FELDSPAR REINFORCED POLYPROPYLENE COMPOSITES: THE EFFECT OF COMPATIBILIZERS, SILANE COUPLING AGENT AND MULTI-WALLED CARBON NANOTUBE ON MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES

by

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LIST OF SYMBOLS

A	area
L	length
L_0	original length
$L - L_0$	change in length
d	outer diameter of fiber
d_i	inner diameter of fiber
E	Young's modulus
E_b	elongation at break
E_C	Young's modulus of composite
E_f	Young's modulus of fiber
E_m	Young's modulus of matrix
TS	tensile strength
T_c	crystallization temperature
T_m	melting temperature
$T_{5\%}$	initial degradation temperature
$T_{90\%}$	end degradation temperature
T_d	degradation temperature
T	time, torque
V_f	fiber volume fraction
wt%	weight percentage
ΔH_c	enthalpy of crystallization
ΔH_m	enthalpy of melting

σ_C	strength of composite (stress)
σ_f	strength of fiber (stress)
σ_m	strength of matrix (stress)
ε	strain
τ	interfacial stress transfer
^0C	degree Celsius
Pa	Pascal
G	Giga
g	gram
Hz	Hertz
K	Kelvin
keV	kilo electron Volt
kV	kilo Volt
M	Mega
M_m	moisture content
M_t	percentage of moisture gain at any time
m	metre
mA	milli Ampere
m^2	square metre
N	Newton
cm	centimetre
cm^2	square centimetre
n	nano

μ	micron
$\%X_c$	percentage of crystallinity
θ	angle of diffraction
$\tan \delta$	mechanical loss factor
W_i	initial weight of the sample
W_f	final weight of the sample
$W_f - W_i$	increase in weight (water absorbed)
E’	storage modulus
E”	loss modulus
G’	shear storage modulus
G”	shear loss modulus

LIST OF ABBREVIATIONS

AAc	Acrylic acid
APTES	3- aminopropyl tri-ethoxy silane
ASTM	American Standard Testing Methods
AR	aspect ratio
ATR	Attenuated total reflection
$CaCo_3$	Calcium carbonate
CNT	Carbon nanotubes
CO_2	Carbon di-oxide
Cu	Copper
CVD	Chemical vapor deposition
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EBSD	Electron back scatter diffraction
EDX	Energy Dispersive X-ray
FE-SEM	Field emission scanning electron microscope
F	Feldspar
FTIR	Fourier transform infrared
HDPE	high-density polyethylene
ICSD	inorganic crystal structure database
IFST	interfacial stress transfer
iPP	isotactic polypropylene
K	Potassium

MAH	maleic anhydride
MFI	melt flow index
MMC	metal matrix composites
MWCNT	multi-walled carbon nanotube
NC	nanocomposite
PE	Polyethylene
PEAA	Poly (ethylene co-acrylic acid)
PMC	Polymer matrix composite
PP	Polypropylene
PP-g-MAH	Polypropylene grafted maleic anhydride
PPAA	Polypropylene acrylic acid
PPEAA	Polypropylene ethylene acrylic acid
SEM	Scanning electron microscope
SiO_2	Silicon di-oxide
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
UTM	Universal testing machine
XRD	X-ray diffraction

KOMPOSIT POLIPROPILENA DIPERKUAT FELSPAR: KESAN PENGSERASI, AGEN PENGKUPEL SILANA, DAN NANO TIUB KARBON BERBILANG DINDING KE ATAS SIFAT-SIFAT MEKANIKAL, TERMAL DAN MORFOLOGI

ABSTRAK

Di dalam kajian ini, felspar telah dipilih sebagai bahan pengisi untuk pelbagai pembebanan pengisi iaitu 10 wt%, 20 wt%, 30 wt%, dan 40 wt% feldspar terisi komposit polipropilena telah disediakan menggunakan teknik pencampuran leburan.. Seterusnya, kepingan komposit dihasilkan menggunakan penekan panas. Ujian tensil telah dilakukan menggunakan mesin pengujian Instron. Didapati kekuatan tensil dan % pemanjangan pada takat putus berkurang manakala modulus tensil dan kekerasan meningkat dengan peningkatan pembebanan pengisi. Agen pengserasi telah ditambah untuk meningkatkan keserasian dan pemprosesan komposit felspar/PP. Dua jenis pengserasi iaitu, polietilena ko-asid akrilik (PEAA) dan polipropilena tercantum-maleik anhidrida (PP-g-MAH) telah digunakan. Agen pengserasi PP-g-MAH menunjukkan peningkatan di dalam kekuatan tensil, modulus Young dan pemanjangan pada takat putus komposit yang lebih tinggi disebabkan peningkatan lekatan antaramuka di antara feldspar dan PP sebagaimana ditunjukkan di dalam kajian morfologi menggunakan mikroscop elektron penskanan (SEM). Kesan agen pengkupel silana, 3-(aminopropil) trietoksi-silana (3-APEs) terawat dengan komposit felspar menunjukkan keputusan yang sama juga disebabkan peningkatan lekatan antaramuka sebagaimana ditunjukkan di dalam kajian morfologi menggunakan SEM. Pengurangan peratus penyerapan air telah diperhatikan untuk komposit feldspar/PP terawat silana dan komposit feldspar/PP/PP-g-MAH. Kesan penguatan nanotiub karbon berbilang dinding (MWCNT) ke atas sifat-sifat mekanik, termal dan morfologi MWCNT diperkuat komposit hibrid felspar/PP telah dikaji. Struktur dan dimensi MWCNT telah dicirikan menggunakan mikroskop elektron transmisi (TEM). Keputusan SEM menunjukkan MWCNT tersebar dengan baik di dalam komposit felspar/PP terutamanya pada pembebanan pengisi yang rendah iaitu 0.1wt% dan menjadi faktor peningkatan kekuatan tensil, pemanjangan pada takat putus, modulus Young, kekuatan fleksural, modulus fleksural dan kekuatan hentaman. Analisis dinamik mekanik (DMA) telah dilakukan untuk mengkaji ransangan dinamik mekanik pada pelbagai suhu dan frekuensi rendah. Modulus simpanan (E’) juga menunjukkan peningkatan. Analisis struktur komposit telah dilakukan menggunakan teknik FTIR dan keputusan menunjukkan puncak-puncak dominan yang melibatkan kumpulah Si-O, C-N, N-CH_3, CNT, C-O dan C-H_x di dalam komposit hibrid dan analisis XRD menunjukkan yang felspar dan MWCNT tersebar dengan baik (exfoliated) di dalam matriks PP.

