containing only carbon and hydrogen atoms. There is a number of different ways to link the monomers together, but PP as a commercially used material in its most widely used form is made with catalysts that produce crystallizable polymer chains. PP can be isotactic, syndiotactic, or atactic, depending on the orientation of the pendant methyl groups attached to alternate carbon atoms. In isotactic PP (the main commercial form), pendant methyl groups are all in the same configuration. Isotactic PP has a high degree of crystallinity [32,33]. In syndiotactic PP, alternate pendant methyl groups have opposite configurations relative to the polymer chain. Syndiotactic PP is produced commercially using metallocene catalysts. In atactic PP, pendant methyl groups have a random orientation with respect to the polymer backbone [34]. Amounts of isotactic, atactic, and syndiotactic segments in a formulation are determined by the catalyst used and the polymerization conditions. Most polymers are predominantly isotactic, with small amounts of atactic polymer.

2.10.1 Crystal structure of PP

PP is a semi-crystalline polymer; varying degrees of crystallinity are possible, depending on the stereochemical structure, the processing or crystallization conditions, and the presence of additives. Crystallinity arises from the stereo regularity in the molecular structure; occasional irregularities such as branching or tail to tail addition during polymerization or the presence of copolymers limit the extent of crystallization [33]. Atactic PP, is predominantly amorphous. Semi-crystalline polymers have high strength, stiffness, density and sharp melting temperatures. Amorphous polymers are tough and ductile, with higher impact strength, lower density, and lower haze. Properties of PP can be adjusted, depending on processing conditions and catalysts, by varying the level of crystallinity [33-36]. Polymer crystallization occurs when melted material solidifies or when a solvent is evaporated. As heat is removed from the melt during processing, molecules begin to lose the ability to move freely, and the melt becomes more viscous. At the crystallization temperature, molecules begin to arrange themselves into crystals, and ordered crystalline regions are formed, along with disordered amorphous regions. Crystal growth may be spontaneous (when the molecular structure is favorable to a highly ordered structure) or may be induced by the presence of a foreign
particle (such as a nucleating agent). The crystallization rate is dependent on the nucleation rate and the rate of crystal growth; as the melt becomes cooler, the nucleation rate increases, while the rate of crystal growth passes through an optimum temperature. Crystallization is generally favored by slower cooling from the melt, and the degree of crystallization can be controlled by the rate of melt quenching and subsequent annealing. Very rapid cooling can suppress crystallization [36].

2.11 Polymorphism

PP can exist in different morphological forms, depending on the tacticity and the crystallization conditions, such as pressure, temperature, and cooling rate. Different forms can coexist and one polymorphic form can change into another as conditions change.

2.11.1 Alpha form of isotactic PP

Polymer chains in the alpha form of isotactic PP form a helical structure in a monoclinic unit cell, with dimensions of 20.8x6.6x6.5 Å and fold into lamellae with thickness of 50 to 200 Å. Radial growth of lamellae is dominant; however, lamella can associate tangentially, with the tangential lamella branching approximately orthogonally from the position place of the radial lamellae. This forms a cross-hatched structure in the lamellae that aggregate to form spherulites [36]. The lamellar structure produces positive, negative and mixed birefringence. Negative birefringence results from spherulites in which radial lamellae are dominant, while positive birefringence is due to spherulites with predominantly tangential lamellae. Both negatively and positively birefringent spherulites form a maltese cross pattern under cross polarizers. The alpha form of isotactic PP is the primary form of PP obtained under normal processing conditions.

2.11.2 Beta form of isotactic PP

Beta form of isotactic PP has a hexagonal unit cell structure, with more disorder than the alpha form. The parallel, stacked lamellae do not show cross-hatching. Lamella have been observed to form sheaf-like spherulitic structures with interconnected boundaries, different from the distinct boundaries of alpha form spherulites, in experiments with high purity beta form PP, this structure resulted in lower elastic moduli and yield strength at a given strain rate and higher impact strength and breaking strain values than alpha form PP. PP can crystallize in the beta form at relatively low isothermal crystallization or in the presence of nucleating agents, such as pimelic acid and calcium stearates [37].

2.11.3 Gamma form of isotactic PP

The gamma form of isotactic PP was initially considered to have a triclinic unit cell with dimensions similar to the alpha form, but the crystal structure was recently reassigned as an orthorhombic unit cell with non-parallel, crossed lamellae. In experiments with PP crystallized at high pressures and different crystallization temperatures, the crossed lamellae formed a feather-like structure. Gamma form PP does not usually form under typical
processing conditions. It can occur in low molecular weight materials during crystallization at elevated pressures, or in chains with regular defects, produced using metallocene catalysts. The alpha form is present at atmospheric pressure, as the pressure is increased; the gamma form begins to coexist with the alpha form until it becomes dominant at a pressure of 200 MPa [37].

2.11.4 Effect of morphology on characteristics of PP

2.11.4.1 Melting temperature
The crystalline structure of a solid semi-crystalline polymer disappears at the melting temperature, $T_m$, when the material undergoes a phase change from solid to liquid. At the melting temperature, physical properties of the material, such as density, refractive index, heat capacity, and transparency change abruptly as the material becomes a viscous liquid [26, 33, 34, 36]. The melting temperature of a polymer varies with the amount of crystallinity. Perfectly isotactic PP resin has a melting temperature of about 171 °C, melting temperature of commercial isotactic resins can range from 160 -166 °C due to atactic material and non-crystalline regions [37]. Melting temperature decreases dramatically with lower crystallinity. Syndiotactic PP resin with a crystallinity of 30 % melts at approximately 130 °C.

2.11.4.2 Amorphous phase of PP
Amorphous (Figure 2.7), regions of the PP resin undergo a glass transition at a temperature between -35 and 26 °C, depending on the measurement method, heating rate, thermal history, and microstructure. The glass transition temperature is related to the amount of free volume in a polymer. Molecules and segments of polymer chains above the glass transition temperature vibrate and move in non-crystalline polymer regions.

![Schematic illustration of chains organization in PP spherulites](image_url)

Figure 2.7: Schematic illustration of chains organization in PP spherulites [36].
At the glass transition temperature, free volume is restricted and only low amplitude vibrations can occur. This movement continues down to absolute zero, temperature where all movement ceases. Resins with lower molecular weight generally have lower glass transition temperatures due to increased free volume at the ends of the polymer chain and lower degrees of chain entanglement. Normal used temperatures of PP are generally between the glass transition and melting temperatures, so that strength and stiffness from the crystalline region are combined with toughness of the amorphous tie regions. The low temperature brittleness of PP is due to its relative high glass transition temperature; as the temperature drops, approaching the glass transition temperature, the resin becomes increasingly brittle, and impact resistance becomes negligible [34,37].

2.12 Properties of PP

2.12.1 Mechanical properties

Mechanical properties of PP are strongly dependent on its crystallinity. Increasing crystallinity increases stiffness, yield stress, and flexural strength but decreases toughness and impact strength. The flexural modulus at 1% displacement of PP with ultra-high crystallinity is comparatively more than the general purpose PP of lower crystallinity. In experiments with alpha form, for isotactic PP, increasing crystallinity increased the growth of cracks and decreased fracture toughness [33,38,39]. Spherulite size affects the strength and ductility of the polymer matrix. In studies of fatigue strength, different crystallization temperatures were used to produce spherulites of different sizes; higher crystallization temperatures produced large diameter spherulites. In fatigue fracture tests investigating the effects of a sharp initial crack, PP with smaller spherulites exhibited more ductile behavior, with more damage ahead of the crack tip and crazing in the surrounding region. Larger spherulite sizes resulted in more brittle behavior, with less material damage. Slow crack growth changed to unstable crack growth at a critical crack length, this length decreased as spherulite size increased [39]. It was proposed that the brittleness was due to the higher crystallization temperature of nucleated PP. Higher crystallization temperatures increase the lamellar thickness and decrease tie-molecule concentrations of amorphous regions; since tie molecules provide mechanical continuity between spherulites, lower tie molecule concentrations would make the amorphous regions of the polymer more susceptible to crack propagation. Semi-crystalline polymers have high strength and have more chemical resistance than amorphous polymers, due to the ordered crystal structure. Semi-crystalline materials are more opaque and can be used at higher temperatures, while amorphous materials are generally more transparent and have greater toughness and ductility. The alpha phase crystallites are usually the predominant part in neat PP, whereas the beta and gamma phase crystallites may develop substantially under some special circumstances, such as with beta phase nucleating agents or under high pressure. The toughness of beta phase PP is higher than that of the alpha phase PP at temperatures both below and above glass transition temperature [32,34,39]
2.12.2 Transparency

Transparency in semi-crystalline polymers is directly related to the crystallinity. Spherulites are much larger than the wavelength of visible light, and the refractive index of crystalline regions is higher than that of amorphous regions. As light rays pass from amorphous to crystalline regions, they encounter the larger spherulites, resulting in light scattering; as a result transparency is lower, and haze is produced. Amorphous materials have lower levels of haze than semi-crystalline materials, and a decrease in crystallinity in a semi-crystalline polymer enhances the clarity. Excessive reductions in crystallinity can result in unacceptable reductions in strength, stiffness, and resistance to softening, so a compromise must be reached that is appropriate for the application [40].

2.12.3 Gas permeability

Polymer chains are arranged randomly in no preferred direction, if the polymer crystallizes in the absence of external forces [33,40]. If the polymer is subjected to external stress immediately after crystallization, the polymer chains align in the direction of external stress. Alignment of polymer chains in oriented materials makes formation of a crystalline structure easier, resulting in increased crystallinity. Stiffness and strength increases when the applied stress is in the orientation direction and decreases compared with unoriented material when the applied stress is perpendicular to the orientation direction [16]. Increased strength results from the covalent bonds between the carbon atoms within the PP chain, and orientation of PP chains. Crystallization can be considered to be associated with the formation of thick lamellas with a high concentration of intralamellar imperfections. The presence of intralamellar defects or voids within the lamellar boundaries will lead to increased permeability. Crystallization can be considered to be associated with the formation of thick lamellas with a high concentration of intralamellar imperfections. Permeability is reduced dramatically due to increased crystallinity; molecules cannot easily diffuse through the crystalline matrix. Permeability to moisture is decreased

2.12.4 Rheology

Rheology is the science of deformation and flow of matter [40]. The rheological properties of PP are important because of the broad range of processing techniques to which PP is subjected, including fiber and film extrusion, thermoforming, and injection molding. The viscosity of PP is most important in the melt state because it relates to how easily it can be extruded or injection molded [32, 39, 40]. The viscosity of PP is related to its molecular weight, and a good estimation of it at low shear rates can be obtained from the melt flow index test. The strain rate dependence of melt viscosity in PP is related to its molecular weight distribution, which is commonly described by the ratio of $M_w$ to $M_n$. As molecular weight distribution of PP broadens, it becomes more shear thinning (less viscous) than a narrower molecular weight distribution PP at the same strain rate [25, 40].
2.13 Ethylene-Vinyl Acetate (EVA)

Ethylene–vinyl acetate copolymers (EVA) are elastomeric materials, and as the ethylene/vinyl acetate ratio varies from 100/0 to 0/100, the polarity covers a broad range from low to high values. Using such a system as models, we can probe the influence of polarity on the behaviour of the blends [41]. EVA is produced by copolymerization of ethylene and vinyl acetate (VA), Figure 2.9 show the basic structure of EVA.

![Figure 2.9: Scheme chemical structure of monomers and EVA copolymer [40].](image)

With increasing proportion of the polar co-monomer VA, the products change from modified PE to rubber-like products. EVA is mainly recognized for its flexibility and toughness (even at low temperatures), adhesion characteristics and stress-cracking resistance. Compared to LDPE, EVA is more polar and less crystalline due to the acetate groups. With increasing VA content, EVA copolymer becomes softer due to the decreased crystallinity. Up to a VA content of 10 wt.%, the density decreases and the crystalline structure is not destroyed. While higher densities usually mean higher stiffness and a higher glass transition temperature, the opposite is true in the case of EVA copolymers. Transparency increases with increasing VA content, the product becomes rubber elastic and the ultimate tensile strength passes through a maximum. Products with up to 10 wt % VA are more transparent, flexible and tougher than LDPE. The high resistance to ESC is especially useful for cable isolation. Between 15 and 30 wt % VA the products are comparable with plasticized PVC. They are very soft and flexible. Compounds with 30 to 40 wt % VA are soft, elastic and highly fillable. Strength and adhesion are the desirable properties for coatings and adhesives. Between 40 and 50 wt.-% of VA rubber-like properties predominate and these products can be cross-linked as cable insulation by either peroxide or radiation [42]. Copolymers with 70 to 95 wt % VA are used for manufacturing of emulsion paints, adhesives and film coatings. EVA is resistant to dilute mineral acids, alkaline substances, alcohols, fats, oils and detergents but not to concentrated mineral acids, ketones, and aromatic or chlorinated hydrocarbons. The resistance to ESC increases with increasing VA content and decreasing melt index. It is significantly higher for EVA copolymers than for comparable LDPE [43].
2.13.1 Crystal structure of EVA

When two or more different monomers unite together to polymerize, the product is called a copolymer and the process is called copolymerization. These possibilities give rise to a number of copolymer classes including (i) random copolymers possessing an arbitrary heterosequence, (ii) alternating copolymers with strictly alternating repeating units, (iii) block copolymers consisting of two or more segments of pure homosequences, and (iv) graft copolymers in which polymeric side chains of one repeating unit are grafted to a strand of another repeating unit, among others block copolymer, and grafted copolymer (Figure 2.10, from left to right) [23,39,40].

![Different copolymer architectures: random copolymer, alternating copolymer, block, graft copolymer (from left to right) [40].](image)

2.13.2 EVA copolymers

Basically three structural attributes of EVA copolymers largely determine the properties of any particular copolymer grade:

2.13.2.1 Weight % vinyl acetate
2.13.2.2 Molecular weight and distribution
2.13.2.3 Molecular branching

2.13.2.1 Weight % vinyl acetate
Vinyl acetate content has two fundamental effects that influence the properties of EVA copolymers. The first effect is to disrupt the crystalline regions formed by the polyethylene segments of the copolymer. Low and medium density polyethylene, produced by the high pressure bulk process typically exhibit degrees of crystallinity in the range of 40-65% which is progressively reduced by increasing VA content until, at some point between 40 and 50 wt% VA, the material becomes completely amorphous. The ability to vary the degree of crystallinity of semi-crystalline EVA copolymers has been of supreme importance in triggering properties for particular end uses and is largely responsible for the unparalleled versatility of these products [43-45]. The second overriding effect of vinyl acetate content results from the polar nature of the acetoxy side chain. Thus, as the vinyl acetate content increases, so does the polarity of the copolymer. Although perhaps less dramatic and obvious than the reduction in crystallinity, this increase in polarity also gives rise to a number of interesting and important properties that are again, in part, responsible for the wide diversity of applications for EVA copolymers [44].
2.13.2.2 Molecular weight and distribution
Apart from molecular weight effect on the viscosity of EVA copolymers, molecular weight also has a major influence on other properties, although, again, it should be appreciated that the effect is invariably modified by the influence of other structural features. The most important properties affected by increasing molecular weight and the sense in which the properties change are illustrated in Table 2.1 [41,43].

Table 2.1: Changes in physical properties of EVA as a function of increasing molecular weight

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>Increases</td>
</tr>
<tr>
<td>Softening point</td>
<td>Increases</td>
</tr>
<tr>
<td>Impact strength</td>
<td>Increases</td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>Increases</td>
</tr>
<tr>
<td>Stiffness modulus</td>
<td>Increases</td>
</tr>
<tr>
<td>Solubility (converse of chemical resistance)</td>
<td>Decreases</td>
</tr>
<tr>
<td>Processability (converse of viscosity)</td>
<td>Worsens</td>
</tr>
</tbody>
</table>

2.13.2.3 Molecular branching
In EVA, short chain branches with less than six carbon atoms are differentiated from “long chain” branches with six carbon atoms that become part of the crystalline network. The primary effect of short chain branches is to disrupt the crystallinity of the polyethylene (PE) segments. Thus the effect of short chain branches on EVA copolymer properties is similar to wt% VA but to a much lesser extent is due to the relatively low number of short branches [43,44]. The primary influence of long chain branches, formed by chain transfer by a growing polymer radical, is to increase the melt elasticity of the EVA copolymer. As mentioned in the previous section on MWD effects, the long chain branches tend to entangle and increase the elastic response of the melt [44].

