CHAPTER 1
INTRODUCTION

1.1 Background

Owing to extraordinary range of physical and mechanical properties, polymeric materials (polymers and plastics) play an essential and ubiquitous role in today’s life. Still, the ever increasing demand for newer, lighter materials with higher strength, greater stiffness, and better reliability has led to extensive research for the development of composite materials. These materials offer a combination of strength and modulus that are either comparable to or better than many traditional materials such as metals or alloys. Owing to their low specific gravities, the strength-to-weight ratios as well as modulus-to-weight ratios make them markedly superior to the metallic materials. In addition, fatigue strength-to-weight ratios as well as fatigue damage tolerances of many composites are excellent and make them viable candidates for many applications. Until recently, the use of composites has primarily been limited to high performance aerospace and sporting applications. However, with the explosion of the information age and higher demand for materials with superior properties from the private sector, composites are now making their way into more common applications. Along with this demand comes the necessity to understand the static and dynamic mechanical behaviour, long term durability, and environmental stability of these materials.

Most composites are reinforced with long continuous or short chopped fibres and are primarily carbon or glass based. On the other hand, the matrix can either be a thermoset or thermoplastic. Furthermore, the interface between these materials must have the proper level of adhesion so that the properties of both materials can be used fully. This must lead to a composite which has a balance of strength, environmental protection, and damage tolerance (Folkes, 1982; Baird and Collias, 1998). Thermosets have accounted for most composite matrices. This is largely due to the low viscosity of thermosetting resins which makes composite fabrication a relatively simple process (Singh, et al., 2002). Epoxies account for most of these thermosetting matrices because they are easy to process, have a low shrinkage upon cure, have good electrical properties, have high chemical resistance, and adhere well to many reinforcing materials. But epoxies have upper use temperature and environmental limitations. This drastically limits their use in many common durability applications. Furthermore, the
high demand for recyclability makes thermosets unappealing. This has spawned new studies investigating the replacement of thermosets with high temperature thermoplastics. In contrast to thermosets, thermoplastics do not have a cross linked structure and therefore can be recycled. Furthermore, thermoplastics have the potential for high volume processing, low cost, and parts with superior impact resistance as compared to their thermosetting counterparts. Thermoplastics also have a very long shelf life, shorter fabrication time, and meet many other requirements such as abrasion resistance and UV resistance. But thermoplastics also have their disadvantages: creep, limited temperature capability, and limited processing techniques (Folkes, 1982).

Although, the use of thermoplastics poses several limitations, efforts are currently being made to synthesize thermoplastics that can be used in a wider range of applications. Initial efforts have looked at using semi-crystalline thermoplastic matrices to enhance thermoplastic composite properties. However, these composites are more complex than amorphous materials, and their microstructures are not well understood. For example, in many semicrystalline polymer matrix composites, interphase morphology between the fibre and matrix termed transcrystallinity is formed due to the presence of the reinforcement. This region forms due to the high nucleation density on the fibre surface, and its effect on the mechanical properties of the composite is not well understood (Folkes, 1982).

There has been much debate in the literature as to whether this region is important in composites, how it is formed, and what effects it has on the composite properties. The recent achievements in nano-composite technology have fuelled the need for new knowledge and findings resulting development of respective polymer nano-composites like polyamide.

For years, fillers have been used extensively to improve properties of polymeric material. Besides the increment obtained in stiffness, hardness, abrasion resistance, and reduced cost of the filled material, the addition of filler to polymer also modify their flow behaviour and consequently their process ability (Zuiderduin, et al., 2003; Wu, et al., 2004; Supaphol, et al., 2007). The use of CaCO₃ as filler in polyamide composites by manufacturers has been growing since further years and today it plays a dominant role as the most widely used filler in polymer composites (Samsudin, et al., 2006; Zhang, et al., 2011). In fact, CaCO₃ in most cases is cheaper than other fillers like talc and it takes an overwhelming proportion of the filler market in plastics (Zhang, et al., 2011). It has been well documented that the general behaviour of adding fillers to
polymers will increase some properties like viscosity and or decrease melt elasticity of the polymer (Lazzarri, et al., 2005).