FELDSPAR REINFORCED POLYPROPYLENE COMPOSITES: THE EFFECT OF COMPATIBILIZERS, SILANE COUPLING AGENT AND MULTI-WALLED CARBON NANOTUBE ON MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES

ABSTRACT

In this research, feldspar was chosen as a filler material where different filler loading viz. 10 wt%, 20 wt%, 30 wt%, and 40 wt% feldspar filled Polypropylene (PP) composites were prepared using melt mixing technique and then the composite sheet was produced using Hot Press. Tensile test was carried out using an Instron universal testing machine where the tensile strength and elongation at break decrease but tensile modulus and hardness increase as the filler loading is increased. Compatibilizers improved the processability and compatibility of the feldspar/PP composites. Two compatibilizers namely polyethylene co-acrylic acid (PEAA) and PP grafted maleic anhydride (PP-g-MAH) were used but PP-g-MAH compatibilizers scored better results by showing marginal increase in tensile strength, elongation at break and Young's modulus of the composites due to the enhancement of the interfacial adhesion between feldspar and PP as shown by scanning electron microscope (SEM). Silane treated feldspar composites using silane coupling agent, 3-(amino propyl) triethoxy silane (3-APEs) also showed similar results due to better interfacial adhesion as investigated by SEM. Feldspar/PP/PP-g-MAH composites and silane treated feldspar/PP composites showed less percentage of water absorption. The effect of multi-walled carbon nanotube (MWCNT) reinforcement on the properties of feldspar/PP hybrid composites was investigated. The structure and dimensions of the MWCNTs were characterized using a transmission electron microscope (TEM). SEM showed that MWCNTs were well dispersed in feldspar/PP composites particularly at low filler loading i.e. 0.1 wt% attributing to the increase in tensile strength, elongation at break, Young's modulus, flexural strength, flexural modulus and impact strength. Dynamic Mechanical Analysis (DMA) was performed to evaluate their responses at different temperatures at low frequency. The storage modulus (E') also improved. Structural analyses were done using Fourier transform infrared (FTIR) spectroscopy technique which showed dominant peaks corresponding to Si-O, C-N, N-CH_3, CNT, C-O, C-H_x groups in the hybrid composites and X-ray diffraction (XRD) which showed feldspar and MWCNT were well dispersed (exfoliated) in the PP matrix.

CHAPTER 1

INTRODUCTION

1.0 Introduction

Products made from polymers contribute strongly to the global economy in terms of performance, reliability, cost-effectiveness and high added value. Among the many reasons why polymers are widely used, two stand out. First, polymers can be operated in a variety of environments and they have useful ranges of deformability and durability which can be exploited by careful design. Second, polymers can often be readily, rapidly and at an acceptable (low) cost be transformed into usable products having complicated shapes and reproducible dimensions. This chapter introduces the polymer matrix composites, importance and current issues of polymer products, focuses on the problem statement and the objectives of this research carried out and finally it outlines the structure of the thesis.

1.1 Polymer Matrix Composites (PMC)

The hybrid organic–inorganic composites are promising materials because they synergistically integrate the advantages of organic polymer and inorganic material, such as, the excellent process properties that are generally considered to be characteristic of polymer, and high modulus and strength that are characteristic of inorganic material. However, the properties of the hybrid organic–inorganic composites are greatly influenced by the length scale of component phase. Important changes in the properties of plastics resulting from the incorporation of special additives permit their use in various fields where the polymer alone would have had small chance to meet certain performance specifications. Fillers and reinforcements are solid additives that differ from the plastic matrices with respect to their composition and structures. They are dispersed uniformly throughout the polymer matrix to obtain the required optimum properties and hence are known as polymer matrix composites.