2.13.3 Influence of the polarity of EVA
The polarity of the dispersed phase (ie; EVA), has a significant effect on the mechanical properties of the blends. Both mechanical and rheological studies reveal that the uncompatibilised PS/EVA blends exhibit some degree of compatibility when the amount of EVA is lower than 30 wt% with high VA content. It can be say EVA with the highest VA content is the most effective impact modifier for PS. Some study reveal that increasing the VA content in EVA increases the polarity of the dispersed phase, approaching that of the matrix (ie; PS) and subsequently improving the compatibility between the two phases in terms of interfacial adhesion [41,42]. The influence of vinyl acetate (VA) content on the compatibility of polystyrene (LS) and EVA blends was studied by many researcher LS/EVA blends containing 0–11 wt% of VA by compression molding, to evaluate the effect of
increasing VA content and polarity in the EVA on the molecular miscibility and/or practical compatibility in the poly blends. Observation found that from the solubility parameter index, differential scanning calorimetry (DSC), ultimate tensile strength and ultimate elongation that the blends are immiscible and incompatible. Modulus, impact strength and leathery transition temperature gave indications of partial miscibility and compatibility, and these improved with increasing VA content in the EVA. Moreover, influence of the graft copolymer on the mechanical properties of LS/EVA blends with higher VA content (18 wt%) is more significant when compared with the blends with lower VA content (10 wt%) [41-45].

2.14 Properties of EVA

2.14.1 Physical properties

EVA copolymers vary in their appearance in thick sections from a somewhat opaque plastic resembling LDPE at 5 wt% VA to a crystal clear, somewhat tacky, rubbery material at higher VA contents. Even at low VA contents the copolymer surface is relatively soft and can be abraded by a fingernail. Although the low VA content materials are opaque in thick sections, in thin film form they can be completely transparent, showing higher clarity than similar films produced from LDPE. This is due to their lower degree of crystallinity. Unlike polyethylenes, the degree of crystallinity is not used to predict density [44]. The density of EVA copolymers is more closely correlated with VA content. The surface hardness of EVA copolymers is related to both molecular weight and the degree of crystallinity. All EVA copolymers can be described as tough, comparatively low modulus materials. Stiffness, or flexural modulus, is mainly determined by crystallinity (i.e. wt% VA) and to a lesser extent by chain branching. In all but exceptional circumstances EVA copolymers give satisfactory service down to -40°C. The flow of EVA copolymers, as with most thermoplastics, is non-Newtonian in character, i.e. viscosity reduces as shear increases [44-46].

2.14.2 Chemical properties

The principal effect of increasing VA content in EVA copolymers is to increase the polarity of the molecules. This allows better incorporation of inorganic fillers or fillers such as carbon black with active surfaces, gives. Due to their more polar nature, EVA copolymers are more permeable to gases and moisture vapor than LDPE. EVA copolymers are less thermally stable than LDPE. Degradation occurs primarily by two mechanisms: oxidation and elimination of acetic acid. Oxidation can be minimized by use of antioxidants, but the elimination of acetic acid cannot be prevented. Fortunately, this problem is minimal at processing temperatures up to 210°C, which is higher than most processors require. UV light causes photo-oxidation of EVA copolymers. This can be minimized by incorporating 2-3% carbon black or other UV stabilizers. As well, EVA crosslinks more easily than LDPE when peroxides are used as free radical sources [43].
2.14.3 Electrical properties

EVA copolymers do not share the excellent dielectric properties of polyethylenes due to the polarity of the vinyl acetate group it has some extent conductivity. This means that EVA is not suitable for use in, for example, telephone or television cable insulation applications where high frequencies are encountered. On the other hand, this does enable the use of radio frequency sealing techniques to be used with films made from EVA copolymers containing more than about 15 wt% VA. In addition, the dielectric strength and volume resistivity of EVA are such that they can be used in low to medium voltage, low frequency applications. EVA'S polar nature allows incorporation of high levels of filler both conductive and non conductive [43-46].

2.15 Concept of Binary Matrix Composite

The properties of polymers can be enhanced by mixing two or more different polymers together to form blends .However, only a small number of combinations of polymers result inmiscible blends, the majority tend to phase separate, modifying the mechanical properties. Some polymer blends can result in enhanced mechanical properties whilst others can reveal poor mechanical properties due to lack of interaction at the interface of the two or more polymers [47]. This is more likely to occur when mixing polar and non polar polymers, for example, as in the case of polyethylene/ethylene vinyl acetate blends. Other factors that can influence the phase separation at macroscopic level are: molecular weight, melting temperature, melting time and annealing temperature. Nevertheless, phase separation can still occur even in polymers that have similar physiochemical properties. It's far widely recognized that EVA has been used within the modification of rigid polymer for higher flexibility, toughness, and resistance to environmental stress cracking. The modifying effect of the EVA copolymer on the mechanical properties of LDPE was studied recently (EVA) have found that the modification of LDPE with EVA copolymer results in an enhancement of the material toughness due to the increase of the adhesive strength at the matrix-rubber particle interface. Increasing the carbon black filler content in the LDPE matrix was leads to an increase in the mechanical strength and a decrease in the elongation at break. The brittleness of the carbon black filled LDPE can be balanced by adding flexible components such as EVA. Specified research at the relation between morphology of LDPE/EVA blends and their mechanical properties, dynamic mechanical properties and electric resistance have been suggested. Ray and Khastgir have found that an interpenetrating polymer network like structure was formed in LDPE/EVA blends with a minimum of 50 wt% EVA in the blend. The tensile strength and elongation at break of different binary matrix system improve with an increase in EVA content up to 50 wt%, after which the change is marginal. Figure 2.11 describe the chronological development of composite having different fraction ratio A/B of components the morphology of polymer blend changes from the insulated inclusions of polymer B within polymer A (at low content of polymer B) to the co-continuous structure at equal content of the phases and further to the inclusions of polymer A within polymer B (at low content of polymer A) [47-49].
Fillers, with a very high aspect ratio, strongly modify the macroscopic properties of the polymer even when a small amount of filler is used. So nanocomposites usually have improved properties compared to neat polymers, such as better mechanical properties and higher thermal stability [49]. Typical examples of conductive components used to prepare this type of conducting polymer include conducting solids (carbon-black, carbon fibers, aluminum flake, stainless steel fibers, metal-coated fillers, metal particles, etc.) and conjugated conducting polymers. Because the conductivity is introduced through the addition of the conducting components, various polymer materials including both amorphous polymers (polystyrene, PVC, PMMA, polycarbonate, acrylonitrile butadiene styrene (ABS), polyethersulphone, polyetherimides, etc.) and crystalline polymers (polyethylene, polypropylene, polyphenylene sulphide,nylons, etc.) can be made electrically conducting [49,50].

2.17 Functions of Fillers / Reinforcements

Polymer needs some modifications in its structure or physical properties to obtain a superior range of functions. One modification technique is adding fillers to a polymer to generate a composite with improved properties, such as enhancement in mechanical strength, electrical conductivity, or thermal stability. The utilization of nanoscale fillers in particular has led to a significant improvement in the properties of the polymer [25,51-52]. The nanoscale fillers are used as reinforcement materials for nanocomposites containing nanoparticles, nanofibers, nanoplatelets, nanoclays, and so forth. However, strong chemical bonding between the nanofillers and the polymeric matrix is compulsory in order to produce a nanocomposite with excellent mechanical properties [52]. Also Filler are considered as additives, since, due to their unfavorable geometrical features, surface area or surface chemical composition, could only moderately increase the modulus of the polymer, while strength (tensile, flexural) remained unchanged or even decreased [50,52]. Their major contribution is in lowering the cost of materials by replacing the more expensive polymer. Other economic advantages are faster molding and processing cycles as a result of increased thermal conductivity and draw.
ability. Reinforcing fillers are characterized by relatively high aspect ratio, \( \alpha \), defined as the ratio of length to diameter for a fiber, or the ratio of diameter to thickness for platelets and flakes. For spheres the aspect ratio is unity, and they have minimal reinforcing capability. A useful parameter for characterizing the effectiveness of a filler is the ratio of its surface area, \( A \) to volume, \( V \), which needs to be high for effective reinforcement [25, 50-53]. In developing novel fillers, the aim of material modifications is to increase the aspect ratio of the particles and to improve their compatibility and interfacial adhesion with the chemically dissimilar polymer matrix. Such modifications may enhance and optimize not only the primary function of the filler, but may enhance additional functions such as thermal conductivity, electrical conductivity, sensor performance etc. The first generation of fillers soon after the commercialization of PP included talc platelets and asbestos fibers for their beneficial effects on stiffness and heat resistance [52, 53]. Other fillers imparted entirely different functions. For example, barium sulfate enhances sound absorption, wollastonite enhances scratch resistance, solid glass spheres add dimensional stability and increase hardness, hollow glass spheres lower density, and combinations of glass fibers with particulate fillers provide unique properties that cannot be attained with single fillers.

2.18 Characteristics of Conventional Fillers

Polymeric materials prepared in combination with organic and inorganic compounds at a nanoscale [25,54] have additional advantages, such as the possibility of obtaining a new material that has the advantages of both organic materials (e.g., light weight, flexibility, and good mold ability) and inorganic materials (e.g., high strength, heat stability, and chemical resistance) [55]. It is known that the composite properties can also change with the dispersion state, geometric shape, and surface quality of the filler particles as well as the particle size [55]. Nanoscale fillers differ from bulk materials and conventional micron-size fillers because of their small size and corresponding increase in surface area. It is expected that the addition of nanoparticles into polymers [50-55] will lead to an unprecedented ability to control the electrical properties of filled polymers. However, the effect of filler on resin properties is dependent on the aspect ratio and size of the particle, the particle size distribution of the filler, filler surface treatment, the dispersion of filler in the polymer [55]. Some reinforcing fillers function by forming chemical bonds with polymer. Other produce enhancements in mechanical properties by occupying volume are that they bind to nearby polymer chains, decreasing the chain mobility and increasing polymer orientation at the filler surface. The increased orientation results in increased stiffness, lower deformability, and increased strength. Reduced mobility results in higher glass transition temperatures in filled polymers, intensifying the inherent brittleness in PP at temperatures below 0 °C, as a result, and many reinforced PP are based on copolymers. High levels of reinforcement can be obtained from fibers due to their high aspect ratio, and the plate-like particles like talc or mica provide more reinforcement than the more spherical carbon black, activated charcoal, alumina, particles. The larger surface areas of smaller particles provide better adhesion to the polymer, and the amounts of coarse and fine particles influence particle packing during compounding and the optical properties of the resin [50,54,55]. The size, shape, and type of filler affect dispersion, in addition to interactions between polymer and filler, filler to filler and processing
parameters. Moreover Filler oriented distribution depends upon the immiscible and miscible blend of polymer matrix by polar and non polar matrix.

2.19 Conductive Filler

2.19.1 Carbon filler

2.19.1.1 Carbon black
Particulate fillers of which carbon black is a notable example are widely used as reinforcing in polymer industries for advanced application in some study. Carbon blacks are produced from the agricultural and forestry waste materials but over the last century those carbon black were obtained from thermal cracking of natural gas, furnace black which is produced by incomplete combustion of oil feed stocks. The production of carbon black is relatively very expensive; therefore researchers found the alternative source i.e. renewable resources such as agricultural waste from which carbon black can be prepared. According to their investigation carbon black can be prepared by the pyrolysis of coal, wood, coconut shell, oil palm shell and other lingo cellulosic materials because they are carbonaceous in nature and reach in organic materials. This biomass can be converted into carbon black thereby reducing unwanted, low-value agricultural residues and underutilized crop into useful, high-value materials in another study. Carbon black is widely used for adsorption of pollutants from gaseous and liquid streams, for recovery of solvents, due to their high adsorptive capacities, porous size and relatively high mechanical strength. It is also used for coating, ink and inkjet application. Carbon materials provide excellent properties for a large spectrum of industrial applications by a researcher. From carbon we obtain the strongest fibers (carbon fibers), one of the best solid lubricants (graphite), one of the best electrically conducting materials (graphite electrodes), the best structural material for high temperature tribological application (carbon–carbon composites). Among the various bio fibers wood apple shell is also a carbonaceous fiber. Still there is no work has been so far done on the chemical modification and analysis of wear behavior of polymer composite incorporating wood apple shell particulates. Some researchers used wood apple shell particulates as an absorbent for the removal of iron or Congo red dye from waste water using wood apple shell carbon [55-57].

2.19.1.2 Graphite
Graphite is a carbonaceous material available commercially at relatively low cost. Its structure consists of carbon layers in an alternating stacked sequence and bonded by weak Vander Waals forces. Expanded graphite (EG) [57] is a layered material as montmorillonite, produced when bulk graphite is exposed to strong oxidizers such as sulphuric acid, nitric acid, or potassium permanganate. Graphene is a sheet of graphite and a two dimensional material which composed of several planar sheets with sp2 bonded carbon atom. The flat carbon sheets of EG has generated huge activity in many areas of science and technology due to its unprecedented physical and chemical properties. In contrast to pristine graphite, the EG sheets are heavily oxygenated bearing hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges. The presence of these functional groups makes EG strongly hydrophilic, which allows graphite oxide to readily swell and disperse in water. The enhanced process ability of EG allows it to be
incorporated into polymer matrices and the scalability. And low cost of this process makes it attractive for industrial applications [57-59].

2.19.1.3 Carbon fibers
Carbon fibers are fine filaments composed of elemental carbon. Structure can vary from amorphous carbon to crystalline graphite, providing a wide range of physical properties. Density ranges from 1.6 to 1.9 g/cm$^3$ [40] Carbon fiber reinforced PP at 10 - 40 % loadings exhibit improved flexural modulus, flexural strength, and retention of mechanical properties in humid environments and greater creep and wear resistance compared with glass fibers [60]. They are more expensive than glass fibers; as a result, their use in PP is generally restricted to applications that require electromagnetic interference and radio frequency interference shielding capabilities [40, 60].

2.19.2 Alumina
Alumina (Al$_2$O$_3$) is commonly used as filler to improve electrical, mechanical and thermal properties ($\lambda \sim 20-30$ W/m·K at room temperature) in insulating composites. Al$_2$O$_3$ has a low thermal expansion, it is resistant to most chemicals, and it is a good electrical insulator with high wear resistance [61]. Aluminum oxide in the form of micro- and nano-filler was studied by many research groups and results of experiments have been presented in many papers. Al$_2$O$_3$ was therefore chosen for comparison and to have a proof-of-concept to build on. [53,61]

2.19.3 Nano clay minerals
The clay minerals are classified as phyllosilicates or layered silicates which contain two structures; 1:1 and 2:1 phyllosilicates [25-29]. The 1:1 phyllosilicates refer to the bonding between one tetrahedral sheet and one octahedral sheet [28]. In contrast, the 2:1 phyllosilicates refer to the layer bonding of two tetrahedral sheets and one octahedral sheet, the octahedral sheet being built-up between two tetrahedral sheets [30]. In PCNs, the 2:1 phyllosilicates structure is the most commonly used clay, especially montmorillonite (MMT). MMT has a 2:1 phyllosilicate structure which exists as a regular stack of layered silicates [37,38]. In addition, MMT exhibits high aspect ratios from 10 to 1,000, a thickness of about 1 nm and the specific surface area of about 750-800 m$^2$/g . The chemical formula of MMT expressed as Mx (Al$_{4-x}$Mg$_x$) Si$_{8}$O$_{20}$(OH)$_4$; M and x represent exchangeable action and the layer charge . The MMT structure consists of two outer tetrahedral sheets (silicate tetrahedral (SiO$_4$)/ central ion: Si$^4+$) and one inner octahedral sheet (aluminum hydroxide or magnesium hydroxide) [29]. The structure of MMT is illustrated in Figure 2.12.
2.20 Micro Composite

A microcomposite consists of a polymer matrix and microsized particles with typical size between 1 and 100 μm. In the case of high filler concentrations (larger than 30 vol. %), composites exhibit much higher thermal conductivity compared to neat polymers. In this case, two important parameters can be claimed that play a major role in determining the thermal conductivity of microcomposites, (i.e. the thermal conductivity of fillers and interaction between them). Fillers of micron size are added to PP in order to reduce costs and enhance mechanical properties. Extenders are inexpensive fillers that are added primarily to increase bulk density, reducing the amount of the more expensive polymer required for the application, although they can increase stiffness and heat resistance. Reinforcing fillers provide a substantial improvement in the mechanical properties, such as tensile strength, heat distortion temperature, and modulus of elasticity. Fillers and reinforcements commonly used in PP are calcium carbonate, talc, mica, glass spheres, and carbon and glass fibers [29, 62, 63]. Maximum concentrations are usually 50 % although higher loadings are used [63].

