CHARACTERISATION AND PROPERTIES OF BENTONITE/POLYPROPYLENE COMPOSITE

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CHARACTERISATION AND PROPERTIES OF BENTONITE/POLYPROPYLENE COMPOSITE

by

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LIST OF SYMBOLS

α	The ratio of length to diameter
A	Area
V	Volume
a	Aspect ratio
l	Length
d	Diameter
µm	Micrometer
Å	Amstrong
m^2	Meter square
g	Gram
Si^{4+}	Silicon ion
Al^{3+}	Aluminium ion
Fe^{3+}	Ferum ion
Mg^{2+}	Magnesium ion
Na^+	Sodium ion
K^+	Kalium ion
Ca^{2+}	Calsium ion
O	Oxygen
OH	Hydroxyl group
x	Degree of isomorphous
M	Monovalent change compensating cation in the interlayer
m/s	Meter per second
w/w	Weight per weight
phr	Part per hundred rubber
wt %	Weight percent
MPa	Mega pascal
T_m	Melting temperature
T_c	Crystallisation temperature
ΔH_c	Crystallisation entrophy
ΔH_m	Melting entrophy
$\% X_c$	Percentage of crystallinity
$T_{5\%}$	Initial degradation temperature
$T_{90\%}$	End degradation temperature

T_d	Decomposition temperature
M_m	Moisture content
D	Diffusion constant
F	Force
σ	Stress
ε	Strain
σ_y	Stress at yield
ε_y	Elongation at yield
$L – Lo$	Change in length
Lo	Original length

LIST OF ABBREVIATION

AAc	Acrylic acid
$Al(OH)_3$	Aluminium hydroxide
APDES	Aminopropyl methyl diethoxysilane
ATH	Aluminium trihydrate
BC	Before century
$CaCO_3$	Calcium carbonate
CEC	Cation exchange capacity
CMC	Ceramic matrix composite
CO_2	Carbon dioxide
CTAB	Cethyl trimethyl ammonium bromide
DAA	Dicarboxylic acid anhydride
DSC	Differential Scanning Calorimetry
EPDM	Ethylene-propylene diene terpolymer
EPR	Ethylene propylene rubber
EPRgMAH	Ethylene propylene rubber grafted maleic anhydride
EVOH	Ethylene vinyl alcohol
FTIR	Fourier Transform Infra Red
GMC	General Motor Corporation
HDPE	High density polyethylene
HMDS	Hexamethyl disilazane
iPP	Isotactic polypropylene
KT-MT	Quarternary-alkylamine-modified-montmorillonite
LICA 12	Titanate coupling agent
LOI	Loss of ignition
MAPP	Maleic anhydride grafted polypropylene
MMC	Metal matrix composite
MTH	Magnesium trihydroxide
PE	Polyethylene
PEAA	Polyethylene acrylic acid
PLA	Polylactic acid
PMC	Polymer matrix composite
PMMA	Polymethyl methacrylate
POFA	Palm oil fatty acid additive

POM	Polarized optical microscopy
PP	Polypropylene
PPAA	Polypropylene acrylic acid
PPEAA	Polypropylene ethylene acrylic acid
PPMAH	Polypropylene-grafted- maleic anhydride
PPgMAH	Polypropylene-grafted- maleic anhydride
PS	Polystyrene
PVC	Polyvinyl chloride
PVT	Pressure volume temperature
RS	Rice starch
SEBS	Styrene ethylene butadiene styrene
SEBSgMAH	Styrene ethylene butadiene styrene grafted maleic anhydride
SEM	Scanning electron microscopy
SiO_2	Silicone oxide
TGA	Thermogravimetric Analysis
TiO_2	Titanium oxide
USA	United State of America
UV	Ultra violet
XRF	X-ray fluorescence

LIST OF APPENDICES

PENCIRIAN DAN SIFAT-SIFAT KOMPOSIT POLIPROPILENA/BENTONIT

ABSTRAK

Projek ini melibatkan penggunaan bentonit sebagai pengisi di dalam termoplastik komposit. Objektif pertama kajian ini adalah untuk mengkaji kesan pembebanan bentonit terhadap sifat komposit PP matriks. Komposit PP pada pembebanan yang berbeza (10–50 wt %) telah diadunkan dengan menggunakan mesin pencampuran dalaman Polydrive Thermo Haake dengan Rheomix R600. Pengisian bentonit ke dalam matriks PP telah menunjukkan peningkatan pada modulus Young’s, kestabilan terma dan kemudahbakaran. Walau bagaimanapun dengan peningkatan bentonit sebagai pengisi, sifat-sifat mekanikal komposit PP-bentonit telah menurun dan peratus penyerapan air telah meningkat. Penurunan dalam sifat-sifat mekanikal telah dibincangkan berdasarkan analisis permukaan rekahan tegangan dan hentaman dengan menggunakan mikroskop penskanan electron (SEM).

Objektif kedua adalah mengkaji pengaruh agen pengserasi atau agen pengkupel terhadap sifat-sifat komposit PP berpengisi bentonit. Empat jenis agen pengserasi dan agen pengkupel telah digunakan di dalam kajian ini iaitu PPMAH, LICA 12, POFA dan PEAA. Pada pembebanan pengisi yang sama, komposit PP terisi bentonit terawat dengan agen pengserasi dan agen pengkupel menunjukkan nilai tork puncak dan tork kestabilan yang lebih rendah berbanding dengan komposit yang tidak terawat. Kekuatan regangan yang lebih tinggi telah dicatat oleh komposit terawat PPMAH diikuti dengan komposit terawat PEAA, LICA 12 dan POFA. Penambahan PPMAH, PEAA, LICA 12 dan POFA telah meningkatkan pemanjangan pada takat putus. Nilai modulus Young telah menunjukkan peningkatan pada semua jenis komposit terawat kecuali komposit terawat POFA. Pada penambahan bentonit dalam julat 10–30 wt %, komposit terawat PPMAH merekodkan nilai kekuatan hentaman tertinggi diikuti dengan komposit terawatt PEAA, LICA 12 dan POFA. Pada penambahan bentonit dalam julat 40-50 wt %, komposit terawat LICA 12 menunjukkan nilai kekuatan hentaman tertinggi diikuti dengan komposit terawat PEAA, POFA dan PPMAH. Nilai penyerapan air terendah telah ditunjukkan oleh komposit terawat PPMAH diikuti dengan komposit terawat LICA 12, PEAA dan POFA. Walau bagaimanapun komposit terawat POFA menunjukkan nilai kestabilan terma tertinggi manakala nilai kestabilan terma terendah ditunjukkan oleh komposit terawat PPMAH. Di samping itu, komposit terawat PPMAH menggalakkan penghabluran melalui peningkatan peratusan darjah penghabluran dalam komposit. Komposit terawat PPMAH, PEAA, LICA 12 dan POFA meningkatkan rintangan kemudahbakaran. Kadar kemudahbakaran paling rendah ditunjukkan oleh komposit terawat LICA12.

