CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There is great deal of potential for nanostructures applications in the technology world. Therefore, much research has been focussed on finding new methods for the preparation and production of these materials and also solutions for solving many of the problems in the way of their production. The form and the methods used towards achieving this goal are dependent on the type of the material of interest and also its application. In the sections that follow, the main methods for nano-particle production which have attracted the interest of many researchers has been explained first. Next, the methods of synthesising polymeric nano-composites are discussed. Finally, the most important experimental characterization methods to analysis nano-particles and polymer composites have been discussed.

2.2 Mineral Fillers

Mineral fillers play an important role as particle reinforcing agents in thermoplastics industry, especially talc and calcium carbonate (CaCO$_3$) (Samsudin, et al., 2006). The purpose of adding inorganic mineral fillers into polymers is not confined to cost reduction but also to fulfil their performance properties, such as increasing the stiffness, dimensional stability toughness, heat distortion temperature, hardness, as well as change the viscosity of the filled material (Zuiderduin, et al., 2003; Modesti, et al., 2005). The properties of particulate filled polymer composites depend on the particles size, shape, loading, dispersion, interfacial bonding, and surface treatment of the fillers (Dangtungee, et al., 2007; Supaphol, et al., 2007). The dispersion of fillers in polymer matrix also influences the physical, mechanical, and thermal properties of polymers.

The degree of improvement not only depends on the judicious choice of filler origin, particle size and shape, and the fraction of filler, but also on the filler surface treatment that promote interaction between the polymer matrix and filler. However, the incorporation of filler in large amounts of resin introduces processing difficulty, whereby the addition of such particulates causes significant increase in the viscosity of thermoplastics. Thus, to obtain the best end properties of the composite product and to
optimize processing conditions, understanding of the rheology of filled melt systems is very important. Hydrophilic feature of mineral fillers usually promote difficulty to combine with most polymeric materials that are usually hydrophobic. Modification of filler not only contributes to reinforcement but is also very useful in increasing the interaction of particles to impart rheological properties, prevent sedimentation, aid dispersion, or prevent agglomeration (Zuiderduin, et al., 2003). Among the various mineral fillers, calcium carbonate, CaCO$_3$ (Albano, et al., 2000; Osman, et al., 2004), zinc oxide, ZnO (Chae and Kim, 2005) and titanium dioxide, TiO$_2$ (Starkova, et al., 2007) have been the most utilized materials. The use of CaCO$_3$ has been primarily due to its availability and low cost (Dangtungee, et al., 2007; Supaphol, et al., 2007).

Several methods have been used to surface-treat the CaCO$_3$ particles to improve the fluidity and dispersion of the filler particles in polymer composites. Surface treatment of CaCO$_3$ reduces the inter particle interaction, enhances the polymer filler compatibility, and results in low increase in viscosity (Kowaleski and Galeski, 1986). Use of low molecular weight of organic compound is the most effective technique to change the particle–particle and polymer–particle interaction (Yue and Cheung, 1991; Suetsugu and White, 1987). With CaCO$_3$, stearic acid is often used as it manifests better mechanical properties by improving dispersion of the filler (Dangtungee, et al., 2007; Dangtungee and Supaphol, 2009).

### 2.2.1 Calcium Carbonate (CaCO$_3$)

Calcium carbonate (CaCO$_3$) is a mineral applied widely as fillers in the areas of plastics, rubbers, paints, papermaking, textiles, pigments, ceramics, medicine, pharmacy and so on, in virtue of its different physical and chemical properties and many of its important technological applications (Hari, et al., 2006; Dong, et al., 2010; Ren, et al., 2011).

Calcium carbonate (CaCO$_3$) is low-priced and widely used as surface coatings in the construction industry. Nano-sized CaCO$_3$ powder is now commercially available and can be used as a raw material for the preparation of super hydrophobic surfaces (Zhang, et al., 2011). Calcium carbonate nucleates in three crystal morphologies: calcite, aragonite, and vaterite. Calcite, easy to find in nature, is more stable than other polymorphs at ambient temperature and atmospheric pressure whereas vaterite is most unstable. Aragonite is less stable than calcite and commonly found in marine organisms and is the high-pressure form of calcium carbonate (Tai and Chen, 1998; Kato, et al.,
2002). It is the main constituent of the shell of bivalve animals, corals, and exquisite pearls. The iridescent colors observed in shells of sea animals such as abalone and in pearls are the result of deposition of minute layers of aragonite (Ganguli, et al., 2008).

Particles have distinctive properties when their crystalline sizes are reduced to submicron range with respect to corresponding bulk materials (Gleiter, 2000), including prominent mechanical/optical properties, high specific surface area and chemical activity, and superior barrier effects especially in polymer matrix. Among the numerous nano-sized materials synthesized within the past decade, calcium carbonate is one of the most useful and abundant materials (Tai and Chen, 2008).

Thus, the nano-sized calcium carbonate can find a myriad of applications. For example, in plastic products, Guo, et al. (2005) found that nano-sized calcium carbonate was able to improve the modulus of polypropylene. Similarly, Jiang, et al. (2005) showed that nano-sized calcium carbonate increased modulus of acrylonitrile-butadine-styrene copolymer and even increased its impact strength under a certain loading range.

In paper application, paper coated with submicron-sized aragonite, compared with traditional use of micron calcite particles, has been demonstrated to improve gloss, brightness and opacity effectively (Dimmick and Mueller, 2006). Dougherty, et al. (2005) applied calcium carbonate of 40nm size as filler in a paper manufacturing process. They proved that paper sheets coated with nano-sized calcium carbonate showed an increase in cross-direction stiffness and a decrease in void count.

In another report related to other industries, it has been shown that when spherical vaterite of 0.23 µm size was added within the toothpaste or dentifrice, the cleaning and abrasiveness characteristics of the paste were remarkably improved. Thus CaCO₃ fine particles with its distinct morphology have specific application (Liu, 2005).

Tai and Chen (2008) have reported controlling the particle morphology, habit and size of calcium carbonate via reverse micro-emulsion technique. Several important operating variables in AOT/isoctane/water reverse micro-emulsion system, such as ω value (water/surfactant molar ratio), S value (water/oil molar ratio), R value (molar ratio of CaCl₂ to Na₂CO₃) and type and concentration of additives, were systematically investigated by them. They showed the ω value had a greater influence than the S value on the particle size and habit of calcium carbonate because it strongly affected the stability and size of aqueous droplets. Also, the droplet size of stable micro-emulsion was much smaller than the particle size.
In 2010, Dong and co-workers prepared CaCO$_3$ nano-particles via micro-emulsion route at room temperature with ethanol and n-hexanol as co-surfactant. This process did not demand any additional energy such as heating or continuous agitation. It is claimed that they are the first to use ethanol as co-surfactant in the synthesis of micro or nano-materials. It is reported that diameter and length of nano-particles were 20-30 nm and 100-300 nm respectively.

Sadowski, et al. (2010) produced calcium carbonate nano-particles in water-in-oil micro-emulsion at 20-23°C temperature. Calcite precipitation experiments were conducted in the presence of poly (ethylene glycol) PEG. Nano-particles synthesized in this way have a spherical shape and almost equal sized varying from 20 to 30 nm.

In 2005, the synthesis of calcium carbonate nano-particles from the carbonation process between CO$_2$ and calcium hydroxide solution was reported by Karagiozov and Momchilova. The reaction was done in micro-emulsion of water in oil at 25°C, which contained normal hexane, calcium hydroxide water solution, and by blowing of CO$_2$ into the micro-emulsion solution. The size of calcium carbonate nano-particles was reported in the range of 20 to 30 nm.

Xiang, et al. (2004), on the size of particles, reported that calcium carbonate nano-particles (20 to 70 nano-meters) were synthesized at room temperature in the presence of terpinoel via carbonation route in ca (OH)$_2$–CO$_2$/H$_2$O system. According to their results, increase in system temperature and density of calcium hydroxide increases the final size of the particles.

Chen, et al. (2004a) produced the precipitated calcium carbonate nano-particles in Rotating Packed–Bed Reactor by reaction between calcium hydroxide and carbon dioxide (CO$_2$). The temperature was maintained at 292 ± 2K. The average size of the synthesized particle was reported to be about 44 nano-meters. The important stage of carbonation process intensity control is the gravitation of CO$_2$. This method, also known as High Gravity Reactive Precipitation (HGRP) needs a high centrifugal force acceleration (at least 2500 times more than the earth gravity acceleration), and therefore, for creating such a high acceleration, needs expensive tools. Though an expensive method, it has some advantages, like less cost involved for preparation of materials used in the carbonation process, higher yield, and easy process control.

Calcium carbonate nano-particles from the chemical and mechanical reaction under the heat process were produced by Takuya and coworkers in 2000. A solid-state displacement reaction:
CaCl$_2$ + Na$_2$CO$_3$ → CaCO$_3$ + 2NaCl

was induced during mechanical milling of a CaCl$_2$+Na$_2$CO$_3$ powder mixture. Heat treatment of the as-milled powder at 350°C helps in the completion of the reaction, and further leads the morphology of particles towards the calcite requiring additional energy. The size of the particles produced is reported to be about 140 nm.

Daibin, et al. (2002) reported the preparation of calcium carbonate nano-wires by micro-emulsion method in Triton X®-100/cyclohexane/water system (a non-ionic surfactant). The nano-wires of CaCO$_3$ were 5-30 nm in diameter. In another report, it was found that calcium carbonate nano-composites exhibited unique and improved properties in polymer composites. In poly vinyl acetate (PVA) matrix, the morphology of the composite was found to be dependent on the filler particle size. The nanoparticles form ‘net like’ dispersion in the matrix, whereas the particles in the micron scale formed ‘islands’ (Kovacevic, et al., 2002). Sunqing, et al. (2000) studied the application of CaCO$_3$ nano-particles as additives in lubricating oils. It was found that CaCO$_3$ nano-particles exhibited good load-carrying capacity, anti-wear and friction-reducing properties.

Mechanical strength of nano-composites has also been reported in literature. Voros and Pukanszhy (1995) reported that tensile strength was affected by the size of the particles and increased with the volume fraction for smaller size of the filler (CaCO$_3$) particles. The highest value of tensile strength was achieved with the smallest particle size. In another study, Pukanszky, et al. (1995) observed that both talcum and CaCO$_3$ lead to an increase of Young’s modulus and that the addition of low strength material decreases it. On the other hand, Young’s modulus variation depends upon the interaction between the filler and the matrix.

The effect of the size (diameter) of CaCO$_3$ particles on the properties of polymeric blends was studied by Zeng and colleagues (2008). The results showed that the composites with the smaller particles presented higher mechanical properties. By adding 40 nm CaCO$_3$ particles into the PVC matrix, the single-notched impact strength of the nano-composite at room temperature was 3.5 times that of the PVC matrix and 4.6 times that of the PVC blend filled with micro-CaCO$_3$. They also obtained better performance of nano-composites with 40 and 80 nm CaCO$_3$ particles compared to the composites with 500 nm and 25µm CaCO$_3$ particles, in terms of tensile and flexural properties.
Kang, et al. (2005a) examined, in water/sodium dodecyl sulfate/ cyclohexane micro-emulsions and found that CaCO$_3$ predominantly formed spherical vaterite instead of the mixture of rhombohedral calcite and round vaterite that forms from the pure aqueous solution. The anionic surfactant lowers local pH and increases super saturation near the surfactant and water interface through ionic interaction with inorganic cations, altering the preferred crystal structure from calcite to vaterite. CaCO$_3$ also formed as vaterite when synthesized in oil-rich micro-emulsions formed with the anionic surfactant sodium bis-2-ethylhexyl-sulfosuccinate, but the crystal structure was surprisingly altered to aragonite with “nano-filament” morphology as the water content in the micro-emulsion was increased (Li, et al., 2003). CaCO$_3$ was shown to grow as elongated “superstructures” consisting of stacks of plate like calcite crystals when synthesized in a mixed surfactant micro-emulsion at high pH (Viravaidya, et al., 2004).

Lazzerri, et al. (2005) reported the rheological and mechanical behavior of CaCO$_3$/HDPE nano-composites on the effect of surface interaction. Surface treatment of the particles was carried out with and without stearic acid. It was found that the addition of 10 volume % CaCO$_3$ to HDPE caused rise of the young’s modulus and yield stress and was also accompanied by a sharp drop in impact strength. The addition of stearic acid has the effect of slightly decreasing both the young’s modulus and yield stress as compared to uncoated composite. As for rheological property, the addition of CaCO$_3$ (with and without surfactant) caused rise in the viscosity with respect to pure HDPE. However, addition of stearic acid resulted in decrease of viscosity. It can be expected that raising stearic acid content cause drop in the level of interaction between particles, reducing the amount and the average size of agglomerates and improves the distribution of the particle in the matrix. Thus the decrease in viscosity may be attributed to a reduction of immobilized polymer fraction because of the lower interfacial tension between the solid particle and surrounding liquid phase when a surfactant layer is present (Lazzerri, et al., 2005). In water/poly(oxyethylene) (1,1,3,3-tetramethylbutyl) phenyl ether/ cyclohexane micro-emulsions, CaCO$_3$ grew into nano-wires 5-30 nm in diameter and more than 10 µm in length (Kuang, et al., 2002).

Many experimental studies have been undertaken using a reverse micelles system to precipitate nano-particles. Copper nano-particles, silver and silver halides, Fe$_3$O$_4$, Pt, Pd, Rh, Cu, Fe and Ir, CdSe, Ni, FeNi, CdS, ZnS, PbS and Ag$_2$S and metal oxides like ZnO, TiO$_2$ have been prepared by such means (Sugih, et al., 2007). Because of the wide application of nano/micro-sized calcium carbonate, the technique to
synthesize calcium carbonate with particle size below 1µm became an interesting research topic. There are several methods to synthesize nano-sized calcium carbonate that they are mentioned in next subsection. It is noteworthy to mention that among the methods mentioned in the following subsection, the water-in oil (W/O) micro-emulsion has been widely used as an ideal medium to prepare inorganic nano-particles, which consists of nano-meter-scale water droplets surrounded by surfactant that are dispersed in oil (Dong, et al., 2010). In this study calcium carbonate nano-particles were synthesized using two reverse microemulsion method and were surface modified by stearic acid.