Hence, the study of such properties like morphological, physical, mechanical, and rheological etc will be important in controlling the filled polymer in processing operation in order to know how the flow would behave under different conditions of temperatures, pressure, etc. Furthermore, availability of CaCO₃ with variation in size, shape and chemical structure will greatly influence the flow of the composite systems. For instance, an important thing of the rheological study is helping one to carry out theoretical analysis of the mechanics of flow for rheologically complex polymeric material in various kind of processing equipment. Such a theoretical study will be useful for designing better processing equipment and determining optimal processing conditions.

1.2 Nanotechnology

In recent years, engineers and scientists have realized that the dynamics of a complex system cannot be understood by considering each of its parts in isolation. In consequence, systems approaches have become dominant across the spectrum of the natural sciences and engineering. The result of consistent endeavors and researches of scientists and researchers in different scientific areas has caused to lead to an emerging interdisciplinary scientific area that can be referred to as nanotechnology (Ghadami, et al., 2011).

‘The first person who pointed out the importance and promising outlook for nano-particle investigations was the outstanding American physicist, Nobel Prize Winner R. Feynman (1960). In his lecture entitled “There’s Plenty of Room at the Bottom. An Invitation to Enter a New Field of Physics,” delivered on December 29th 1959 at the California Institute of Technology, Feynman paid attention to the problem of substance structure control on the scale of ultra-small distances. In particular he pointed out that “… when we have some Control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do … The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed” (Sysoev et al. 2009). Nowadays, realization of Feynman’s scientific dream is called nanotechnology. The term “nanotechnology” was introduced into everyday life in 1974 by the Japanese
scientist Taniguchi at the conference of the Japan Society of Precision Engineering (Tretyakov, 2008).

Nanotechnology is the fusion of material science, chemistry, physics, and engineering sciences for creation of a suitable method or a process for constructing of useful structures and producing of tools which at least possess a nano-metrical dimension in the size of 1 to 100 nano-meters (i.e. 1 nm to 100 nm; 10^{-9} m to 10^{-7} m) (Alberts, et al., 1989; Murday, 2002; Sysoev, et al., 2009). These materials due to their nano-metrical dimensions can possess unique biological, chemical, physical, and mechanical characteristics in comparison with similar materials which are possessing big nano-metrical dimensions. Generation of nano-metric structures (nanostructures), make the following developments possible: controlling the essential (basic) properties of materials like melting point, magnetic behavior, color, thermal properties, absorbability and charging capacity without any change in chemical nature. Therefore, it is predicted that in near future, nanotechnology may give rise to an efficient extensive industrial revolution (Murday, 2002).

Nanotechnology investigations embrace various fields of science and engineering, including physics, chemistry, electronics, mechanics, biology, medicine, aviation and cosmonautics, and other, more narrow, branches of human activity. With the advent of advanced equipment (lithographs of nanometre resolution, precision vacuum systems for sputtering, etching, epitaxy, and others) and methodologies (chemical processes for the synthesis of nano-particles, molecular clusters, and their assembling into more complex systems) intensive “construction” of nano-objects and nano-systems began. At first, mostly traditional methods were used for these purposes, and then newly developed, original methods appeared (Andriyevsky, 2006; Alencar, et al., 2006).

The 7th International Conference on Nano-structured Materials recommended the following classification of nano-materials (Tretyakov, 2008):

1. Nano-porous structures;
2. Nano-particles;
3. Nano-tubes and nano-fibres;
4. Nano-dispersions (colloids);
5. Nano-structured surfaces and films;
As is clear from the above list, nano-materials are objects of molecular physics, or, using chemical terminology, they are objects of physical chemistry. However, in this branch of science there are no sharp boundaries between physics and chemistry. Among the types of nano-materials listed above the most interesting for physicists are the ones composed from nano-particles, nano-tubes, and nano-fibers, because they are the most promising for practical applications (Tretyakov, 2008).