Di dalam kajian ini analisis percantuman maleik anhidrid (MAH) ke atas rantaian PP telah dilakukan. Kajian menunjukkan 0.51 % MAH telah berjaya dicantumkan ke atas rantaian PP. Ini dapat dibuktikan melalui kaedah pentitratan dan dapat disokong melalui analisis FTIR. Analisis FTIR mengesahkan kewujudan kumpulan karbonil anhidrid di dalam julat panjang gelombang 1785 – 1795 cm^{-1} dan 1865 cm^{-1}. PP tercantum MAH telah digunakan sebagai matriks dan disikan dengan bentonit melalui kaedah ‘in-situ’. Sifat-sifat mekanikal komposit PP tercantum MAH terisi bentonit lebih tinggi daripada komposit PP terisi bentonit kecuali sifat pemanjangan pada takat putus. Komposit PP tercantum MAH terisi bentonit menunjukkan peratus penyerapan air yang lebih rendah. Keputusan analisis ujian DSC pula menunjukkan pengurangan peratusan darjah penghabluran yang hadir di dalam komposit PP tercantum MAH terisi bentonit. Walau bagaimanapun, suhu penguraian telah meningkat kepada 480°C dan meningkatkan rintangan kemudahbakaran.

CHARACTERISATIONS AND PROPERTIES OF BENTONITE/ POLYPROPYLENE COMPOSITES

ABSTRACT

This project was concerned with the application of bentonite filler in thermoplastics composite. Thus, the first objective of this project was to study the effect of bentonite loading on properties of polypropylene (PP) matrix composites. Polypropylene composites at different bentonite loading (10-50 wt %) were compounded using a Polydrive Thermo Haake with Rheomix R600. The inclusion of bentonite into PP matrix improves the Young's modulus, thermal stability and flammability. However, the use of bentonite reduces the mechanical properties and also increases the percentage of water absorption as increasing filler loading. The reduction in mechanical properties can be explained from the analysis of Scanning Electron Microscopy (SEM) micrograph of the tensile and impact fractured surfaces.

Secondly, the influences of compatibilisers or coupling agents on properties of bentonite filled PP composites have been investigated. Four types of compatibilisers or coupling agents were used in this project namely; polypropylene-graft-maleic anhydride (PPMAH), titanate (LICA 12), polyethylene-graft-acrylic acids (PEAA) and palm oil fatty acid additive (POFA). At similar filler loading bentonite filled PP composites with compatibilising or coupling agent exhibit lower peak and stabilization torques than the similar composites but without compatibilising or coupling agents. The highest tensile strength was recorded by the composites treated with PPMAH followed by composite treated with PEAA, LICA12 and POFA, respectively. The addition of PPMAH, PEAA, LICA12 and POFA improved the elongation at break as compared to uncompatibilised (PPBT) composite. The addition of compatibilisers or coupling agents into PP-bentonite composites further improved the Young's modulus of the composites except for the composites with POFA treatment. At typical bentonite loading of 10-30 wt %, PPMAH treated composite recorded the highest impact strength followed by the composites treated with PEAA, LICA 12 and POFA, correspondingly. At higher filler loading, typically at 40-50 wt % of bentonite loading, the highest recorded impact strength was for composites treated with LICA 12 and followed by composites treated with PEAA, POFA and PPMAH, respectively. The incorporation of PPMAH into bentonite filled PP composites shows the lowest water absorption characteristic followed by composites treated with LICA 12, PEAA and POFA treatment respectively. However the presence of POFA in PP-bentonite composites demonstrates the highest thermal stability and the lowest was recorded by PPMAH treatment. Besides that the PPMAH treatment was capable of inducing crystallisation as indicated by increasing the percentage of crystallinity presence in the composites. The application of PPMAH, PEAA, LICA 12 and POFA improved the flammability of PP-bentonite composites. The lowest burning rate was achieved by LICA 12 treated PP-bentonite composites.

Grafting of maleic anhydride onto PP back bone was investigated in this project. 0.51 % of maleic anhydride (MAH) was successfully grafted onto the PP chain. It was determined by titration method and the evidences are supported by FTIR analysis which confirmed the existing of carbonyl anhydride group in the region of 1785-1795 cm^{-1} and 1865 cm^{-1}, respectively. Maleic anhydride grafted PP (PPgMAH) was used as a matrix and filled with bentonite via in-situ method. The mechanical properties of bentonite filled PPgMAH composites were higher than bentonite filled pure PP except for elongation at break. PPgMAH/bentonite composites demonstrate lower percentage of water absorption than PP/bentonite composite and DSC results revealed the reduction in the percentage of crystallinity. However, the decomposition temperature has increased to 480°C and also improved the flammability.

CHAPTER 1

INTRODUCTION

1.0 Introduction

Minerals used as fillers in plastic compounds have traditionally been used to reduce material costs by replacing a portion of the polymer with a less expensive material. However, nowadays many functional fillers or mineral modifiers are required to modify processing characteristics or finished part properties. Many are now also being used to reduce the level of more expensive additives such as pigments, flame retardants and impact modifiers.

According to a study by Principia Consulting, total North America demand for minerals used as reinforcements, pigment extenders and fillers in a variety of end-use applications in 2002 exceed 15 millions tons, valued at $ 1.9 billion (www.principiaconsulting.com). Among all mineral markets outlets, Principia finds the plastics industry to be the most intriguing as it consumes the highest value-added minerals – with an average price tag of $225/ton, almost twice the industry average – and demand for minerals in plastics has the highest forecast growth, at over 5% per year.

A wide variety of minerals are employed as plastics additives, including calcium carbonate ($CaCO_3$), talc, alumina hydrate, silica, mica, kaolin, diatomite, dolomite and wollastonite. Since 1980, demand or these additives has increased on average 7% a year in volume terms, compared to an annual increase in the US demand for plastics of only 4-5%. In 1980, 9% of all plastics compounds are incorporated with minerals but this percentage had grown to 15% by 2002 (www.principiaconsulting.com).

Minerals clays are technologically important and are mainly composed of hydrated aluminosilicate with neutral or negative charge (Murray, 2000). Therefore, a large number of new composites based on synthethic polymer and clay minerals have been recently investigated (Liu & Wu, 2001; Fornes et al., 2001).

Moreover, clay mineral was used as filler in glycerol-plasticized Cara'starch films in order to improve the mechanical properties. DMA results showed that the composites films give rise to three relaxation processes, attributed to a transition of the glassy state of the glycerol-rich phase, to water loss including the interlayer water from the clay structure, and to the starch-rich phase. A film obtained with 30% in w/w of clay showed an increase of more than 70% in the Young's modulus compared to non-reinforced plasticized starch (Wilhem et al., 2003).