2.21 Nanotechnology

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers [1,3,25,27]. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term
nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, that modern nanotechnology began (web). For example, the swords that were made from Damascus steel were very flexible (Figure 2.13), sharp and stiff. Many centuries later it was discovered that ancient Muslim smiths were inadvertently using carbon nanotubes within the metallic matrix of the blade in the 17th century [25-27, 40].

![Figure 2.13: Illustration of the change of a physical property as a function of particle size [64].](image)

### 2.22 Emergence of Nanocomposites

Nanotechnology is now an important interdisciplinary thread in fundamental research. Nanoscience is still in a nascent stage but its impact on the world economy can already be seen since significant potential clearly exists [25,30]. For the field of electrical power engineering, one of the promising materials that were born by nanotechnology is the nanocomposite (NC). Since 1984 when the term „nanocomposite” was mentioned for the first time [24,25], it has been generally accepted by the scientific community. A nanocomposite may be defined as a composite system that consists of a polymer matrix and homogeneously dispersed filler particles having at least one dimension below 100 nm. Polymers are the most common materials (thermoplastics, thermosets or elastomers) that are used for nanocomposite manufacture. Over the past decades, polymer nanocomposites have involved considerable interest in both academia and industry [24,62-64]. The outstanding properties of NC are attributed to the large surface area to volume ratio of the nanoadditives [62,65]. The size reduction of particles allows tailoring of the physical properties of composites. Every property has a critical length scale, and if a nanoscale item is made smaller than the critical length scale, the fundamental physics of that property change drastically (Figure 2.13). Smaller particles display a much larger surface area for interaction with the polymer for the same microscopic volume fraction than larger particles [5, 8, 65,66]. It is currently thought the reason for such dramatical change of the characteristics of nanocomposites due to the interactions that occur at nanoparticle-matrix interfaces. Figure 2.14a,b illustrates how the interface area gets more important for smaller particles.
Major effects on the macroscopic properties can be obtained already at low concentrations, because of the large interfacial area of nanoparticles (see Table 2.2) [64-66].

Table 2.2: Interaction zone of particle in respect of atom.

<table>
<thead>
<tr>
<th>Interaction zone Particle diameter, nm</th>
<th>Number of atoms in a particle</th>
<th>Fraction of surface atoms in a particle, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>250,000</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>30,000</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>4,000</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>80</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>99</td>
</tr>
</tbody>
</table>

### 2.23 Conductive Polymers Nanocomposites

The nanocomposite can be conductive when blending insulating polymers with conductive ingredients such as carbon blacks, carbon fibers, metal particles or conducting polymers such as polyaniline [49]. The transfer conditions of the electric charge and heat flow determine the electrical and thermal conductivity level in the heterogeneous polymer-filler system, in which the conductive phase is formed by dispersed metallic or carbon filler. The influence of the type of polymer matrix and filler on the electrical characteristics of the composite has been studied in many works. Although in some publications it was observed that the percolation behavior of the conductive composite depends on both filler particle shape and spatial distribution within the polymer matrix, as a rule, the equations and models used do not contain any parameters linked with the filler particle shape and conductive phase topology [49-53]. Concerning the thermal conductivity of such composites, in spite of several models for two-phase systems [51], there are only a few publications on the study of the correlation between structure and thermal properties [48-51]. As a consequence, a range of so-called conductive polymer can find their applications in many fields such as floor heating elements, electronic equipment, important strategic materials such as electromagnetic interference (EMI) shielding [51], apart from the conventional application of semi-conducting materials for dissipation of static electricity. More recently conductive composites have been used for sensing components [53]. Compared with metallic conductor, conductive polymer nanocomposites have the advantages of ease of shaping, low density, and wide range of electrical conductivities as well as corrosion resistance [48-53, 67]. However in respect of conductivity for polymer composite we can address two major conductivity.
2.24 Electrical Conductivity

A polymer matrix having a electrical conductivity \( \sigma_p \) is filled with dispersed filler having a conductivity \( \sigma_c \), the composite prepared gains a conductivity value \( \sigma \). When the filler volume fraction reaches a critical value \( \varphi_c \) (so-called percolation threshold), particle agglomerates is formed and, consequently, the composite becomes conductive \([55-59,67]\) due to continuous network. As the filler concentration increases from \( \varphi_c \) to the filling limit \( F \), the value of \( r \) increases rapidly over several orders of magnitude, from the value \( r_c \) at the percolation threshold to the maximal value \( \sigma_m \). Below the percolation threshold, the conductivity of the composite is equal to the polymer conductivity \( \sigma_p \). The typical dependence of the logarithm of conductivity on the filler volume fraction \( (\varphi_f) \) is shown in Figure 2.15.

![Figure 2.15: Correlation of structure with conductive properties of composite [47].](image)

One of the most important characteristics of the filler polymer composite is the filler packing factor \( F \) \([67]\). The value of \( F \) depends on the particle geometry and on the possibility of the skeleton or chained structure formation. The parameter \( F \) is a limit of system filling and equal to the highest possible filler volume fraction at a given type of packing:

\[
F = \frac{V_f}{V_f + V_p}
\]

Where \( V_f \) is the volume occupied by the filler particles at the highest possible filler fraction and \( V_p \) the volume occupied by the polymer. However for monodispersed spherical particles, \( F \) is equal to 0.64 where as for polydispersed filler particles it will be increase. This phenomena is related to percolation volume of conductive sites \( (\varphi_c) \) by the relation

\[
\varphi_c = X_c F
\]

Where \( X_c \) is a critical parameter which is related to percolation capability of the system for a given packing factor\( (F) \) and percolation volume\( (\varphi_c) \)[48,51,53].
We can identify two immiscible polymers, a-polymer and b-polymer (see Figure 2.15) which are to be filled with the conductive filler. Denoting the critical fraction of the conductive filler required ensuring conductivity in the a-polymer is $\phi_a$ and the critical fraction of the a-phase required to ensure connectivity in b-polymer as $\phi_b$, the critical fraction of the conductive filler in the total ternary blend is

$$\phi_c = \phi_a \phi_b$$

We can extend the approach to higher levels of percolation

$$\phi_c = \phi_a \phi_b \ldots \phi_n$$

Where $\phi_n$ is the threshold of co-continuity of the (n-1)-polymer blend in the n-polymer. A multiple percolation approach allows, at least theoretically, for the feasibility to obtain a CPC material with as low a level of conductive material as desired.

### 2.25 Thermal Conductivity

The thermal conductivity has been important since the Stone Age, when humans started looking for materials, which can keep warm for a long time or the other way around – to cool down in a short period of time. Thermal conductivity (K), along with radiation and convection is a mechanism of heat transfer. Convection is the energy transfer within liquids and gases by direct particle interaction. Radiation is the energy transfer by means of emission and absorption of energetic particles or waves. This physical constant is defined as the quantity of heat that passes through a unit cube of a material in a unit of time, when the difference in temperature between the opposite sides of the cube is 1K. The first clear statement of the proportionality between heat flow and temperature gradient was made in 1822 by Fourier. When materials are subjected to a steady-state heat flow (H), a temperature gradient ($dT/dt$) is produced in the materials along the direction of the heat flow. Both parameters are related by the equation:

$$H = K \left( \frac{dT}{dt} \right)$$

Where K is a proportionality constant with the unit W/m·K and is referred to as the thermal conductivity of a material [70].

The concept of heat conduction in dielectric solids is often discussed with the help of the Debye kinetic model.

$$K = \frac{1}{3} c \nu l$$

where C is the specific heat per unit volume, $\nu$ is the average phonon propagation speed, and l is the mean free path of a phonon. l is in the order of a few nanometers at room temperature and of a few microns at low temperatures close to absolute zero. The mean free path l decreases with increasing temperature. The specific heat can be rewritten as $C=C_p \rho$, where $C_p$ is the heat capacity and $\rho$ is the density of a material. The product of velocity and mean free path of a phonon is known as thermal diffusivity D, i.e. $D = \nu l$. Thus, the thermal conductivity is related to the thermal diffusivity as in [69].

$$K = \frac{1}{3} C_p \rho D$$

There are a few mechanisms by which heat can be transmitted through a solid. Thermal conductivity requires a transport of thermal energy. Different types of carriers like electrons,
phonons (atom vibrations) or photons can be considered for this transport. In the polymeric materials heat is conducted by phonons, the thermal vibrations of the atoms. In metals the thermal conduction is almost entirely due to electron transport. In alloys and semiconductors both transport mechanisms can make comparable contributions to the thermal conductivity [51,53].

2.25.1 Thermal conduction mechanism

Polymeric nanocomposite materials show a weak thermal conductivity. Thermal conductivities of insulating polymer materials are usually 1-3 orders lower than those of ceramics and metals. Due to the chain-like structure of polymers, the heat capacity consists of the contribution of two mechanisms: (a) lattice vibrations and (b) characteristic vibrations, which originate from internal motions of the repeating unit. The lattice (skeleton) vibrations are acoustic vibrations, which give the main contribution to the thermal conductivity at low temperatures. The characteristic vibrations of the side groups of the polymer chains are optical vibrations, which become visible at temperatures above 100 K. Another mechanism for thermal conductivity - is caused by various types of phonon propagation processes. Phonons travel at the speed of sound but during travel, there are several types of phonon scattering occur (e.g. phonon-phonon scattering, boundary scattering, scattering from static point imperfections, dislocations of atoms, stacking faults, grain boundaries [53-59]. The scattering of phonons in composite materials is mainly due to the interfacial thermal barriers, resulting from acoustic mismatch and flaws associated with the filler-matrix interface. Polymeric material must meet below criteria to be regarded as high thermal conductive:

a) Low atomic mass
b) Strong interactions or chemical bonding with polymer
c) Simple crystal structure
d) Low anharmonicity in the molecular vibrations
e) Lowering the number of thermally resistant junctions
f) Forming conducting networks by suitable packing; and
g) Minimize filler-matrix interfacial defects or voids.

To meet such criteria some scientist discovered that polymer filler composite with agglomerates of particles is more efficient in enhancing the thermal conductivity than a nanocomposite with well dispersed nanoparticles [51,53]. This is most likely due to the formation of percolated pathways or networks and to recover all above feature. The main approach to an effective improvement of the low thermal conductivity of polymers is to fill them with particles with high thermal conductivity. One must take consider about temperature, pressure, density of the polymer, orientation of chain segments, crystal structure, the degree of crystallinity and many other factors may affect the thermal conductivity of polymers [48,58-60,70].
2.26 Reasons for Interest in Conductive Nanocomposite Technology

Although several conducting polymers nanocomposite have been prepared but they do not suitable for in traditional electrical applications, like wiring, transmission cables etc. rather are applicable for very emerging field mentioned below [25,26]

2.26.1 Polymeric batteries

One of the most advance applications of conducting polymers, that was the focus of attention world-wide, was that of light-weight batteries. While a lot of the nanocomposite were tried to develop ultrathin batteries but most of them are under research to get desired properties, specifically with respect to stability of energy. Thus, the prospect of a polymeric battery is still alive and is awaiting further technological refinement. Figure 2.12 a

2.26.2 Electrochromic displays

Electrochromic display is another interesting application which utilizes the electrochemical doping and undoping of conducting polymers. The basic idea, in such devices, is to effect a significant change in the colour (both the wavelength of absorption and its intensity) upon application of an electric potential. Because of their very high absorption coefficients ($10^5 \text{ cm}^{-1}$) in the visible range of the electromagnetic spectrum, only very thin films are required to provide display devices with high contrast and a very broad viewing angle which can be possible by conductive polymer nanocomposite with high processibility [49,50,72]. Thus, by the ultimate development of nanocomposite can generate, other interesting and innovative applications, such as electrochromic windows and other applications in the automotive industry are being actively pursued. Electro-chromic windows, for instance, are windows in buildings/automobiles which can be made to go from low transmitting (during the day) to high transmitting (during the night); the switching in such systems occurs upon application of an electric potential. Figure 2.16 b

Figure 2.16: Emerging application of conductive polymer nanocomposite [23].
2.26.3 Conducting fabric

The unique electromagnetic shielding and microwave absorbing properties of such a fabric are expected to find many interesting applications. Conductive fibers provide lightweight alternatives to heavy metal wiring in a variety of settings, including aerospace, where weight is always a chief concern. This is an area where NASA is always seeking improved materials [25,58-51]. The fibers are also more cost effective than metals. In the case of electronics that are confined to small spaces and subject to severe stress, copper is prone to breaking and losing connection over time. Flexible conductive polymer nanocomposite eliminates that problem. They are more supple and stronger than brittle metal like copper and, thus, find good use in these and similar situations. Fibre produce from conductive polymer nanocomposite chips have the potential applications include power distribution lines; additional aircraft and aerospace wiring systems; automotive wiring harnesses; missile guidance wires; electro textiles for military, medical, and consumer applications; lightweight deployable antennas; thermal blankets and clothing; flexible keyboards; giant area flexible circuits for energy harvesting; electrostatic charge dissipation; and battlefield monitoring and reporting of vital signs and wound locations on soldiers[64], Figure 2.16 c.

2.26.4 Light Emitting Diodes

Other exciting phenomena, that have caught the imagination of both scientists and technologists alike, are the phenomena of photoluminescence and electroluminescence in conductive polymers. A conventional LED thermal management system is composed of a heat spreader, thermal interface material (TIM) and heat sink. Copper and aluminum alloys are typically used for heat spreader. Silicon based grease, gels; phase change materials (PCM) have been used as TIM. There are continuous needs on increasing the TC (thermal conductivity) of TIM or decreasing the thermal interfacial resistance of TIM. Some recent progress has been made on using a conductive nanocomposite for TIM application. In order to achieve higher TC, the promising approach is conductive particle or fibre filled polymer nanocomposite [48-51,64,71], Figure 2.12 d.

2.26.5 Electronic packaging

Demandable power density and miniaturization have made the thermal management one of the major challenges for the semiconductor industry. The objective of thermal management is to ensure that temperatures of all components in the system are maintained within their functional temperature range. Thus, there should be effective thermally conductive path for heat dissipation and eliminating hot spots in electronic parts. However, for that sector conductive polymer nanocomposite have an emerging need era. [51,64,65].

2.26.6 Tissue engineering

Many cell types, including neurons, osteoblasts, fibroblasts, and skeletal myoblasts (SMs), respond to electrical stimuli. The conducting polymer has been recognized as a promising
scaffold and neural prostheses because of excellent biocompatibility and ability to transfer charge from a biochemical reaction, ability to entrap and adjustably release bio-molecules (also called reversible doping), ability to easily vary its electrical and biological properties to better match the special medical applications (including neural probes, nerve drug-delivery devices) [64-69]. Compared with metals and semiconductors (e.g., gold, iridium and silicon), which have been applied in neural probes and neuro-sensors [48-49], conductive polymer (CP) have advantages over them, including inexpensiveness, easy synthesis and versatility. Furthermore, CPNC(conductive polymer nanocomposite) can adjust the level and time of electrical stimulation in neural-tissue engineering applications, and even can create substrates with higher surface area. Electrical stimulation (ES) has many noted beneficial effects, such as enhanced nerve regeneration in vivo. CPNC lend themselves as excellent novel scaffolds for a more efficient delivery of this stimulus type by which we believe they will revolutionize the world of tissue engineering [51,71-73].

### 2.26.7 Biosensors

Electroactive biomaterials are a part of a new generation of „smart“ biomaterials that allow the direct delivery of electrical, electrochemical and electromechanical stimulation to cells [71] which is a promising property to apply in a sensor. The family of electroactive biomaterials includes conductive polymers, electrets, piezoelectric and photovoltaic materials. Electrets and piezoelectric materials allow the delivery of an electrical stimulus without the need for an external power source, but the control over the stimulus is limited. Conductive polymers, on the other hand, allow excellent control of the electrical stimulus, possess very good electrical and optical properties, have a high conductivity/weight ratio and can be made biocompatible, biodegradable and porous. Furthermore, a great advantage of conductive polymers is that their chemical, electrical and physical properties can be tailored to the specific needs of their application by incorporating antibodies, enzymes and other biological moieties. In particular, CPNC biosensors may be usually involved muscle, bone, cardiac and nerve, due to excellent mechanical match between polymer and tissues [71-74].

CPNC have, thus, come a long way from purely laboratory curiosity to a class of materials that can find end use in a wide variety of commercial products, ranging from batteries to biosensors. Such a development is a classic example that serves to illustrate the wide range of expertise, starting from chemists, physicists, biologists and technologists, that is required to take some invention in the laboratory to the market place [51,71,74].