1.3 Practical Applications of Nanotechnology

Consideration and investigation on generation of nano-structured materials and application of them in different areas of sciences and industries is relatively new field and the first research articles in this area, has been nearly published since last two decades. In 1985, Harry Kroto and Richard Errett Smalley in Rice University succeeded to synthesize the molecular cages, C60, from carbon atom. In 1991, the first carbon nano-tubes (CNTs) with extremely high mechanical strength, exceptional electrical and highly thermal resistance properties have been presented by Sumio Iijima. This was the milestone for building and development of nano-composites which may be used in military industries, air-space and the other engineering applications (Murday, 2002). According to the opinion of foreign military experts, applications of nanotechnology in the military industry could have a greater impact on the character of future military operations than even the invention of gunpowder (Bocharov, et al., 2006). To date, CNTs are being employed to usher a new revolution in the field of advanced materials and systems (Murday, 2002).

Big pharmaceutical companies have developed their researches to decrease the dimension or size of drug powders or particles. It has been proved that the finer and smaller drug particles cause the better and sooner digestion and adsorption inside the body within the digestion system. Therefore, decreasing the particle size cause to lower the assimilation time of drug into the body and consequently, the necessary dose of required drug will be diminished. The other main proposition of nanotechnology is the possible emergence of nano-robots. Manufacturing of special systems are still under investigation for the sake of arranging atoms by using the concept of self assembly. This makes possible automatic manufacturing of products without any traditional workforce like copying in Xerox machine. Nanotechnology advances have opened several new fields of activity based on nano-materials. This has led to the birth of molecular electronics, which rests upon the quantum properties of nano-objects.
(Smalley, 1997; Grungberg, et al., 2007). The electronic Industry with the miniaturization trend of electronic parts and tools have been developed and doing research (working) in the smaller dimensions leads to manufacturing a tool which is able to manipulate single atoms of proteins in potato and also replication of soil, air and water atoms from their original atoms (Kamel, 2007).

One of the most important nanotechnology applications is the creation of new materials, which can lead to radical transformations of industrial technologies. The main directions of activity in this area are listed below (Kamel, 2007):

1. Design of information technology devices,
2. Synthesis of nano-sized metal composites (oxidemetal materials),
3. Manufacturing of fire-resistant plastics and reinforcing materials in the form of dispersed nano-particles.

Nano-catalysts are amongst the other useful achievements of nanotechnology. Using of nano-catalysts due to their very large ratio of area to volume (so called, aspect ratio) increases the performance of nano-catalyst to react with different reactants. Finally, in addition to the nano-catalysts efficient role in increasing the rate of chemical reactions and especially combustion reaction, nano-particles may also be able to significantly decrease the pollution caused by different environmental pollutants. The most likely technical capabilities of nanotechnology can be summarized as following (Murday, 2002; Apresyan, et al., 2009):

1. Novel inventions
2. Manufacturing of self-assembled products
3. Manufacturing extremely high speed computers with a rate of billion fold of recent conventional computers
4. Safe and cost-effective travels to space
5. Medical nanotechnology may conquer over deadly diseases and may provide early symptoms of different diseases so as help very old people and prevent their ailments and occurring of pre-matured early death.
6. Re-survival of declined animals and plants
7. Organization and fertilization of agricultural lands etc.

The above-mentioned issues are merely the limited number of expected products of nanotechnology. The human being is subjected to an accelerated and powerful social revolution that is originated from the science of nanotechnology. In the near future, a group of scientists may be able to manufacture the first nano-metric robot which can be
replicated (or it is able to do replication). It is expected that during the next several years, production of five billions of trillions of nano-robots may make all industrial processes totally automized and all current workforce may not be required. Frequent access to the plenty of consumption goods and materials will be made easy and they will be inexpensive, durable and stylish. Pharmaceutical industries will experience a fast quantum movement on ahead. So, due to these changes and the other main reasons, the lifestyle of people will be essentially revolutionized all over the world and the behavioural pattern of men will be affected by this obligatory trend (Apresyan, et al., 2009). Nanotechnology is not an independent, isolated circle but rather one that overlaps all of the existing circles and will continue to grow as the field is developed, as shown in Figure 1.1.