### 2.3 Methods of Synthesis of Nano-particles

There are various methods for nano-structured material production. In general, the nano-particles production methods may be broadly classified as top-down and bottom-up methods. Therefore, the different methods for the production of such materials may belong to either of these two groups (Tseng, et al., 2005; Bratton, et al., 2006; Wong, et al., 2009). Attrition or milling is a typical top-down method, whereas the colloidal dispersion is a good example of bottom-up in the synthesis of nano-particles. There are advantages and disadvantages in both methods. Among others, the biggest problem with top-down approach is the imperfection of the surface structure. It is well known that the conventional top-down techniques such as lithography can cause significant crystallographic damage to the processed patterns (Das, et al., 1993), and additional defects may be introduced even during the etching steps (Vieu, et al., 2000; Harper, 2003). For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on surface. Such imperfections would have a significant impact on physical properties and surface of nano-structures and nano-materials, since the surface over volume ratio in nano-structures and nano-materials is very large. The surface imperfection would result in a reduced conductivity due to inelastic surface scattering, which in turn would lead to the generation of excessive heat and thus impose extra challenges to the device design and fabrication. Regardless of the surface imperfections and other defects that top-down approaches may introduce, they will continue to play an important role in the synthesis and fabrication of nano-structures and nano-materials. Bottom-up approach is often emphasized in nanotechnology literature, though bottom-up is nothing new in materials synthesis. Typical material synthesis is to build atom by atom on a very large scale, and
has been in industrial use for over a century. Examples include the production of salt and nitrate in chemical industry, the growth of single crystals and deposition of films in electronic industry. For most materials, there is no difference in physical properties of materials regardless of the synthesis route provided that chemical composition, crystallinity, and microstructures of the material due to kinetic reasons. Consequently, the material exhibits different physical properties. Bottom-up approach refers to the build-up of a material from the bottom: atom by atom, molecule by molecule, or cluster by cluster. In organic chemistry and/or polymer science, we know polymers are synthesized by connecting individual monomers together. In crystal growth, growth spices, such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nano-materials. There are several reasons for this. When structures fall into a nano-meter scale, there is little choice for a top-down approach. All the tools we have possessed are too big to deal with such tiny subjects. Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and nano-materials such produced are in a state closer to a thermodynamic equilibrium state. On the contrary, top-down approach most likely introduces internal stress, in addition to surface defects and contaminations (Cao and Wang, 2004). 

Figure 2.1 is a concise expression of the production process of nano-structured materials by up-down and bottom-up methods are presented (Kelsall, et al., 2005; Wong, et al., 2009).

2.3.1 The Breakdown and Mechanical Method

The mechanical breakdown method is a customary method and an example of up-down technique for production of nano-structured materials. Unlike the bottom-up method, the material does not form/create from original atomic clusters and prepared only through breakdown and intensive plastic deformation of these materials. Due to easy performance and relatively inexpensive equipments necessary in the laboratory scale, and its capability to produce a vast majority of materials, the method has found versatile applications. However, the main limitations of this method are:

1. It is difficult to synthesize nano-particles of size less than 100nm,
2. It is not easy to control the process,
3. The shape and the morphology of particles are completely irregular (they have no definite geometrical form).
4. The environmental pollution originating from the mill atmosphere,
5. Particle assembling and incorporation during milling and consequently, broad particle size distribution.

![Diagram of nano-scale materials synthesis](image)

**Figure 2.1** Schematic of nano-scale materials synthesis (Kelsall, et al., 2005; Wong, et al., 2009).

In this process, high energy stirring mills are usually used. Nano-particles are generated based on the shear stresses applied on the particles. The energy is transferred to particles through ball mills, **Figure 2.2**. This energy is dependent on the sliding speed, size and the number of balls, weight ratio of ball to the powder, milling time and also mill atmosphere. If the energy is good enough, it is possible to fabricate a homogeneous composite consists of different ingredients in nano-metric dimensions. In this method, the high hardness materials like aluminum oxide and zirconium oxide are used as a ball for breakdown (Kelsall, et al., 2005).
2.3.2 Synthesis by Wet Chemical Processing

In this method, chemical synthesis of nano-material is based on the manipulation of atoms and molecules for reaching to a nano-structured material, called bottom-up architecture. The original material in solid or liquid state can be solved as salt or organic metal in suitable solvent (dependent on the reaction type). When the concentration of product in solution is reached to a saturation limit, the condensation step begins and particle nucleus generates. The nucleation can occur in homogeneous or heterogeneous states which depend on the stable nucleus formation with or without the help of external factors. Reaction and mass transfer rates are influenced by factors like reactants concentrations, temperature, pH and reagent stirring rate (convection). To get dispersed particles i.e. unassembled particles and/or narrow particle size distribution, it is necessary that all nucleons (nucleus) are formed at the same/similar time and dimension growth is done without secondary nucleation or particle assembling (Kelsall, et al., 2005; Pandey, et al., 2009; Darezereshki, et al., 2010; Bahadur, et al., 1992). Many important methods for the production of nano-particles fall in this category and are described in the following sections.

2.3.2.1 Sol-Gel Method

Sol-Gel process is the most popular chemical method for synthesizing nano-metric materials. In this process, the inorganic network is prepared as a colloidal suspension (sol) and finally, during the formation process of gel, the liquid phase is
removed from it. The main steps of sol-gel process are shown in Figure 2.3. The generated polymeric gel is formed as three-dimensional structure which causes the cavities or porous spaces to join together and to be incorporated. After drying or shrinkage, it will form a rigid and strong solid. The final products can be designed so that it causes joining of the nano-porosities together and consequently have the high specific surface area.

![Diagram of sol-gel process]

Figure 2.3 Schematic of general steps of sol-gel process for nano-particles synthesis (Kelsall, et al., 2005).

In sol-gel process, sol-to-gel conversion is often done by pH change or the change of solution concentration. The advantage and the major application of sol-gel process lies in the synthesis of products with high purity and obtaining a homogeneous nano-structured material at low temperature. Sol-gel method is also used for metallic nano-oxides production. Another attraction of this method is in the production of inorganic materials like glasses, and/or ceramic materials at a very low temperature in comparison to other methods (Valles Lluch, et al., 2009; Kizilkaya, et al., 2010; Chowdhury and Bould, 2010). For example, Liu, et al. (2001) prepared nano-sized CaCO$_3$/SiO$_2$ composites by the sol-gel process of CaCO$_3$ and Na$_2$SiO$_3$ in an agitated tank reactor, with an average 40 nm composite size of sol-gel coated CaCO$_3$. Nano-CaCO$_3$ particles have also been prepared using a micro-emulsion technique consisting of sodium dodecyl-sulphate (SDS)/isopentanol /cyclohexane/water (Sunqing, et al., 2000). Nano-particles of calcium carbonate in the reaction system of Ca (OH)$_2$/H$_2$O-CO$_2$ were also synthesized by Shi-Cheng, et al. (2000). They reported that the increase in temperature and mass fraction of the Ca (OH)$_2$ suspension increased the particle size of the final product.

### 2.3.2.2 Colloidal Method

Colloidal methods are based on precipitation processes in solutions (Weller, 2003; Zou, et al., 2008; Sau and Rogach, 2010). In this method, the preparation of nano-particles is based on providing a consistent flow of solvent “colloidal sol”. Also, there is usually a need for generating a very fine dispersed system which has a very high free energy for breaking and decomposing solid structure (Kim, et al., 2010). For
instance, solutions of different ions can be mixed under controlled conditions of temperature and pressure to form insoluble precipitates. By controlling the nucleation and growth kinetics, particles of various sizes and morphologies can be produced. The method has been implemented in bulk solutions and also in confined systems such as reverse micelles. To control the process of nucleation, ultrasonic or sono-chemical effects have also been employed. A wide range of metal, metal oxide and organic nanoparticles have been produced by colloidal wet chemical approach (Perez, et al., 2005). Due to fine crystals of nano-particles and consequently larger specific surface area of materials and the colloidal systems, they tend to join together, leading to particle bulking and assembling. Mechanism of nano-particle production by colloidal methods is shown in Figure 2.4. This phenomenon is basically related to strong Van Der Waals attractive force between particles and second, to low repulsion forces to overcome the intrinsic energy barrier. The magnitude of this energy barrier and particles bulking intensity is dependent on the equilibrium of the attractive and repulsion forces between particles.

![Figure 2.4](image)

**Figure 2.4** Mechanism of nano-particle production using vapour/liquid phase/colloidal methods (Perez, et al., 2005).

By increasing the repulsion forces, particle bulking and assembling can be prevented. Addition of chemical additives to colloidal solution causes the adhesion of cluster surfaces together and blocking the voids (free volumes or spaces) and consequently growth process can be prevented. These additives consist of polymeric surfactants and/or electrostatic materials which cause the adhesion of cluster surfaces. With further treatment on the colloidal systems which consists of colloid conditioning with regard to surface charges on it, nano-particle structures can be synthesized.
Colloidal methods belong to relatively simple and cost-effective methods and can be widely used for production of semiconductor or metallic nano-crystals. The intrinsic and essential problems of colloidal method are that in most of colloidal solutions, the phenomenon of ageing occurs causing increase in the particle size with passage of time (Dutta and Hofmann, 2003; Kim, et al., 2010). One of the most important styles of this method (wet chemical processing) is the micro-emulsion method and is discussed in chapter-3.

2.3.3 Gas Phase Synthesis Method

This class includes all methods for nano-powder production resulting from the reaction between one or more gases (Dutta and Hofmann, 2003); gas-phase synthesis being a well-known chemical synthesis technique for an extensive variety of nano-sized particles. Since the potential of ultra-fine and especially nano-sized particles in high-performance applications has been identified, the scientific and commercial interest has increased immensely, disclosing this field as a most important technology of the future (Wang, et al., 2008; Ruud van Ommen and Yurteri, 2010). Gas phase synthesis is based on homogeneous nucleation of a supersaturated vapour and subsequent particle growth by condensation, coagulation and capture, as shown in Figure 2.4 (Perez, et al., 2005). The supersaturated vapour can be generated in many ways depending on the chemical nature of the material, but typically by heating a solid and evaporating it into a carrier gas phase. The super saturation is achieved by cooling or by chemical reaction or by some combination of these. The supersaturated vapour can nucleate homogeneously in the gas phase and also heterogeneously by contact with surfaces. The nuclei grow by collision and condensation to give rise to a distribution of particle sizes and morphologies. Depending on the heating and cooling processes used, a wide range of gas phase methods such as flame pyrolysis (fumed silica, TiO2), furnace flow reactors (Ag, Ga, Al, PbS, Pb, Si, Ge), laser induced vaporization and pyrolysis (silica and iron), thermal and microwave plasmas (metals and metal oxides), sputtering (metals), and laser ablation have been employed (Weller, 2003; Zou, et al., 2008). The continuous-gas-phase production method is under consistent development. The intrinsic advantages of this method are:

1. Exact control of the particle size, shape, crystallinity and chemical compound of the resulting powder,
2. High purity of final product,
3. Convenient control of reaction mechanisms.

Cluster condensation can be affected to occur when the vapours reach to the super-saturation limit and the atomic clusters are formed into the vapour phase (Dutta and Hofmann, 2003).

2.3.3.1 Gas Phase Production in the Furnace

Use of furnace is the simplest approach for gas-phase generation and is the desired method for high vapor-pressure materials. Electrical arc or electron beam have also been used to transfer to transfer energy. The atoms of the original material vaporized and passed through the reactor (furnace). Furnace atmosphere is either inert or consists of gaseous reactants. For materials with low vapor-pressure, organo-metallic compound can be used (Dutta and Hofmann, 2003; Deepak and Tenne, 2008; Buznik and Kuryavyi, 2009). The resulted hot vaporized atoms from the original material through creating the homogeneous nucleation can be caused to a decrease in the energy of system and finally are condensed, Figure 2.5. For the production of powder-type composite, different gases like hydrogen or a mixture of several gases are passed to the reaction chamber (furnace). By controlling the velocity of the exhausted nucleons from the super-saturation medium, the particle size can be governed.

Figure 2.5 The simple schematic of nano-structured materials from gas-phase (Dutta and Hofmann, 2003).

The size and the quality of the distribution of atomic clusters are dependent on the following parameters (Dutta and Hofmann, 2003):

1. The velocity of vaporization (the level of applied energy to the system),
2. The velocity of condensation,
3. The velocity of cluster exhaustion.

This method is quite simple and laboratory procedures can easily be converted to semi-industrial and industrial scale.

### 2.3.3.2 Flame Assisted Ultrasonic Spray Pyrolysis

Ultrasonic spray pyrolysis may be employed to generate an aerosol from a dilute aqueous metal salt solution, resulting in the production of particles with a narrow size distribution (Dutta and Hofmann, 2003; Kalyana, et al., 2005). A review by Messing and colleagues (1993) has shown that spray pyrolysis has been used for the synthesis of particles of micron size, producing various metal powders. Tsai and co-workers (2004) used ultrasonic spray pyrolysis and found that uniform particles of 90 nm could be synthesized from smaller droplets whereas larger droplets generated porous particles. Pluym, et al. (1993) used three types of aerosol generators in synthesizing solid, spherical, micron-sized silver metal particles and observed that the effect of precursor concentration on the particle size was weak and mostly dependent on the aerosol droplet size. Yuan, et al. (1998) used flame-assisted ultrasonic spray pyrolysis technique to synthesize ceramic powders in micron and submicron size range by controlling the concentration of precursor solution. Kim synthesized hollow spherical silica particles using ultrasonic flash pyrolysis by adding a small amount of urea to the sodium silicate solution (Kalyana, et al., 2005). A schematic diagram of the spray pyrolysis reactor system is shown in Figure 2.6.