Bentonite is a kind of clay mineral and used for various applications, including pet absorbent, pitch control, ceramics manufacture, and as filler in the polymer, paint and cosmetics industries. Particles of bentonite have the shape of platelets due to the layer structure of the mineral. It is well known that the basal surfaces are hydrophobic, while the edge surfaces are hydrophilic (Yariv, 1992; Chander et al., 1975). The hydrophobicity of the basal surfaces arises from the fact that the atoms exposed on the surface are linked together by siloxane (Si-0-Si) bonds and, hence, do not form strong hydrogen bonds with water. The edge surfaces, on the other hand, are composed of hydroxyl ions, magnesium, and silicon and substituted cations all of which undergo hydrolysis. As a result, the edges are hydrophilic, and they can form strong hydrogen bonds with water molecules and polar substances (Feurstenau et al., 1988; Ciullo, 1996; Rayner and Brown, 1973).

In many of the industrial applications, this dual surface property of the mineral plays an important role. In the paper industry, for the pitch and sticky control applications, the hydrophilic property of the edges allows the particles to be dispersed in aqueous media, while the hydrophobic property of the basal surfaces attract the sticky hydrophobic substances present in wood pulp.

For filler applications, proper control of the adhesion between bentonite filler and the matrix is essential in controlling the property of the composite material. The strength of adhesion depends on the surface properties of the filler and of the matrix. In general, strong filler-matrix interactions result in improved processability, impact strength, and surface quality, while interactions that are too weak lead to decrease strength and increased deformability of the composite (Pukanszky, 1995). The role of acid-base interactions is crucially important in the use of minerals as filler.

It is well known that mineral fillers interact with polymers by acid-base interactions. For example, halogenated polymers such as polyvinylchloride are acidic and tend to interact strongly with basic fillers such as alumina and calcium carbonate (Fowkes, 1983). In this regard, if the hydrophilic edge surface area of bentonite is appreciably higher, strong acid-base interactions between bentonite filler and polymer matrix would be expected. As a means of controlling the filler–polymer matrix interactions and improving the processability and properties of particulate filled polymers, bentonite filler is treated with appropriate compatibilisers or coupling agents.

1.1 Background of the present research

Many researchers have investigated the substitution of ceramic materials by the clay in plastics composite (Özdilek et al., 2005). While simple clay minerals are extensively used as fillers in elastomers, their use in thermoplastics is more restricted (Rothon, 2003) due to the character and extent of interaction at the polymer-filler interface, the homogeneity of filler distribution, the filler orientation in the case of filler anisometric particles, and the polymer-filler adhesion (Díez-Gutiérrez et al., 1999).

Among inorganic compounds, special attention has been paid to clay minerals because of their small particle size and intercalation properties. Clay and clay minerals such as montmorillonite, hectorite, saponite, koalinite, etc, were widely used as filler in rubber for many years mainly for reducing polymer consumption and lowering the cost (LeBaron et al., 1999).

The clay minerals are composed of silicate layers at 1nm thick and between 200 and 300 nm in the lateral dimensions (Alexandre and Dubois, 2000). The internal and external cations can be changed by other inorganic or by organic cations ion (LeBaron et al., 1999; Alexandre and Dubois, 2000), for examples quaternary alkyl ammonium ions. Organophilic modification makes the silicate compatible with the polymer. These entering guest molecules can either simply increase the distances between the still-parallel layers in an intercalation process or randomly entirely disperse the separate layers in an exfoliation. The optimal performance of polymer/clay composites is achieved when the clay fillers are uniformly dispersed in the polymer matrix.

Nowadays, the development and characterisation of polymer/clay composites has been subjected to raising interest especially in nanosize filler. The studies have been carried out by several workers (Gloaguen and Lefebure, 2001, Jian et al., 2003, Varghese and Karger-Kocsis, 2003, Varghese et al., 2003). The possibility of substituting carbon black by white fillers as reinforcements of natural rubber, in particular an octadecylamine-modified monmorillonite has been carried out by Arroyo et al., (2003). They found that the organoclay gives rise to a higher degree of crosslinking as compared to the counterpart with carbon black, which is reflected in a considerable increase in mechanical properties of the elastomer. In fact, the organoclay behaves as an effective reinforcing effect than carbon black while retaining the elasticity of the elastomer. Only 10 phr of the organoclay are enough to obtain a similar mechanical behaviour as the compound with 40 phr of carbon black. It can be assumed that the organic treatment of the silicate increases the interlayer spacing which allows the dispersion of silicate layers into the matrix at a nanoscale level and improves the filler-matrix compatibility.

Even though, many study have been done on polymer/clay composites up to nanosize but there is no particular study was mentioned about the polypropylene with bentonite. Actually very rare in the literature reported about the application of bentonite in thermoplastic composites especially in micron size. Therefore, this research was carried out in order to determine the performance of bentonite in thermoplastics, in particular polypropylene.

1.2 Problem statements

The application of fillers in thermoplastics or thermoset generated a special interest in the world of polymer engineering nowadays. Many kinds of filler have been introduced so far in order to increase the number of filler selections in the market. Fillers could be conveniently classified into two groups, i.e., natural or synthethic. Natural fillers are categorised as agriculture and industrial waste which contribute much attention on cost saving. Mineral fillers also considered as natural as well since they come from deposit of the earth, for example talc, calcium carbonate, kaolin and silica. On the other hand, synthetics filler are much more expensive.

The usage of common mineral fillers, as mentioned earlier, has been established in the research world. Perhaps combination of two of them, in research and development stage, or may be some of them, are already established in the market; so-called as hybrid quite familiar. The needs for new types of filler for composite application are inevitable in order to produce a composite with new set of properties. As far as mineral filler is concerned bentonite is relatively new type of filler with promising properties. Therefore, this project mainly focussing on mineral filler known as bentonite and the potential of bentonite to perform as filler in polypropylene matrix has been investigated.

The third component which use as compatibilisers or coupling agents are commonly introduced to the composite systems in order to improve the interaction between filler and matrix. They are many type of compatibilisers or coupling agent in the market, but the choice depends on the matrix and filler itself. In this study there are four types of compatibilisers or coupling agents used in bentonite filled polypropylene composites system namely; polypropylene grafted maleic anhydride (PPMAH), titanate coupling agent (LICA 12), polyethylene acrylic acids (PEAA) and palm oil fatty acids additive (POFA). The utilisation of POFA as a new type of compatibiliser for thermoplastic composite has been introduced in this research work.

Besides the common practice using compatibilisers or coupling agents, a new approach was introduced in this project. Here, a modification of polypropylene has been carried out in the laboratory via melt blending method and has been used as a matrix in the composite system.