![Figure 1.1 Nanotechnology encompasses all fields.](image)

In the past decade, nanotechnology has grown into a billion dollar research enterprise with an explicit aim of rapid commercial deployment, as shown in Figure 1.2. The definition of nanotechnology offered by the US National Nanotechnology Initiative (NNI) is: “the understanding and control of matter at dimensions of roughly 1 to 100 nano-meters (a nano-meter is one-billionth of a meter), where unique phenomena enable novel applications” (Roco, 2007).
1.4 Polymers

Polymeric materials are widely used due to their unique attributes: ease of production, light weight, and often ductile nature. However, polymers have lower modulus and strength as compared to metals and ceramics (Tseng, et al., 2002; Arbatti, et al., 2007; Zhou, 2008; Lim, et al., 2008). One way to improve their mechanical properties is to reinforce polymers with inclusions (fibers, whiskers, platelets, or particles). The embedding of inclusions in a host matrix to make composites, which gives material properties not achieved by either phase alone, has been a common practice for many years. Using this approach, polymer properties can be improved while maintaining their light weight and ductile nature (Rong, et al., 2001; Shen, et al., 2007; Aravinda, et al., 2007; Xu, et al., 2008). Improvements in properties can often be found even at relatively low filler content (Wu, et al., 2002). Recently, processing techniques have been developed to allow the size of inclusions to go down to nanoscale.

1.4.1 Polyamide-66

Polymers containing an amide group –CONH– as a recurring part are called Polyamides or nyons. Polyamides are crystalline polymers typically produced by the condensation of a diacid and a diamine (Araujo, 2007; Barbosa, et al., 2008). There are several types and each type is often described by a number, such as nylon 66 or Polyamide-66 (PA66). Poly (hexamethylene adipamide) (PA66), is one of the most
famous engineering thermoplastics because of its excellent physical and mechanical properties (Won, et al., 2001). Nylon was discovered by Wallace Hume Carothers in 1935 at the Dupont Company and the introduction of PA66 as toothbrush filaments by DuPont in 1938 was the first polyamide application (Kohan, 1973). In recent years, the increasing interest in polyamides results from their higher melting points to extend the boundaries of this polymer type to satisfy more stringent high temperature automobile and electronic applications (Kroschwitz and Mark, 2003).

PA66 is a semicrystalline polymer that is synthesized by stepwise polymerization between a diacid and a diamine (Elzein, et al., 2002; Baldi, et al., 2006). The first integer of PA 66 represents the number of carbon atoms in the diamine and the second integer belongs to the number of carbon atoms in the dicarboxylic acid (Seymour and Carraher, 1984). The synthesis reaction is given in Figure 1.3 (Elzein, et al., 2002; Baldi, et al., 2006).

![Figure 1.3 Synthesis reactions of diadic polyamides.](image)

1.4.2 Crystalline Structure of Polyamide-66

PA66 (nylon-66) has a polymorphic structure and two phase crystallinity arises from the different spatial arrangement in the hydrogen bonding between the oxygen in the carbonyl group of one polyamide molecular chain and the hydrogen attached to the nitrogen in the neighbouring polyamide molecular chain. It cannot readily be drawn to high extensions because of the presence of intermolecular hydrogen bonding. Both crystalline and amorphous phases have hydrogen bonds within their structure and the hydrogen-bonded crystallites behave like quasi-cross links during drawing, restricting
the achievable drawing ratio and limiting control over polymer microstructure (Vasantha, et al., 2004).

The crystal structure of PA66 is composed of triclinic α and β form with one chemical per unit cell (Kohan, 1973). The lower temperature α phase contains chain folded sheets and is a consequence of the linear hydrogen bonds, imparted by progressive shear of chains, between amide groups in the adjacent chains within the sheet (Kang, et al., 2005b). The molecules are in the fully extended zigzag conformation. The higher temperature β phase is not a distinct phase in the thermodynamic sense and it results in a slight perturbation of α phase (Kohan, 1973). The intersheet shear of chains occurs alternately in c direction rather than progressively within pleated sheets of chains joined by hydrogen bonds (Kang, et al., 2005b). Interaxial angles of triclinic structure of PA66 are unequal and it is of low symmetry (Kohan, 1973). Schematic representation of PA66 unit cell is shown in Figure 1.4 (Chow, et al., 2004; Lu, et al., 2004).