One of the disadvantages of this method is final product (nano-particles) assembling. For controlling the size and the dimensions of the final product, the intensity of flame should be controlled and remain homogeneous. Due to the fact that the production medium is oxidative, this method is only suitable for oxide nanoparticles synthesis (Dutta and Hofmann, 2003).
2.3.3.3 Gas Condensation Processing

In this method, the original (metal/inorganic) material is vaporized under the heat resulting from the collision of an electron beam and/or a spark at a pressure of 1-50 Mbar in the medium of inert gases like Ar, Ne and Kr. Then, the atomic clusters are created from the homogeneous nucleus and by incorporating other atoms. By changing the gas pressure, it may possible to control the contact time of clusters within the gas media and thereby enabling the adjustment of particle growth. A simple expression of the quality of nano-metric powder produced by means of this method is presented in Figure 2.7.
The particle size distribution of the resulted nano-powder follows from a normal distribution (uniform and homogeneous). For collection of the nano-particles produced, the liquid nitrogen cooling rotating wheel is exploited. The synthesized nano-particles are within the range of 2 to 50 nm. Further, the resulting nano-powder is reported to have no particle bulking or assembling tendency (Dutta and Hofmann, 2003; Sivaprahasam, et al., 2010).

2.3.4 Chemical Vapor Condensation

In Chemical Vapors Condensation, Figure 2.8, unlike gas condensation processing’ a hot wall of a reactor is used and therefore, depending on the process parameters, it is possible to control the nano-particle nucleation. Trials have been undertaken to optimize the effective parameters so that the homogeneous nucleation of particles in the gas flow may be accelerated. This goal can be achieved by adjusting the duration time of nano-particles in the reactor.

![Figure 2.8](image)

**Figure 2.8** A schematic of the chemical vapors condensation (CVC) method (Dutta and Hofmann, 2003).

The duration time can be changed by controlling the inlet gas pressure and also the temperature of the hot wall of the reactor. Indeed, with controlling the effective parameters, it is possible to produce both nano-metric powders and thin layers of materials which can be deposited on the substrate. In comparison with the previous methods, it is possible to produce different kinds of nano-powders like carbides, nitrides and compounded powders like barium titanate in this method. It is almost possible to produce all nano-powders by the gas-phase synthesis method. Depending on
the powder type required, method should be selected in order to achieve the desired purity, particle size, assembling degree and the type of powder phase to be compatible with the requested application for it (Dutta and Hofmann, 2003).

2.4 Nano-composites Preparation Methods

Organic/inorganic composite materials have been extensively studied for a long time. When inorganic phases in organic/inorganic composites become nano-sized, they are called nano-composites. Organic/inorganic nano-composites are generally organic polymer composites with inorganic nano-scale building blocks. They combine the advantages of the inorganic material (e.g., rigidity, thermal stability) and the organic polymer (e.g., flexibility, dielectric, ductility, and processability). Moreover, they usually also possess special properties of nano-fillers leading to materials with improved properties. A defining feature of polymer nano-composites is that the small size of the fillers leads to a dramatic increase in interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings (Landfester, 2001; Qi, et al., 2007). Inorganic nano-scale building blocks include nano-tubes, layered silicates (e.g., montmorillonite, saponite), nano-particles of metals (e.g., Au, Ag), metal oxides (e.g., TiO$_2$, Al$_2$O$_3$), and semiconductors (e.g., PbS, CdS) (Balazs, et al., 2006; Schadler, et al., 2007). Nano-composites are prepared from the distribution (admixture and distribution) of material nano-particles (distributed phase) in matrix (constant phase). Matrix can be mono-sectional or poly-sectional and it can be a metal, ceramic, and / or polymeric material. The distributed phase can be a material like fortifier, conductor, softener, resistant, and some other materials. Making good samples of polymer matrix nano-composites is a challenging area drawing considerable effort. Researchers have tried a variety of processing techniques to make polymer matrix nano-composites. These include melt mixing, polymer solution, in situ polymerization, and other approaches. Creating one universal technique for making polymer nano-composites is difficult due to the physical and chemical differences between each system and various types of equipment available to researchers. Each polymer system requires a special set of processing conditions to be formed, based on the processing efficiency and desired product properties. Different processing techniques in general do not yield equivalent results (Jordan, et al., 2005).
In the next section, some most important methods for preparation of nano-composites which have attracted the interest of many researchers have been discussed. Different methods for preparation of polymeric nano-composites and those used in practice are available in published literature. Based on the starting materials (consistent phase), these methods can be classified in three categories:

1. Solution polymerization,
2. Melt polymerization, and
3. In-situ polymerization.

In addition, few other methods like sol-gel process and the bonding between polymer/monomer to clay layers are also indicated in the clay-polymer hybrids (Sinha and Okamoto, 2003). Based on the shape of the reinforcing materials, nano-composites may also be classified into three categories: particulate, layer to layer, and fabric types (Dutta and Hofmann, 2003).

2.4.1 Preparation of Particulate Nano-composites

The polymeric composites containing particulate reinforcements have the widest applications in the routine materials. One of the most effective factors on the reinforcement of fabricated composite properties is the quality of mixing and the degree of homogeneity of the mixing of the reinforcing particles in the polymer matrix. There are several techniques for preparation of this group of nano-composites: (a) mixing of nano-particles with the polymer solution, (b) mixing of nano-particles and melting polymer, (c) In-situ polymerization, and (d) the use of ultrasonic waves for dispersion of nano-particles (Thompson, et al., 2003).

2.4.1.1 Mixing the Nano-particles with a Polymer Solution

This method is suitable for the intercalation of polymers with little or no polarity into layered structures and production of thin films with polymer intercalated layers is facilitated. However, the use of expensive and environmentally unfriendly inorganic solvents is one of the major drawbacks (Sinha and Okamoto, 2003).

For a given polymer, there are solvents that dissolve the polymer well and solvents that do not dissolve the polymer. The former solvents are called “good solvents” and the latter “nonsolvents”. The concentration of the polymer in the good solvent can be as high as 100%, yet the solution remains clear and uniform. Adding a nonsolvent to the solution causes the polymer to precipitate, if the nonsolvent mixes
with the good solvent. A solvent with an intermediate quality dissolves the polymer to some extent. Amorphous polymers (transparent in the solid state; to be precise, it is not a solid but rather a supercooled liquid) are usually easy to dissolve in the good solvent. In contrast, crystalline and semicrystalline polymers, i.e. nylon 6, 6, (opaque in the solid state) are sometimes not easy to dissolve. Within a crystallite, polymer chains are folded into a regular, thermodynamically stable arrangement. It is not easy to unfold the chain from the self-locked state into a disordered state in solution even if the latter state is thermodynamically more stable. Heating may help the dissolution because it facilitates the unfolding. Once dissolved, polymer chains take a random coil conformation unless the chain is rigid (Teraoka, 2002). Even then, many researchers have used this route to prepare both thermososes and thermoplastic polymer nano-composites.

Thompson, et al. (2003) succeeded preparing metallic oxide/polyimide nano-composites through mixing the nano-particles with polymer solution. Indium tin oxide (0.0520 g) was combined with 8.5 ml of DMAc (N,N-Dimethyl Acetamide) in a sample vial and the vial was partially immersed in an ultrasonic bath for 90 min. Polyamide (1.73 g) was added to the mixture and sonication was continued overnight. A film was cast from the suspension on plate glass and was subsequently dried to a tack-free state in a low humidity chamber followed by drying for 1h each at 50, 100, 150, 175, and 225°C in a forced air oven. The strength and elongation gained to rupture for the nano-composites thus produced were found to be less than those of pure polymers while the hardness was greater than the pure polymer materials.

Pourabas and Raeesi (2005) prepared acrylonitrile – butadiene–styrene terpolymer (ABS) nano-composites containing montmorillonite (MMT) by means of mixing the nano-particles in the polymer matrix. The procedure has been reported as follows. ABS (10 g) was dissolved in 200 ml Tetrahydrofuran (THF) by mixing at 50°C. A dispersed mixture of 0.5 g MMT in 200ml ethanol was prepared to the ABS/THF solution under homogenizing condition at 60°C. The dispersion solution of MMT/ethanol was added drop wise during 0.5-h total time. After precipitation, the supernatant liquid was decanted and the solids collected over a filter paper. After washing several times with ethanol and distilled water, the product was dried at 80°C for 24-h in an oven producing ABS/MMT nano-composites. A schematic illustration of nano-composite synthesis by this method is given in Figure 2.9.
2.4.1.2 The Mixing of Nano-particles and Polymer Melt

Melt processing, an efficient, rapid and environmentally friendly method for dispersion of nano-particles in a polymer matrix, is one of the most preferred techniques from industry point of view owing to its ease of scale-up. It is commonly used for processing thermoplastic polymers. The nano-filler or any other additive is added to the melt and homogenously mixed with application of shear mixing. A lot of effort has been directed towards dispersing nano-particles in polymer matrix using melt processing method (Hornbostel, et al., 2006; Xiao, et al., 2007).

Bikiaris, et al. (2005) succeeded in preparing Isotactic Polypropylene (IPP) nano-composites containing siliciumoxide (SiO$_2$) nano-particles through melt mixing. In all nano-composites Poly (propylene-g-maleic anhydride), PP-g-MA was added as a compatibilizer in three different amounts, 1, 2.5 and 5 wt%, based on the SiO$_2$ content. The mixing section, after the nano-particle feeding, enhanced the compounding and also increased the residence time of the mixture in the barrel. Prior to the melt processing, silica nano-particles were dried for 24-h at 105°C. The IPP pellets were fed into the throat of the extruder, while SiO$_2$ nano-particles were introduced separately through a downstream side feeding port into the polymer melt. After completing the mixing of the compound into the extruder, it was ejected from the extruder and rapidly contacted with cold water by floating into it. It was subsequently cut to required pieces and sizes for the second stage of testing. From the study of mechanical properties, it was realized that tensile strength and impact strength increase up to a SiO$_2$ content of 2.5 wt% leading to the conclusion that silica nano-particles act as reinforcing agents.

method showed higher modulus and strength compared to pure Nylon 6. Schematic illustration of melt intercalation process is shown in Figure 2.10.

![Intercalation process between a polymer melt and an organically modified layered silicate (Vaia and Giannelis, 1997).](image)

**Figure 2.10** Intercalation process between a polymer melt and an organically modified layered silicate (Vaia and Giannelis, 1997).

### 2.4.1.3 In-situ Polymerization of Nano-particles/Monomer

In-situ polymerization is a method commonly used to improve the dispersion and compatibility between different phases (Jia, et al., 1999; Jian-Ming, et al., 2004; Li, et al., 2006). The technique has the advantage that the reinforcement is on molecular level and grafting of polymer molecules onto the walls of carbon nano-tubes can be easily done. One can go to very high loading of nano-tubes without any processing problem. This method has been mainly used for preparing insoluble or thermally unstable polymers (Jia, et al., 1999).

Li, et al. (2006) synthesized the MWNT/poly-p-phenylene benzobisoxazole (PBO) nano-composite by in-situ polymerization of dichlorides and diacids under sonication. With strong stirring, stir opalescence formed indicating a nematic phase, and dry-wet spinning technique was used to spun composite dope.

Earlier, Jian-Ming, et al. (2004) using the above method successfully prepared PMMA (Poly-methyl methacrylate) nano-composites containing calcium carbonate. Investigation on the structure of nano-composite samples showed a good grafting of PMMA on the calcium carbonate nano-particles. A diagrammatic presentation of the synthesis of nylon 6/clay nano-composites is shown in Figure 2.11.
2.4.1.4 Ultrasonic Method of Nano-particle Dispersion

Ultrasound is a well-established method for particle size reduction in dispersions and emulsions and ultrasonic processors are used in the generation of nano-size material slurries, dispersions and emulsions because of the potential in de-agglomeration and the reduction of primaries (Kuldiloke, 2002).

Evora and Shukla (2003) succeeded in producing polyester nano-composites containing titanium oxide (TiO$_2$) nano-particles through ultrasonication, Figure 2.12. The nano-composites so prepared had higher hardness compared to pure polymer.
2.4.2 Layered Nano-composites Preparation Methods

As pointed out earlier, during the last few years, the utility of inorganic nano-particles as filler for enhancing the polymer performance has been established. One such technology consists of a polymer and organically modified layered filler (organo-clay) which has shown exhibit remarkably improved mechanical and other properties compared to those of virgin polymers or conventional composite (micro/macroc-omposites) (Okamoto, 2006; Katoh and Okamoto, 2009). Layered nano-composites generally consist of a layer of organic polymer placed between the inorganic layers.

2.4.2.1 Intercalation of Polymer or Pre-polymer from Solution

Intercalation compounding is to intercalate monomer or polymer into the interlayer space or gallery of silicate layers to reduce interlayer attraction, and progressively cause the nano layers to exfoliate and homogeneously disperse in polymer matrix, then realize the compounding of polymer and inorganic silicates on nano-scale. On the whole, intercalation compounding includes two methods: monomer in-situ intercalation polymerization, and direct polymer interaction, which can be applied respectively by two approaches, either solution intercalation or melt intercalation (Wenhua and Guangjie, 2004). The method is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. Nematic liquid crystal Polymer Layered Silicate (PLS) nano-composites have also been prepared using this method in various organic solvents, such as toluene and DMF (Sinha and Okamoto, 2003).

This method is reported to be good for the intercalation of polymers with little or no polarity into layered structures, and facilitates production of thin films with polymer-oriented clay intercalated layers. However, from commercial point of view, this method involves the copious use of organic solvents, which is usually environmentally unfriendly and economically prohibitive. As early as in 1992, Aranda and Ruiz-Hitzky reported the preparation of PEO/MMT nano-composites by this method. The nature of the solvents is of critical importance in this method as it facilitates the insertion of polymers between the silicate layers, while the polarity of the medium is a determining factor for intercalations. The high polarity of water causes swelling of Na\(^+\)-MMT, provoking cracking of the films. Methanol is not suitable as a solvent for high molecular weight PEO, whereas water/methanol mixtures appear to be useful for intercalations, although cracking of the resulting materials is frequently
observed. PEO intercalated compounds derived from the homoionic Na\(^+\)-MMT can satisfactorily be obtained using anhydrous acetonitrile or a methanol/acetonitrile mixture as solvents (Sinha and Okamoto, 2003).