1.3 Objectives of study

The objectives of this study are:

1) To investigate the ability of bentonite to serve as filler in polypropylene matrix.

2) To study the effect of bentonite loading on mechanical properties, water absorption characteristics, flammability, thermal stability, and morphological properties of PP composites.

3) To investigate the effect of compatibilisers or coupling agents on the properties of bentonite filled polypropylene composites and determine the most suitable compatibilisers or coupling agents that could be used to boost the desired properties of the bentonite filled polypropylene.

4) To investigate the grafting percentage of maleic anhydride onto polypropylene and maleic anhydride grafted polypropylene was used as a matrix.

5) To study the mechanical, morphological, thermal and flammability properties and water absorption characteristic of bentonite filled PPgMAH composites.

1.4 Organisation of the thesis

This thesis has been divided into seven chapters all together. Each chapter gives the information about the research interest as mentioned in the objectives earlier.

- **Chapter 1** covers the introduction of the thesis. It contains a general overview about mineral filler, a brief introduction about research background, a problem statement, objectives of the project and organisation of the thesis.
- **Chapter 2** contains some fundamental concepts of polymer matrix composites together with some review of related works reported in the literature.
- **Chapter 3** explains the material specifications, research methodology and finally experimental procedures which are carried out in the study.
- **Chapter 4** discusses the preliminary study on application of bentonite as filler in polypropylene composites.
- **Chapter 5** discusses the modification of bentonite filler coupling or compatibilising approach.
- **Chapter 6** discusses maleic anhydride grafted polypropylene as a matrix and filled with bentonite via in-situ method.
- **Chapter 7** concludes the finding of the project and the evaluation has been made in order to assess the achievements of the objectives. Some of suggestions for further study have been explained.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter will cover the fundamental on the definition and classification of composites followed by a brief overview of composite materials explaining their increasing use in a wide range of engineering structures. The role of polymer matrix, fillers and extenders with particular interest focused on filler-matrix interaction will be described in this chapter. Subsequently, a literature survey was done on various published works on polymer composites, particularly those related to this work. Works on other polymer composites were also extensively reviewed.

2.1 Composite: Definition and classification

The introduction of a second component into polymers is an accepted and frequently used method to modify their properties and to obtain new materials with improved characteristics, i.e. polymer composites. Composite materials play an important role in the most progressive manufacturing industry in the world.

Polymer composites were first developed during the 1940's, for military and aerospace applications. The word 'composites' has a modern ring but the deliberate combination and orientation of dissimilar materials to achieve superior properties is an ancient and well-proven practice. In fact, the use of high strength fibres to stiffen and strengthen a weak matrix material is probably a concept older than the wheel.

2.1.1 Definition of composite

Composite materials may be defined as materials having two or more distinct components or phases and their components have significantly different physical properties and thus, the composite properties are noticeably different from the individual component properties. Composites consist of one or more discontinuous phases embedded in a continuous phase. The discontinuous phase is usually harder and stronger than the continuous phase and is called the reinforcement or reinforcing material, whereas the continuous phase is termed the matrix (Matthews, 1994).

Thus, one can classify bricks made from mud reinforced with straw and horsehair, which were used in ancient civilisations over 5000 years ago, as composites. Other examples of primitive composites include the Professional Way in ancient Babylon (1750 BC), which was made from bitumen reinforced with plaited straw (Ashby and Jones, 1988), and the Egyptian mummy cases made from papyrus and resin (1000 BC). Paper is a composite, as is concrete; the ancient Romans knew both. Perhaps more representatives of modern composite are Mongolian bows, which are laminates of wood, animal tendons, and silk; and Japanese samurai swords, which contain thousands of alternating layers of tough, ductile steel and hard oxide (Kroschwitz, 1987).

In addition to synthetic composites, there are also many natural composites (particularly those which must bear load) including wood, bone, muscle and bamboo. Based on this explanation, wood can be considered as a polymer composites since wood is a mixture of two polymers namely, hemicellulose and lignin (Steven, 1990). Bone is a composite of collagen and other proteins and calcium phosphate salts. The shell of mollusk as shown in Figure 2.1 is made of layers of hard mineral separated by a protein binder (Xanthos, 2005).

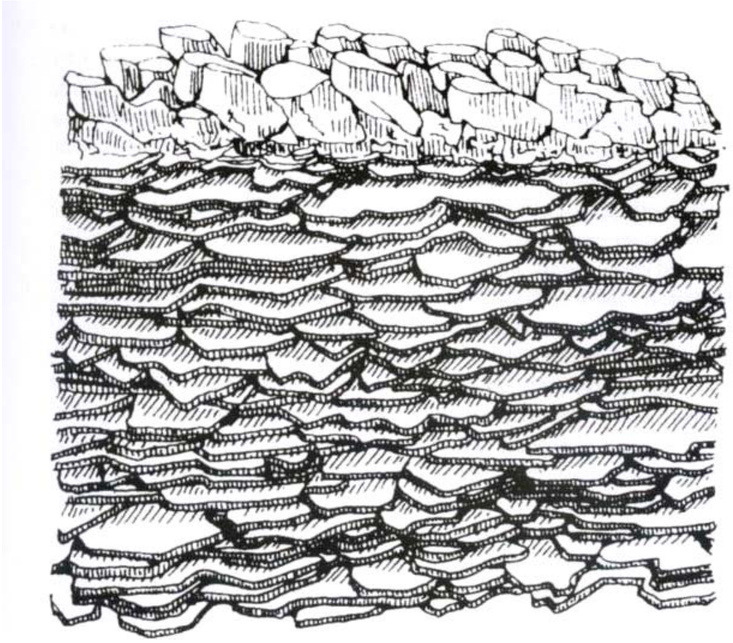


Figure 2.1: A natural composite: the shell of a mollusk made up of layers of calcium salts separated by protein (Xanthos, 2005)

A synthethic composite could be seen in Figure 2.2 whereby a similar platy structure providing a tortuous path for vapors and liquids can be obtained by embedding mica flakes in a synthetics polymeric matrix (Xanthos, 2005).