Ideal unit cell of PA66 consists of all trans chain conformations hydrogen bonded into sheets (ac plane (010) plane) and the intersheet stacking is controlled by van der Waals interaction (Lu, et al., 2004). The growth axis of crystalline lamellae is in “a” direction. The number of H bonds between the two faces of the lamellae determines the thickness, it is about 4xc for bulk PA and it is nearly 6 nm for PA66. The angle between the c axis and the direction normal to the chain folded plane is 13°. As a result, the angle between the C=O transition moments and the average angle between the normal to the chain folded plane is equal to 13° (Elzein, et al., 2002). The good balances of properties are improved by the semicrystalline structure. The crystalline regions enhance the stiffness, strength, chemical resistance, creep resistance, temperature stability and electrical properties; while the impact resistance and high elongation are affected by the amorphous region (Kohan, 1973).
In many applications polyamides have been reinforced with mineral fillers like aluminium or calcium silicates or with glass and carbon fibers. Mineral fillers result in increase of modulus and elasticity and tensile strength, decrease in elongation, while glass or carbon reinforced fibers result in improved Izod impact strength. In reinforced or filled polyamides the issue is the efficiency of bonding agents and the aspect ratio that is the length to diameter ratio of the fiber in the final product. The applicability of polyamides in different applications has been enlarged with the emergence of nano-composites. Improved properties in terms of strength, heat deflection temperature, dimensional stability, gas barrier, flame retardancy, and electrical conductivity can be listed as highlighting features of polyamide nano-composites (Araujo, 2007; Barbosa, 2008). Figure 1.5 shows various applications of polyamides (Morgan and Wittbecker, 1959).

### 1.5 Composites

Since thousands of years, men have been using natural and engineered composite materials. Materials like wood, i.e. polymer-polymer composite made of cellulose fibers in a lignin and hemicelluloses matrix, or bone, i.e. polymer-ceramic composite made of hydroxyapatite reinforced with collagen fibers, teeth or ivory, are natural composites. In ancient Egypt, more than 5000 years ago, brick makers used to add short lengths of straw to Nile mud mixed with sand and water, in order to improve
the mechanical properties of the bricks. Like in Mesopotamia, this combination of materials was also employed to make tubes designed for the transportation of water. Examples of more recent composites are concrete (cement-gravel and sand composite), cermets (ceramic-metal composite), reinforced rubber (carbon–polymer composite), arborite (paper-melamine composite), etc. By definition, a composite material is made of two or more constituents with significantly different physical and chemical properties and which remain separate and distinct within the final structure. This combination (hopefully) leads to a synergy of structural (e.g. mechanical) and/or functional (e.g. electronic, optical, etc.) properties compared to each constituent separate (Utracki, 1995).

![Figure 1.5](image-url)

**Figure 1.5** Nylon readily tailored to market needs (Morgan and Wittebecker, 1959).

These constituents of a composite can be classified in two categories: the matrix, i.e. the dispersing or continuous phase and the reinforcement, i.e. the dispersed phase. Because of the large variety of types of matrices (metallic, inorganic, polymeric, etc.) and dispersed phases (fibers, particles, crystals, etc.), the design potential of composite materials is extremely large (Utracki, 1995). Nowadays, one of the most widely used categories of materials is based on fibers randomly dispersed in a matrix,
notably an organic polymer matrix. This specific type of composites has gained a growing importance since the beginning of the eighties, and the continuous technological improvement of these materials has opened the way to large application domains ranging from sport equipments, leisure activities, entertainment, to advanced technologies (like in automobile, aeronautics, etc.). Depending on the intrinsic properties of the added filler, not only the mechanical performances of the matrix can be improved, but also the fire resistance, the electrical and/or the thermal properties, etc (Lu, et al., 2006; Lu and Wong, 2007).