Next to cellulose, Chitosan is the second largest natural biopolymer. Wang, et al. (2005) prepared montmorillonite/chitosan composites with high efficiency by means of solution method. Chitosan solution was prepared by dissolving chitosan (CS) in a 2\% (v/v) aqueous acetic acid solution at a concentration of 2 wt\% followed by centrifuging to remove the insoluble. MMT, swelled by 50 ml distilled water was added to 50 ml chitosan solution followed by stirring at 60\(^\circ\)C for 6-h. Next, MMT/CS solutions were cast on a plastic dish at 60\(^\circ\)C for 48-h. The dry films still contained a small quantity of the solvent (HAc), which formed chitosonium acetate, termed as HAc-CS-x (x is concentration of MMT). CS/MMT nano-compo-sites were prepared by the same procedure as HAc-CS/MMT nano-composites. After drying, the films were soaked in 1 M aqueous NaOH for 5-h to neutralize the acid followed by rinsing in distilled water to neutral and then dried at 60\(^\circ\)C for 24-h. These are termed as CS-x (x is the content of MMT). The authors have observed that increasing the amount of montmorillonite resulted in the enhancement of the modulus and stiffness level of nano-composites samples.

### 2.4.2.2 Melt Intercalation Method

The melt intercalation method is one of the most studied processes, since it permits the straightforward preparation of nano-composites by melt extrusion of the polymer with the silicate (Acierno, et al., 2007). Nano-composites comprising of a semi-crystalline polymer matrix are particularly attractive due to their dramatic improvement in heat distortion temperature (HDT) and modulus provided by the nanoparticle reinforcement. Polymer/clay nano-composites of semi-crystalline thermoplastics such as nylon-6 poly-ethylene terephthalate (PET) and poly-butylene-terephthalate (PBT) have been studied in detail (Acierno, et al., 2007; Berti, et al., 2009).

Maiti, et al. (2003) are the first to report the structure and some of the material properties of PHB/layered silicates obtained by melt intercalation using commonly used polymer processing techniques. The materials have been characterized for their properties with the main focus on the biodegradation aspect. Different types of organoclays were tested: a MMT modified with dimethyloctadecylamine, and two
types of organomodified synthetic fluoromicas which led to intercalated PHB-based nano-composites.

In 2006, Xu and colleagues successfully produced poly-propylene-carbonate (PPC)/montmorillonite (MMT) nano-composites by melt intercalation method. Prior to melt blending, PPC and OMMT were dried at 80°C for several hours under vacuum to remove moisture that could induce degradation reactions of PPC. PPC and various amounts of OMMT were first jumbled in a plastic box and then melt-blended at 130°C for 5 min using a Brabender internal mixer at screw speed of 40 rpm. Upon completion of mixing, the nano-composite was removed from the mixing chamber, and cooled for future use. PPC samples were also processed in the same way for the purpose of comparison. Thermogravimetric analysis showed that the thermal decomposition temperature rises with the increase of filler content. The storage modulus and Young’s modulus of the nano-composites were much higher than that of virgin PPC, indicating the reinforcement by the incorporation of MMT into PPC matrix (Xu, et al., 2006). Melt intercalation has many advantages over solution polymerization and in-situ polymerization. It is compatible with the industrial processes and environmentally benign because of the absence of organic solvents. The polymers whose properties are not suitable for in-situ polymerization or solution polymerization can be processed by melt intercalation (Sinha and Okamoto, 2003).

2.4.2.3 **In-situ Intercalative Polymerization**

The melt intercalation method is a physical process and no chemical reaction is occurs during the preparation. The in-situ intercalative polymerization method consists of swelling of silicate layer in the liquid monomer so that the polymer can be formed between the intercalated sheets. In this method, the nano dimensional clay is dispersed in the monomer, which is then polymerized (Messersmith and Giannelis, 1993; Uthirakumar, et al., 2004). The monomer may be intercalated with the help of a suitable solvent and then polymerized as illustrated in the schematic in Figure 2.13. The advantages of using the in-situ polymerization method include: ease of handling, the speed of the process, and better performance of the final products. Generally, the process of in-situ polymerization involves three continuous steps. First, the nano-scale additives are pretreated with appropriate surface modifiers and then the modified additives are dispersed into monomer(s). This is followed by bulk or solution polymerization; the nano-composites are formed in-situ during polymerization.
Obviously, the important factors that affect the properties of composites are the dispersion and the adhesion at the polymer and filler interfaces. Inorganic particles may disperse homogeneously in the polymer matrices when they are pre-modified by a coupling agent. The polymers studied include PA, PET, PA66, PI, N,N'-bismaleimide-4,4′-diphenylmethane polymer, PMMA, PHEMA, PVA, acrylic polymer, epoxy polymer, PU, PCL and poly-butylene-succinate (Uthirakumar, et al., 2004).

![Figure 2.13](image)

**Figure 2.13** Schematic of nano-composite synthesis by in-situ polymerization (Messersmith and Giannelis, 1993).

This method was used by Jia, et al. (2002) to prepare poly-aniline-dodecylbenzensulfonic acid (PANI-DBSA) nano-composites. Thirty grams of MMT clay was added to 600 g water and vigorously stirred at 80°C for 3 hr to produce a fine aqueous dispersion. The subsequent addition of aniline and DBSA (in stoichiometric ratio) into the clay-water dispersion was either at ambient temperature or at 80°C in a water bath. The monomer-clay-water dispersion was stirred for 2 hr (dispersion at 80°C was under nitrogen purge), and then cooled down while stirring to about 0°C in an ice bath. A solution of APS (stoichiometric ratio with aniline dissolved in 50 g of water) was added drop wise to initiate the polymerization. A color change from white through blue to dark green was observed during the polymerization process. The induction period and polymerization time were recorded from the beginning of the oxidant addition to the reaction mixture until the color turned pale blue and dark green, respectively the PANI-clay composite. The precipitate was filtered, washed with de-ionized water and dried under vacuum at 60°C overnight. The product was finally pulverizes into a fine powder.
2.4.3 Fibrous Nano-composite Preparation Methods

Carbon nano-tube and nanofiber reinforced polymer nano-composites and micronsized carbon fiber-based polymer composites look set to have a significant impact on emerging advanced products ranging from aerospace, automotive and PEM (proton-exchange membrane) fuel cell parts, to surgical implants and to components for nano-electronics. The area of micron-scale carbon fiber filled composites, unlike that of the emerging field of carbon nano-tube and nano-fiber-based nano-composites, is relatively mature (Gunter, 2006).

Micron-sized carbon fibers can be classified in terms of the precursor fiber materials as PAN (polyacrylonitrile)-based, mesophase or isotropic pitch-based, rayon-based, and phenolic-based. The synthesis process involves a heat treatment of the precursor fibers to remove oxygen, nitrogen, and hydrogen to form the carbon fibers. It is well established in the literature that the mechanical properties of the carbon fibers are improved by increasing the crystallinity and orientation, and by reducing defects in the fiber. The best way to achieve this is to start with a highly oriented precursor and then maintain the initial high orientation during the process of stabilization and carbonization through tension. Carbon fibers are used in many applications as a reinforcing agent of polymeric matrices because of having specific modulus, high strength and excellent thermal and electrical properties. CNT (Carbon Nano Tube) and CNF (Carbon Nano Fiber) having specific properties have been studied in detail (Maschmann, et al., 2006).

2.4.4 Sol-gel Method

Sol-gel reactions have also been extensively studied for several decades as a method to prepare ceramic precursors and inorganic glasses at relatively low temperatures. The sol-gel process has been widely used to create novel organic-inorganic composite (hybrid) materials and have been termed as “ceramers” (Huang, et al., 1985).

Poly-dimethyl-siloxane/HTiNbO₅ nano-composites were prepared through sol–gel process by Stephan Bruzaud and coworkers. 3-Amino-propyl-diethoxy-methylsilane can be grafted onto TiNbO₅ by direct reaction without using any solvent. 3-Amino-propyl-diethoxy-methylsilane and the mineral were introduced in the reactor under stirring at room temperature during 48h, followed by addition of small quantity of hydrochloric acid (12 mol/l) added to the mixture as reaction catalyst. The resulting
product was washed three times with toluene and dried under vacuum at 50°C overnight, Figure 2.14. Good and homogeneous mixing of HTiNbO₅ layers in the polymer matrix has been one of the most important characteristics of nano-composite samples which resulted by the above method (Beigbeder, et al., 2005).

Carbon nano-tube reinforced alumina matrix nano-composite was fabricated by Chan, et al. (2005) through sol-gel process. The schematic procedure for the fabrication process of carbon nano-tube reinforced alumina nano-composite is shown in Figure 2.15.

![Figure 2.14 Schematic illustration of the grafting poly (3 aminopropylmethysiloxane) on to HTiNbO₅ layers (Beigbeder, et al., 2005).](image)

Aluminum tri-sec-butoxide (Al (OBu⁴)₃) was used as a precursor of alumina. The multi-wall carbon nano-tubes, fabricated by CVD using alumina-supported catalyst, have dimension of 15–30 nm in diameter, 10–50µm in length. Alumina sol was synthesized by Yoldas’ process, which consists of hydrolysis and peptization of aluminum hydroxide (AlOOH). The carbon nano-tubes dispersed as suspension within ethanol were added to alumina sol during the gelation process. The carbon nano-tube/alumina gel was dried at 350°C for 6 hr. The carbon nano-tube/alumina composite powders were fabricated by calcinations of gel powder at 1250°C for 1 hr under 10 Pa vacuum. The resulting nano-composite samples had better mechanical properties than the pure polymer (Chan, et al., 2005).
Figure 2.15 Schematic diagrams for sol–gel process for fabrication of CNT reinforced alumina composite powders (Chan, et al., 2005).

Rajatendu, et al. (2005) produced nylon 66/in situ silica hybrid nano-composites by sol–gel technique. They first dissolved a commercial grade of PA66 in 85% formic acid to prepare a 10 wt% PA66 solution. Different amounts of TEOS (Tetraethoxysilane) were carefully added to this 10 wt% PA66 solution at room temperature (30°C). The solutions in beakers were covered with polyethylene (PE) films and allowed to stand at room temperature for 12 hr to allow the hydrolysis and condensation reactions of TEOS to continue and were then finally poured onto thoroughly cleaned glass plates for room temperature drying in a fume hood to constant weight. The resultant films were vacuum dried for 24 hr at 80°C for obtaining self-standing films with approximate thickness of 100-150 µm ready for testing. Thermogravimetric analysis showed decreasing thermal properties of the resulting samples in comparison to the pure polymer.

2.5 Uses of Nano-particles

It is commonly accepted that the addition of nanosize fillers into polymers can enhance polymer properties. Different types of nanosize fillers are widely used to make advanced composite materials.
2.5.1 Use of Nano-particles for Improving Polymers Properties

While a large number of researches have reported the fabrication of nano-composites with polymeric matrix, yet, there is no general agreement on the mechanism by which the properties of the polymer matrix improve by the addition of the nano-particles. This may be attributed to the fact that the emerging field of nanotechnology/nano-composites lacks confirmatory experimental results. Also, there is lack of complete and comprehensive theoretical studies in this field. Polypropylene (PP) because of its resistance to water, chemical and fuel (gasoline) has been widely used as sheets and molded parts. In addition, PP has low volume, good mechanical properties and low cost. However, its resistance to impact or in low temperature is very weak. Therefore, in order to reinforce and modify of its properties, different elastomers and polymers are added to it (Cayer-Barrioz, et al., 2006; Hanim, et al., 2008). For example, ethylene-diene-polypropylene terpolymer can improve PP resistance to impact intensively. With addition of some filler like talc, calcium carbonate, titanium oxide, magnesium oxide and glass fibers, the properties of PP can be improved (Hanim, et al., 2008).

For filler contents greater than 5%, the stiffening effect of the filler counterbalanced the negative effect of premature de-bonding. The maximal stress and its corresponding strain increase with increasing CaCO₃ content in the case of AST and AA treatments. Tensile tests performed at 353 K on neat PA66 and on the 5% composites systematically displayed a ductile behavior. The data of Table 2.1 show that the stress level at the yield point, σ_max, decreases significantly as compared with that at room temperature, whereas the elongation at failure, ε_f, increases far beyond the corresponding value at room temperature. Young’s moduli at 353 K were much smaller than at room temperature, Table 2.1, because of the fact that the PA66 amorphous phase is rubbery at that temperature. Notwithstanding, a stringent 2.5-fold increase of Young’s modulus was observed at 353 K for the 5% CaCO₃ composite as compared with unfilled PA66 (Cayer-Barrioz, et al., 2006).
Table 2.1 Mechanical Properties of the 5% CaCO₃ Composites at $1.52 \times 10^{-2}$ s⁻¹ and 353 K (Cayer-Barrioz, et al., 2006).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mechanical behavior</th>
<th>E (MPa)</th>
<th>$\sigma_{\text{max}}$ (MPa)</th>
<th>$\varepsilon_{\text{max}}$ (%)</th>
<th>$\varepsilon_{\text{f}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>Ductile</td>
<td>440±10</td>
<td>55±2</td>
<td>20±3</td>
<td>105±54</td>
</tr>
<tr>
<td>PA66-5</td>
<td>Ductile</td>
<td>1640±140</td>
<td>63±5</td>
<td>12±4</td>
<td>15±6</td>
</tr>
<tr>
<td>PA66-AST5</td>
<td>Ductile</td>
<td>2000±80</td>
<td>63±2</td>
<td>13±1</td>
<td>20±4</td>
</tr>
<tr>
<td>PA66-AA5</td>
<td>Ductile</td>
<td>1470±160</td>
<td>62±6</td>
<td>16±1</td>
<td>26±1</td>
</tr>
</tbody>
</table>

The SEM images of composite samples showed that filler particles are an obstacle to the polymer deformation. So that in the round of particles, the matrix caused to be more stretched and because of the lack of good enough adhesion and weak interface, small cavities have been formed. Further, due to consistent application of stress, the cavities make bigger and are subsequently incorporated together to form still bigger cavities, and finally the sample suddenly breaks (Zebarjad and Bagheri, 1999). The variation in the impact energy as a function of weight percent of calcium carbonate showed that with increasing the weight percent of calcium carbonate, impact resistance decreases. This phenomenon can be attributed to the following factors:

1. Decrease in the ability to move in the molecular chains of polymers by filler phase which causes the composite to be more brittle,

2. The weak interface between particles and polymer matrix which causes to form a place for micro cracking nucleation, and crack progresses through this way (Zebarjad and Bagheri, 1999).