### 2.27 Formation and Structure of Conductive Particle Filled Polymer Nanocomposite

Formation of CPNC is critical due to the matching of optimum characteristics on respect of mechanical and conductivity. Thus the number of the conductive particles is insufficient to form a continuous conducting path below $\varphi_c$ Figure 2.17a, the conductive domains are insulated from each other by the polymer medium and the electrical conducting behavior could not be observed.
Figure 2.17: Schematic representation of conductive particles dispersed in a polymer matrix at different particle volume fractions: (a) $\varphi < \varphi_c$ (b) $\varphi = \varphi_c$ (c) $\varphi > \varphi_c$ [64].

In the vicinity of $\varphi_c$, the isolated conductive particles appear to contact each other forming a continuous network for transportation of electrons which is called percolation threshold. (Figure 2.17b). During formation of nanocomposite the nanostructures are oriented in such way that it formed this network in low filler load to achieve optimum properties. Immediately after the percolation threshold (Figure 2.17c), a slight increase in the concentration of conductive particles may greatly increase the bridges in the conducting network. The insulating composite is thus transformed into a conducting material in a bumping fashion. Further increase in the concentration of the conductive particles, however, may only cause the volume of the conducting domains to increase without any significant increase in the pathways for electrons resulting a monotonic increase in conductivity [48, 51, 53]. However, to design such system one may have target to create this conductive pathway in nanocomposite in programming manner. For that, conducting polymer composites of low percolation thresholds have also been developed by using a binary host of immiscible polymer blends by some researcher[48,51], Figure 2.18.

Figure 2.18: Co-continuous phase of binary nanocomposite [40].
In the binary polymer systems, the conductive particles may favorably localize at the interface of the polymer blends or within one of the polymer phases. The selective localization of the conductive particles at the interface of polymer blends is particularly interesting not only because percolation threshold in low filling load are achievable in programmable manner at the interface region between two co-continued polymer phases but also because mechanical properties of the composites may be improved by the in situ interfacial modification[48,53,56,59].

2.28 Method of Preparation of Nanocomposites

In general, there are three methods used in the preparation of polymer nanocomposite, including, in situ polymerization, solution process, and melt intercalation (Figure 2.19). All the methods are aimed to achieve single layer dispersion of the layered silicate in the polymer matrix, because a high surface area is directly associated with the enhanced properties of polymer-clay nanocomposites [27, 28, 30]. The degree of interaction between the clay and polymer matrix, which ultimately determines the morphological structure within the nanocomposite, is not only dependent on the properties of the modified clay and the polymer, but also the method by which the two components are blended.

2.28.1 In-situ polymerization technique

For in situ polymerization method, the initiator or catalyst is usually pre-fixed inside the nanoparticle, and then the nanoparticle is engorged by a monomer solution, Figure 2.20.
Polymerization occurs in the presence of this exchanged nanoparticle to form the polymer and cross link between the inserting elements [25, 2-6]. With this technique the driving force is the interaction between monomer and particle surface. It is suitable for low or non-soluble polymers. Particle distribution depends on the diffusion rate of monomers in the gallery.

2.28.2 Solution process

In solution blending, nanoparticle is dispersed in an appropriate solvent while dissolving the polymer in the same solvent [25-27]. When the solvent is evaporated (or the mixture precipitated), the nanoparticle kinetically trapping to the polymer to form a nanocomposite structure. There are two immiscible phases present, an aqueous (continuous) phase containing initiator and a non aqueous (discontinuous) phase containing the monomer or polymer. Spontaneous exchange requires a negative variation in the Gibbs free energy. The diminished entropy due to confinement of the polymer is compensated by an increase due to desorption of intercalated solvent molecules. The process is illustrated schematically in Figure 2.21.

2.28.3 Melt Compounding

A polymer and nanoparticle mixture is annealed above the $T_g$ or $T_m$ of the polymer in either static or flow conditions. The polymer chains spread from the molten mass into the nanoparticle galleries to form hybrids according to the degree of particle penetration. The decreased entropy in this case is compensated due to the greater conformational energy of the aliphatic chains of the alkylammonium cations due to the increase in the size of the galleries caused by insertion of the polymer. Semi-quantitative calculations show that this gain is enough to offset the loss of entropy and make the process isoentropic. Maintenance of spontaneity requires enthalpy as the driving force. The process is illustrated schematically in Figure 2.22.
Manufacturing Process

Polymer processing has elementary operations, namely, 1) handling of particulate, 2) melting, 3) pressurization and pumping, 4) mixing, 5) devolatilization. Among all, mixing is the main element of most polymer processing operations to obtain high-quality products [2,3,30-34].

2.9 Melt mixing

Melt mixing is a well-known method for compounding polymer blends or composites. In this process, nanofillers are introduced into the polymer at a high temperature where the matrix is molten. Polymer macromolecules should move easily at high temperatures in their low viscosity state during the mixing process. Polymer chains are expected to penetrate between nanofillers, and intercalate the nanolayers or nanoparticles. The melt mixing process for the nanocomposites with different filler loadings was carried out using one of the following two mixers, Haake Batch Mixer or Miniature Batch Mixer. The choice of mixer depended on the scale of the material, and included a defined and controlled temperature, time and rotor speed (shear).

2.9.1 Haake batch mixer

Melt intercalation was performed in the Thermo-Fisher Haake Rheomix Series 600® internal batch mixer with twin Banbury blades, Figure 2.23a to make polymer nanocomposites. The mixing volume is 70 cm$^3$ and filling factor used is about 0.78 for most of the polymers.

Figure 2.22: Nanocomposite formation by melt blending technique [39].

Figure 2.23: Melt-intercalation mixers; a) Haake internal [36], b) Miniature batch [39], and c) APAM [75].
2. 29.1.1 Miniature batch mixer
Melt intercalation was performed in a smaller mixer custom developed in our laboratory. This batch mixer, as shown in Figure b, has exactly the same system and structure as the Haake Rheomix 600, but with a small chamber size of 2.4 cm$^3$. This makes the mixer ideal for small scale experiments, with a limited material amount, Figure 2.23b.

2. 29.1.1 Alberta polymer asymmetric mini mixer (APAM)
Alberta Polymer Asymmetric Minimixer (APAM) is the name of another custom miniature mixer which was developed by our research group in 2004, Figure 2.23c [71-75]. This mixer was built to achieve flow regimes similar to industrial mixers and has temperature and rotation frequency (Revolutions per minute (RPM)) control in addition to torque and melt temperature measurement. Its complex flow pattern is the same as that observed in a standard, two-rotor laboratory internal batch mixer, such as the Haake Rheocord series 600, but in a simple, one-rotor configuration. The asymmetric design of the rotor exerts sufficiently high shear rates, elongational flow and reorientation to obtain both a well-dispersed and well-distributed material [24,71-76]. PP The small scale of the chamber’s cavity volume of approximately 2 cm$^3$ makes the mixer ideal for laboratory experimental purposes. The cup has an inner diameter of 13 mm and a height of 25 mm. The rotor, similar to a roller blade has a helical cut and a length of 25 mm, with an alternating diameter. The temperature of the chamber is measured and controlled to maintain a steady state via the heating band around the mixer and using temperature measured by the thermocouple in the outer cup.

2.30 Importance of the Melt Compounding Process
Melt processing is environmentally sound since no solvents are required, making the production of industrially significant polymers practicable. It shifts the nanocomposite production downstream by giving end-use manufacturers many degrees of freedom with regard to final product specifications (e.g. selection of polymer grade, choice of filler, level of reinforcement, etc.). Application of this process also minimizes capital costs due to its compatibility with existing processes [31,32].

2.30.1 Molding

Different forming methods and equipment, such as injection molding or compression molding, were used to shape the polymer materials into samples for different tests and characterizations. In this thesis, all of molding was conducted using a hot compression press setup.

2.30.2 Compression molding
A Carver hot press with heating/cooling platens, Figure 2.24 was used for both compressions molding and curing of the polymer composites. The temperature and pressure of process were controlled at the desired values according to the type and final purpose of the molded material.
The heating system was a series of cartridges heaters. The cooling system of the press comprised of cold water flowing through tubes embedded in the mold.

Figure 2.24: Hot press machine for making composite.
CHAPTER THREE
EXPERIMENTAL PROCEDURE
3.1 Sample Preparation

3.1.1 Materials used

Polypropylene (PP) is generally used in consumer commodities, non-woven fiber, insulating applications, and this was used as the matrix polymer for the nanocomposites with a copolymer ethylene - vinyl acetate (EVA) which is used to develop flexibility. The specification of the material is given in Table 3.1. Two different fillers were used in the research which are aluminum oxide (alumina) and activated carbon, their specification also given below in Table 3.1. The fillers have a size variation, so both types can be connected to each other fibers and also facilitate homogeneous dispersion in order to obtain the best properties. In this work, all these materials were used as obtained from the suppliers. The use material pictures are shown in Figure 3.1.

Table 3.1: Specification of used material in the analysis.

<table>
<thead>
<tr>
<th>Material Specification</th>
<th>Polypropylene</th>
<th>Ethylene-vinyl acetate(EVA)</th>
<th>Conductive Activated Carbon</th>
<th>Aluminium oxide (Alumina)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Marlex® HGZ-120SP</td>
<td>Sipchem EVA 2018</td>
<td>Merck &amp; Sigma-Aldrich</td>
<td>Merck &amp; Sigma-Aldrich</td>
</tr>
<tr>
<td>Density</td>
<td>0.904 g/cm³</td>
<td>0.935 g/cm³</td>
<td>0.15 - 0.44 g/cm³</td>
<td>3.94 g/cm³</td>
</tr>
<tr>
<td>Processing Temperature</td>
<td>190 - 260 °C</td>
<td>150 – 230 °C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Melt Flow Rate</td>
<td>(230°C/2.16 kg) 12 g/10 min</td>
<td>190°C / 2.16 kg 2.0 g/10 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>8-10 %</td>
<td>&gt;400%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Average Particle size</td>
<td>-</td>
<td>-</td>
<td>63 μm to 200 μm</td>
<td>≤ 100 μm</td>
</tr>
<tr>
<td>Average Particle Size After Grinding</td>
<td>-</td>
<td>-</td>
<td>≤ 100 nm</td>
<td>≤ 100 nm</td>
</tr>
<tr>
<td>Melting Point</td>
<td>160-170°C</td>
<td>87 °C</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.1: Materials used in analysis; (a) PP, (b) EVA, (c) activated carbon (AC) and (d) alumina.
3.1.2 Development of polymer composite

In this thesis there are two composites actually used 1) microcomposite and 2) nanocomposite, both was developed in automated mixing followed by nanoparticle preparation by grinding. Automatic mixing was done by internally develop mixing unit.

3.1.3 Nanoparticle preparation

For preparing nanoparticle, we followed three step processes by means of grinding, which are a) hand grinding of bulk respective particle, b) ball milling by means of ceramics pot and ball and c) again hand grinding.

a) Hand grinding of bulk respective particle

After the procurement of particle it was grinded by means of mortar pastel for about 18 hr followed by subsequent drying in 3 hr interval to demoisturize the sample and better grinding action below Figure 3.2.

![Figure 3.2: Mortar pastel of carbon particle to make it nanoparticle.](image)

b) Ball milling by means of ceramics pot and ball

Hereafter to make the particle finer it was subjected to ball milling by means of locally develop ceramics pot and ball with drying in 8 hr interval to de moisturize the sample. The ball milling process time vary with respect to particle. (Figure 3.3) As in this research two bulk particle used, so ball milling time are as follows:

- Activated Charcoal (Carbon Particle): 72 hr
- Alumina: 120 hr
c) **Second stage hand grinding**

Finally, the ball milled particles are hand grind to make the particle uniform in respect of size distribution for 2 hr. If any particle not be grinded, this process ensures to make it nanoparticle. The grinding process is similar to previous one. Final grounded particle are shown in Figure 3.4.

![Figure 3.4: Final nanoparticle after three step process; (a) carbon and (b) alumina.](image)

### 3.1.4 Development of nanocomposite

#### 3.1.4.1 Sample plan

There are five category sample was develop for the whole study. These are representing in following table for Table 3.2 to Table 3.5.
Table 3.2: Binary matrix reinforced by single particle system (microcomposite)

<table>
<thead>
<tr>
<th>Sample Name (Carbon:Alumina)</th>
<th>Matrix system (wt%)</th>
<th>Particle content (wt%)</th>
<th>Sum of filler (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>EVA</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>0:0</td>
<td>60</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>1:0</td>
<td>54</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>0:1</td>
<td>54</td>
<td>40</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.3: Binary matrix reinforced by binary particle system (microcomposite)

<table>
<thead>
<tr>
<th>Sample Name (Carbon:Alumina)</th>
<th>Matrix system (wt%)</th>
<th>Particle content (wt%)</th>
<th>Sum of filler (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>EVA</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>3:2</td>
<td>54</td>
<td>40</td>
<td>3.6</td>
</tr>
<tr>
<td>2:3</td>
<td>54</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>1:4</td>
<td>54</td>
<td>40</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 3.4: Binary matrix reinforced by single particle system (Nanocomposite)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Matrix system (wt%)</th>
<th>Particle content (wt%)</th>
<th>Sum of filler (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>EVA</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>Carbon 2%</td>
<td>58</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Carbon 4%</td>
<td>56</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>Carbon 6%</td>
<td>54</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>Alumina 2%</td>
<td>58</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Alumina 4%</td>
<td>56</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>Alumina 6%</td>
<td>54</td>
<td>40</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 3.5: Binary Matrix reinforced by binary particle system (Nanocomposite)

<table>
<thead>
<tr>
<th>Sample Name (Carbon:Alumina)</th>
<th>Matrix system (wt%)</th>
<th>Particle content (wt%)</th>
<th>Sum of filler (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
<td>EVA</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>2:3</td>
<td>54</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>1:4</td>
<td>54</td>
<td>40</td>
<td>1.2</td>
</tr>
</tbody>
</table>


3.1.4.2 Design and development of polymer melting and blending unit

The result of thesis mostly related to blending of particle with the matrix, a proper mixing unit is a crucial parameter. So for that we internally developed a polymer melting and blending unit, Figure 3.5, which is a small polymer mixing and melting equipment design to meet the requirement of scientific research requirements. The basic working principle of this equipment can mix the polymeric materials uniformly with a uniform temperature control system by means of well designed insulation materials, internal drum wall thickness and well design agitator. The highest rotation speed of the equipment reached 60 rpm which makes it suitable for varied polymer materials. During the operation the materials will carry out axial and radial motion at same time to mix the materials thoroughly and uniformly within a short time due to its designed lock and lifting handle. The highest temperature reached to 450°C can cover most of the processing polymer research with various filler particle, fiber etc. With wide rotation speed (0~60 rpm) make it suitable for varied polymer materials. With digital rotation speed display (0~60 rpm) various speed control, temperature display (0-450°C), temperature control, stable operation make the device excellent use for various research purpose like polymer composite with reinforce fiber, particle, conductive particle etc. A handle is attached to the internal mixer which makes it faster processing of melted materials after operation. However, this device is equipped with well design parts and set their respective function to produce efficient blending materials.

3.1.4.3 Mixing using melting and blending unit

An internal mixer was used to disperse activated carbon, graphite, alumina, nanoclay and their mixtures in the PP/EVA matrix by melt mixing at 190°C, the mixing chamber capacity being 400 gm. Before melt mixing, the particle weighted in a certain amount (Figure 3.6a) then the mixture of particle was hand ground for 30 min in an internal granite mortar (Figure 3.6b) and all the materials were dried for 2 hours in an oven at 100°C (Figure 3.6c).
Figure 3.6: Progressive stage in automatic mixing of polymer nanocomposite; a) weighting the particle, b) hand grinding and c) drying.

To begin with, all compounds were mixed at 190°C in an internal mixer using a 30-rpm mixing rate to insert sufficient shear rate to the mixer to ensure homogeneous mixing. The mixing procedure involved adding the oven dried PP/EVA pellets (Figure 3.7a) into the preheated (at 190° for 10 min) rotating mixer (Figure 3.7b) and keep the polymer pellets in the mixing chamber condition for 5 min (Figure 3.7c).

Figure 3.7: Progressive stage in automatic mixing of polymer nanocomposite; a) preheating the mixer, b) oven dried PP/EVA pellets and c) keep the polymer pellets.

Then, allowing the polymer to mix for 7 min prior to the addition of the particle, after which the compound was allowed to mix for an additional 5 min with particle (Figure 3.8). This procedure insured a uniform distribution of particle within the base polymer.