The use of inorganic fillers is a usual practice in the plastics industry to improve the mechanical properties of thermoplastics which are commonly known as polymer composites. Polymer composites play an important role in the engineering field due to their high strength to weight ratio and better corrosion resistance. These materials usually comprise of an effective polymeric matrix in which fibers and/or small filler particles are thoroughly dispersed in composite systems. The filler must be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing [Shui, 2003]. Polypropylene (PP) based composite material is one of the many composite systems that are successfully utilised in engineering applications. PP has been known for its good mechanical properties and processability, which allows it to accept numerous types of natural and synthetics fillers. Its versatility has also led to the possibility of producing particulate-filled composites [Pukanszky and Karger-Kocsis, 1995].

The incorporation of fillers such as talc, calcium carbonate ($CaCO_3$), mica, kaolin and wollastonite into thermoplastics is a common practice in the plastics industry, wherein it helps to reduce the production costs of moulded products. Fillers are also used to improve the working properties of thermoplastics, such as the strength, rigidity, durability, and hardness [Bledzki and Gassan, 1998; Khunova *et al.*, 1999]. Thus, the aim of this study is to investigate the potential of a new filler viz, feldspar with PP as this filler has not been used in polyolefin groups. Feldspars are a group of minerals that have similar characteristics to each other type of feldspar due to similar structure. It is an aluminium silicate with exchangeable cations and reactive OH groups on the surface. All feldspars have low symmetry, being only monoclinic to triclinic. They tend to twin easily and one crystal can twin up multiple times on the same plane, producing parallel layers of twinned crystals. They are slightly hard, at around 6 on Mohs scale, and have an average density at 2.55 to 2.76 g/cc. They have a rather dull to rarely vitreous luster. Crystals tend to be blocky. Some feldspar may be triboluminescent. They have two directions of cleavage which are at nearly right angles. Feldspars also tend to crystallize in igneous environments, but are also present in many metamorphic rocks[http://www.galleries.com]. Feldspar is the most important single group of rock forming silicate minerals. K-feldspar as $KAlSi_3O_8$ consists of three different entities (K_2O, Al_2O_3, SiO_2). Feldspar structures can be described as an infinite network of tetrahedral SiO_4 and AlO_4, which is a stuffed derivative of the SiO_2 structures with substitution of Al for some Si into tetrahedral sites, and accommodation of K into voids [Cetinkaya, S. *et al.*, 2007].

One way of compatibilising PP with inorganic particles is by using functionalized polyolefin e.g. PP grafted with maleic anhydride (PP-g-MAH). Unfortunately, there have been only limited achievements in the functionalisation of polyolefin especially PP, which have not succeeded either during its polymerization or in the post-polymerization processes. In addition, the improvement of the interfacial bonding between the hydrophilic fillers and the hydrophobic matrix (PP) has been an important issue in the research field, because the interfacial adhesion between the filler and PP plays an important role in determining the properties of the composites.

Other methods of compatibilising PP and inorganic filler is by modifying the filler surface using coupling agents such as silane, titanate, and also by grafting small molecules such as acrylic acid, maleic anhydride, and acrylic esters onto the polyolefin chain. Modified PP such as PP grafted-maleic anhydride (PP-g-MAH) is successfully used as a compatibiliser in PP based composite because it can efficiently improve the fiber–matrix bonding due to the formation of covalent linkages and hydrogen bonds between the maleated anhydride and the hydroxyl groups of the fillers [Bledzki and Gassan, 1998; Khunova *et al.*, 1999]. Other than PP-g-MAH, much cheaper and nonreactive compatibilisers have also been successfully employed in polymer with lack of reactive groups particularly, PP and PE.

1.2 Polymer Composites

In recent years, polymer composites have attracted great interest. Especially, nanocomposites offer new technological and economical benefits. The incorporation of nanometer scale reinforcement (e.g. layered silicates of clay, nanofiber, nanotubes, metal nanoparticles in polymeric materials) may dramatically improved selected properties of the related polymer. These nanocomposites exhibits superior properties such as enhanced mechanical properties, reduced permeability and improved flame retardency [Ray and

Okamoto, 2003]. Polymer nanocomposites with layered silicate represent a hybrid between organic and inorganic materials. Polymer layered-silicate nanocomposites are currently prepared in four ways: in-situ polymerization, intercalation from a polymer solution, direct intercalation by molten polymer (melt compounding) and sol-gel technology. Direct polymer melt intercalation is the most attractive because of its low cost, high productivity and compatibility with current processing techniques (Alexandre and Dubois, 2000]. Numerous researchers described polymer-clay nanocomposite based on single polymer matrix, including PP, polyamide, polystyrene, polyimide, epoxy, poly (methyl metacrylate), unsaturated polyester, polycaprolactone and polycarbonate. Naturally occurring montmorillonite is the most abundant member of the smectite family of clays. Naturally occurring montmorillonite is incompatible with most polymers because of its hydrophilic nature. Ion exchange is widely practiced to modify the montmorillonite's surface to increase its compatibility with hydrophobic polymer [Zanetti *et al.,* 2000].