Chen and Cheung (2002) prepared Polypropylene (PP) and calcium carbonate nanocomposites and measured its elastic properties. The average primary particle size of the CaCO₃ nano-particles was measured to be about 44 nm. Based on the results of elemental analysis, it can be concluded that the sample contains more than 98 wt% CaCO₃ with a small amount of impurities including MgO, Fe₂O₃ and Al₂O₃. Figure 2.16 shows that the weight loss is small, until the temperature is above 400°C. At 550°C, the weight loss is about 5 wt%. These results indicate that CaCO₃ nano-particles can be used as filler for most thermoplastics, because most processing temperatures are below 400°C (Chen and Cheung, 2002). It is known that the dispersion of filler in the polymer matrix can have a significant effect on the mechanical properties of the composites. The dispersion of inorganic filler in a thermoplastic is not an easy process.
The problem is even more severe, when using nano-particles as filler, because the nano-particles have a strong tendency to agglomerate. Consequently, homogeneous dispersion of the nano-particles in the thermoplastic matrix is a difficult process. A good dispersion is achieved by surface modification of the filler particles and appropriate processing conditions.

The TEM micrographs of the nano-composites containing; 4.8, 9.2 and 13.2 volume percentage of CaCO₃ show that good dispersion is achieved. Most CaCO₃ aggregates are broken down to primary particles. This should maximize the interfacial interaction between the nano-particles and the polymer. However, more aggregates are found for the nano-composite with a high concentration of CaCO₃ (Chen and Cheung, 2002).

![Figure 2.16 TGA curve of CaCO₃ nano-particles (Chen and Cheung, 2002).](image)

To determine the optimal mixing time, three mixing times, 15, 30 and 45 min were used. The mechanical properties, which can be significantly affected by the dispersion of the nano-particles in the composites, were measured. Figure 2.17 shows the impact strength of the composites prepared with different mixing times. The results suggest that the impact strength is not significantly affected by mixing time. The other mechanical properties of the nano-composites are also found not being affected by the mixing time. These results indicate that a mixing time of 15 or 30 min is adequate. The tensile stress-strain curves of the pure PP and the nano-composites are shown in Figure 2.18.
Fig. 2.17 The Izod impact strength of the nano-composites prepared with different mixing times (Chen and Cheung, 2002).

Figure 2.18 Stress-Strain curves of the nano-composites and pp (Chen and Cheung, 2002).

Results have indicated that a decrease in the spherulite size and crystallinity decreases the modules of PP, because large spherulites are believed to have a much higher load-bearing capability. The TEM results indicate that the aspect ratio of the nano-particles is low. Hence, a significant increase in the modulus must be caused by the strong interaction between the polymer and filler, because of the large interfacial area between them.

There are two counter forces that affect the mechanical properties of these nano-composites: the reinforcing and nucleating effects of the CaCO₃ nano-particles. In addition, the strong interaction between the filler and the polymer increases the tensile
strength, as well as yield strength nucleating effect of the CaCO$_3$ nano-particles produces the opposite effects. A reduction in the size of the spherulites generally reduces the yield and ultimate tensile strengths, but increases the ultimate elongation (Chen and Cheung, 2002).

Poly-vinyl chloride (PVC) is one of the major thermoplastics used today, and a large amount of PVC is produced worldwide (Costa, et al., 2009). However, process ability and thermal stability of PVC are inferior to those of other commodity plastics, like polyethylene and polystyrene. Much improvement of the inferior properties of PVC has been carried out by the incorporation of additives such as plastizers, heat stabilizers, lubricants, fillers and copolymerization with other monomers. Amongst these methods, compounding PVC with inorganic fillers is a convenient and efficient method (Xie, et al., 2004).

Xie, et al. (2004) produced poly-vinyl chloride (PVC)/CaCO$_3$ nano-composites by in-situ polymerization process and evaluated their thermal, rheological and mechanical properties. The storage modulus of pure PVC and containing 1, 2.5, 5 and 7.5 wt% of CaCO$_3$ in the temperature range studied (<60°C) was found lower than the PVC/CaCO$_3$ nano-composites. For example, at 23°C, the storage modulus of the PVC/CaCO$_3$ nano-composites increased (by a maximum ~18%) with increasing CaCO$_3$ nano-particle loading. It confirms that well-dispersed CaCO$_3$ nano-particles stiffen the PVC matrix. However, when the nano-particle is 7.5 wt%, the stiffening effect is progressively reduced with increasing temperature most probably due to the agglomeration of CaCO$_3$ nano-particles. Figure 2.19 shows the loss factor (tanδ) versus temperature for these nano-composites.

Thermogravimetric analysis (TGA) of the samples has also been reported. Figure 2.20 shows the variation of storage modulus with temperature for pristine PVC and PVC/CaCO$_3$ nano-composites up to 7.5 wt% of nano-particles. The glass transition temperatures ($T_g$) of the PVC phases in pristine PVC and PVC/CaCO$_3$ nano-composites are listed in Table 2.2. Clearly, the glass transition peak of PVC in PVC/CaCO$_3$ nano-composites tends to shift towards a marginal but definitely higher temperature as the CaCO$_3$ nano-particles loading is increased (to < 7.5 wt%). These results confirm that well dispersed nano-particles restrict the motion of PVC segmental chains. As with the storage modulus, agglomeration of CaCO$_3$ nano-particles at 7.5 wt% loading weakens the interaction between PVC chains and nano-particles so that the $T_g$ decreases (Xie, et al., 2004). Figure 2.21 shows the thermogravimetric ($T_g$)
curves for the pristine PVC and nano-composites to 400°C. From these curves, the 5% weight loss temperature ($T_{5\%}$) and maximum weight loss temperature ($T_{max}$, defined as the peak on the derivation of the $T_g$ curve) are obtained and listed in Table 2.2.

![Figure 2.19](image1.png)

**Figure 2.19** Variation of tan $\delta$ with temperature for PVC and nano-composites (Xie, et al., 2004).

![Figure 2.20](image2.png)

**Figure 2.20** Variation of storage modulus with temperature for PVC and nano-composites (Xie, et al., 2004).

It is evident that maximum decomposition at $T_{max}$ corresponds to dehydrochlorination. In addition, the thermal stability of PVC at 190°C is important for its processing, and as given in Table 2.2, the weight residue of the PVC/ CaCO$_3$ nano-composites is higher than that of pristine PVC. Therefore, PVC/CaCO$_3$ nano-composites have good thermal stability, required for their processing (Xie, et al., 2004).
Table 2.2 $T_g$ and TGA results of PVC and PVC/CaCO$_3$ nano-composites (Xie, et al., 2004).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°c)</th>
<th>$T_{5%}$ (°c)</th>
<th>$T_{max}$ (°c)</th>
<th>Weight residue at 190 (°c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVC</td>
<td>81.7</td>
<td>254.01</td>
<td>275.30</td>
<td>98.6</td>
</tr>
<tr>
<td>PVC/2.5%</td>
<td>82.8</td>
<td>257.80</td>
<td>280.30</td>
<td>99.1</td>
</tr>
<tr>
<td>PVC/5.0%</td>
<td>83.1</td>
<td>258.02</td>
<td>276.40</td>
<td>99.2</td>
</tr>
<tr>
<td>PVC/7.5%</td>
<td>81.9</td>
<td>261.03</td>
<td>276.33</td>
<td>99.1</td>
</tr>
</tbody>
</table>

Figure 2.21 Thermogravimetric (TG) curves for the pristine PVC and nano-composites (Xie, et al., 2004).

Figure 2.22 Rheological curves for the pristine PVC and nano-composites at 175°C (Xie, et al., 2004).

Rheological properties: The rheological properties of polymer materials are important for their processing. These are most often studied by using capillary rheometry. Thus, the rheological behaviors of pristine PVC and PVC/CaCO$_3$ nano-
composites were examined by a capillary rheometer and the results at 175°C are given in Figure 2.22. All these materials exhibit non-Newtonian and shear thinning characteristics in the range of applied shear rates. The linear relationship between log $\eta_a$ and log $\gamma$ in Figure 2.22 suggests a power law ($\eta_a = k\gamma^{n-1}$), where $k$ is a constant and $n$ is the power law index. Figure 2.23 shows that, at low shear rates ($<100$ s$^{-1}$), $\eta_a$ of PVC/CaCO$_3$ nano-composite with 2.5 wt% CaCO$_3$ nano-particles is higher than the pristine PVC; but at larger loading of nano-particles $\eta_a$ is lower. At high shear rates ($>100$ s$^{-1}$), $\eta_a$ of all PVC/CaCO$_3$ nano-composites are lower than pristine PVC, and decreases with increasing content of nano-particles (Xie, et al., 2004).

Mechanical properties: The mechanical properties of the PVC/CaCO$_3$ nano-composites indicate that CaCO$_3$ nano-particles stiffen and toughen PVC. At 5 wt% nano-particles, optimal properties were obtained in Young’s modulus, tensile yield strength, elongation-at-break and Charpy notched impact energy. Variations curves of these properties are presented in Figure 2.24 to 2.26.

![Figure 2.23](image)

**Figure 2.23** Effect of the nano-particle content on apparent viscosity of the PVC/CaCO$_3$ nano-composite (Xie, et al., 2004).

Detailed examinations of failure mechanisms of impact and tensile specimens showed that CaCO$_3$ nano-particles acted as stress concentrators leading to interface debonding/voiding and matrix deformation. These mechanisms lead to impact toughening of the nano-composites (Xie, et al., 2004). As an important inorganic filler or pigment, calcium carbonate (CaCO$_3$) has been used in many fields (Wu, et al., 2004; Liu, et al., 2006).
In 2004, Wu and coworkers examined the effect of CaCO₃ nano-composites on poly-vinyl chloride (PVC) properties. Figure 2.27 presents the notched Izod impact strength of PVC/nano-CaCO₃ composites at various weight ratios, which indicated that the nano-CaCO₃ particles had a remarkable toughening effect on PVC. The impact strength of pure PVC was 53.4 J/m, and it increased slightly to 76.5 J/m for the PVC/nano-CaCO₃ composites. Predictably, the impact strength increased gradually with increasing the nano-CaCO₃ particles content.

Figure 2.24 Variation of tensile yield strength of nano-composite with nano-particle loading (Xie, et al., 2004).

Figure 2.25 Variation of Young’s modulus of nano-composite with nano-particle loading (Xie, et al., 2004).
Predictably, the impact strength increased gradually with increasing the nano-CaCO₃ particles content. The toughness of PVC was improved by a factor of 3 with addition of 30 wt % nano-CaCO₃ particles. Although extensive literature reported that micro-sized CaCO₃ fillers had a positive effect on toughness of PVC the improvement in Izod impact strength was moderate. The tensile strength and elongation at break of PVC/nano-CaCO₃ composites at various weight ratios are presented in Figure 2.28.

The PVC/nano-CaCO₃ composites, at a weight ratio of 95.5, exhibited a slightly higher tensile strength than that of pure PVC, which revealed that the nano-CaCO₃ particles gave a strength enhancement on the PVC matrix like the normal micro-sized
CaCO$_3$ filler. However, a further increase in the nano-CaCO$_3$ particle contents resulted in a decrease in the tensile strength. This may be a result of the poor filler–polymer interaction (Wu, et al., 2004).

![Figure 2.28](image)

**Figure 2.28** Tensile strength and elongation at break of PVC/nano-CaCO$_3$ composites vs. nano-CaCO$_3$ content (Wu, et al., 2004).

On the other hand, the elongation at break kept a continuous increase with increasing the nano-CaCO$_3$ content. This may be attributed to the increasing deformation of the matrix caused by the energy dissipating in toughening (Wu, et al., 2004). It could also be found, as shown in Figure 2.29, that Young’s modulus of PVC/nano-CaCO$_3$ composites gave higher performance with increasing the nano-CaCO$_3$ content, which could be attributable to the improvement of rigidity of nanocomposites due to introduction of rigid filler into the PVC matrix. The effect of chlorinated polyethylene (CPE) contents on notched Izod impact strength of PVC/CPE/nano-CaCO$_3$ composites against the nano-CaCO$_3$ content is shown in Figure 2.30. Comparing the binary nano-composites with ternary nano-composites in the same PVC/nano-CaCO$_3$ proportion, the Izod impact strength of ternary nano-composites is much higher than that of the binary one (Wu, et al., 2004). At the same time, the greater the CPE content, the higher the Izod impact strength. The remarkable improvement in impact strength shows how important the effect of CPE is on the nano-composites. It is well known that CPE is a good impact modifier for PVC, and a toughening effect for the PVC/CPE system can be observed only when the CPE content is higher than 15 wt.%.
Figure 2.29 Young’s modulus of PVC/nano-CaCO$_3$ composites vs. nano-CaCO$_3$ content (Wu, et al., 2004).

Figure 2.30 Notched Izod impact strength of PVC/CPE/nano-CaCO$_3$ composites vs. nano-CaCO$_3$ content (Wu, et al., 2004).

The effect of CPE content on tensile properties of PVC/CPE/nano-CaCO$_3$ composites has also been studied by tensile testing, as reported in Figures 2.31 to 2.33. The tensile strength and Young’s modulus of the ternary nano-composites are lower compared to pure PVC, as a result of introduction of CPE, which, as a flexible polymer, would soften the composite materials. However, the decrease in tensile strength for the ternary nano-composites is continuous and slight, compared to the strongly negative influence of nano-CaCO$_3$ for binary nano-composites.

Apparently, CPE is miscible with PVC. The nano-CaCO$_3$ particles are surface modified with CPE by preparing the CPE/nano-CaCO$_3$ master batch, which functions
to strengthen the interaction between PVC and nano-CaCO₃. As a result, the mechanical properties could be enhanced partially. The same reason could be given for the increase in elongation at break and Young’s modulus with increasing the nano-CaCO₃ content. The morphology of PVC/CPE/nano-CaCO₃ composites was also studied by the authors. Comparing the TEM micrographs of ternary nano-composites with those of binary ones, the dispersions of the particles in PVC matrix for both were reported to be quite similar. However, the individual particle size of ternary nano-composites was slightly larger than that of binary ones from the TEM micrographs (Wu, et al., 2004).