Figure 3.8: Mix up nanoparticle to mixing chamber.
3.1.4.4 Hot molding

Samples for characterization were prepared in the form of circular disks (90mm diameter, 9 mm thick) and rectangular (150 mm X 150 mm X 2.5 mm) sheet. These samples contained either one carbon particle or the mixtures of hybrid particle, and the sample composition was different not in variable volume fraction of the filler(s) but the relative amounts of the two/three fillers. Samples were prepared in such a way that they contained particle in an isotropic way to the direction of heat flow. To obtain the desired samples, the composite, as obtained from the internal mixer (Figure 3.9a). The molten polymer transfer to a aluminum mold followed by silicon spraying and wrapping by a heat resistant paper to avoid any type of scratch on the final cast. Thereafter, the sample molded into a Fontunehy-draulic compression press at a pressure of approximately 30 KN for 5 min at 190°C followed by temperature cycle from 0 C- 160 C and 160 C to 190 C, (Figure 3.9b). Then the sample allowed to solidify by passing water through the hot press plate at the same pressure and after cooling the resulting composite is taken to store in sealed plastic bags for the further test (Figure 3.9c). An optical microscope was used to observe the morphology of the microcomposites, and to verify the expected particle dispersion.

Figure 3.9: Progressive stage in molding of conductive polymer nanocomposite; a) the melted composite obtained from the internal mixer, b) hot pressed the molten sample and c) final solidified sample.

The schematic of sample making by hot press are presented below in, Figure 3.10

Figure 3.10: Schematic of sample preparation of compression molding in hot press.
3.1.5 Development of micro composite

Development of micro composite via automatic mixing is similar to development of nanocomposite via same process which describe below.

3.2 Characterization of Polymer Nanocomposites

In order to obtain some points about the characteristic properties of the materials produced, we need some methods testing the specifications which allow us to describe the requirements. Main purpose of a standard is to make a bridge between thoughts with using same language to communicate. The product specifications, such as mechanical properties (tensile, flexural, and impact) thermal properties ($T_g$, $T_d$, $T_m$ etc.) and morphological properties (homogeneity etc.), can be expressed using standard test methods defined by authorized foundations, like the American Society for Testing and Materials (ASTM).

3.2.1 Mechanical Tests

The mechanical properties are often the most important sources to make a decision about product specifications. The material selection for a variety of end-use applications is mostly dependent on these properties, such as tensile strength, modulus, elongation and impact strength [30,31].

3.2.1.1 Tensile Tests

Tensile test is a measurement of the ability of a material to applied forces tending to pull it apart and observe the extent of material stretches before breaking. Different types of plastic materials are often compared based on tensile property data (i.e. strength, modulus, and elongation data). Tensile tests were conducted according to ASTM D 638-01 [77] using an Instron UTM machine (system Id 3369J8567, maximum capacity 50KN) Figure 3.11. Each test was continued until tensile failure. As a testing machine, the machine of a constant-rate-of-crosshead movement, containing a stationary member carrying one grip, and a movable member carrying the second grip, is used. The specimens are conditioned using standards of procedures. The recommended test conditions are 23°C as a standard laboratory atmosphere and 65% percent relative humidity.

![Figure 3.11: (a) Schematic of tensile test and (b) Instron UTM machine.](image)
There are basically five different testing speeds mentioned in the ASTM D638 Standard. As the specimen elongates, the resistance to the tension increases, and it is detected by a load cell. The tensile strength can be calculated by dividing maximum load in Newton’s by the original minimum cross sectional area of the specimen in square millimetres, and the result can be explained in the term of megapascal (MPa). The tensile strength at yield and at break (ultimate value) is calculated.

\[
\text{Ultimate Tensile Strength}(\Sigma) = \frac{\text{Max Load } (N)}{\text{Cross Section Area } (\text{mm}^2)} \tag{1}
\]

\[
\text{Tensile Strength at Yield } (\text{MPa}) = \frac{\text{Max. Load at Yield point } (N)}{\text{Cross Section Area } (\text{mm}^2)} \tag{2}
\]

\[
\text{Tensile Strength at Break } (\text{MPa}) = \frac{\text{Load recorded at break } (N)}{\text{Cross Section Area } (\text{mm}^2)} \tag{3}
\]

Tensile modulus and elongation values are derived from the stress-strain curve. If the specimen gives a yield load larger than the load at break, percent elongation at yield is calculated; if not, percent elongation at break is calculated. [38]

\[
\text{Strain} = \frac{\text{Change in Length (elongation)}}{\text{Original Length (gauge length)}} \tag{4}
\]

\[
\varepsilon = \frac{\Delta L}{L} \tag{5}
\]

Elongation at yield: \(\Delta L = \varepsilon \) (the value at the yield point) \(* L \tag{5}
\]

Percent Elongation at yield = \(\Delta L \times 100\) \tag{6}

Tensile modulus (the modulus of elasticity) can be determined by extending the initial linear portion of the load-extension curve and dividing the difference in stress obtained from any segment of section on this straight line by the corresponding difference in strain, expressing the result in the unit of megapascal (MPa) [76].

\[
\text{Tensile Modulus} = \frac{\text{Difference in Stress}}{\text{Difference in corresponding Strain}} \tag{7}
\]

Figure 3.12: Photograph of a tensile test specimen.
3.2.1.2 Flexural Tests

Flexural strength is the ability of the material to applied bending forces perpendicular to the longitudinal axis of the specimen. The stresses induced by flexural load are a combination of compressive and tensile stresses (Figure 3.14), and properties are calculated in terms of the maximum stress and strain occurring at the outside surface of the test bar [77]. These test methods are generally applicable to rigid or semi rigid materials.

Two basic methods, including a three-point loading system utilizing center loading on a sample supported beam, and a four-point loading system utilizing two load points, are employed to determine the flexural properties. The former is designed particularly for materials undergoing small deflections, whereas the latter particularly for materials with large deflections during testing. The test specimens used for flexural testing are obtained from sheets, plates or molded shapes by cutting as bars with rectangular cross section. Specimen shown in, Figure 3.15a.

Flexural strength is equal to the maximum stress in the outer fibers at the moment of break, and calculated using the following equation,

$$\sigma_f = \frac{3FL}{2bd^2} \quad \text{(8)}$$

where; $\sigma_f$ is the stress in the outer surface at mid span (MPa), $F$ is the load at a given point on the load-deflection curve, $L$ is the support span (mm), $b$ and $d$ are the width and the depth of beam tested, respectively (mm). The max. strain in the outer fibers occurs at mid span is calculated as follows,

$$\varepsilon_f = \frac{6Dd}{L^2} \quad \text{(9)}$$

where; $\varepsilon_f$ is the maximum strain in the outer surface (mm/mm), $D$ is the maximum deflection of the center of the beam (mm), $L$ is the support span (mm). The modulus of elasticity is the
ratio, within the elastic limit of stress to corresponding strain, and can be represented by the slope of the initial straight-line portion of the stress-strain curve, calculating as follows.

\[ E_f = \frac{L' m}{4bd^3} \]  \hspace{1cm} (10)

where; \( E_f \) shows the modulus of elasticity in bending (MPa) and \( m \) is the slope of the tangent to the initial straight line portion of the load-deflection curve (N/mm). In this work we follow ASTM D790M with sample size total length of the specimen is taken as \{SP (length of support span= 16d) + (20-30 mm)\} Figure 3.15 b[78].

![Figure 3.15: (a) Flexure test specimen and (b) flexure test specimen dimension.](image)

3.2.1.3 Hardness Test

The hardness of plastics is most commonly measured by the Shore® (Durometer) test or Rockwell hardness test. Both methods measure the resistance of plastics toward indentation and provide an empirical hardness value that doesn't necessarily correlate well to other properties or fundamental characteristics. Shore hardness, using either the Shore A or Shore D scale, is the preferred method for rubbers/elastomers and is also commonly used for 'softer' plastics such as polyolefins, fluoropolymers, and vinyls. The hardness of the composite was measured using a shore hardness testing machine as shown in Figure. Shore Durometer is one of several measures of the hardness of a material. Hardness property of composite was measured using shore A, D scale. Figure 3.16

![Figure 3.16: (a) Hardness test specimen and (b) Shore D.](image)

3.2.2 Thermo Gravimetric Analysis (TGA)

TGA tests can be performed under different atmospheres, such as air, \( N_2 \), and also using different heating protocols, depending on the type of material and purpose of the test. For our
composites, the tests were conducted under N$_2$ atmosphere. The important data obtained from the TGA are: (1) the thermal decomposition onset of the materials, which shows the thermal stability and (2) it provides important data which help to design application oriented materials and gives information to understand the structure-property relationships. Moreover, TGA data will help to quantify the amount of possibly damaging, deteriorating volatiles, and maximum operating temperature of the nanocomposites. In this work, Thermal gravimetric analysis (TGA) was done using a TA instruments’ (TGA Q50 V6.4) series. The samples were cut into small pieces in block by using suitable cutter and then this block is slice to fit in sample holder of about 20 mg. The test was carried out 650 C from room temperature at a heating rate of 10°C/min in nitrogen gas atmosphere.

3.2.3 Differential Scanning Calorimetry (DSC)

The crystallization behavior, detection of phase transition, and crosslinking procedure of materials are studied by differential scanning calorimetry (DSC) test. The test has been conducted using a SII EXSTAR TMA SS6300, SII Nanotechnology, Japan. The most important results from studies are: (1) melting temperature (Tm), (2) any miscibility of binary matrix examine by DSC. These data can be used to determine the amount and type of crystals and phase structure; gelation temperature, maximum operating temperature, changes in the heat capacity. The samples were cut into small pieces in block of 3mm X 3mm X 2.5mm using suitable cutter and then this block is slice to fit in platinum pan of about 20 mg. The test was carried out 300°C from room temperature at a heating rate of 10°C/min in nitrogen gas atmosphere.

3.2.4 Fourier Transform Infrared

Fourier transform infrared (FTIR) spectroscopy is a technique for performing qualitative and quantitative analysis of the molecular structure and chemical bonds of organic compounds, achieved by analyzing how the sample absorbs a light beam at each wavelength [48-52]. The term "infra-red" covers the range of the electromagnetic spectrum between 0.78 and 1000 μm. In the context of infra-red spectroscopy, wavelength is reported as "wavenumber" $2\pi/\lambda$, which has the unit cm$^{-1}$. It gives quantative information like identifying a material, following a chemical reaction, providing information for determining the molecular structure, elucidating conformational information, or for a host of other purposes. In this study solid sample of nanoparticle and composite both are tested to get clear understanding matrix and particle with Cary 630 FTIR spectrometer with co-addition of 32 scans. The sample prepared in powder collected by scratching of the composite by a saw was placed on the sample holder and the spectroscopy was carried out.

3.2.5 Microscopic imaging

Electron microscopy imaging is a technique of imaging the ultrastructure of materials using electron beams. Two types of electron microscopy imaging were used in this work, scanning electron microscopy (SEM) and optical microscopy.
3.2.5.1 Optical microscopy
Light or optical microscopy is the primary means for scientists and engineers to examine the microstructure of materials. The basic techniques developed in metallography are not only used for examining metals, but also are used for examining ceramics and polymers. The sample of nanocomposite are prepared by grinding by using automatic grinder to clean the surface as well as to open up inner side of the sample, after grinding it was observe in optical microscopy followed by cleaning with methanol.

3.2.5.2 Field Emission Scanning Electron Microscopy (FESEM)
A Field Emission Scanning Electron Microscopy (FESEM) produces images by scanning a sample with a focused beam of electrons. The electrons interact with atoms in the sample and produce detectable signals which contain information about the sample's surface topography and composition. This method of imaging provides information about external morphology, chemical composition, crystalline structure, and orientation of materials. The tensile fracture surface of nanocomposite was prepared for microstructural analysis. Before place the sample in test chamber in FSEM it was dried 100 C for 10 min in a oven for demoiturising. The interfacial localization between of particle in the matrix and tensile fracture surfaces of the nanocomposite were examined using a Scanning Electron Microscope [JEOL JSM 7600F, Japan]. The micrographs are presented in the Results and Discussion section.

3.2.6 Thermal conductivity measurement
A steady-state heat-conduction technique similar to that described in ASTM D5470 standard was used to measure the thermal conductivities of the samples by lee disk apparatus, Figure 3.17.

![Figure 3.17: Concept of the experimental technique; (a) basic concept of test principle and (b) experimental set up of Lee” Disc apparatus](image)

The test was continued at room temperature of about 29°C and 90% R.H. with the sample size 90mm dia and 10mm thickness. Thermal conductivity, k, is the property of a material that indicates its ability to conduct heat. Conduction will take place if there exists a temperature gradient in a solid (or stationary fluid) medium. Energy is transferred from more energetic to less energetic molecules when neighboring molecules collide. Conductive heat flow occurs in
direction of the decreasing temperature because higher temperature is associated with higher molecular energy. Fourier’s Law expresses conductive heat transfer as:

\[ H = KA \frac{(T_1 - T_2)}{x} \]  

……………(11)

Where \( H \) is the steady-state rate of heat transfer, \( k \) is the thermal conductivity of the sample, \( A \) is the cross-sectional area of the sample having a radius \( r \) and \((T_1 - T_2)\) is the temperature difference across the sample thickness \( x \) (Figure 3.17a), assuming that the heat loss from the sides of the sample is negligible. To keep the loss from the side small, the sample is made in form of a thin disk with a large cross-sectional area compared to the area exposed at the edge. Keeping \( A \) large and \( x \) small produces a large rate of energy transfer across the sample. Keeping \( x \) small also means that the apparatus reaches a steady state (when temperature \( T_1 \) and \( T_2 \) are constant more quickly. When steam flows for some time, the temperatures recorded (Upper disk, \( T_1 \) and Lower Disk, \( T_2 \)) gradually remain steady. After the steady state, the lower disk heated directly by the burner till its temperature is about \( T_2 + 10^\circ C \). Then the burner was removed and allowed “C” to cool whereas simultaneously record the cooling time for every \( 1^\circ C \) decrease the temperature of the system. Variation of the temperature of the Brass disk with a time of cooling was plotted as shown in (Figure 3.17). A tangent is drawn at the steady state temperature \( T_2 \).

\[ H = ms \frac{(dT)}{dt} \]  

……………(12)

From the above equation the thermal conductivity, \( K \) can be determined as,

\[ K = ms \frac{(dT / dt) x}{A(T_1 - T_2)} \]  

……………(13)

Also simple DSC measurements can be used to rapidly determine the thermal conductivity of polymers and other materials with similarly low values with an accuracy of about \( \pm 10 \) to \( \pm 20\% \). Under stationary conditions, the heat flow, \( \varphi \), through a body with a thermal resistance, \( R_s \), is proportional to the temperature difference, \( \Delta T \):

![Figure 3.18: Cooling curve for measuring the tangent to determine thermal conductivity.](image)
\[ \varphi = \frac{1}{R_s} \Delta T \] .................................(14)

The thermal resistance, \( R_s \), of the material is given by the material-dependent thermal conductivity and the geometry of the body:

\[ R_s = \frac{h}{K A} \] .................................(15)

Here \( K \) is the thermal conductivity, \( A \) the cross-sectional area, and \( h \) the height of the measured body. As \( R_s \) is much smaller can be neglected and \( K \) can be determined from a single melting curve. Combining equation 15 and 16

\[ K = \frac{\varphi \ h}{\Delta T \ A} \] .................................(16)

The all basic data to measure the thermal conductivity collected from reference data base and calculation was done by above equation.

3.2.7 Water absorption test

The specimens for water absorption test had dimension 39mm×10mm×4.1mm. After oven drying, the weight of all the specimens were taken and recorded. Next, the specimens were immersed in the distilled water according to ASTM D 570-99. After 24 hours, the percentage increase in weight during immersion was calculated using following Equation [79-81]:

Increase in weight, \( \% = \frac{(weight \ wet - weight \ dry)}{weight \ dry} \times 100 \)
CHAPTER FOUR
RESULTS AND DISCUSSION
4.1 Selection of Base Matrix

Tensile properties of the different proportion of polypropylene (PP) and ethylene vinyl acetate (EVA) were examined to select the basic matrix. This study was targeted to select a PP/EVA blend which can increase draw ability and flexibility of the ultimate develop composite. For that blend with 10, 20, 30 and 40 wt % of EVA in the PP matrix were tested for % elongation and flexibility. The % elongation was increased with the increase of EVA concentration, Figure 4.1. As PP is a rigid polymer having % elongation 6 where as EVA is a very elastic resin having % elongation of about 400%, so their perfect blend would be also a elastic material, which is actually reflect in result.