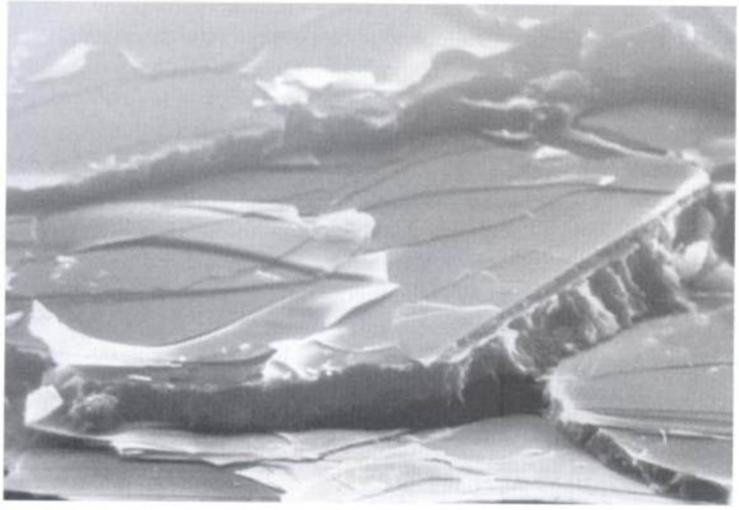


Figure 2.2: A synthetics composite: SEM photograph of a cross-section of a fractured mica thermoset composite showing mica flakes with thickness 2.5μm separated by a much thicker polymer layer (Xanthos, 2005).

Chiang and Huang (1999) have given a similar but little broad and simple definition for polymer composites. They defined polymer composite as a polymer mixed with filler. In the plastics industry, reinforced plastics are defined and/or used interchangeably with "composites" or "advanced composites". This is because, reinforced plastics are defined as a polymer resin matrix with a reinforcing agent or agents which improved strength and stiffness, compared to neat resin (King, 1972).

2.1.2 Classification of composite

There are several types of composites. They are classified into three main classes, grouped according to the nature of the matrix. Most composites in industrial used are based on polymeric matrices (PMC); thermosets and thermoplastics. These are usually reinforced with fibre such as glass and carbon. They commonly exhibit marked anisotropy, since the matrix is much weaker and less stiffer than the fibres. Other type of composites is based on metallic matrices (MMC) such as aluminium and titanium and ceramic matrices (CMC) (Hull and Clyne, 1996).

A broad classification of polymer matrix composite has been explained by Robert Eller Associates, Inc. in their website (http://www.robertellerassoc.com/). The polymer matrix composites families are divided into two major group; thermoplastics and thermosets. A thermoplastics composite covers four main groups, i.e. glass mat, fibre reinforced, natural fibre thermoplastics composites and mineral reinforced thermoplastics. While thermosets composites are separated into two main groups only, i.e. glass carbon reinforced and natural/synthethic fibre reinforced. The details of the classification on polymer composites are shown in Figure 2.3.

Alger (1989) has classified polymer matrix composites (PMC) into three main categories;

1. Polymer-polymer combinations (polymer blends)

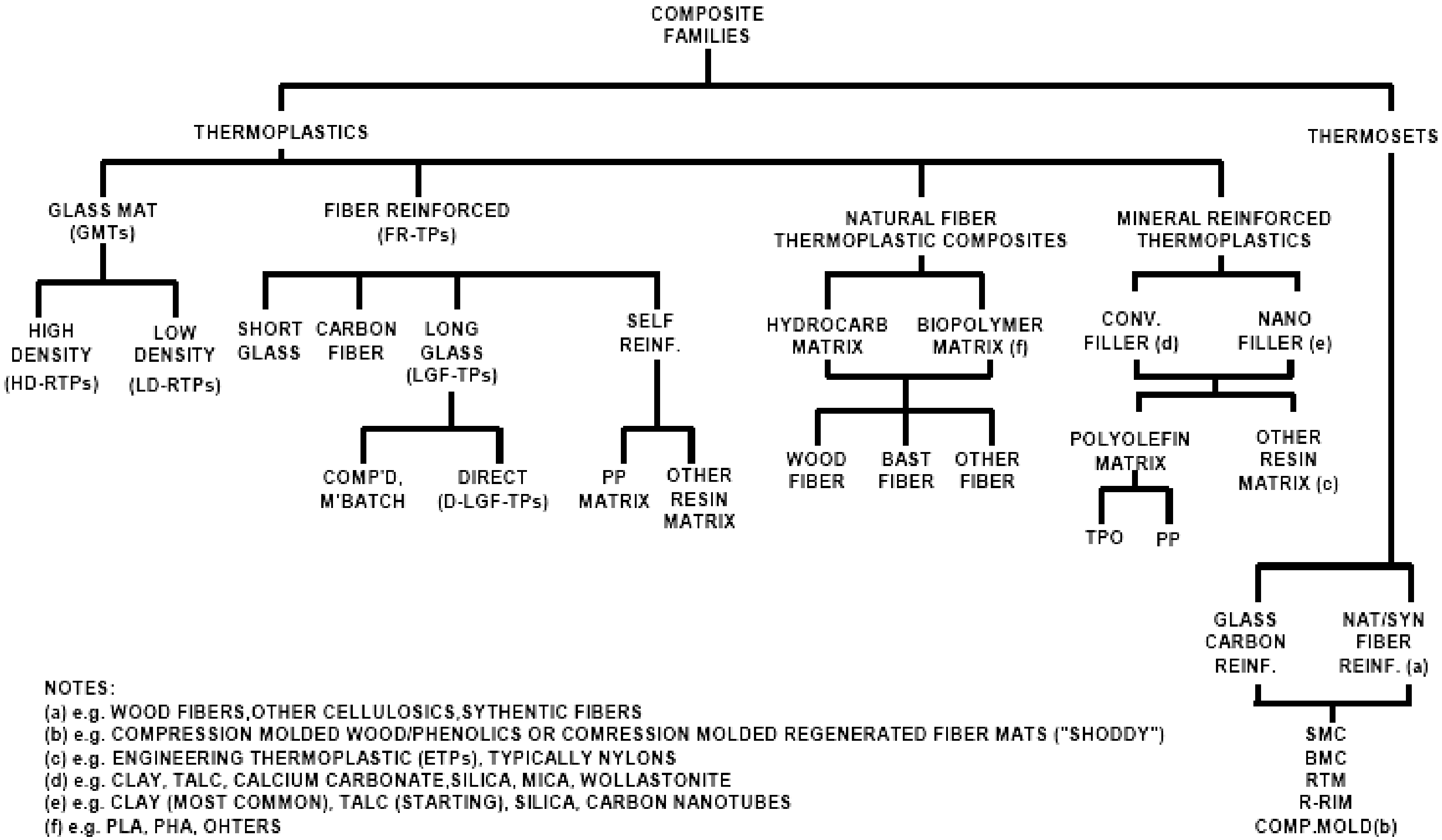
2. Polymer-gas combinations (expanded, cellular or foamed polymers)
3. Polymer-stiff filler combinations of:
    (1) Polymer-fibre – Discontinuous or short fibre
        - Continuous fibre
    (2) Polymer-particulate filler
    (3) Polymer-hybrid filler

Agarwal & Broutman (1990) and Rattana (2003) also classified composites material into two broad groups on the basis of reinforcement geometry:

(1) particulate-filled materials consisting of a continuous matrix phase and a discontinuous filler phase made up of discrete particles which can be spherical, cubic, block and platelet (or flake), and

(2) fibre-filled composites. A fibre is characterized by the fact that its length is much greater than its cross-sectional area.