1.2.1 Polypropylene composite

PP has also been tested for the preparation of composites. However, no direct intercalation of PP in simply organically modified layered silicates has been observed so far as PP is non-polar to correctly interact with the modified layers [Alexandre and Dubois, 2000]. Maleic anhydride-modified PP (MAH-g-PP) oligomer had been used to separate the silicate layers in the PP matrix. Maleic anhydride (MAH) gives a sufficient polarity to modified PP to diffuse between the silicate layers in order to obtain intercalated nanocomposites [Kawasumi *et al*., 1997]. They have reported the preparation of PP-clay hybrid via simple melt mixing of three components, i.e. PP, MAH-g-PP oligomer and clay intercalated with stearylammonium. It is found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids: the intercalation capability of the oligomers in the layers and the miscibility of the oligomers with PP. The basic role of a filler is to “fill’ i.e. increase the bulk at low cost, thereby improving economics while, by definition, the main function of a reinforcing filler is to improve the physical and mechanical properties of the basic polymer.

1.2.2 Hybrid Composites

Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials. Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. One of the most successful examples is the group of composites which are formed by the incorporation of a basic structural material into a second substance, the *matrix*. Usually the systems incorporated are in the form of particles, whiskers, fibers, lamellae, or a mesh. Most of the resulting materials show improved mechanical properties and a well-known example is inorganic fiber-reinforced polymers [Kickelbick, 2007].

The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, a hybrid material is a material that includes two moieties blended on the molecular scale.

Commonly one of these compounds is inorganic and the other one is organic in nature. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species [Kickelbick, 2007].

Although we do not know the original birth of hybrid materials exactly it is clear that the mixing of organic and inorganic components was carried out in ancient world. At that time the production of bright and colorful paints was the driving force to consistently try novel mixtures of dyes or inorganic pigments and other inorganic and organic components to form paints that were used thousands of years ago. Therefore, hybrid materials or even nanotechnology is not an invention of the last decade but was developed a long time ago [Kickelbick, 2007].

Apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials [Kickelbick, 2007].

1.3 Current Issues

In the automobile industry, polyolefins especially PP have become the most important plastics, replacing not only steel but also other plastics such as ABS, PVC etc., The reason is the versatility offered by the possibility of modifying PP, which allows us to use similar raw materials for forming almost all the plastics parts of vehicles. For eg, elastomer modified PP's which are of different degree of toughness offer a more favourable cost performance ratio than other materials and allow innovation design concepts. Moreover, apart from economic consideration, PP represents many advantages in-term of easy processing and recycling [Almeras *et al*., 2003].

1.4 Problem Statements

Polymer composites are the area of interest for most of the researchers. The enormous availability of material resources around us especially thermoplastics, make them a vulnerable subject for research. More over thermoplastics are easily manufactured and are light in weight which is advantageous. There are many kinds of fillers which have been introduced so far in order to increase the variety of fillers and their combinations to obtain mixture of properties. The use of common mineral fillers and fibres has been established in the material research field for some years. However, combination of both mineral particulate filler and fibre reinforcement together are still under development stage. The needs for new types of fillers for polymer composites application are inevitable in order to produce a composite with new set of properties.

Initially, PP and feldspar composites were prepared to improvise the mechanical properties and also to reduce the cost. There has to be an inclusion of a compatibilizer to improve the compatibility between the feldspar/PP composites. Further reinforcement of the composites with nano-scale filler such as MWCNTs in the mineral/polymer composites (eg. feldspar/PP composites) is expected to improve the strength, stiffness and rigidity of the feldspar/PP composites. The issues to be addressed are the characteristics of the nanotubes present within the polymer matrix such as the dispersion uniformity, tube size and their loading amount.

The following approaches have been identified as a potential route to meet this goal. They are:

i. The inclusion of untreated feldspar into the thermoplastic matrix (PP) to form feldspar/PP (control) composites by melt-mixing method.
ii. Addition of compatibilizers such as PP grafted maleic anhydride (PP-g-MAH) and polyethylene- co-acrylic acid (PEAA) during the melt-mixing of feldspar/PP composites.
iii. The inclusion of silane treated feldspar into the PP matrix by melt-compounding.
iv. The reinforcement of MWCNTs into the feldspar/PP composites by melt-mixing which gives a better uniform dispersion of the MWCNTs.

However, several studies have indicated that the above mentioned approaches have their own potentials and limitations. Generally, the inclusion of mineral particulate filler will reduce some of the mechanical properties such as strength and toughness. On the contrary, the reinforcement with a small proportion of MWCNTs may help to produce a good balance of mechanical and thermal properties of the composites.

1.5 Objectives of research

The present research work proposal aims to develop a new advanced polymeric hybrid composite materials namely MWCNT/feldspar/PP composites and to evaluate their mechanical, thermal and morphological properties.

The objectives of this research are listed below:

- to evaluate the mechanical, thermal, and morphological properties of feldspar/PP composites.
- to study the effect of compatibilizers and coupling agents on the mechanical, thermal and morphological properties of the feldspar/PP composites.
- to investigate the effect of reinforcement of MWCNTs in feldspar/PP composites.

1.6 Outline of thesis structure

The study focuses on the properties of feldspar/PP composites and the effect of compatibilizers, coupling agent and multi-walled carbon nanotube reinforcement on feldspar/PP composites.

Chapter 1 will introduce some basic information about composites, polymer matrix composites, definition and concept about hybrid composites, the use of compatibilizers for better properties. It also states the problem statement, objectives of the research and organization of thesis structure.

Chapter 2 discusses the literature review on various published works on polymer composites and carbon nanotubes reinforced polymer nanocomposite, particularly those that are closely related to this work.