![Figure 4.1: Variation of % elongation (drawability) against relative weight ratio of PP: EVA.](image)

Moreover, the immiscible theory was also supports this phenomenon. As the PP/EVA is immiscible blend, so no chemical bond (discuss later) was formed in their blend rather than mechanical interlocking at interfacial zone. This is why the elasticity was increased with the increase of elastic part in final blend. As like the elastic behavior the phenomenon was also similar in case of flexibility. Obviously the flexibility is proportional to elasticity which ultimately reflects in result, Figure 4.2.

![Figure 4.2: Variation of flexural strength against relative weight ratio of PP: EVA.](image)
The aims of present research was to develop a composite of better drawability, thermal conductivity with improve or no loss of mechanical property. So, the optimum concentration PP: EVA (60:40) was selected for further study, as it gives the maximum elongation and flexibility. Moreover, as the PP itself is a rigid polymer with good strength, so further reduction of PP will reduce the mechanical property of develop composite from its expected level.

4.2 FTIR Spectroscopic Analysis

The FTIR spectra of pure polymer, matrix and the particle reinforced composite was performed to know their identity and also to ensure any chemical change during manufacturing process. Figure 4.3 shows the FTIR spectra of pure PP, the characteristic absorption peak at around 2952 cm\(^{-1}\), 2914 cm\(^{-1}\), 2870 cm\(^{-1}\), 2840 cm\(^{-1}\), 1453 cm\(^{-1}\), 1375 cm\(^{-1}\) and 720 cm\(^{-1}\) represents the methyl symmetric C–H stretching, methylene asymmetric C–H stretching, methyl asymmetric C–H stretching, methylene symmetric C–H strong stretching, methylene \(-\text{CH}_2\)- scissoring, methyl symmetrical C–H bending and methylene \(-\text{CH}_2\)- rocking respectively [81]. All the peaks are enough support to define the PP matrix in the study. The absence of other peak meets the requirement that there are no chemical reactions occur during processing. Some peaks also show slight variation from its standard value may be for system aberration.

![Figure 4.3: FTIR spectrum of pure polypropylene (PP).](image)

Further FTIR spectral analysis was done on pure EVA sample and the spectra as represented in Figure 4.4. The absorption peak at around 2914 cm\(^{-1}\), 2847 cm\(^{-1}\), 1464 cm\(^{-1}\), 1375 cm\(^{-1}\), 1300 cm\(^{-1}\) and 720 cm\(^{-1}\) represents methylene asymmetric C–H stretching, methylene symmetric C–H stretching, methylene \(-\text{CH}_2\)- scissoring, methyl symmetrical C–H bending, methylene \(-\text{CH}_2\)- twisting, methylene CH\(_2\)- rocking respectively. In addition there are another important peak found which represent the aliphatic –C=O ester group in 1730 cm\(^{-1}\). So all the peaks strongly support the chemical structure of EVA which have all the functional group[81].
Figure 4.4: FTIR spectrum of pure Ethylene vinyl acetate (EVA).

Figure 4.5 represents the FTIR spectral analysis for PP/EVA blend where all characteristics peaks are found like 2914 cm$^{-1}$, 2847 cm$^{-1}$, 1730 cm$^{-1}$, 1464 cm$^{-1}$, 1375 cm$^{-1}$, 1300 cm$^{-1}$, and 720 cm$^{-1}$ represents methylene asymmetric C–H stretching, methylene symmetric C–H stretching, aliphatic –C=O ester stretching of EVA, methylene -CH$_2$- scissoring, methyl symmetrical C–H bending, methylene -CH$_2$- twisting and methylene -CH$_2$- rocking respectively. It is clear that no new peak will seen which just prove the overlapping the two FTIR spectra of PP/EVA. It is also prove the miscibility of the PP/EVA matrix [10,81].

Figure 4.5: FTIR spectrum of polypropylene (PP)/ethylene vinyl acetate (EVA) matrix at PP/EVA (60/40) wt%.

In case of PP/EVA/carbon composite all the absorption peak are present in the FTIR spectra. The conductive carbon particle is individual one, which have no chemical bond at all. So, there was no new peak appeared when the sample is blended with activated carbon nanoparticle. This also proves the absence of chemical bond between carbon particles and the PP/EVA matrix. Figure 4.4 shows the all absorption peaks for PP/EVA/activated carbon.
Figure 4.6: FTIR spectrum of carbon particle reinforced polypropylene (PP)/ethylene vinyl acetate (EVA) composite at PP/EVA/carbon (54/40/6) wt%.

The FTIR absorption peak of PP/EVA/alumina also observed and shows in Figure 4.6. Here a new peak was appeared at 1088 cm\(^{-1}\) which is characteristics peak for alumina (Al\(_2\)O\(_3\)) nanoparticle [82, 83].

Figure 4.7: FTIR spectrum alumina particle reinforced polypropylene (PP)/ethylene vinyl acetate (EVA) composite at PP/EVA/alumina (54/40/6) wt%.

Finally investigation was done on binary matrix (PP/EVA) by binary particle (activated carbon/alumina) system, the FTIR of that sample shown in Figure 4.7. Here similar pattern found like previous blend. Generally PP is non polar and EVA is polar, so their blend always produce immiscible matrix [15,16]. Now, from above FTIR spectral analysis revealed no additional peaks other than the characteristics peaks in the composites. This proves that there was no chemical bond creates in the composite, which indicate the complete immiscibility of matrix. Moreover, the nanoparticles are only mechanically bonded to matrix, as they did not create any bond with PP/EVA matrix, Figure 4.8. Also the major peak intensity remains constant, means the concentration of PP/EVA (54/40) throughout the composite was remain constant.
Figure 4.8: FTIR spectrum of carbon and alumina particle reinforced polypropylene (PP)/ethylene vinyl acetate (EVA) composite at carbon: alumina (2:3) within 6 wt% of particle in PP/EVA (54/40) wt%.

4.3 Mechanical Properties

4.3.1 Tensile properties

4.3.1.1 Tensile strength

In general, properties obtained from tensile test consist of the ultimate tensile strength, tensile modulus, and elongation at break. Determining of tensile strength and other tensile properties is important for evaluation of different polymers and component designs, design of plastic components for load-bearing applications, and, finally, for determining the specifications and predicting in-service performance of plastics. In that perspective, tensile test of developed polymer composite was perform from micro composite to nanocomposite range in various proportion of microparticle and nanoparticle. Tensile behavior of polymer composite containing microparticle shown in Figure 4.9 where 6 wt% of filler is maintain either single particle (carbon or alumina) system or binary particle (carbon: alumina) system. The tensile strength shown at single particle either activated carbon (AC) or alumina is lower than that of binary particle system (carbon: alumina) in the microcomposite. This is due to the larger particle size of micro particle reduces the interfacial wetting of polymer to particle which result low strength even create weak point or aggregation in case of alumina which result lowering the composite strength down to basic matrix. Similar phenomena also found by some researcher [84, 85]. In contrast, for binary particle system in PP/EVA matrix initially increases the tensile strength with increase of alumina particle portion in the carbon: alumina ratio. This is due to there are a two types of dispersion possibility activated carbon particle to alumina particle, particle to matrix which increase the possibility to entangle, wettability with particle to matrix lead to higher strength [86]. After a certain activated carbon: alumina ratio the strength again tend to fall due to the higher alumina particle create the same phenomena mention earlier.
As the continuation of search to nanocomposite, Figure 4.10 shows the tensile strength of individual activated carbon particle in PP/EVA matrix. Here, the tensile strength of the nanocomposite shows a minor increasing trend compared with that of the matrix. For the nanocomposites, if there is some deal of particle de-bonding from the matrix happening prior to the obvious plastic deformation of the matrix, generally the strength will reduce. Hence, the improvement in the tensile strength supplies a proof that the interaction between the nanoparticles and matrix is enough to restrict the considerable matrix yielding. The similar pattern for carbon filler was observed by [86]. After the formation of some aggregates, these properties are decreased at higher concentration. This is directly related to the microstructure of nanocomposites because the size of aggregates increases by increasing the nanoparticle content, the same phenomenon was observed by several researchers [86-88].
Similarly for alumina nanoparticle, the tensile strength in Figure 4.11 shows an increasing trend up to 6 wt%. Generally, binary matrix technique produces more interfacial area or interfacial zone (IZ) than that of conventional micro particulate composite. Other than the particle dispersion, the property of interfacial zone plays an important role in determining the property of the nanocomposite [16,81]. As interfacial zone is higher in binary matrix system, so interaction of particle to matrix is higher. Also, entanglement of particle to matrix is higher as a result the strength gives an increasing trend than that of microcomposite [84].

Figure 4.11: Variation of tensile strength against different concentration of alumina nanoparticle in PP/EVA matrix.

However, the 6 wt % nanoparticle reinforcement give best result in all composite. So, the binary particulate composite was investigated within the 6 wt% of activated carbon: alumina to PP/EVA (54/40) matrix, in Figure 4.12 shows. The tensile strength in binary matrix by binary particle (B/B) composite system was higher than that of binary matrix by single particle (B/S) system. This trend is similar to that of micro particulate composite which due to better dispersability, wetability, more entanglement with polymer to polymer chain and polymer to particle at interfacial zone. Moreover, this trend also a contribution of nano size particle in the PP/EVA matrix. The alumina particle shows better result in carbon: alumina than when it was used as single particle (alumina) in the matrix. This is due to its nature of agglomeration, [88] which also gives a drastically bad result in micro particulate composite.

Figure 4.12: Variation of tensile strength against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.
4.3.1.2 Tensile (Young’s) Modulus

Tensile modulus also increases with converting the composite from binary matrix by single particle to binary matrix by binary particle, shown in Figure 4.13 for micro particulate composite. The modulus of a composite material depends on the ratio of filler modulus to that of the matrix. Since both activated carbon and Al₂O₃ have higher modulus, more rigid structure, the modulus increases and in case of binary matrix by binary particle system it will increases with the increase of Al₂O₃ particle because alumina is more rigid than activated carbon. Furthermore individually alumina does not give the expected increase in modulus due to the tendency of alumina particles to agglomerate in the structure. This effect can be seen in Figure 4.19 at 6 Wt % of alumina loading. This agglomeration effect also ceases the increase in stiffness of the composite having activated carbon: alumina ratio 1:4.

![Figure 4.13: Variation of tensile modulus against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.](image)

Further observation in nanoparticulate composite represent for individual particle as well as binary particle. The Young’s modulus for activated carbon particulate composite shows in Figure 4.14, increases with the increase of particle content. This is a general trend for stiffening the base matrix by the particle loading increases due to Therefore, the property of interfacial zone plays a main role in determining the property of the nanocomposite, in addition to the particle dispersion. It is reported that the interfacial interaction can be improved between the particles and the matrix by increasing interface zone. In the presence of strong interfacial interaction, the load transfer across the nanoparticle-matrix interface takes place very easily, which provides the raise in the tensile modulus. This observation, which is in similar with [4, 89], can be explained by the fact that the fillers have higher stiffness than the matrix and are able to improve the modulus of the composite.
In addition for alumina particle, The Young’s modulus is good enough higher than that of activated carbon due to its higher modulus contribution to the matrix. However, all other supportive clause mention above is similar for both particle, Figure 4.15 shows the relation for alumina.

In binary matrix by binary particle system the Young’s Modulus shows better result, Figure 4.16. Thus, PP/EVA nanocomposites exhibit their higher mechanical performance at concentration 6wt% while, in binary matrix by binary particle composite give better modulus than that of binary matrix by single particle. Moreover, with the increase of relative nano alumina ratio to carbon, the Young’s modulus also increases, this observation also support by
several study [52,86]. This can be happen due to low nano alumina content, partial tensile strain can be transferred to nano alumina embedded in matrix under tensile stress, which leads to the increase of Young’s Modulus [52]. With further addition of nano alumina at activated carbon: alumina ratio 0:1 more agglomerates of nano alumina form in matrix and many defects are introduced into the polymer matrix. This is due to difficulty of homogeneously dispersing nano alumina by melt mixing. This effect is similar with some researcher [36,52,86] These defects lead to the decrease of Young’s Modulus. However, in all the cases the mechanical properties are higher than PP/EVA matrix.

![Graph showing Young's Modulus variation against carbon:alumina ratio](image)

Figure 4.16: Variation of tensile modulus against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.

**4.3.1.3 Elongation at break**

In pure PP/EVA matrix shows the better elongation in the develop composite, it is also reported by many researcher[5,88,89],this is due to the higher elastic property of EVA of about 400 % Elongation which directly affect the rigid polymer PP of about 6%. Figure 4.17 shows the result of micro particulate composite where % elongation decreases drastically with the increase of alumina particle content in the binary matrix by binary particle microcomposite. At only carbon loading have slight impact on % elongation due to the softness of carbon particle which interact with matrix without giving sufficient stress concentration, which also support by strength and modulus result. However, at high alumina contents the particles agglomerate giving rise to stress concentration. Since the alumina particles have rigid structures, the actual elongation of the pure resin decreases as more rigid is loaded to the matrix. However, individually alumina cannot change the elongation rather increase interfacial de-bonding results more elongation than normal pure PP/EVA.
Figure 4.17: Variation of % elongation against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.

As the elongation is reciprocal of the stiffness of a material, the results show that the filler imparts a greater stiffening effect [4,81,90]. Figure 4.18 shows a decrease in elongation at break for composites containing activated carbon (AC) nanoparticle. This indicates that the presence of activated carbon in the matrix reduces the ability of the sample to deform by restricting the mobility of the polymer chains. This is similar with the researchers [41,52,86,90]. Also, the particles are almost evenly distributed in the matrix amorphous region as well as in interfacial zone which restricts the flexibility of the chain segments, leading to a decrease in elongation at break [81,86].

Figure 4.18: Variation of % elongation against different concentration of carbon nanoparticle in PP/EVA matrix.

It was seen that by the addition of alumina nanoparticles in Figure 4.19, elongation is drastically dropped. The percentage of elongation at break is approximately 33% to 20%. The dramatic reduction in elongation at break implied that the ductility of matrix has been reduced with the presence of nano alumina particles. This observation can be explained from crystallinity phenomena. This effect of alumina nanoparticle to composite was also observed by some researcher [18,52,53]. However, as EVA having varying degree of amorphousness which will block by adding Al₂O₃ particle, result the reduction of its elasticity ultimately fall the elongation of nanocomposite [41,52,86].
Figure 4.19: Variation of % elongation against different concentration of alumina nanoparticle in PP/EVA matrix.

The elongation at break of binary matrix by binary particle composite also shows the similar reduction, but the pattern is different from binary matrix by single particle composite, although the same (6%) particle wt% was maintained. In the binary activated carbon: alumina particle system give more rigidity than that of single particle, Figure 4.20. This is due to the more entanglement of polymer chain with particle occur on interface zone by the two types of dispersion behavior discussed before. Also the Al$_2$O$_3$ is a hard which somewhat increase crystallinity of EVA will result this reduction of % elongation [4,90,88]. However in single Al$_2$O$_3$ and activated carbon not give such drastically reduction due to aggregation behavior of Al$_2$O$_3$ and for latter particle itself is soft particles which will slight reduce the % elongation. Moreover all the perspective the toughness is increase of the composite in perspective of major matrix. So at binary particle content nanofillers act as reinforcement agents, but at single formed aggregates act as mechanical failure concentrators thus reduce elongation at break.

Figure 4.20: Variation of % elongation against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.
4.3.2 Flexural properties

4.3.2.1 Flexural strength

Flexural strength shows similar trend to tensile strength values, as explained before. Owing to the nature of the flexural test, strength values are greater than those of tensile samples. In flexural testing the upper half of specimens is in compression while the lower half is in tension. Thus, cracks cannot easily propagate towards the compression side. The compressive stresses tend to close the cracks rather than opening them leading to ductile behavior and higher strength. In composite containing micro particle activated carbon not affect the flexural strength due to its soft nature where the hard alumina also cannot affect the flexural strength due to no uniform stiffening of composite which supports aggregation theory [88]. In contrast for activated carbon: alumina ratio to the microcomposite shows in Figures 4.21, increase uniform stiffening result from uniform dispersion particle.

![Figure 4.21: Variation of flexural strength against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.](image)

Again the dispersion system of particle in the composite give pattern like Figure 4.22 was the main responsible for stiffening according to flexural loading behavior. However, increase alumina content in binary matrix by binary particle system also give an adverse effect on this pattern of figure 4.21, results in adverse effect on flexural testing.