The properties of composite materials are strongly influenced by the properties of the components, the geometry of the filler phase (size, shape and size distribution), the morphology of the system and the nature of the interface between the phases.



NOTES:
(a) e.g. WOOD FIBERS,OTHER CELLULOSICS,SYTHENTIC FIBERS
(b) e.g. COMPRESSION MOLDED WOOD/PHENOLICS OR COMRESSION MOLDED REGENERATED FIBER MATS ("SHODDY")
(c) e.g. ENGINEERING THERMOPLASTIC (ETPs), TYPICALLY NYLONS
(d) e.g. CLAY, TALC, CALCIUM CARBONATE,SILICA, MICA, WOLLASTONITE
(e) e.g. CLAY (MOST COMMON), TALC (STARTING), SILICA, CARBON NANOTUBES
(f) e.g. PLA, PHA, OHTERS

Figure 2.3: A broad classification of polymer matrix composites (http://www.robertellerassoc.com/)

2.2 Advantages and disadvantages of polymer composites

Composite materials have established themselves as high performance engineering materials and are relatively common place in a wide range of structural applications. Presently, the aircraft, automotive, marine, leisure, electronic and medical industries make extensive use of fibre-reinforced plastics. Composites are currently used to provide huge benefits with an emphasis on lower production and lifetime costs featuring prominently. One of the main characteristics of composites is the possibility of optimising the fibre stacking sequence to provide solution for structural needs.

Among the advantages of high performance polymer matrix composites are the followings:

- Weight savings are significant, frequently ranging from 20 to 50% of the weight of conventional metallic designs.
- The high torsion stiffness requirements of various vehicles, particularly high speed aircraft, can be satisfied.
- Corrosion resistance is outstanding.
- Impact and damage tolerance characteristics are excellent.
- Improved dent resistant is normally achieved (composite panels do not damage as easily as thin sheet metals).
- Flexibility in selection and changing of styling and product aesthetic considerations is an important feature.
- Thermoplastics have rapid processing cycles, making them attractive for high-volume commercial applications which traditionally have been the domain of sheet metals. Furthermore, thermoplastics can be re-formed and re-shaped.
- Low thermal expansion can be achieved.

- Manufacturing and assembly are simplified because of part integration (joint/fastener reduction) which reduces costs.

Many polymer-matrix materials absorb moisture, which can reduce their mechanical properties as a result of an increase in internal stresses and a possible change in dimensions. Thermal degradation due to oxidation may occur in polymer-matrix composites materials subjected to elevated temperatures. The characteristics anisotropy of composite materials are difficult to detect visually, and this it may add complexity to the design process. It is also worth commenting on the relative cost of composites compared to metallic or organic materials (i.e. wood, stone, etc).

In terms of their cost per tonne, composite materials are somewhat more expensive and restricted their use in some fields of application. Damage induced by impact loads may be difficulty to detect visually, making it laborious to assess the potential loss in residual mechanical properties. Nevertheless, other considerations such as operational costs, manufacturability, disposability, availability, health risks, durability and serviceability, play important role in the evaluation and selection of the appropriate materials for a specific application.

2.3 Applications of polymer composites

The composite industry, however, is relatively new compared to the traditional materials industry such as metal and ceramics. Polymer composite materials are widely used in variety of applications, ranging from engineering and aerospace structures to medical and surgery components replacing metallic materials such as aluminium and titanium alloys. Polymer composites, offering light weight coupled with high strength and stiffness properties are also being used in the manufacture of satellites, high performance aircraft, and luxury sailboats as well as submarines.

The principal features of these materials that make them so capable as engineering materials are their high specific strength and stiffness (strength–to–weight and stiffness-to-weight, respectively), which allow for significant weight reductions with little or no less in performance compared to considerably more dense metallic structures. The outstanding properties of polymer composites materials have led to their use in a wide range of structures. The marine industry is also a major user of composite materials. The marine environment presents a challenge for engineering materials. Materials that cannot withstand this severe environment are subjected to corrosion, rot, decay and loss of strength when used in marine applications. Polymer composite materials have proven their ability to withstand this environment, and in many cases, have essentially replaced less suitable materials.

A good example is the rapid and nearly total replacement of wood with glass reinforced plastics in small pleasure boats (Broutman et al., 1974). The use of composites materials in high-speed boats also reflects the high performance of these materials in marine environments. Other applications for composites materials can be found in freight containers, the ocean engineering industry, the building industry, chemical plants, appliances, sport equipment, etc.

2.4 Flake filled polymer composites

Thin flakes offer attractive features for an effective reinforcement. They have primarily a two-dimensional geometry and hence impart equal strength in all direction in their plane compared to fibres that offer a unidirectional reinforcement. Their incorporation normally imparts higher stiffness, higher resistance to heat distortion, which leads to lower shrinkage and a decrease in the coefficient of thermal expansion. However, the increase in tensile strength is rather limited and ductility is often decreased. In order for flakes to provide full reinforcement potential, platelets are required that have as high an aspect ratio as possible and a strong adhesion to the matrix. These two conditions are necessary to ensure efficient stress transfer between the two components. In addition, polymers filled with plate-like particles posses an extremely high resistance to the permeation of gases and liquids, which is attributable to flakes or platelets being aligned parallel to the surface of the film or sheet during processing (Bissot, 1990).

Flakes are especially effective in increasing the moduli of composites. Typical flake fillers include mica, kaolin, graphite, glass flakes, aluminum flakes, and aluminum diboride (Nielsen and Landel, 1994; Newman and Meyer, 1980). Such materials support the constraints in all direction in a plane of reinforcement, and often have the behavior of biaxially oriented materials. Unlike fibre, materials with planar orientation of the flakes provide reinforcement with high strength and stiffness in two directions: the longitudinal direction and the in-plane transverse direction, i.e. typically a direction perpendicular to the length of the flakes in the plane of the film or sheet. Materials with planar orientation of flakes have extremely high resistance to the permeation of gases and liquids.

The addition of platelet fillers distributed in the polymer film can greatly increase the diffusion pathway; permeating molecules are forced to go around impermeable flakes creating a tortuous path for the diffusing species. The use of mica in ethylene vinyl alcohol (EVOH) copolymers was reported to show a threefold increase in oxygen barrier properties (Bissot, 1990). In addition, composite barrier performance was shown to be proportional to its filler aspect ratio.

Concerted survey is presented of the existing theories for predicting the strength and modulus of particulate-filled polymeric composites. The macroscopic behaviour of particulate composites is affected by the size, shape, and the distribution of the inclusions. The interfacial adhesion between the matrix and inclusion is also important. The limitation of theoretical models in describing these parameters and expressing the experimental data on the macroscopic behaviour has been demonstrated by Ahmed and Jones (1990).