Chapter 3 discusses the material specifications, research methodology, and finally all experimental procedures carried out in this research in order to evaluate the mechanical, thermal, morphological and structural characteristics.

Chapter 4 discusses on the effect of feldspar loading on the mechanical, thermal and morphological properties, the effect of compatibilisers and coupling agents on the mechanical, thermal and morphological properties, the effect of multi-walled carbon nanotube reinforcement on feldspar/PP composites. The effect will be presented by means of data table, graphs, electron micrograph of the feldspar particles, SEM/TEM images of MWCNT, the fractured surface of the PP and MWCNT/feldspar/PP hybrid composites were also included and analyzed.

Chapter 5 presents some concluding remarks on the present work and the evaluation made in order to assess the achievements of the objectives. Some of the suggestions for further research works have also been listed.

Details about the reference materials were reported in the References. Finally, the abstracts of the paper published in journals and conference proceedings were presented in the Appendices.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter will cover the basic definition of polymer composites and their classification, followed by the historical developments of polymer composites and their applications. The role of polymer matrix especially PP and their structure, particulate mineral fillers viz. feldspar particles and their structure, carbon nanotube reinforcing filler will be discussed. Subsequently, a literature survey was done on polymer composites and those related to the present research work.

2.1 Historical Background

2.1.1 Polymers: Plastics

The year 1967 was a significant year for plastics. One event, related to American pop culture and one that some of us tend to remember, is the advice given to the young graduate played by Dustin Hoffman in the movie “The Graduate”. The prophetic words told to the new graduate – “I just want to say one word to you, Ben. Just one word – plastics” – where a symbol of the times and a sign of things to come. The same year that the movie was showing in the theaters, the volume of plastics’ production surpassed that of all metals combined. Today, almost forty years later, plastics production is six times higher than in 1967, while production of metals has barely doubled. However, to be fair, in the popularity contest between metals and plastics we can always present the data differently, namely by weight. This way, the tonnage of metals produced worldwide is over twice the tonnage production of polymers. Neverless, the fact is that today the volume of polymers produced is three times larger than that of metals. In fact, the world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century. Figure 2.1 shows the graphical representation of the World's annual plastics production in millions of tons.

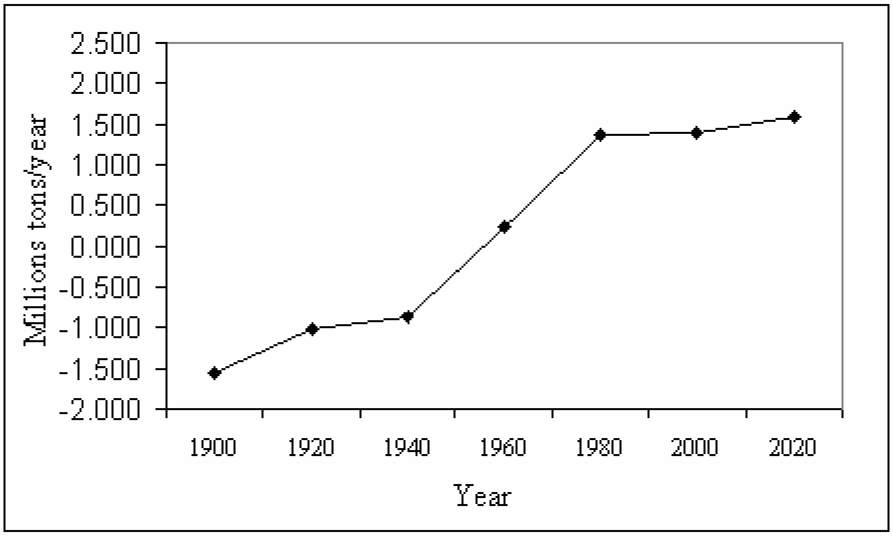

Figure 2.1 World annual plastics production since 1900 [Utracki, 1995].

There has been a steady increase in the world annual plastics production throughout the years, with slight dips during the oil crisis in the mid-1970s and during the recession in the early 1980s. In the developed countries, the growth in annual polymer production has diminished somewhat in recent years. However, developing countries in South America and Asia are now starting to experience tremendous growth. With the exception of recession years, the growth in US polymer production has been declining in the past 20 years to approximately 4% of annual growth rate. Since 1970, China has seen the highest annual growth in the world, ranging from a maximum approximately 50% between 1976 and 1977 to a low of 2% between 1980 and 1981. According to a soon-to-be-released updated report from Business Communications Company, Inc. - RP-234 Polymer Nanocomposites: Nanoparticles, Nanoclays and Nanotubes, the total worldwide market for polymer nanocomposites reached 24.5 million pounds valued at US$90.8 million in 2003 (about $3.71/lb). This market has grown at an AAGR (average annual growth rate) of 18.4% (US$211.1 million) during 2008.

There are over 18,000 different grades of polymers, available today in the US alone. In 1993, 90% of the polymers produced in the US were thermoplastics. However, in a 1995 worldwide projection, thermoplastics account for 83% of the total polymer production [Progelhof and Thomas, 1993].

It is a fact that some time now, polymers have become an indispensable material in everyday life. From sports to medicine, and from electronics to transportation, polymers are not only a material that is often used, but also the material that in many cases make it possible. One can sum it up with Hans Uwe Schenck's often quoted phrase – "Without natural polymers, there would be no life; without synthetic polymers, no standard of living."