![Figure 4.22: Combination of soft and hard polymer.](image)
Flexural strength of nanocomposite containing single nanoparticle, Figures 4.23 shows for activated carbon. Initially the strength keep constant but with the increase of particle increase the flexural strength which is due to the interfacial adhesion between activated carbon and the polymer matrix is strong, in case of activated carbon this adhesion is whatever but the particle itself is soft enough which result slight increase in flexural strength.

Figure 4.23: Variation of flexural strength against different concentration of carbon nanoparticle in PP/EVA matrix.

In case of alumina nanoparticle, the situation is different only 2 wt% of particle inclusion increase the flexural strength, Figures 4.24. The strength of interaction depends on the surface energy of the components. Silicates, aluminates, and titanates usually have high surface energy that leads to relatively strong interaction between the matrix and the filler. Rasheed [22] also explained that the flexural properties are strongly affected by the quality of the interface in composites. The static adhesion strength, entanglement in addition to the interfacial stiffness, acts as a main function to increase the filler reinforcement. It is expected that the flexural strength is further slightly enhanced with the addition of nano alumina particles loading, since they are rigid materials, and, by increasing the amount of their loading, rigidity of the nanocomposites increased, and hence ductility decreased.

Figure 4.24: Variation of flexural strength against different concentration of alumina nanoparticle in PP/EVA matrix.
In binary matrix by binary particle nanocomposite the similar trend of tensile strength was found than binary matrix by single particle (B/S) nanocomposite. Figure 4.25 shows that in binary matrix by binary particle system the flexural strength increase with the increase of alumina content due to two reason, one is high surface energy of alumina [91] leads to increase adhesion strength, entanglement and another is orientation pattern like Figure 4.14, this orientation act more compactly when the inter particle distance reduce which is obvious in nanocomposite. Moreover B/S system does not fully support such organization which describe before.

![Figure 4.25: Variation of flexural strength against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.](image)

**4.3.2.1 Flexural modulus**

As illustrated in Figure 4.26, flexural modulus increases as the stiff particle alumina content increases, and shows maxima at activated carbon: alumina ratio 3:2 in a fixed 6 wt% loading. After this ratio further increase in alumina decrease in the sample modulus is mostly due to imperfections resulted from aggregates (non-uniform structures) in the composition. This behavior of non-uniform stiffening is higher in B/S particle system of alumina.

![Figure 4.26: Variation of flexural modulus against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.](image)
In binary matrix by single particle system, Figure 4.27 where activated carbon shows good stiffness with the increase of particle content which support by many researchers [91-95]. More interfacial zone in PP/EVA matrix, more interaction with particle, more blockage of chain, decrease the mobability increase the flexural modulus which is max loading of 6 wt%.

Figure 4.27: Variation of flexural modulus against different concentration of carbon nanoparticle in PP/EVA matrix.

This phenomenon is rougher in case of hard filler like Al₂O₃ nanoparticles. Flexural modulus (FM) reported in this section points out that the nanocomposites emulate the rigidity of填料s and change from the normally flexible plastic to stronger materials. Figure 4.28 shows a pattern for nanocomposite indicating that nano Al₂O₃ particles cause the rising in flexural modulus. In general, when hard/rigid filler is integrated into the polymer matrix, the modulus will be enhanced [4,91]. Also nanoparticles inclusion increases the ability of nanocomposite interface to transmit elastic deformation that causes increasing of the flexural modulus values [90,92].

Figure 4.28: Variation of flexural modulus against different concentration of alumina nanoparticle in PP/EVA matrix.
In Figure 4.29, shows the combination effect of binary matrix by single particle system (B/S) and binary matrix by binary particle (B/B) system. Where, it was seen there is a linear increase in modulus in B/B system from B/S system. However, the flexural strength is higher in B/B system. This is due to the blockage of interfacial zone as well as matrix empty amorphous region by binary particle (carbon :alumina). Surface morphological study also support it which will discuss later [89,94].

**Figure 4.29:** Variation of flexural modulus against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.

### 4.3 Hardness (Shore D)

The hardness of the polymer composite containing microparticle shows in Figure 4.30. As the EVA itself is soft material (Shore A 20), so mainly it effect the ultimate PP/EVA matrix hardness. However, the inclusion of particle in binary matrix by single particle system give a slight increase in hardness which is due to stiffening behavior of particle inclusion [89, 91]. Furthermore in binary matrix by binary particle system there will be a slow increase of hardness value with the increase of alumina content on the ratio activated carbon: alumina. This is due to increase of compactness in interfacial zone as well as amorphous zone of EVA matrix.

**Figure 4.30:** Variation of hardness (Shore D) against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.
The similar trend was revealed in nanocomposite either it is binary matrix by single particle or binary matrix by binary particle. The nano particle has no great impact on hardness rather than a slight increase. In case of binary matrix by single particle system activated carbon give max hardness at 6 wt% further increase literally have no effect on hardness, Figure 4.31 shows that.

Figure 4.31: Variation of hardness (Shore D) against different concentration of carbon nanoparticle in PP/EVA matrix.

The nano alumina initially has no effect on hardness up to 4 wt%, Figure 4.32. But in 6 wt% it gives a good shift of hardness to ultimate nanocomposite. This is happen due to the creation of filler agglomeration site inside the matrix body [90,84].

Figure 4.32: Variation of hardness (Shore D) against different concentration of alumina nanoparticle in PP/EVA matrix.

The shore hardness of binary matrix by binary particle nanocomposite also has the similar trend like microcomposite which indicates there are no detritions of mechanical property rather than slight increase. Moreover all result are higher than that of basic matrix, Figure 4.33 shows the phenomena.
4.4 Thermal Properties

Thermal properties are critical to the performance, lifetime, and reliability of electronic devices. With the miniaturization, integration and functionalization of electronics and the emergence of new applications such as light emitting diodes, thermal dissipation and thermal stability becomes a challenging problem. Addressing this challenge requires the development of novel polymer-based composite materials with enhanced thermal properties. So in this study it was the main concern to develop polymer nanocomposite with better thermal performance, which is discussed below.

4.4.1 Thermal conductivity

In this study the thermal conductivity of the polymer composite was investigated with particle content as minimum as possible. Throughout the study binary matrix system PP/EVA (54/40) wt% was used and particle reinforcement of 6 wt% was maintained in nanocomposite as well as in microcomposite. The samples were designed in such way that to observe single particle (carbon or alumina) effect to binary particle (carbon: alumina) effect on thermal conductivity of the composite. From Figure 4.34, the alumina content individually has low effect on thermal conductivity of the composite. Even, the thermal conductivity of alumina is higher than that of other element in the composite system. This is due to the creation of non uniform filler agglomeration site inside the matrix body that possibly acts as a void initiation, which results hinder of phonon scattering leads to bad thermal conductor. The phenomenon was similar in case of carbon particle reinforcing microcomposite. This will prove that the isolated particles have little effect on the enhancement of the thermal conductivity until the particle form a continuous pathway through the matrix. Moreover, the shape of carbon particle assumed to be spherical while in actual practice they are irregular shaped [83]. In binary matrix by binary particle composite system, the senerio is different. Initially, thermal conductivity increases slightly with the previous composite due to isolated alumina particle aggregation in activated carbon: alumina ratio. However, the scenario will change when the alumina content increases in the fixed 6 wt% of particle. This is due to the higher alumina
creates a continuous network in interfacial zone of PP/EVA matrix which gives a higher thermal conductivity of the composite, Figure 4.35 clear that. The carbon particle creates a contact between the alumina networks which also accelerate thermal conductivity. This is why there is a shifting of thermal conductivity at activated carbon: alumina ratio of 1:4 [83,84].

![Figure 4.34: Variation of thermal conductivity against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.](image1)

The thermal conductivity (TC) also depends upon the particle size, Figure 4.35 shows that a gradual increase in conductivity with increase nanosized activated carbon. This is due to the distribution of the particles varies with particle content and particle size, which determines the properties of the composites [85,86]. Chain orientation has been the most explored route to increase thermal conductivity in polymers. However, usually high thermal conductivity can be obtained only in the orientation direction. As in PP/EVA matrix system there will produce a co-continuous structure. This structure have more interfacial zone of polymer to polymer interfacial place. This zone is a good location to create conductive pathway for activated carbon. Therefore, thermal conductivity can be significantly higher with the increase of activated carbon [87].

![Figure 4.35: Variation of thermal conductivity against different concentration of carbon nanoparticle in PP/EVA matrix.](image2)
Similar trend was found for the nano alumina in Figure 4.36, but this can be described not only by the dispersion theorem or interfacial interaction but also crystalline phenomena. Crystalline polymers generally have higher thermal conductivity than amorphous ones. In amorphous polymers, thermal conductance path that follows the chain conformation is essentially random, which reduce and causes phonon scattering [85]. Crystallization can increase the intrinsic order, which is likely responsible for higher thermal conductivity in [86]. In case of PP/EVA this can be attributed to lowering the possible phonon scattering created by vibrational mode of side group methyl and amorphous EVA by locking these sides by hard and high conductive alumina. In addition, as investigated by all-atom model molecular dynamics simulation [95], mechanical stretching is able to orient polymer chains that have very high thermal conductivity (TC). Thus enhance the TC of bulk polymers, which can be insert by nano alumina.

Figure 4.36: Variation of thermal conductivity against different concentration of alumina nanoparticle in PP/EVA matrix.

There is further improvement of thermal conductivity found in binary matrix by binary particle (B/B) nanocomposite system than that of binary matrix by single particle nanocomposite. From figure 4.37, literally have adruft shifting in binary matrix by binary particle sample; this phenomena can be describe by both dispersion theorem and crystalline theorem. As binary particle in relative ratio of carbon: alumina give both effect on nanocomposte describe above, so this shifting occur. In the B/B system PP/EVA matrix responsible to give more interfacial zone, activated carbon is soft nanosized particle ensure good dipersion and nano Al is responsible to give somewhat crystalline interaction make the B/B nanocomposite ideal for fulfill condition for High thermal conductivity: (1) strong intermolecular mechanical trape to replace weak interactions; (2) the intermolecular bonds must connect as closely as possible to polymer backbone; (3) homogeneous distribution of these bonds at a concentration above percolation threshold to form a continuous thermal network; in further give such adruft shifting in thermal conductivity. It can say for B/B composite, at the higher alumina content creates a continuous network which gives a higher thermal conductivity of the composite and the carbon particle creates a contact between the alumina networks which convert the whole matrix as conductive sheet. That”s why; we found a shifting of thermal conductivity [95].
4.4.2 DSC

This particular apparatus allows the user to analyze the physical or chemical response taking place within a sample by monitoring the energy changes occurring throughout heating, cooling or isothermal cycles. The user is, therefore, able to characterize a range of chemical or physical changes taking place within the analyzed substances (melting, crystallization, glass transition, solid-solid transition, enthalpy of fusion or crystallization, reaction enthalpy, polymerization and pyrolysis). To know such type of information about miscibility of PP/EVA matrix, interfacial entanglement or change in crystallinity, the DSC study done on some selective sample from nanocomposite which shown in Figure 4.38. The main concern of this study to develop better conductive nanocomposite without deterioration of mechanical property. So for the DSC analysis we target some typical sample which fill up the thesis target as well as can represent the whole nanocomposite system.
From Figure 4.38 and table 4.1, the PP/EVA blend has two melting peaks, indicating immiscibility of EVA and PP [90]. Which provide sufficient prove to create co continuous network and better interfacial zone in the matrix. The B/S system composites, containing (activated carbon: alumina=1:0) show a slight increase in PP and EVA melting point from pure PP/EVA matrix (activated carbon: alumina=0:0). It indicate the change in crystal structure or crystallinity of the matrix due to inclusion of carbon nanoparticle. This is also support by increase in enthalpy. Moreover, these phenomena also support by second matrix EVA. The amount of EVA will remain constant throughout the study but the enthalpy
increase with the increase of alumina particle. Which indicate the crystallinity of second matrix also somewhat increase with the increase of alumina. This is because the alumina accumulates in amorphous region of EVA and this alumina absorbs heat during melting. In contrast, the melting point and enthalpy of PP was increased with the increase of carbon particle. Which indicate the crystallinity of PP also increase with the increase of carbon particle. So, the result indicates that the PP is centric to carbon and EVA is centric to alumina. The trend of the curve confirms that a completely immiscible blend was formed, and that neither polymer had an influence on the melting behavior of the other polymer [92]. The peak temperatures of PP and EVA melting in the composites are also not significantly different from those of pure PP/EVA. This shows that nanoparticle either it is single or binary is situated primarily in the interfacial zone of both phase and strongly interacts with both at interfacial zone. As a result of this interaction, the chains are somewhat immobilized by the particles, which results in a better mechanical property in composite than that of PP/EVA. It has been reported that the addition of nanoparticle to a PP/EVA blend causes increase in enthalpy which indicates increase in crystallinity of PP/EVA. This effect is more severe in amorphous polymer EVA [90].

4.5 Water Absorption Test

To know the damping behavior of sample water absorption (WA%) is fastest method. Water absorption could lead to a decrease in some of the properties and needs to be considered when selected for applications. From Figure 4.39, it is clear that there is slight variation in WA compare to neat matrix.

![Figure 4.39: Variation of water absorption percent against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of microparticle at PP/EVA (54/40) matrix.](image)

As activated carbon and alumina itself have good water absorption [96,98], so generally they increase the water absorption in the binary matrix by single particle composite. In contrast binary matrix by binary particle system the water absorption remains constant due to keep
constant of particle wt%. Also good entanglement of particle with matrix lead to block of absorption side of this particle results the slight improve of water absorption in B/B system. In Figure 4.40, give result of binary matrix by single particle nanocomposite system where there is increasing trend show with inclusion of activated carbon content. A model was observed in some study [96,98].

![Graph of water absorption percent against different concentration of carbon nanoparticle in PP/EVA matrix.](image1)

**Figure 4.40:** Variation of water absorption percent against different concentration of carbon nanoparticle in PP/EVA matrix.

In this category the particle size reduce which leads to better surface area means better contact area with water molecule could give a gradual increase in water absorption [98], although the value of water absorption is somewhat small. Similar trend was found in the case of alumina nanoparticle [98,100,101], in Figure 4.41. After a certain content 4 wt% there is a shift of absorption which can directly affect by high water centricity by alumina [100,101].

![Graph of water absorption percent against different concentration of alumina nanoparticle in PP/EVA matrix.](image2)

**Figure 4.41:** Variation of water absorption percent against different concentration of alumina nanoparticle in PP/EVA matrix.
In addition, individual particle aggregation behavior rather than chain to particle interaction also affects the formation of micro cracks at the interface region [52,86,100]. This can increase the diffusion transport of water via them. Furthermore a capillarity mechanism becomes active here. So, water molecules flow through the interface of particle and matrix, leading to a greater diffusivity [98]. Even, the nanoparticles were distributed homogeneously in interfacial zone in binary matrix by binary particle system. But the water absorption do not changes with relative nanoparticle addition, in Figure 4.42. This indicates that the good interfacial entanglement and wetability with particle to matrix and this phenomenon block the absorption side of particle [101].

![Figure 4.42: Variation of water absorption percent against relative ratio of carbon and alumina reinforcement within 6 wt% concentration of nanoparticle at PP/EVA (54/40) matrix.](image)

Moreover it is obvious that all of water absorption value shows slight change to pure PP/EVA matrix. This indicates the slight change of hydrophobicity of both polymers by inclusion of particle; as the particle wt% is always remaining constant [101].

### 4.6 Comparative Study

From the previous discussion this is clear that the binary matrix by binary particle (B/B) composite system is more effective than binary matrix by binary particle (B/B) composite system. Moreover, this is true for both microcomposite to nanocomposite.so in this section some comparative analysis will be one among the all micro composite to nano composite in respect of B/B composite system. From the comparative (Figures 4.43 to 4.49) bar graphs it is quite noticeable that the B/B nanocomposite showed better mechanical properties and thermal properties than binary matrix by binary particle microparticulate composite. This due to the low adhesion or mechanical trapping in interfacial zone (IZ) of binary immiscible matrix as the micro particle show lower dispersion, aggregation, wettability, low acquiring the amorphous region. [85,88].This drawback mostly recover by incorporating nano sized particle with the same ratio of matrix. the thermal conductivity in binary matrix by binary particle micro composite although show better property, but it is enhance in nanocomposite up to a limit [86].
4.6.1 Tensile properties

The inclusion of high strength material will improve the composite overall strength and stiffness, so the develop composite also showing the same trend [99,100]. In addition in show betterment with reduction of particle size from micro to nano when all other ratio is fixed. Figure 4.43 shows the combine effect of carbon: alumina ratio to PP/EV matrix for micro and nano particle.