![Figure 2.31 Tensile strength of PVC/CPE/nano-CaCO₃ composites vs. nano-CaCO₃ content (Wu, et al., 2004).](image)

Nano-CaCO₃ particles were encapsulated with a CPE layer through preparation of the CPE/nano-CaCO₃ master batch. During preparation of the ternary nano-composites through melt mixing the PVC and master batch, the CPE layer was not broken down during the processing of the PVC and master batch. Finally, in the PVC matrix, the nano-CaCO₃ particles act as “core-shell” particles with an elastomeric shell and rigid core. This is schematically illustrated in Figure 2.34 (Wu, et al., 2004).
Figure 2.32  Elongation at break of PVC/CPE/nano-CaCO$_3$ composites vs. nano-CaCO$_3$ content (Wu, et al., 2004).

Figure 2.33  Young’s modulus of PVC/CPE/nano-CaCO$_3$ composites vs. nano-CaCO$_3$ content (Wu, et al., 2004).

Distinct from the rigid particle toughening mechanism for PVC/nano-CaCO$_3$ composites, the toughening effect for ternary nano-composites can be attributable to a rubber-toughening mechanism, because the nano-CaCO$_3$ particles encapsulated with the CPE layer play a role of elastomer particles in the matrix. This mechanism is in good agreement with the observed notched Izod impact strength of ternary nano-composites. To verify the above conclusion, they also observed the TEM micrograph of the PVC/CPE blend that as shown in Figure 2.35. It was found that the CPE domain had a particle size ranging from 100 to 200 nm, which was much larger than the particles observed in the TEM micrographs of ternary nano-composites. This result
confirmed the fact that the nano-CaCO₃ particles were encapsulated with the CPE layer (Wu, et al., 2004).

**Figure 2.34** Scheme of the processing for PVC/CPE/nano-CaCO₃ composites (Wu, et al., 2004).

**Figure 2.35** TEM micrograph of the PVC/CPE blend stained at a weight ratio of 97:3 (Wu, et al., 2004).

**Figure 2.36** shows the impact fractured surface of PVC/nano-CaCO₃ binary and PVC/CPE/nano-CaCO₃ ternary nano-composites, which demonstrated completely different fracture behaviors. In **Figures 2.36 a, b, and c**, which are based on the binary nano-composites, it may be seen that the fracture surface is smooth and featureless. It is also noticed that better particle dispersion in the matrix tends to form smaller agglomerates. However, it is also observed that massive plastic deformation on the fracture surface of binary composites is accompanied by a large number of voids,

65
which was might have been caused by matrix cavitations due to the addition of the nano-CaCO\textsubscript{3} particles. On the other hand, as demonstrated in Figure 2.36 d to f, the fracture surface of the ternary nano-composites had a highly plastic deformation exhibiting high-impact energy. This extensive plastic deformation of the matrix was accompanied by the crack propagation. A characteristic feature of the fracture surface of the ternary nano-composites is the formation of thread-like striations perpendicular to the direction of the crack propagation (Wu, et al., 2004).

![SEM micrographs of the PVC/nano-CaCO\textsubscript{3} composites at a weight ratio of: (a) 95/5, (b) 90/10, (c) 80/20; and the PVC/CPE/nano-CaCO\textsubscript{3} composites at a weight ratio of: (d) 95/3/5, (e) 90/3/10, (f) 80/3/20 (Wu, et al., 2004).](image)

**Figure 2.36** SEM micrographs of the PVC/nano-CaCO\textsubscript{3} composites at a weight ratio of: (a) 95/5, (b) 90/10, (c) 80/20; and the PVC/CPE/nano-CaCO\textsubscript{3} composites at a weight ratio of: (d) 95/3/5, (e) 90/3/10, (f) 80/3/20 (Wu, et al., 2004).

Rheological properties: the apparent viscosities of pure PVC, and PVC/nano-CaCO\textsubscript{3} and PVC/CPE/nano-CaCO\textsubscript{3} composites measured in the capillary rheometer at 180°C, are shown in Figure 2.37.
Figure 2.37 Plots of apparent viscosity vs. non-Newtonian shear rate for the PVC/nano-CaCO₃ binary and PVC/CPE/nano-CaCO₃ ternary composites and PVC/CPE blend (Wu, et al., 2004).

The PVC/nano-CaCO₃ binary composites had a much higher viscosity than pure PVC in all ranges of the shear rates carried out in this experiment. It was observed that the introduction of rigid filler into PVC reduced the flow ability of PVC, and hindered the disentanglement of the molecular chains of PVC. The increase in melt viscosities of binary composites is due to these two effects. When CPE was introduced to PVC/nano-CaCO₃ binary composites, the viscosity of ternary nano-composites was lower than that of the binary ones in the same PVC/nano-CaCO₃ proportion (Wu, et al., 2004).

Chen et al. (2004b) investigated the effects of nano-scale calcium carbonate (nano-CaCO₃) particles on the properties of Polyvinyl chloride (PVC) and PVC/Blendex (BLENDEX 338). The impact strengths of the composites are presented in Figure 2.38.
Figure 2.38  Notched impact strength of the composites as a function of nano-CaCO$_3$ content (Chen, et al., 2004b).

It can be seen that PVC/Blendex blend exhibits much better impact performance than PVC, and the impact strength of PVC/nano-CaCO$_3$ binary composites and PVC/Blendex/nano-CaCO$_3$ ternary composites can be increased simultaneously in a broad range of nano-CaCO$_3$ content. For example, the impact strength of the binary composites reaches the maximum value of 39 J/m when 15 phr nano-CaCO$_3$ is introduced, about 30% higher than that of pure PVC (30 J/m), while the maximum impact strength of the ternary composites is 819 J/m, which is about 81% higher than that of PVC/Blendex blend (453 J/m). This result suggests a much better toughening effect of nano-CaCO$_3$ on PVC/Blendex matrix than that on PVC matrix. The SEM micrographs of the impact-fractured surfaces of the composites are shown in Figure 2.39 (Chen, et al., 2004b). Referring to Figure 2.39 (b), cavities can be found on the fracture surface of the ternary composites, some of which are occupied by CaCO$_3$ particles. These cavities are much larger than the particles, suggesting cavitations happen during the samples being impacted. Since no cavity is observed on the fracture surface of PVC/Blendex blend, as shown in Figure 2.39 (a), the presence of CaCO$_3$ particles must be responsible for the cavitations. This cavitation could absorb large amounts of energy, leading to the improvement of the composites’ impact strength.
On the other hand, few cavities can be observed on the fracture surface of PVC/nano-CaCO₃ binary composites, Figure 2.39 (c). This indicates that the toughening effect of nano-CaCO₃ on pure PVC is restricted to the mechanical coupling between the filler and polymer matrix, and no cavitation is involved. Figures 2.40 and 2.41 represent the yield strength and elongation at break of PVC/nano-CaCO₃ binary composites and PVC/Blendex/nano-CaCO₃ ternary composites, respectively. The yield strength of the ternary composites is slightly decreased with the increase of nano-CaCO₃ content, while that of the binary composites can be increased when the nano-CaCO₃ is below 10 phr. An interesting phenomenon is that the elongation at break of the binary composites can be greatly increased when a low content of nano-CaCO₃ is introduced. That is quite different from many other composites based on spherical nano-scale fillers, which exhibit either decreased or no changed elongation at break with the addition of fillers. It also can be seen from Figure 2.40 that the elongation at break of the ternary composites generally decreases with nano-CaCO₃ content (Chen, et al., 2004b).
Flexural modulus: as shown in Figure 2.42, the flexural moduli of PVC/nano-CaCO$_3$ binary composites and PVC/Blendex/nano-CaCO$_3$ ternary composites enhance with the increase of nano-CaCO$_3$ content independent of the filler dispersion state. Classically, composites based on spherical mineral fillers and polymer matrix exhibit improved elastic moduli with the increase of the filler concentration, due to the rigidity of fillers and the strong interaction between the filler and polymer matrix (Chen, et al., 2004b).
Jiang, et al., 2005, investigated reinforced effect of nano-sized and micron-sized calcium carbonate on acrylonitrile-butadiene-styrene (ABS). Micron-sized inorganic fillers have long been used in polymer industry to increase modulus and/or lower costs of the products. As expected, the moduli of MCC (micron-sized calcium carbonate)/ABS and NPCC (nano-sized precipitated calcium carbonate)/ABS composites improved with increasing filler contents as shown in Figure 2.43.

NPCC was in cubic shape and there was no strong polymer/NPCC interaction at the interface. Therefore the reinforcing effect of NPCC was much less than that
reported in the literature. Indeed, the moduli of NPCC/ABS were even lower compared to MCC/ABS composites at the same filler content. This could be due to more uneven dispersion of NPCC than MCC in ABS matrix as revealed by SEM micrographs. In addition, modulus was calculated in the linear elastic region of the composites. Within this small strain, the stress was not high enough to break the bonding between the particles and ABS matrix. Therefore the larger interfacial area of NPCC/ABS did not contribute to modulus enhancement at this stage. On the other hand, the large size MCC particulates might be more effective in impeding the deformation of the polymer chain than small NPCC, and hence lead to higher moduli of MCC/ABS composites (Jiang, et al., 2005). In general, the enhancement of modulus by inorganic fillers is achieved at the expense of tensile and impact strength, due to the filler-polymer interfacial weakness. As shown in Figures 2.44 and 2.45, ultimate tensile strength and impact strength of MCC/ABS decreased with higher filler contents. Although the tensile strength of NPCC/ABS also decreased, the rate of decline is less.

![Figure 2.44](image)

**Figure 2.44** Tensile strength of NPCC/ABS and MCC/ABS composites with different powder contents (Jiang, et al., 2005).

At the same filler contents, NPCC/ABS had a higher tensile strength than its counterpart, especially at high filler ratios, **Figure 2.44**. At low filler ratios, the differences were small. As explained above, the modulus of NPCC/ABS is smaller than that of MCC/ABS due to the small strain when the modulus was calculated. With rising strain, the stress increased to the threshold of the particle/polymer bonding strength. At this stage, a larger interfacial area meant higher load the specimen could withstand.
Therefore NPCC/ABS, with larger interfacial area, had higher ultimate tensile strength than MCC/ABS. The difference in impact strength between the two composites was much more significant, as can be seen in Figure 2.45. NPCC/ABS had much higher impact strength than its micron-sized counterpart over most of the wt% range. At small filler contents (≤ 8 wt%), the impact strength of ABS was basically maintained or even slightly improved by the addition of NPCC, whilst the modulus increased by 49% at the same time. This shows the great advantage of using NPCC as strengthening fillers in polymer processing (Jiang, et al., 2005).

![Figure 2.45](image)

**Figure 2.45** Impact strength of NPCC/ABS and MCC/ABS composites as a function of powder loading (Jiang, et al., 2005).

### 2.5.2 Influence of Particle Size: From Micro to Nano-meter

As pointed out earlier, enhancement of the modulus and hardness of polymers are quite often achieved by the application of micrometer size inorganic particles; however, this may lead to a reduction in the material ductility. Even though, either by decreasing the particle size or by enhancing the particle volume fraction, the strength can be improved; in some cases the fracture toughness and modulus remain fairly independent of the particle size, even when going down to the nano-scale (Ng, et al., 2001). The changes in other properties resulting from particle content and size depend on the type of loading applied. In order to improve the wear resistance, various kinds of micro-sized particles, e.g., TiO₂, ZrO₂, CaCO₃, Sic, and copper compounds (CuO, CuS, CuF), can be incorporated into different polymer matrices, e.g., polyether-ether-ketone (PEEK) (Bahadur and Gong, 1992), polyamide (PA) (Bahadur, et al., 1992), poly-
phenylene sulfide (PPS) (Schwartz and Bahadur, 2001), and poly-tetrafluoro-ethylene (PTFE) (Tanaka, 1986). The improvements of the wear resistance can be due to physical, mechanical (the enhanced modulus and hardness) and chemical (the improved bonding between transfer films and metallic counterparts) reasons. PEEK, PPS, and PA are attractive semi-crystalline thermoplastics for tribological applications due to their special features, e.g., the high-temperature resistance of PEEK and PPS, and good wear resistance of PA. The incorporation of micrometer scale inorganic particles led to two opposite trends in the wear resistance, as it was clearly demonstrated in studies of Bahadur and co-workers (Bahadur and Gong, 1992; Schwartz and Bahadur, 2001). It was found that CuO and CuS are very effective in reducing the wear rate of PEEK and PA11, whereas ZnF, ZnS, and PbS increased the wear rate of PA11.

2.5.3 Influence of the Nano-particle Volume Content

Agglomeration is considered as a general problem of polymer nano-composites, especially for higher contents of nano-fillers. Figure 2.46 illustrates the correlation among particle diameter, distance, and volume content (based on the assumptions of spherical particles, cubic distribution and ideal dispersion). It should be noted that agglomerations may easily happen for smaller particles at higher filler contents due to the reduced inter-particle distance. So far, various inorganic nano-particles, e.g., Si₃N₄, SiO₂, SiC, ZrO₂, Al₂O₃, TiO₂, ZnO, CuO, CaCO₃, may be incorporated into different matrices, in order to improve their wear performance. In most of these cases, optimum nano-particle filler contents can be acquired, at which the wear resistance of polymers is the best. It may also be noted that high filler contents lead to deterioration of the wear properties, which may be due to the tendency of particle agglomeration. It is of utmost importance that the nano-particles must be uniformly dispersed rather than being agglomerated in order to yield a good property profile (Wang, et al., 1997; Wang, 1998).
Dispersion is the process of breaking apart large agglomerates and ensuring wetting of the particle surface to ensure particle separation. Dispersants are used to maintain particle separation by steric hindrance or electrostatic stability and stearic acid is a normally used chemical dispersant. Ultrasonic agitation is a common method for dispersing agglomerates. The duration, acoustic power and temperature affect the extent of agglomeration: it has been found that short durations of 1 – 3 minutes are sufficient to form a well dispersed suspension. Once the agglomerates have been broken up by ultrasound, stearic acid adheres to the surface of the particles and prevents further agglomeration (Stachowiak and Batchelor, 2001).