2.4.1 Types of particulate fillers

Hancock and Rothon, (2003) have classified particulate fillers into two major group i.e., particulate fillers from the natural origins (mineral filler) and synthethic particulate fillers. However, Katz and Milewski, (1987) classified them into four major groups i.e., mineral fillers, metallic, conductive and magnetic fillers, carbon black and organic fillers and lastly is spherical fillers.

The most important mineral fillers used are carbonates, clays and talc, while others silicates are also of interest. Calcite (calcium) and dolomite (calcium-magnesium) are the main carbonate fillers and very widespread. The other carbonate mineral of any importance is, in fact, a mixture of two carbonates: hydromagnesite and huntite. Clay minerals are aluminium silicates of either the two layered koalinite type or three layered montmorillonite type. Only three clay minerals are commonly used in the polymer industries, kaolinite, montmorillonite and chlorite. Talc (magnesium silicate) is widespread but is commonly found with other magnesium minerals such as magnesite. Carbon black is one of the synthethic particulate fillers, others such as fumed silicas, aluminium hydroxide (ATH), magnesium hydroxide, dawsonite, and antimony trioxides and pentoxide.

2.4.2 Particulate filler characteristics

The word ‘fill’ is synonymous with the action of filling, cluttering or dumping as these very common human activities. It also means saturate, penetrate, infiltrate, impregnate, pack, quench all of which are consistent with what fillers are designed to do. The saturate and pack spaces depending on parameters listed below;

1. Primary particle size and surface area
2. Particle/aggregate shape after dispersion
3. The magnitude of the interaction between the particle surface of the filler and matrix or the interface characteristics (associate with surface chemistry).

In addition, mechanical properties of the filler, filler friability, and processing technique used to prepare the composites, matrices properties and chemical treatments performed on the filler and matrix play an important role in deciding the final properties of the composites.

The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness and sometimes creates special properties, originating from the synergetic effect between the component materials. Among inorganic compounds special attention has been paid to clay mineral in the field of nanocomposites because of their small particle size and intercalation properties (Alexandre and Dubois, 2000; Murray, 2000).

According to Riley et al., (1990) mineral filler can change the characteristics of a polymer in two ways; firstly, the properties of the particulates themselves (size, shape and modulus) can have a profound effect, especially upon mechanical properties. Whilst most minerals have a large modulus relative to the polymer, a wide range of sizes and aspect ratios may be encountered. The largest dimension of a mineral filler particle may be anything from 0.1 micron to several tens of micrometers, whilst aspect ratios may be in the range 1 to a few hundred. Secondly, the particles may cause a change in the micromorphology of the polymer which may then give rise to differences in observed bulk properties. For example, the surface of the filler may acts as a nucleator for semi-crystalline polymer and may thereby alter the amount or type of crystallinity.

Xanthos (2005) explained that the reinforcing fillers are characterized by relatively high aspect ratio, α, defined as the ratio of length to diameter for a fiber, or the ratio of diameter to thickness for platelets or flakes. For spheres, which have minimal reinforcing capacity, the aspect ratio is unity. A useful parameter for characterizing the effectiveness of a filler is the ratio of surface area, A, to its volume, V, which needs to be as high as possible for effective reinforcement. Figure 2.4 shows that maximizing A/V and particle-matrix interaction through the interface require α > 1 for fibers and 1/α <1 for platelets (McCrum, 1997).

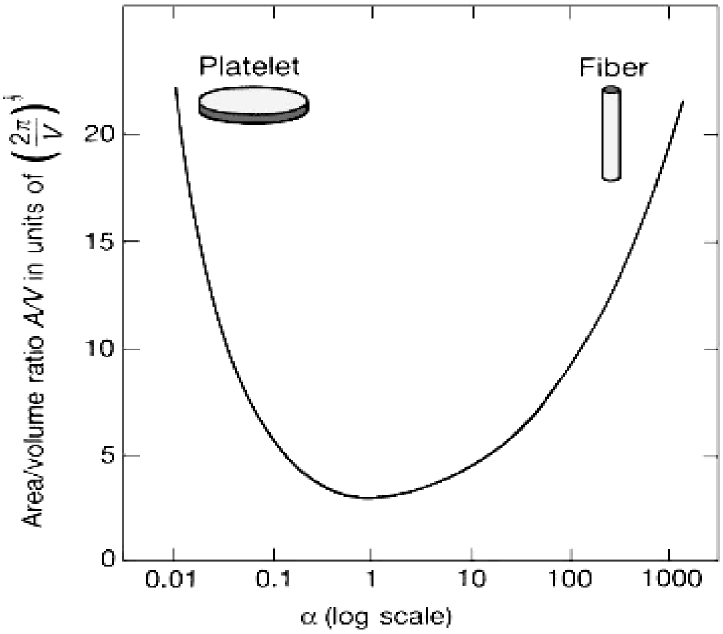


Figure 2.4: Surface area to volume ratio A/V, of a cylindrical particle plotted versus aspect ratio, a = l/d (Mc Crum et al., 1997).

Fillers, as the name implies, have commonly been employed to cheapen or extend a product with and evident change or modification of the properties of the unfilled materials such as hardness, rigidity, viscosity or colour. Gradually, the realization grew that by the selective use of fillers, certain properties of the unfilled material could be enhanced or even exceeded and a reinforcement of properties was possible. So as the conclusion, the introduction of filler to a polymer matrix can be either to enhance the general properties, to introduce specific characteristics and reduce the cost or to achieve combination of some of them. However, the performance of fillers depends on their characteristics.

2.4.2.1 Particles size

For natural filler it will have been determined by the origin and mineralogy of the deposite from which it has been extracted, by the method used in mining, and by separation procedures used during processing. For synthethic fillers, size will be determined by the conditions used in its synthesis such as precipitation and possibly by the drying and any coating procedures. Size is an easy property to measure reproducibly using a variety of technique including sieving, sedimentation, optical scattering and diffraction from particulate suspensions.