1.5.1 Polymer Composites

Since the last century, polymeric materials have been widely used in many areas, such as in civil life and military applications. Now polymers are the fastest growing materials in the world. Between 1980 and 1990, the production of plastics increased by 62% while that of steels decreased by 21%. The annual overall production of polymeric materials has exceeded that of metal materials if computed in volume (Utracki, 1995). A composite is a type of material that consists of two or more components with largely different chemical or physical characteristics. The preparation of a composite from two or more materials is one of the most important approaches to produce new materials, because few pure materials fulfill the strength, design, and cost requirements of modern applications. In the 1960s, polymer composites became one of the research focuses in materials science. Since then, many conventional polymer composites have been prepared. These composites possess better chemical or physical properties than pure polymeric materials, such as high strength and modulus, good dimensional stability, improved chemical and corrosion resistance, and various functionalities (Garces, et al., 2000; Lau, et al., 2005; Yasmin, et al., 2006). Polymer composites are prepared by mixing polymers with inorganic materials such as reinforcing fibers (e.g., glass, carbon, aramid etc.) and particulate solids (e.g., talc, carbon black, calcium carbonate, mica etc.). Such composites exhibit physical properties synergistically derived from both the organic and inorganic components, for example, they show superior mechanical properties and higher heat deflection temperature compared to the pristine polymers while maintaining processibility (Eitan, et al., 2003; Andrews and Weisenberger, 2004; Zhang, et al., 2006; Lu, et al., 2006; Lu and Wong, 2007). Modification of organic polymers through the incorporation of additives yields, with few exceptions, multiphase systems containing the additive
embedded in a continuous polymeric matrix. The resulting mixtures are characterized by unique microstructures or macrostructures that are responsible for their properties. The primary reasons for using additives are:

1. property modification or enhancement;
2. overall cost reduction;
3. Improving and controlling of processing characteristics.

Important types of modified polymer systems include polymer composites, polymer–polymer blends, and polymeric foams (Zhou, et al., 2007).

1.5.2 Polymer Nano-composites

Although, polymers possess less stability and low module in comparison with metals and ceramic, and one of the best ways for modifying of their mechanical characteristics is the use of addable such as filling (calcium carbonate is used as a filling in nutrition, paint making, pharmacy, and plastic). Therefore, making of composites in various methods has become a usual affair since last years. Nano-composites are composites in which at least one of the phases shows dimensions in the nanometre range (1 nm = 10^{-9} m) (Roy, et al., 1986; Choa, et al., 2003; Fischer, 2003; Pandey, et al., 2005).

Nano-composites are creating from the distribution (admixture and distribution) of material nano-particles (distributed phase) in Matrix (constant phase) (Choa, et al., 2003; Roy, et al., 2005; Marosfoi, et al., 2006; Hedicke, et al., 2006; Kim, et al., 2007; Passaglia, et al., 2008; Chaisan, et al., 2009). Matrix can be mono-sectional or poly-sectional and it can be a metal, ceramic, and or polymeric material and distributed phase can be a material like fortifiers, conductors, softeners, resistant, and some other materials. The way of mixing and distributing of particles in polymer matrix is a vital and distinguishable factor in nano-composite treats and various methods are invented and used for this case. But yet, finding of a universal method to be responsible for all polymers and addable is a hard task. Because, every polymer possesses its own physical and chemical nature, furthermore, the available tools for researchers are various. Any polymer needs its own process conditions and we should find them according to the process efficiency and products favourite characteristics (Marosfoi, et al., 2006; Hedicke, et al., 2006; Kim et al., 2007). Totally, there is not any simple process to make nano-composites. It seems that methods like, Micro-emulsion, Melt Mixing, Extrusion, and Compression molding would be the selected methods of the
researchers. Briefly, decision-making about the application of various methods depends on extent of particles distribution for any researcher.

1.6 Nano-particles

Nano-scale materials are commonly characterized by at least one dimension in the nanometer range (1 nm = 10^-9 m) (Rao, et al., 2004). Nano-particles are defined as particles with size in the range of 1 to 100 nm at least in one of the three dimensions. Because of this very small size scale, they possess an immense surface area per unit volume, a high proportion of atoms in the surface and near surface layers, and the ability to exhibit quantum effects. The resulting unique properties of nano-particles cannot be anticipated from a simple extrapolation of the properties of bulk materials. Nano-particles exist with great chemical diversity in the form of metals, metal oxides, semiconductors, polymers, carbon materials, organics or biological. They also exhibit great morphological diversity with shapes such as spheres, cylinders, disks, platelets, hollow spheres and tubes, etc. Nano-particles can be generated via a number of synthetic routes based on gas, liquid or solid phase approaches. The synthesized nano-particles have to be surface modified in most cases, in order to passivate and stabilize them since their nano-scale renders them chemically very reactive and/or physically aggregative. The nano-particles are also surface functionalized in order to meet the needs of specific applications. Nano-particles serve as the fundamental building blocks for various nanotechnology applications (Shenhar, et al., 2005; Perez, et al., 2005). The transition from micro-particles to nano-particles yields dramatic changes in physical properties (Hussain, 2006). Nano-particles in general have high surface area for a given volume (Luo, 2003). The enormous diversity of the nano-particles, as shown in Figure 1.6, arising from their wide chemical nature, shapes and morphologies, the medium in which the particles are present, the state of dispersion of the particles and most importantly, the numerous possible surface modifications the nano-particles can be subjected to make this an important active field of science (Shenhar, et al., 2005).
Figure 1.6 Various features contributing to the diversity of engineered nano-particles:
The same chemical can generate a wide variety of nano-particles.