2.6 Experimental Characterization Techniques

Analytical techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are generally used to elucidate the structure of polymer nano-composites (Salavati-Niasari, et al., 2007; Petroski, et al., 2009). In the following sections, the characterization techniques used for the analysis of CaCO$_3$ nano-particles and micro-nano-composites are briefly explained.

2.6.1 X-ray Diffraction (XRD)

The structure of nano-composites has typically been established using X-ray diffraction (XRD) analysis. XRD is a non-destructive analytical technique for
identification and quantitative determination of long-range order in various crystalline compounds. The wavelength ($\lambda$) of X-rays is characteristic of the target anode material used and is given by (Klugg and Alexander, 1974; Moore and Reynolds, 1997):

$$\lambda = \frac{hc}{E}$$

(2.1)

Where, $h$ is the Planck’s constant, $c$ is the velocity of light and $E$ is the energy of the photon. Since the wavelength of X-ray is comparable to the atomic size, they can be effectively used to measure the structural arrangement of atoms in materials. In laboratory instruments X-rays are produced in tubes having copper (Cu) or molybdenum (Mo) anodes, which emit x-rays corresponding to wavelengths of 1.54 Å and 0.8 Å, respectively. X-rays interact with electrons in atoms. When X-rays collide with electrons, some X-rays from the incident beam are deflected away from the incident direction. If the wavelengths of these scattered X-rays remain unchanged, the process is called an elastic scattering (Thompson Scattering) in that only the momentum is transferred during collision (Klugg and Alexander, 1974). These are the X-rays that are measured in diffraction experiments. They carry information about the electron distribution in materials. On the other hand, during inelastic collision (Compton Scattering), X-rays transfer some of their energy to the electrons and so the scattered X-rays will have different wavelength than the incident X-rays. X-rays diffracted from different atoms interfere with each other. If the atoms are arranged in a periodic fashion, as in the case of crystals, the peaks in the interference pattern will correspond to the distribution of atoms. The peaks in an X-ray diffraction pattern are directly related to the atomic distances by Bragg’s law (Klugg and Alexander, 1974; Moore and Reynolds, 1997):

$$n\lambda = 2d_{hkl} \sin \theta$$

(2.2)

Where, $\lambda$ is the wavelength of X-ray, $d$ is the inter-planar distance; $\theta$ is the scattering angle and $n$ an integer representing the order of the diffraction peak, as shown in Figure 2.47.
Figure 2.47 Schematic for Bragg’s law (Klugg and Alexander, 1974).

X-ray diffraction data can be collected by using either reflection or transmission geometry, Figure 2.48. X-rays scattered or reflected from the sample are detected in the reflection mode, Figure 2.48 (a). The reflected x-rays interfere with each other such that in the diffractogram, intense peaks are obtained at corresponding d values, according to the Bragg’s law. The peak position, intensity, and shape provide important information about the long-range order in the material. For example, the apparent crystal size (D) can be quantitatively calculated by Scherrer’s formula (Klugg and Alexander, 1974):

\[ D = \frac{0.9 \lambda}{\beta_o \cos \theta} \]  \hspace{1cm} (2.3)

Here, \( \beta_o \) is the half width of the crystalline peak in radians. In the transmission mode, a circular cone of transmitted rays through the sample incident on an area detector giving a circular ring like pattern is observed, Figure 2.48 (b). The radius of the circular ring corresponds to the inter-planar distance. The intensity along the circumference of the circle gives the intensity along the azimuthal angle (\( \chi \)), which gives information about orientation of the scattering entities in the sample. XRD can be very effectively used for intercalated composites, containing silicate layers arranged in a periodic spacing of a few nano-meters. However, XRD has limited use in completely disordered exfoliated state, where the layered structure is completely lost.
2.6.2 Transmission Electron Microscopy (TEM)

Conventional optical microscopes can investigate structure to the resolution of few micrometers. But much higher resolution is required for the investigation of fine structural details of the polymer nano-composites. A transmission electron microscope (TEM) is used to observe the fine scale structure (Klugg and Alexander, 1974). A TEM functions exactly as its optical counterpart except that it uses a focused beam of electrons instead of visible light to "image" the specimen and gain insight about the structure and composition. The four basic operations involved are:

1. A stream of electrons is formed and accelerated towards the specimen using a positive electrical potential.
2. This stream is confined and focused using a metal aperture and magnetic lenses into a thin, monochromatic beam, (magnetic lenses are circular electro-magnets capable of projecting a precise circular magnetic field in a specified region).
3. The focused beam is impinged on the sample by a magnetic lens.
4. The energetic electrons then interact with the irradiated sample. These interactions and effects are detected and transformed into an image.

A schematic of a TEM is illustrated in Figure 2.49 (Klugg and Alexander, 1974; Garces, et al., 2000).

Figure 2.48 Schematic of X-ray diffraction geometries (a) reflection mode (b) transmission mode (Klugg and Alexander, 1974).
2.6.3 Scanning Electron Microscopy (SEM)

When the domain size is in the range of < 1 μm to 10 nm, scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM) are necessary. It is a qualitative technique. A schematic of a scanning electron microscope is shown in Figure 2.50 (Klugg and Alexander, 1974). Samples in the SEM can be examined “as is” for general morphology, as freeze fractured surfaces or as microtome blocks of solid bulk samples. In addition, the SEM can be used to study liquids or temperature sensitive polymers on a Cryostage. The SEM is also used to do X-ray/elemental analysis. X-ray analysis and mapping of the particular elements present is useful for the identification of inorganic fillers and their dispersion in compounds as well as inorganic impurities in gels or on surfaces and curatives, e.g., aluminum, silicon, or sulfur in rubber compounds and Cl and Br in halo butyl blends (Hieda, et al., 2008; Petroski, et al., 2009).
2.6.4 Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is the most widely used thermal method and is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry, a continuous graph of mass change against temperature (Thermogravimetric, TG curve) is obtained when a substance is heated at a uniform rate or kept at constant temperature. Sometimes, one may plot time (t) in place of T. TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature. In a TG curve of single stage decomposition, there are two characteristic temperatures; the initial $T_i$ and the final temperature $T_f$, Figure 2.51.

$T_i$ is defined as the lowest temperature at which the onset of a mass change can be detected by thermo balance operating under particular conditions and $T_f$ as the final temperature at which the particular decomposition appear to be complete (Willard, et al., 1986; Brown and Brown, 2000). Sometime, one records the Derivative Thermogravimetric (DTG) curves. A DTG curve presents the rate of mass change ($dm/dt$) as a function of temperature, or time (t), Figure 2.52, when the substance is heated at uniform rate. In this figure, the derivatives of the curve are shown by dotted lines. The reactions in the thermo-balance can be run under different environments like nitrogen, argon, helium, and oxygen. Moreover, TGA can be used in the quantitative determination of the components in a mixture (Barbara, 2002).
Figure 2.51 A typical TG curve (Willard, et al., 1986).

Figure 2.52 TG Curve, note the plateau of constant weight (region A), the mass loss portion (region B), and another plateau of constant mass (region C) (Brown and Brown, 2000).

2.6.5 Differential Scanning Calorimetry (DSC)

DSC, shown schematically in Figure 2.53, is a technique of non-equilibrium calorimetry in which the heat flow into or away from the polymer compared with the heat flow into or away from a reference is measured as a function of temperature and time (Seymour and Carraher, 1984). The difference in the energy supplied between the sample and the reference is attributed to various thermal events like the glass transition, crystallization and melting. Other processes such as evaporation and chemical reactions can also take place (Rodriguez, et al., 2003).
The polymer sample is held in an aluminum pan with a crimped-on lid. The reference is mostly an empty reference pan. The temperature change between sample and the reference is detected by separate platinum resistance heaters, which are controlled by the signals from platinum resistance thermometers. The difference in power needed to keep both at the same temperature is amplified and provides information on thermal events. The heating of both the sample and the reference material continues at a constant rate until heat is emitted or consumed by the sample. If the change in the temperature is endothermic, the temperature of the sample will be less than that of the reference. The temperature of the sample is raised to the reference temperature since a constant temperature has to be maintained for both the reference and the sample. The current required to keep the temperatures constant is recorded and heat of transition, crystallization or melting is measured by calculating the area under the resulting curve (Seymour and Carraher, 1984).

Figure 2.53 Differential scanning calorimetry (Rodriguez, et al., 2003).

Heat capacity increases at $T_g$ where the temperature of the sample is reduced below its previous level relative to the reference. In contrast to the smooth dip of $T_g$, a sharper dip is observed at $T_m$ since large amounts of heat are required to melt the crystals at constant temperature. These two thermal events appear on the endothermic side of DSC thermogram shown in Figure 2.54 while crystallization is on the opposite exothermic side because of the heat evolved upon formation of crystals (Rosen, 1982).
The sample purity, identity, the heat of transition, the heat of reaction, the phase diagram, the specific heat, the rate of crystallization, melting or reaction and the activation energy can be determined by the help of DSC thermograms (Seymour and Carraher, 1984).

2.6.6 Fourier Transform Infrared Spectroscopy (FTIR)

In contrast to the field of scanning probe microscopy Fourier Transform Infrared (FTIR) spectroscopy is an excellent tool for chemically characterizing a wide variety of materials including polymers and ceramics. In a conventional FTIR spectrometer, infrared radiation emitted by the source is split into two beams by a beam-splitter; one beam is reflected off of a fixed mirror while the other is reflected off of a moving mirror as shown in Figure 2.55. Because the two beams travel different distances to reach the detector, there is a phase difference between them at the detector. This phase difference is referred to as the optical retardation and is represented by the symbol $\delta$. The sweeping motion of the movable mirror causes a continuous change in the optical retardation. Therefore, the output from the detector consists of the intensity $I$, as a function of $\delta$ and is referred to as an interferogram. In the experiments described in the referred work, the intensity was described in units of volts. In traditional infrared spectroscopy techniques, such as transmission FTIR spectroscopy, the sample is generally placed just before the detector (see Figure 2.55) and its absorption spectrum is encoded within the interferogram. Fourier transformation of the interferogram yields
the absorption spectrum of the sample (Gupta and Kothari, 1997; Griffiths and Haseth, 2007).

Figure 2.55 FTIR Spectroscopy setup for transmission experiment.

The energies of the infrared (IR) photons lying between 0.001 eV and 1.6 eV are not sufficient to excite electronic transitions, but they cause rotations and vibrations of molecules or atomic groups. Polymer analysis is done in the medium IR (ν= 4000 to 200 cm⁻¹). Correlation tables can be used to analyze group frequencies. Group frequency phenomena imply that the masses of atoms and bonding strength in certain frequency ranges arrange into absorption bands corresponding to certain atomic groups. Analysis is done by comparison to published characteristic vibrations for specific chemical groups. Figure 2.56 shows an example for such a classification (Gunter, 1986).

Figure 2.56 General spectral positions of CC– and CX– valency vibrations (Gunter, 1986).
2.6.7 Ultraviolet and Visible (UV-Vis) Absorption Spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. UV light is part of the electromagnetic spectrum. It is at the higher end of energy compared to visible light and is followed in energy by X-rays and the Gamma rays as can be seen Figure 2.57.

![Electromagnetic spectrum](image)

**Figure 2.57** Electromagnetic spectrum (Jang and Jeong, 2006).

UV energy absorbed by plastics can excite photons, which then create free radicals. While many pure plastics cannot absorb UV radiation, the presence of catalyst residues and other impurities will often act as free radical receptors, and degradation occurs. It only takes a very small amount of impurity for the degradation to occur, e.g. trace parts per billion values of sodium in polycarbonate (PC) will initiate color instability. All types of UV can cause a photochemical effect within the polymer structure, which can be either a benefit or lead to degradation of some sort to the material (Jang and Jeong, 2006). UV-Vis can be used to measure energy-band gap. The band gap energy is the energy needed to break a bound in the crystal. When a bound is broken, the electron has observed enough energy to leave the valence band and jump to
the conduction band. The width of the band gap determines the type of the material (conductor/semiconductor/insulator) that is served (Medeiros, et al., 2007).

2.6.8 Rheological Properties of Nano-composites

The flow behaviour of polymer melts is of great importance in polymer manufacturing. Therefore, the description of flow phenomena by rheological studies is highly desirable to assist in the material processability on industrial scale (Krevelen & Hoftyzer, 1976).

2.6.8.1 Molecular Weight Determination

Dilute solutions (~2%) are used to determine the molecular weights of polymers via the viscosity method. Relative viscosity, the ratio of solution viscosity ($\eta$) to the pure solvent ($\eta_o$), is utilized. Also reduced viscosity is defined as $(\eta - \eta_o) / \eta_{oc}$, where $\eta$ is the viscosity of a solution of concentration c (in g/l). The relative viscosity dependence on concentration can be represented as a power series, as follows:

$$\frac{\eta}{\eta_o} = 1 + [\eta]c + k([\eta]c)^2 + \cdots \text{etc.} \quad (2.4)$$

For low concentrations the terms above $c^2$ can be ignored and the remaining equation is known as the Huggins equation:

$$\frac{\eta - \eta_o}{\eta_{oc}} = [\eta] + k[\eta]^2c \quad (2.5)$$

Finally intrinsic viscosity can be calculated taking the limit of this equation:

$$[\eta] = \lim_{c \to 0} \left[ \frac{\eta - \eta_o}{\eta_{oc}} \right] \quad (2.6)$$

Intrinsic viscosity can be determined experimentally by linearly extrapolating a plot of $(\eta - \eta_o) / \eta_{oc}$ vs. c or $(\eta / \eta_o - 1) / c$ vs. c to find the y-intercept. One of the most commonly employed viscometers, the Ubbelohde, is shown in Figure 2.58.
Experiments are run to determine the time for the solution to flow through the capillary relative to a standard sample. Also, the ratio of the efflux time to that of pure solvent \((t_o)\) can be taken as equivalent to the relative viscosity ratios as follows:

\[
\frac{(t - t_o)}{t_{oc}} = \frac{(\eta - \eta_o)}{\eta_{oc}}
\]

Mark-Houwink equation is used to determine the relative molecular weight:

\[
[\eta] = KM^\alpha
\]

Where \(K\) and \(\alpha\) are constants which depend on the solvent, the type of the polymer and temperature of the system. In order to take into account the presence of clay, Einstein’s law of viscosity has been used in the literature (Sibel and Goettler, 2004). Einstein’s law of viscosity applies for the viscosity of a dilute dispersion of spheres. Several assumptions in this theory are (a) the particles are solid spheres (b) their concentration is very small. According to this theory:

\[
\frac{\eta}{\eta_o} = 1 + 2.5 \phi
\]
Where \( \phi \) represents the volume fraction occupied by the particles, \( \eta \) measures the viscosity of the dispersion; \( \eta_o \) measures the viscosity of the solvent (Hiemenez, 1977).