The appropriate particle size for consideration can itself vary according to whether one is dealing with powder flow, behaviour during compounding and dispersion, or the properties of the final composites. These different types of particles are generally described as primary or ultimate particles, agglomerates and aggregates. The types of particles are necessary to clarify the terminology as two contradicting convections are widely used. The need is to distinguish between collections of particles that are weakly and strongly bonded together. The term agglomerate for weakly bonded particles collections and aggregate for strongly bonded ones. The chosen terminology is, however, at least as widely used and is especially prevalent in the carbon black industry. An idealized view of particle type and breakdown with work during composite formation is presented in Figure 2.5 (Rothon, 2003)

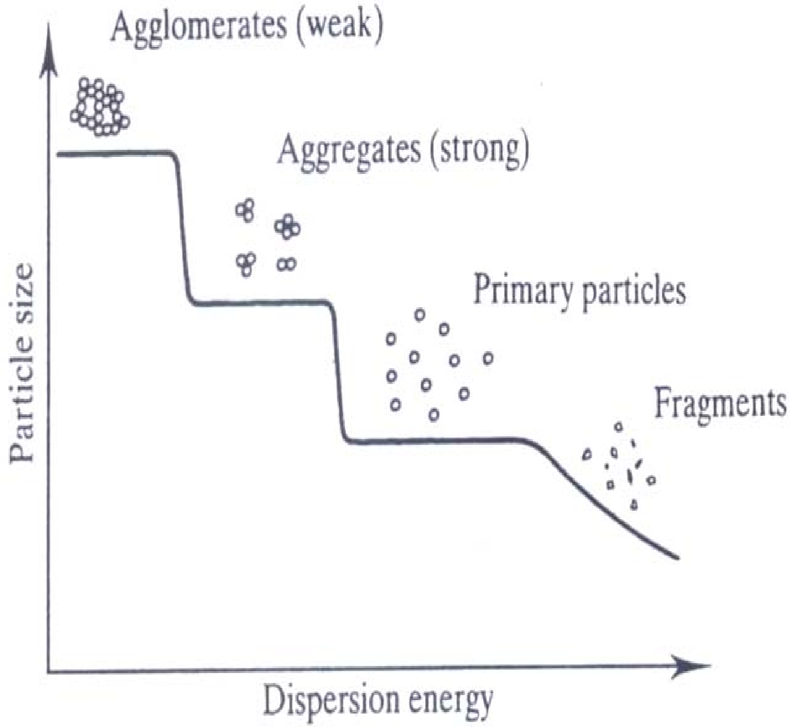


Figure 2.5: Idealised view of the way filler particles disperse and of the different form of particle types that might be encountered (Rothon, 2003)

Figure 2.6 shows the further complication arises when agglomerates form from initially well-dispersed systems. These agglomerates are sometimes referred to as flocs and can arise due to loss of colloidal stability in polymerizing systems, or to reticulation (filler network formation) above the glass transition, especially in cured elastomers, an effect often observed with carbon blacks. The most difficult situation to deal with is synthetics products, especially those formed by precipitation. This is where quite strong, complex aggregates are present, in addition to agglomerates. These aggregate often break down slowly, leading to a drawn-out step in the effective profile. The effective particle size will then be critically dependent on the exact processing conditions and will be very difficult to predict in advance.

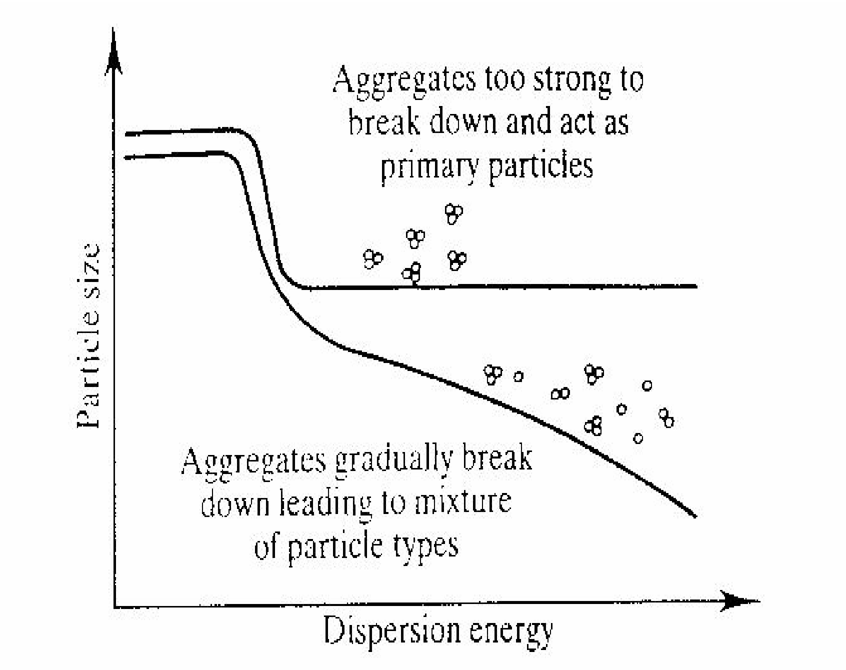


Figure 2.6: Complex particle dispersion behaviour, as often encountered with fine, precipitated fillers (Rothon, 2003)

Improvements in the physical properties are directly related to filler particle size. The increase of modulus and tensile strength is very much dependent on the particle size of the filler; smaller particulate fillers imparting greater reinforcement to the filled polymer. Since particle size is directly related to the reciprocal of surface area per gram of filler, it is the increase in surface area that is in contact with the polymer phase which probably leads to the increase in reinforcement. Reducing particle size also simply results in a greater influence of polymer-filler interaction.

In addition to average particle size, the particle-size distribution also has a significant effect on reinforcement. Particulate fillers with a broad particle-size distribution have better packing in the polypropylene matrix, which results in a lower viscosity than that provided by an equal volume of filler with a narrow particle-size distribution.

Another important concern in reinforcement is the presence of large particles or agglomerates in the polypropylene. These agglomerates not only reduce the contact between filler and matrix but function as failure initiation sites which would lead to premature failure of materials. This is based on the assumption that particle size of the filler in diameter is in the same order of magnitude of the distance between the crosslink sites in the matrix elastomer, which is about 500 Å (Manson and Sperling, 1976). It is reported that effective filler particle size is usually below the 40 µm and the finer particles of particles size less than 5 µm offer an improved physical properties. However, it is difficult to suggest an optimum particular particle size for filler. It is depend on the various other factors such as filler type, filler loading, chemical treatment, matrix type and the processing technology.

Nakamura et al. (1999) performed a study on the effect of particle size, shape and interfacial adhesion on the properties of a 50 wt % (35 volume %) silica filled epoxy system. In their study, they utilised different particles sizes of irregular shaped and spherical silica particles (the latter are typically produced by fusing the former in a flame to round their shape). Furthermore, in addition to the untreated state, the particles were also treated with two silane compounds (aminopropyl methyldiethoxysilane, APDES, and hexamethyl disilazane, HMDS). The particles treated by APDES and HMDS exhibit the well adhered and poorly adhered particles, respectively. The authors noted that the flexural strength generally increased with decreasing particle size in both the untreated and well adhered system, whereas it was independent of size in the poorly adhered system. The flexural strength was higher in the order where systems with well adhered shows better properties compared to that of untreated system. On the other hand, the system with irregular shape shows well adhered and untreated systems produce better flexural strength compared to that adhered system.