In the nano-scale range, the materials structures and properties differ significantly from those of single atoms or molecules but also from bulk materials. These unique properties bring nano-scale materials into an emerging wide area of applications. One of the interesting properties of nano-scale materials is the decreasing melting temperatures with decreasing size as an effect of the increasing number of surface atoms. Since the number of surface atoms increases with smaller particles, these atoms can be more easily rearranged than those in the centre of the particles, and thus the melting process can start earlier (Klabunde, 2001). As can be seen in Figure 1.7, there is a dramatic decrease of the melting points for particles smaller than 3-4 nm (Castro, et al., 1990). The effect of the increasing number of surface atoms with decreasing particle size also makes small metal nano-particles becoming a highly reactive catalyst as the area of surface active centers for catalytic processes will also increase (Klabunde, 2001).
Another interesting point of nano-particles is their magnetic property. Whilst magnetic bulk materials are usually formed from multiple magnetic domains, small magnetic nano-particles often consist only of one domain and exhibit a phenomenon known as super-paramagnetism. In this case the overall magnetic coercivity is lowered as a result of random processes of the particle magnetization due to thermal fluctuations (Kelsall, et al., 2005). Concerning optical properties, the effect of the reduced dimensionality on the electron structure has a strong impact on the valence band and the conduction band (Kelsall, et al., 2005). Optical emission and absorption depend on the transition between these bands. For this reason, semiconductors and metals, in particular, show large changes in their optical properties, such as the colour being a function of the particle size. For example, colloidal solutions of gold nano-particles have a deep red colour which becomes progressively more yellow with increasing particle size.

The classification of nano-scale materials depends generally on the number of dimensions which exist in the nanometer range. By reason of this dependence on the dimensions, nano-scale materials can be classified as: zero-dimensional (e.g. nanopores), one-dimensional (e.g. laminate structure), two-dimensional (nano-wires/nanotubes), and three-dimensional structure (e.g. super lattices). This classification system is useful in describing the type of the structure of the nano-scale materials one would like to produce. In Table 1.1, a list of the typical size and dimensions of nano-scale materials is shown (Rao, et al., 2004).
Table 1.1 Typical sizes of some nano-scale materials.

<table>
<thead>
<tr>
<th>Form</th>
<th>Size</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocrystals</td>
<td>Diameter, 1…10 nm</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>Nanowires</td>
<td>Diameter, 1…10 nm</td>
<td>Metals, semiconductors, oxides sulphides, nitrides</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>Diameter, 1…10 nm</td>
<td>Carbon, layered metal</td>
</tr>
<tr>
<td>Nanoporous solids</td>
<td>Pore Diameter, 0.5…10 µm</td>
<td>Zeolites, phosphates, etc.</td>
</tr>
<tr>
<td>2-dimensional array</td>
<td>Several 2nm …2µm</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>Surface and thin film</td>
<td>Thickness, 1…1000 nm</td>
<td>Variety of materials</td>
</tr>
<tr>
<td>3-dimensional structures</td>
<td>Several 3nm…3µm</td>
<td>Metals, semiconductors, magnetic materials</td>
</tr>
<tr>
<td>(super lattices)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For this study, the nano-sized inclusions are defined as those that have at least one dimension in the range 1–100 nm. The experiments are expected to show the nano-scale reinforcement and bring new phenomena, which contribute to material properties. In this work, the interest is in how the properties of polymer matrix composites are altered by introducing nano-sized versus micron-sized reinforcement, and what additional factors contribute to the material response of nano-composites. With the recent developments in the nano-science and nanotechnology fields, the correlation of material properties with filler size has become a point of great interest. As a result, much of the work is still ongoing and there is yet to be a definite conclusion on the effect of nano-sized inclusions on properties of polymer systems.