2.1.2 What is a composite?

A composite is a material having two or more distinct constituents or phases and thus we can classify bricks made from mud reinforced with straw, which were used in ancient civilizations, as a composite [Hull and Clyne, 1996]. A versatile and familiar building material which is also a composite is concrete is a mixture of stones, known as aggregate, held together by cement. In addition to synthetic concrete there are naturally occurring composites of which the best known examples are bone, mollusc shells and wood; bone and wood. Within the last forty years there has been a rapid increase in the production of synthetic composites, those incorporating fine fibres in various plastics (polymers) or mineral particulated fillers in various plastics (polymers) dominating the market. Predictions suggest that the demand for composites will continue to increase steadily with metal and ceramic based composites making a more significant contribution.

Composites make up a very broad and important class of engineering materials. World annual production is over 10 million tones and the market has in recent years been growing at 5-10% per annum. Composites are used in a wide variety of applications. Further more, there is a considerable scope for tailoring their structure to suit the service conditions [Hull and Clyne, 1996].

Composites materials have fully established themselves as workable engineering materials and are now relatively commonplace around the world, particularly for structural purposes. Early military applications of polymer matrix composites during World War II led to large-scale commercial exploitation, especially in the marine industry, during the late 1940's and early 1950's. Today, the aircraft, automobile, leisure, electronic and medical industries are quite dependent on fibre-reinforced plastics, and these composites are routinely designed, manufactured and used. Less exotic composites, namely particulate or mineral filled plastics are also widely used in industry because of the associated cost reduction [Mathews and Rawlings, 1999].

Some typical applications of polymer matrix composites are listed in Table 2.1 which gives an overview of all the products that are made using polymer composites in different industrial sectors.

Table 2.1: Some applications of polymer matrix composites (Adapted from Hull, 1981)

Industrial sector	Examples
Aerospace	Wings, fuselage, radomes, antennae, tail-planes, helicopter blades, landing gears, seats, floors, interior panels, fuel tanks, rocket motor cases, nose cones, launch tubes.
Automobile	Body panels, cabs, spoilers, consoles, instrument panels, lamp-housings, bumpers, leaf springs, drive shafts, gears, bearings.
Boats	Hulls, decks, masts, engine shrouds, interior panels.
Chemicals	Pipes, tanks, pressure vessels, hoppers, valves, pumps, impellers.
Domestic	Interior and exterior panels, chairs, tables, baths, shower units, ladders.
Electrical	Panels, housings, switchgear, insulators, connectors.
Leisure	Motor homes, caravans, trailers, golf clubs, racquets, protective helmets, skis, archery bows, surfboards, fishing rods, canoes, pools, diving boards, playground equipment.

2.1.3 Types of composite materials

Many useful engineering materials have a heterogeneous composition. Metals for instances, are often used in the form of alloys. The addition of a small percentage of another metal, such as copper, magnesium or manganese, is necessary to prevent plastic deformation occurring in aluminium at very low stresses an increase in carbon content from 0.1wt% to 3 wt% is a primary determinant in whether a ferrous alloy becomes mild steel or a cast iron. Concrete, which like cast iron, has good compressive but poor tensile properties, consists of a hard aggregate embedded in a metal silicate network [Ward and Hadley, 2002].

Both human and animals depend on natural composites for their living. Bones must be stiff and yet able to absorb significant amount of energy without fracturing; they also provide anchor points for muscles, which are composite. The skeletal material of plants, and in particular wood, provides a splendid example of the desirable properties of a composite. As a gross simplification, its structure can be considered in terms of an array of relatively stiff fibres embedded in a more compliant matrix. The matrix permits to be redistributed among the fibres, so retarding the onset of fracture at stress concentrations.

A further form of composite is one where the second component acts as filler. Carbon black in vehicle tyres is an example of filler needed to provide the required properties. Each carbon particle provides an anchorage for many rubber molecules, and so assists in the redistribution of stress; and the carbon is also essential to obtain the desired hysteresis behaviour and abrasion resistance. A much simpler application of filler is the use of sawdust or other cheap powder in mouldings made from a thermosetting or a thermoplastic. Although the mechanical properties of the base material are degraded (except possibly for impact resistance), they are still adequate for the proposed application, and the product cost is reduced. Good adhesion between the fibre and matrix will assist in reducing stress concentrations, and transverse cracks will grow only with difficulty across a fibrous composite [Ward and Hadley, 2002].