![Figure 4.43: Variation of tensile strength considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix.](image)

All the tensile strength is higher in binary by binary (B/B) composite due to better dispersibility, wet ability, more entanglement with polymer to polymer chain and polymer to particle at interfacial zone will give such result [90,94]. In B/B microparticulate composite, better dispersibility, wet ability, more entangle occur and as all parameter is fixed except the particle size. So it is a clear indication that all the cause for improving the properties is directly effect by nanoparticle in positive way. In further, from Figure 4.44, it was observed that alumina gives more stiffness than that of carbon and other host material of the developed composite, so the young’s modulus also higher except one the ratio of activated carbon: alumina (1:4), which was the indication of forming aggregation at larger microparticle size [93,95].

![Figure 4.44: Variation of tensile modulus considering two relative ratios of carbon: alumina in (54/40) matrix.](image)
From Figure 4.45, the elongation at break shows a consistency in micro composite through nanocomposite due to high elastic of about 400%, EVA content in the matrix. As because of its high amorphous zone not affected by particle; ultimately give a consistent elastic behavior of composite.

![Figure 4.45: Variation of % elongation considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix.](image1)

### 4.6.2 Flexural properties

From Figures 4.46 reveal the flexural strength comparison for microcomposite and nanocomposite.

![Figure 4.46: Variation of flexural strength considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix.](image2)

All the sample give better flexural strength, which increase with the increase of alumina content due to two reason, one is high surface energy of alumina [91] leads to increase adhesion strength, entanglement and another is orientation pattern like Figure 4.26, this orientation act more compact when the inter particle distance reduce which is obvious in nanocomposite also the nature of flexural loading. Moreover the surface area is higher in nanocomposite than that of micro composite which slightly increases this strength. Figure
4.47 shows a pattern for nanocomposite indicating that nano alumina particles cause the rising in flexural modulus.

![Graph showing variation of flexural modulus](image1)

Figure 4.47: Variation of flexural modulus considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix

Flexural modulus reported in this section points out that the nanocomposites emulate the rigidity of fillers and change from the normally flexible plastic to stronger materials. In general, when hard/rigid filler is integrated into the polymer matrix, the modulus will be enhanced [89,90]. Also nanoparticles inclusion increases the ability of nanocomposite interface to transmit elastic deformation that causes increasing of the flexural modulus values [89, 91].

4.6.3 Hardness (Shore D)

From Figure 4.48, it is observed that the size of particle has quite effect on the matrix hardness as the filling load in the matrix maintain only 6 wt%. The hardness is directly related to the inclusion particle as well as host matrix [101]. The PP/EVA matrix itself soft matrix where as the EVA is very soft (Figure 3.16). So the hardness of in B/B system gives a slow increase of with the increase of alumina content on the ratio of activated carbon: alumina. This is due to increase of compactness in interfacial zone as well as amorphous zone of EVA matrix.

![Graph showing variation of Shore hardness](image2)

Figure 4.48: Variation of Shore hardness considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix.
4.6.4 Thermal conductivity

Both micro and nanocomposite give better thermal conductivity in binary matrix by binary particle composite compare to PP/EVA matrix, due to breaking of alumina agglomerates in the binary matrix. Where individual alumina create more agglomerates, which leads to create void initiator which phonon scattering of thermal conductivity (TC). From Figure 4.49 it is clear that the particle size have a breakthrough effect on TC because in amorphous polymers (PP/EVA matrix), thermal conductance path that follows the chain conformation is essentially random, which reduce phonon scattering [83, 85].

![Figure 4.49: Variation of thermal conductivity considering two relative ratios of carbon: alumina in PP/EVA (54/40) matrix.](image)

Crystallization can increase the intrinsic order, which is likely responsible for higher thermal conductivity [95]. In case of PP/EVA this can be attributed to lowering the possible phonon scattering created by vibrational mode of side group methyl and amorphous EVA. The combination of activated carbon: Al₂O₃ lock these side by hard and high conductive alumina and activated carbon particle also give a contact between two Al₂O₃ particle, make the B/B composite ideal for Thermal conduction. All the mention phenomena can be fulfill by nanoparticle where as microparticulate partially support it. In addition, as investigated by all-atom model molecular dynamics simulation [86], mechanical stretching (melt blending) is able to orient polymer chains that have very high thermal conductivity and thus enhance the TC of bulk polymers, which can be insert by nano alumina with combination of activated carbon. That’s why the nanocomposte give a better thermal conductivity than microparticulate composite. In case of activated carbon: alumina (2:3) give a rise in TC of 170% from micro to nano where as activated carbon: alumina (1:4) give a rise of 23%, both are consider as a adruft shifting compare to PP/EVA [83, 86].

4.6.5 Water absorption characteristics

From Figure 4.50 it is observed that water absorption increase from micro to nano particulate system. This is happen due to the higher volume to surface area; better surface area means better contact area with water molecule could give a gradual increase in water absorption. Also it is already clear that in binary particle the dispersion of Al and activated carbon
particle is good which also ensure the water contact and absorption. Also activated carbon and Al itself have great water absorption, so that in all perspective it improves water absorption.

Figure 4.50: Variation of water absorption percent considering two relative ratios of carbon and alumina in PP/EVA matrix.

4.7 Surface Morphology

To study the morphology and microstructure of the nanocomposites and nanoparticles, SEM was carried out. Scanning electron microscopy used a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. It has been found out that filler dispersion and adhesion with the polymer matrix are the basis for efficiently enhancing the mechanical behavior of composites [4]. Fine control of the interface morphology of the nanocomposites is one of the most serious factors to convey the desired mechanical properties on such materials. As discuss before activated carbon particle grinded for 90 hr whereas the alumina grinded for 140 hr. So we analysis the low grinding particle for ensuring the particle size, Figure 4.51 shows the particle size distribution of activated carbon, from where it is clear that the particle mostly in nano sized and also they have good surface geometry (nanorod and spherical) which will help to mechanical entanglement, wet ability in interfacial area and create conductive pathway in the matrix.

Figure 4.51: SEM micrograph of activated carbon.
Figure 4.52, represent the SEM image of tensile fracture surface for PP/EVA (60/40) matrix. The image clearly revealed that both polymers create a co-continuous phase. This co-continuous phase would facilitate the particle to locate in interfacial zone rather than the matrix body. As a result good wetability and entanglement occur at the interfacial area. This leads to good stress distribution from the matrix to the filler throughout the tensile loading [19, 26, 27]. Also such type of co-continuous phase gives a route to particle for creating conductive pathway of conductive particle.

Figure 4.52: SEM micrograph of tensile fracture surface of PP/EVA (60/40) wt% composite.

The tensile fracture surfaces of PP/EVA matrix containing 6 Wt % of carbon microparticulate composite was investigated, in Figure 4.53. As per expectation there are some agglomerates of carbon particle found which actually responsible for lower mechanical property. However, there is some uniform distribution of carbon micro particle with good interfacial bonding which gives a uniform stress distribution. Figure 4.54, show the highlighted point (1) in Figure 4.53 with high magnification.
Figure 4.53: SEM micrograph of tensile fracture surface of PP/EVA/carbon (54/40/6) composite containing.

Figure 4.54: Highlighted point (1) of tensile fracture surface of figure 4.53.

Similar pattern of the tensile fracture surfaces of PP/EVA matrix containing 6 Wt % of alumina microparticulate composite was investigated, in Figure 4.55. As per expectation there are some agglomerates of alumina particle found which are bigger. In addition it has several voids in its structure make it very weak to withstand against stress. The microstructure of this sample revealed for its worst mechanical properties.
Figure 4.55: SEM micrograph of tensile fracture surface of PP/EVA/alumina (54/40/6) microcomposite.

The SEM micrograph of binary matrix by binary particle composite containing activated carbon and alumina was shown in Figure 4.57 where it was revealed how uniformly particle are distribute to the interfacial zone (IZ) which actually made possible to give some unique characteristics.

Figure 4.56: SEM micrograph of tensile fracture surface of PP/EVA/carbon/alumina composite containing carbon: alumina (2:3) in PP/EVA (54/40) microcomposite.
Also a crucial point (1) in Figure 4.56 shows in Figure 4.57 with high magnification, which revealed the formation of conductive pathway of activated carbon and Al at interfacial area. So for the uniform particle distribution and conductive pathway, this sample gives better result among the micro composite.

Figure 4.57: Highlighted point (1) of tensile fracture surface of figure 4.56 showing conductive network of conductive nanoparticle.

In case of nanocomposite the tensile fracture surfaces of PP/EVA matrix containing 6 Wt % of carbon nanoparticle were investigated. A typical fracture surface is presented in Figure 4.58, where the similar pattern of single particle composite was observed but for particle size reduction gives more uniformity in agglomeration, bonding or entanglement. The micrograph shows some void is the weak point for crack propagation and failure. But compare to the micro particle structure are more uniform and gives some extended properties which we discuss respective section.

Figure 4.58: SEM micrograph of tensile fracture surface of PP/EVA/carbon (54/40/6) nanocomposite.
Similar composition of nanocomposite having nano alumina investigated following, Figure 4.59, where also find uniformity in particle interfacial distribution and bonding.

![Figure 4.59: SEM micrograph of tensile fracture surface of PP/EVA/alumina (54/40/6) nanocomposite.](image)

In this investigation also revealed that some of the nanoparticle also interact with EVA phase and make good bond, which ultimately increases the mechanical property as well as thermal conductivity. But according to the previous study alumina particle always tries to agglomerate [93], which is also found in that study. Moreover, this investigation shows some conductive pathway (Figure 4.60), which prove to bumping the thermal conductivity on this nanocomposite.

![Figure 4.60: Highlighted point (1) of tensile fracture surface of Figure 4.60 showing conductive network of conductive alumina nanoparticle.](image)
In Figure 4.61, finally the SEM investigation done on particle containing activated carbon: alumina (1:4), in the micrograph it is clear to form a wider conductive pathway than before which reveal the reason of higher thermal conductivity. Also the sample give clear prove of interfacial location of activated carbon and alumina particle (Figure 4.62) and their strong bonding, entanglement and wet ability (Figure 4.63). To be a unique nanocomposite this micrograph support all condition, that”s why the property of this composite also unique than other which is the main purpose of this study.

Figure 4.61: SEM micrograph of tensile fracture surface of PP/EVA/carbon/alumina composite containing carbon: alumina (1:4) in PP/EVA (54/40) nanocomposite.
Figure 4.62: Nanoparticle at interfacial zone of PP/EVA/carbon/alumina composite containing the relative ratio (1:4).

Figure 4.63: Highlighted point (1) of tensile fracture surface of Figure 4.62 showing good bonding of PP/EVA/carbon/alumina composite containing the relative ratio (1:4) of nanoparticle.
CHAPTER FIVE
CONCLUSION
In the present research, binary matrix (polypropylene, PP and ethylene vinyl acetate, EVA) by single particle (carbon or alumina) and binary matrix by binary particle (activated carbon: alumina) composites were fabricated with hot press technique following pre-melting and blending of a fixed 6 wt% of filler. The fabrication system was done both for microparticle and nanoparticle in binary matrix, which is named, respectively, microcomposite and nanocomposite. The particles used as a microparticle in microcomposite were converted to nanoparticle by means of ball milling and hand grinding in a mortar pastel. After development of the composite; it was characterized by several techniques such as FTIR, tensile, flexural, thermal conductivity, DSC, SEM and water absorption tests. The main concern of this study is to develop a composite, which have better thermal conductivity without deterioration in the mechanical properties of the basic matrix materials. Also to find out whether organic (activated carbon) or in-organic (alumina) nanoparticles is good for functional property (thermal conductivity) enhancement or not. Throughout the study PP/EVA used as binary matrix and alumina/carbon used as binary particle, where PP/EVA/particles have 54/40/6 (wt%) in combination. After the detail investigation the following final conclusions have been made from this research:

a. The tensile strength of composites of the binary matrix reinforced by binary particles increased with increasing alumina content in relative particle ratio of activated carbon and alumina. But, when the reinforcing particles are used individually in the composite, relatively inferior tensile strength has been observed. Similar trend was also found in tensile modulus. However, addition reinforcing particles separately did not decrease the tensile strength to any level lower than the base level of the binary matrix PP/EVA, which indicates no deterioration of mechanical property of the basic matrix materials have been caused by particle addition.

b. The percent elongation of the developed composite is decreased with the increase in the alumina particles in the binary matrix. The same phenomena have also been found when the particles are used individually in the composite. However, there is important target to select such PP/EVA matrix for composite design, which is to improve the draw ability of pure PP. In this study, it is found that whatever the particle content the %elongation is always greater than pure PP, which is the indication of the fulfillment of the basic research target, the good draw ability of the ultimate nanocomposite.

c. As like tensile strengths, flexural strength and flexural modulus also increased with the increase in the content of alumina particle in the relative ratio of activated carbon and alumina in the nanocomposite. The flexural strength and flexural modulus are optimum at activated carbon and alumina ratio of 1:4 in the nanocomposite.

d. Detail SEM analysis revealed that, in the case of binary PP/EVA polymer, co-continuous phase of the participating polymers is formed. SEM study also revealed more reinforcing particles in the interfacial locations of the co-continuous phases and that the interfacial bonding between the co-continuous phase and the reinforcing particles are quite good. Concerning this, composites with activated carbon: alumina
to 1:4 in both nanocomposite and microcomposite showed better reinforcing particles pathways.

e. In the case of PP, EVA and PP/EVA binary matrix, characteristics peaks of various molecular bonds have been observed in the FTIR spectra. However, after addition of micro or nano particles of carbon or alumina no additional peak other than characteristics peak of basic polymer matrix has been found. This interesting observation suggests that no additional bond formation occurred during the composite formation.

f. DSC was carried out to justify the miscibility and any change of crystallinity in the polymer matrix. In DSC spectra two characteristics peaks were clearly observed that indicates the presence of two immiscible co-continuous phases in the PP/EVA binary polymer composite. After inclusion of the reinforcing particles in the polymer matrix, a slight increase in the melting points of both polymers PP and EVA to higher temperatures was also observed in the DSC investigation.

g. Thermal conductivity was determined by Lee disc apparatus. Individually EVA has higher thermal conductivity than that of PP and that their blend PP/EVA matrix also shows lower thermal conductivity compared to that of the single EVA. However, it is better than that of the single polypropylene.

h. The PP/EVA binary matrix containing single filler either activated carbon or inorganic alumina particle exhibited lower effect on thermal conductivity. The binary matrix shows slight increase on thermal conductivity when it is reinforced with activated carbon. But the increment in the thermal conductivity is more significant when alumina is added as reinforcing particle. The above observation is consistent for both microcomposite and nanocomposite.

i. The composites containing binary reinforcing particle show better thermal conductivity in both microcomposite and nanocomposite, where the thermal conductivity of nanocomposite is 23% higher than that of the microcomposite. Also it was observed that the ultimate thermal conductivity of the developed nanocomposite is nearly 13 times higher than that of the pure PP with 6 wt% of nanoparticle and 10 times of that of the PP based microcomposite.

So, after analysis the details characteristics it can be wind up that the binary matrix (PP/EVA) reinforced by binary particle (activated carbon/alumina) shows the optimum result in all perspective than binary matrix (PP/EVA) by single particle (activated carbon or alumina). The present study would provide practical and theoretical supports for thermal conductive polymer composites with good synthetic properties.
Future Work

Materials research is moving towards ever more controllable and predictable material properties. These properties can be mechanical, self-corrective or optical, and they may be related to permeability, reactivity, shape memory, density, electric conductivity or thermal conductivity. The future world leads to smart materials, nanostructure materials and self controllable materials. For that perspective the present study is just forwarding towards the future. Today, conductive polymer composite is intense research era for miniaturization of electronic device and to meet the imagination of human. So, this study has broadened future perspective, some are listed below:

1. To develop electrically conductive material as well as thermally conductive materials by the use of same technique named binary by binary composite system.

2. In this study two particles was used, this investigation can also be continued for functionalized particle, functionalized fiber, carbon nanotube, grapheme or other high conductive fibre, to developed multi functional nanomaterials.

3. By the use of conductive novel particle this materials can be converted to tunable materials which can change its self structure by stimuli of environment.

4. High strength smart fibre can be designed for smart textile application.

5. This study also can be extended to design smart biomaterials for the use in tissue engineering where it can control the growth of tissue by thermal or electrical action.

6. The similar study can carried out to develop the nanofibre with suitable spinning system, which can be useful fibre to design artificial organ.
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