1.7 Relevance and Importance of this Study

Through this comprehensive study, it is envisaged to develop a polyamide nano-composite via an ideal method with modified, improved and modelled properties. The success of this project will widen the applications of nylon-66/CaCO₃ nano-composites in areas such as fibre, furniture, automotive parts like fans, grilles, etc. and enable it to be considered as a possible substitute for conventional petroleum based plastics.
1.8 Objectives and Scope of the Study

The basic objectives of the present study may be stated concisely as:

1. To synthesize calcium carbonate nano-particles by the reverse microemulsion method and subsequent surface modification of the particles by stearic acid followed by their physical, thermal and optical characterization. The same nano-particles are to be used in the synthesis of polymer nano-composites.

2. To synthesize micro-composites (ordinary composites) and nano-composites of polyamide-66 (nylon-66) using polymer solution method, under different conditions and filler quantity.

3. Morphological, thermal, optical, rheological and mechanical characterization of the micro- and nano-composites synthesized.


One of the most important aspects of material development in thermoplastics engineering is to achieve a good combination of mechanical properties and process ability at a moderate cost. As far as mechanical properties are concerned, the main target is to strike a balance of elastic modulus, strength and elongation. Material development for specific exotic applications is a vast subject of Material Science and Engineering. The scope of this research shall be limited to the following tasks.

1. To investigate the conditions for the synthesis of CaCO₃ nano-particles through the reverse micelles (micro-emulsion) method,
2. Surface modification of synthesised nano-CaCO₃ particles by reverse micro-emulsion technique in stearic acid,
3. To explore the synthesis route for making nylon-66/CaCO₃ micro and nano-composites by polymer solution method using micro-nano CaCO₃ as fillers,
4. To explore the effect of surfactants and speed of reactions on size and morphology of CaCO₃ nano-particles and micro-nano composites,
5. To examine the physical, thermal and optical properties of CaCO₃ nano-particles,
6. To examine the physical, mechanical, rheological, thermal and optical properties of nylon-66/CaCO₃ nano-composites,
7. To examine the physical, mechanical, rheological, thermal and optical properties of nylon-66/CaCO₃ micro-composites,
8. To compare the properties of the developed micro- and nano-composites with that of virgin nylon-66.

9. In order, to predict the mechanical properties of developed micro-and nano-composites some modeling shall be done.

1.9 Organisation of the Thesis

The research work has been presented in seven chapters. The current chapter-1 was aimed at introducing the subject and background of nano-materials research and their prospective applications. This is followed by an overview of the research presented in the next chapters of the thesis and has ended with a clear elucidation of the objectives and the scope of the work.

A comprehensive literature review in the areas related to this study is presented in chapter-2. The main strategies developed over the recent years for incorporation of filler, CaCO$_3$ in this case, into a polymer matrix has been covered in detail. This chapter has the pretension to give an exhaustive overview and also illustrate the main strategies with some appealing examples. The details of reverse microemulsion method used for the synthesis of CaCO$_3$ nano-particles have been described in chapter-3.

Chapter-4 is devoted to the description of some of the theoretical models proposed in the literature for the prediction of Young’s modulus and Yield strength of micro- and nano-composite materials based on component properties. These models have been used to predict the mechanical properties of the composite samples synthesised in this work.

Chapter-5 presents the details of the materials, instruments/equipments and the experimental procedures used for the synthesis and surface modification of the nano-particles and preparation of micro- and nano-composites of nylon 6, 6/CaCO$_3$.

Chapter-6 may be called the heart of the thesis. Details of the method used for the synthesis and surface modification of CaCO$_3$ nano-particles and the subsequent preparation of polymer micro- and nano-composites are presented in two main sections. Physical, morphological, optical, thermal, rheological and mechanical characterization procedures are presented in adequate details. Results obtained from the analyses are discussed in exclusive terms.

Conclusions drawn from this research and some recommendations for future work are listed in chapter-7. The thesis ends with a comprehensive list of references referred in this work, a select bibliography and few appendices.