Many materials are effectively composites. This is particularly true of natural biological materials, which are often made up of at least two constituents. In many cases, a strong and stiff component is present, often in elongated form, embedded in a softer constituent forming the matrix. However, this definition is not sufficient and three other criteria have to be satisfied before a material can be said to be a composite. First, both constituents have to be present in reasonable proportions, say greater than 5%. Secondly, when the constituent phases have different properties and the composite properties are noticeably different from the properties of the constituents, then these materials are recognized as composites. For example, plastics, although they generally contain small quantities of lubricants, ultra-violet absorbers, and other constituents for commercial reasons such as economy and ease of processing, do not satisfy either of these criteria and consequently are not classified as composites. Lastly, a man-made composite is usually produced by intimately mixing and combining the constituents by various means. It is a known that composites have two (or more) chemically distinct phases on a micro or a nano scale, separated by a distinct interface, and it is important to be able to specify these constituents. The constituent that is continuous and is often but not always, present in the greater quantity in the composite is termed as matrix. The normal view is that it is the properties of the matrix that are improved on incorporating another constituent to produce a composite. A composite may have a ceramic, metallic or polymer matrix. The second constituent is referred to as the reinforcing phase, or reinforcement, as it enhances or reinforces the mechanical properties of the matrix. In most cases the reinforcement is harder, stronger, and stiffer than the matrix, although there are some exceptions for eg. ductile metal reinforcement in a ceramic matrix and rubber like reinforcement in a brittle polymer matrix. At least one of the dimensions of the reinforcement is small, say less than 500μm and sometimes only of the order of a micron. The geometry of the reinforcing phase is one of the major parameters in determining the effectiveness of the reinforcement; in other words, the mechanical properties of the composites are a function of the shape and dimensions of the reinforcement. We usually describe the reinforcement as being either fibrous or particulate [Mathews and Rawlings, 1999].

Particulate reinforcements have dimensions that are approximately equal in all directions. The shape of the reinforcing particles may be spherical, cubic, platelet or any other regular or irregular geometry. The arrangement of the particulate reinforcement may be random or with a preferred orientation, and this characteristic is also used as a part of the classification of composite structure. In the majority of particulate reinforced composites the orientation of the particles is considered, for practical purposes, to be random.

A fibrous reinforcement is characterized by its length being much greater than its cross-sectional dimension. However, the ratio of length to the cross-sectional dimension, known as the aspect ratio, can vary considerably. In single-layer composites long fibres with high aspect ratios give what are called as continuous fibre reinforced composites, whereas discontinuous fibre composites are fabricated using short fibre of low aspect ratio. The orientation of the discontinuous fibres may be random or preferred. The frequently encountered orientation in the case of a continuous fibre composite is termed as unidirectional and the corresponding random situation can be approximated to by bidirectional woven reinforcement. Multilayered composites are another category of fibre reinforced composites. These are classified as either laminates or hybrids. Laminates are sheet constructions which are made by stacking layers (also called as plies or laminae and usually unidirectional) in a specified sequence. A typical laminate may have between 4 to 40 layers and the fire orientation changes from layer to layer in a regular manner through the thickess of the laminate, eg. $0/90^0$ stacking sequence results in a cross ply composites. Hybrids composite are usually multilayered composites with mixed fibres and are becoming commonplace. The fibres may be mixed in a ply or layer by layer and these composites are designed to benefit from the different properties of the fibres employed. For eg. A mixtue of glass and carbon fibres owing to the low cost of glass fibres, but with mechanical properties enhanced by the excellent stiffness of carbon. Some hybrids have a mixture of fibrous and particulate reinforcement [Matthews and Rawlings, 1999].

Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials. Many of the well-established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Most of the resulting materials show improved mechanical properties and a well-known example is inorganic fiber-reinforced polymers. Apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers. Blends are formed if no strong chemical interactions exist between the inorganic and organic building blocks. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components.

After having discussed the above examples one question arises: what is the difference between inorganic–organic hybrid materials and inorganic– organic nanocomposites? In fact there is no clear borderline between these materials. The term nanocomposite is used if one of the structural units, either the organic or the inorganic, is in a defined size range of 1–100 nm. Therefore there is a gradual transition between hybrid materials and nanocomposites, because large molecular building blocks for hybrid materials, such as large inorganic clusters, can already be of the nanometer length scale. Commonly the term nanocomposites is used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used if the inorganic units are formed *in situ* by molecular precursors, for example applying sol–gel reactions. Examples of discrete inorganic units for nanocomposites are nanoparticles, nanorods, carbon nanotubes and galleries of clay minerals as shown in Figure 2.2 (a), (b) and (d). Usually a nanocomposite is formed from these building blocks by their incorporation in organic polymers, inorganic clusters or nanoparticles with specific optical, electronic or magnetic properties in organic polymer matrices. These organic polymers are usually in macromolecules as shown in Figure 2.2 (c). However, sometimes a controlled aggregation can also be required, e.g. percolation of conducting particles in a polymer matrix increases the overall conductivity of the material. If the organic polymerization occurs in the presence of an inorganic material to form the hybrid material one has to distinguish between several possibilities to overcome the incompatibilty of the two species. An important area with respect to potential applications of hybrid materials and nanocomposites is the ability to design these materials on several length scales, from the molecular to the macroscopic scale. The enhancement of mechanical and thermal properties of polymers by the inclusion of inorganic moieties, especially in the form of nanocomposites.