### 2.6.9 Mechanical Behaviour of Semicrystalline Polymers

This discussion of mechanical properties is restricted to only tensile properties of semicrystalline polymers. The schematic of stress-strain curve for a typical semicrystalline is shown in the Figure 2.59 along with different stages of ductile deformation of a tensile specimen (Schultz, 1974).

![Figure 2.59 Schematic of the mechanical behaviour of the semicrystalline polymer (Schultz, 1974).](image)

### 2.7 Properties of Nylon-66 (PA66)

#### 2.7.1 Mechanical Properties

In recent years, demands have increased in using polyamide (PA) to replace certain metals and thermosets in the automotive vehicle and power train systems, and lawn or garden tools with addition of different fillers like fibers, talc and CaCO\(_3\) (Jia, et al., 2006; Sonawane, et al., 2010).

PA66 has moderately high tensile strength, limited modulus, excellent toughness and adhesive properties depending on its semicrystalline structure. It is a very important solution in many applications because of the combination of significant thermal and mechanical properties, high resistance to chemicals, durability to fatigue and abrasion. Despite all these advantages and its high resistance to crack initiation, its
crack propagation resistance is rather low. When a crack exists, it breaks easily (Kohan, 1973 and 1995). Its impact strength is improved by blending it with terpolymers of ethylene and propylene containing carboxylic acid groups (Seymour and Carraher, 1984). Molecular weight, moisture content, temperature and the presence of additives affect the final mechanical properties. Moisture increase gives a steady increase in impact strength for PA 66, just like the temperature increases, as a result of increasing plastication, although at very low temperatures moisture can embrittle nylon. PA 66 is notch-sensitive and the unnotched impact strength is dramatically reduced when a notch or flaw is introduced into the material. Sharp angles have to be avoided during the design of different parts. Incorporating impact modifiers in the polymer matrix can considerably reduce the notch sensitivity. The strength and stiffness can be remarkably increased through the aid of adding a reinforcing agent to the polymer whereas a sharp decrease is observed in both of them upon the addition of plasticizers that promote ductility, flexibility and impact strength (Kroschwitz and Mark, 2003). PA66 has a low coefficient of friction and melt viscosity. Friction coefficient value is lowered below that of graphite when water is present in the medium. The low melt viscosity is related to many methylene groups between the amide stiffening groups and it may readily be extruded to produce un-oriented filaments. Strong fibers of these filaments can be produced by stretching and aligning the chains in a specific direction so that the intermolecular forces are more effective (Seymour and Carraher, 1984). Sonawane, et al. (2010) reported a relation between weight percentage of filler loading (nano- and commercial CaCO₃) and tensile strength of polyamide composites shown in Figure 2.60.

Sonawane and colleagues found the tensile strength of nano-CaCO₃ filled polyamide nano-composites is higher than that of commercial CaCO₃ filled polyamide composites. Also, the tensile strength of 11nm CaCO₃ was found to be more improved than that of 23 and 17nm sizes of CaCO₃. The tensile strength was recorded to be 8 and 7MPa for 1wt% loading of 11 nm CaCO₃ and commercial CaCO₃ respectively. However, at 4 wt% loading of the two materials the tensile strength was observed to be 9 and 7.2 MPa, respectively. It means nano-filler provide higher tensile strength compared to commercial CaCO₃. This increment in tensile strength is due to uniform dispersion of nano-filler throughout the matrix (Sonawane, et al., 2010). It was also found that the Young’s modulus of nano-CaCO₃ filled polyamide nano-composites was higher than that of commercial CaCO₃-filled polyamide composites and that with an
increase in weight percentage of filler loading, elongation at break decreases, Figure 2.61.

![Graph showing tensile strength of polyamide filled with various sizes of CaCO₃](image1)

**Figure 2.60** Tensile strength of polyamide filled with various sizes of CaCO₃ (Sonawane, et al., 2010).

![Graph showing Young's modulus of polyamide filled with various sizes of CaCO₃](image2)

**Figure 2.61** Young’s modulus of polyamide filled with various sizes of CaCO₃ (Sonawane, et al., 2010).

Phang, et al. (2009) prepared nylon 66/clay nano-composites by melt compounding. Based on XRD studies, they reported that organoclay was well dispersed into nylon 66 matrixes, **Figure 2.62**, and that both the Young’s modulus and tensile strength steadily increased with clay content, **Figures 2.63 and 2.64**.
Figure 2.62 XRD patterns of the pristine and modified clay, neat PA66 and PA66/clay nano-composites (Phang, et al., 2009).

Figure 2.63 Young’s modulus of nylon 66/clay nano-composites (Phang, et al., 2009).

Figure 2.64 Tensile strength of nylon 66/clay nano-composites (Phang, et al., 2009).
2.7.2 Electrical Properties-Moisture Absorption

Nylons are frequently used in electrical applications especially for the combination of their mechanical, thermal, chemical and electrical properties. Their insulating properties are fairly good at low temperatures and humidities and are generally suitable for low frequency, moderate voltage applications (Kroschwitz and Mark, 2003).

The water sensitive amide groups of PA66 are responsible for the good dyeability and diminishing of fair to good non-conductive electrical properties (Seymour and Carraher, 1984). Moisture absorption is dependent on the degree of crystallinity and the polar amide groups around which water molecules can become oriented. Increasing the length of aliphatic groups in the chain can decrease moisture absorption just like the melting point. Impact strength can be increased by making the polymer more flexible resulting from the plasticizing effect of water absorption related to hydrogen bonding interruption in the amorphous regions (Kroschwitz and Mark, 2003).

2.7.3 Thermal Properties

The glass transition temperature of aliphatic polyamides is rather low (40-70°C) and composition does not affect T_g to any great extent (Kang, et al., 2005b). The heat deflection temperature of PA 66 is about 75°C and it has a linear expansion coefficient of 8x10^{-5} cm/cm °C. Its high melting point (about 265°C) is a function of both the strong hydrogen bonding between the chains and the crystal structure. High melting points permit materials to retain significant stiffness above T_g and almost up to the melting point (Seymour and Carraher, 1984). Despite the fact that PA 66 has good thermal stability, it tends to degrade when held for long periods of time at high temperatures. The adipic acid segments can cyclize, leading to chain scission, the production of cyclopentanone and derivatives and evolution of carbon dioxide and ammonia. Crosslinking occurs and the material turns into an intractable gel along with reduction of molecular weight (Kroschwitz and Mark, 2003).

Chae and colleagues (2006) examined DSC cooling scan of nylon-66 and nylon-66/ferrite nano-composites, Figure 2.65 and effect of ferrite nano-particles on the degradation process of nylon-66, Figure 2.66. They reported that the presence of ferrite nano-particles less than 1 wt% increases the crystallization temperature (T_c) of nylon-66 with the loading level. This indicates that the ferrite nano-particles act as a nucleating agent, leading to a small degree of super-cooling. However, further addition
decreases $T_c$ with ferrite content and produces even lower $T_c$ than that pure nylon-66 at circa 1.3°C at as high as 10 or 20 wt % as can be seen in Figure 2.65. While comparing the onset temperature ($T_{0.1}$) of the degradation at which 10% degradation occurs, it was observed that only Ny66-0.1 showed a slight enhancement of thermal stability by giving higher $T_{0.1}$ than that of pure nylon-66 at 7.3°C, Figure 2.66. However, further incorporation of ferrite nano-particles induces a negative effect on the thermal stability of nylon-66 matrix.

Figure 2.65 DSC cooling scans thermograms of nylon-66 and nylon-66/ferrite nano-composites (Chae, et al., 2006).

Figure 2.66 TGA curves of nylon-66 and nylon-66/ferrite nano-composites (Chae, et al., 2006).
2.7.4 Optical Properties

Most of the polyamides are opaque in thicknesses over about 2.5 mm and transparent below 0.5 mm. The opacity is due to light scattering at sphereulite boundaries. A further reduction in light transmission can be obtained by increasing crystallinity and the number of sphereulites via use of nucleating agents. However, transparency is enhanced by reducing the rate of crystallization and sphereulitic nature. Quenching the melt during fabrication and by modifying the polymer via copolymerization or plasticization are some of the ways of accomplishing it (Kroschwitz and Mark, 2003).

Kotek and co-workers (2011) demonstrated that the extent of hydrogen bonding can be quantified using FTIR spectroscopy. An FTIR spectrum was taken for PA 66 film, PA66-GaCl₃ complex and regenerated PA66 film, shown in Figure 2.67.

![Figure 2.67 FTIR spectra of regenerated PA 66 and PA 66-GaCl₃ complex (Kotek, et al., 2011).](image)

Infrared spectra of as-received PA 66 film and regenerated PA66 film are similar, suggesting that the regenerated films do not have much complexed material in the sample. The band at 3300 cm⁻¹ was attributed to N-H stretching and the band at 1640 cm⁻¹ was attributed to C=O stretching vibrations. These two vibrations strongly depend on hydrogen bonding interaction between the PA66 chains (Kotek, et al., 2011).

Fourier-transform IR confirmed the chemical structure of the nylon 6,6, showing absorptions for all required chemical groups: N-H stretch at 3304 cm⁻¹, C-H stretch at 2860-2940 cm⁻¹, amide-I at 1632 cm⁻¹, and amide-II at 1540 cm⁻¹.
Suzuki, et al. (2001) reported that fiber polymers have no inherent absorbance in the visible range but may exhibit absorbance below 300 nm. The UV absorbance has been grouped into none, low, moderate, and high absorbance peaks/increases. Fiber polymers with no to very low absorbance at < 300 nm were cotton, ramie and viscose. Low absorbance was demonstrated by di- and tri-acetate, nylon 6 and nylon 66 polyamides at < 300 nm. Figure 2.68.

2.7.5 Determination of Molecular Weight by Viscometry

In order to reach the desired properties, the molecular weight must be strictly controlled when polyamides are used as engineering plastic materials. Haggenmueller, et al. (2006) determined the viscosity average molecular weight of nylon 6-6 by capillary viscosimetry using an Ubbelohde viscometer with a kinematic viscosity constant of 0.003 mm²/s². The efflux time of nylon 6,6 solutions in 90 % formic acid was measured at concentrations from 2.23 to 10.41 mg/ml at 25°C. The relative viscosity, which is proportional to the efflux time, was plotted as a function of concentration; the intrinsic viscosity was then determined from this plot using the Huggins and Kramer equations. The Mark-Houwink equation is presented by equation 2.8 (Suzuki, et al., 2001; Haggenmueller, et al., 2006). While $K = 3.53E-4$ and $a = 0.786$, for nylon 6, 6 in 90% HCOOH at 25°C (Bandrup and Immergut, 1975) was used to determine the viscosity averaged molecular weight ($M_v$) from the intrinsic viscosity measurements, resulting in a $M_v \approx 35,000$ g/mol (Haggenmueller, et al., 2006).
However, Song, et al. (2008) reported the viscosity average molecular weight of nylon 6, 6 using an Ubbelohde viscometer at room temperature in the range of 11,000–12,000 which was lower than the commercial product.

2.8 Critical Summary

Fillers were initially added to materials in the quest for cost reduction and bulk increase. They also influenced optical, electrical, mechanical and rheological properties and affected durability and morphology of the materials. It was reported that the effect of fillers on resin properties depends primarily on the particle size distribution, shape, surface area and chemical composition. Particle size and shape affect both the properties of the final product and also the processing conditions.

Calcium carbonate has been the most widely used filler in the plastic industries as it is inexpensive and can be added up to high loadings of 60% weight. Even though generally used as an extender, it can improve stiffness and impact strength, especially with fine micron particles. Different methods have been reported in literature for the synthesis of CaCO$_3$ nano-particles; however, microemulsion method is an ideal method due to its high degree of dispersion, very low size, and good enough potential to control the chemical reaction. Lower cost is another attractive feature. It has also been reported that agglomerations may easily happen for smaller particles at higher filler contents due to the reduced inter-particle distance.

Reverse micro-emulsion (w/o) system of surfactant (Span®80 & Tween®80)/Toluene/water has been used for the first time to synthesize CaCO$_3$ nano-particles in this study.

It has been also reported that modulus is the most frequently measured and modelled property because it is determined at very low deformations and the analysis based on linear visco-elasticity. It can be used to develop the relationship of property and structure. The addition of rigid particle fillers like calcium carbonate may increase the modulus of polymer when there is good adhesion or even with poor adhesion since thermal coefficients impose a squeezing force on the filler by the matrix preventing relative motion. It has also reported that yield stress and tensile strength may be reduced because calcium carbonate modifies the shape of the polymer matrix and often induces yield points. Calcium carbonate reduces the effective cross section of the matrix and leads to increased internal stress facilitating failure at lower external load in comparison with unfilled polymer. However, mechanical properties of prepared micro-
and nano-composites by polymer solution, as a common method, i.e. Young’s modulus, yield stress, elongation at yield and break has been examined in the present study.

While XRD, SEM, TEM, TG/DTA and DSC techniques have been the usual methods used for the characterization of the polymers and composites, optical and rheological properties of nylon-66/CaCO₃ micro- and nano-composites have so far not been reported in literature. Optical property studies using UV-Vis spectrophotometry provides energy band gap and Urbach’s energy and is useful in determining whether a material is conductor/semiconductor or insulator. Chemical structures of the polymer composites using FT-IR studies have also not been reported so far. The optical and rheological properties have been studied in the present work, for the first time.