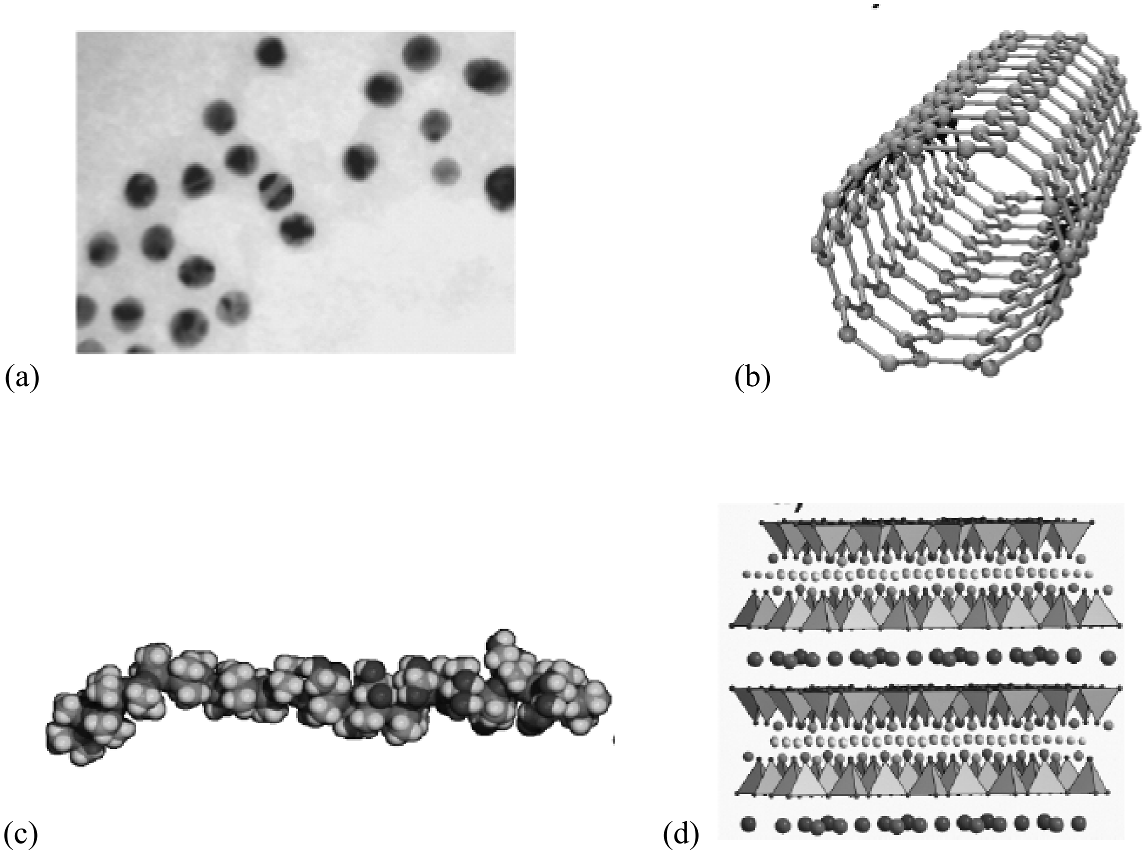

Figure 2.2 (a) Inorganic building blocks used for embedment in an organic matrix in the preparation of hybrid composites (a) nanoparticles (b) nanotubes (c) macromolecules (d) layered materials

Medical materials are also one typical application area of hybrid materials, as their mechanical properties can be tailored in combination with their biocompatibility, for example nanocomposites for dental filling materials. Many methods used are more related to the characterization of amorphous organic polymers. The heterogeneous nature of hybrid materials means that generally a variety of analytical techniques has to be used to get a satisfactory answer to structure– property relationships [Kickelbick, 2007].

2.1.4 Carbon Nanotubes (CNTs)

CNTs, long, thin cylinders of carbon, were discovered in 1991 by S. Iijima. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in the recent years and a large amount of research has been dedicated to their understanding. Currently, the physical properties are still being discovered and disputed. What makes it so difficult is that nanotubes have a very broad range of electonic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). With unique atomic structure and very high aspect ratio, carbon nanotubes (CNTs) have extraordinary mechanical properties (such as high strength and unique flexibility), making them ideal reinforcing materials in composites [Hone *et al*., 1999; Unger *et al*., 2002; Sun and Zhao, 2005]. CNTs incorporated composites represent a new frontier in materials science because the reinforcement scale has changed from micrometers to nanometers.

2.2 Polymer Matrix

2.2.1 Polypropylene Matrix

PP is one of the most important and widely used commercial thermoplastics polyolefin polymers. Its consumption is still increasing more rapidly than the total for all thermoplastic. This polymer and its blends and composites find wide application in automotive parts, extruded profiles, cable insulation, footwear, packaging industry, etc [Karger-Kocsis, 1995].

This situation is likely to continue in the future due to following reasons:

- Relatively low cost product due to low monomer cost and well established polymerization technology, compared with other thermoplastics.
- PP can be modified for a variety of applications through copolymerization, orientation and other techniques.
- The ease in processing of these polymers allows their use in most commercial fabrication techniques.

PP is a linear hydrocarbon polymer containing little or no unsaturation. The presence of methyl group attached to alternate carbon atoms on the chain backbone can alter the properties of the polymer in number of ways [Brydson, 1995]. The repeating unit of PP is shown in Figure 2.3. The most significant influence of the methyl group is that it can lead to products of different tacticity, ranging from complete isotactic and syndiotactic structures to atactic molecules. The isotactic is the most regular since the methyl groups are all disposed on one side of the molecule. The isotactic polymer is stiff, highly crystalline and with a high melting point. The melting point of isotactic is 165 ^{0}C. Within the range of commercial polymers the greater mount of isotactic material the greater the