

**RHEOLOGICAL BEHAVIOR OF TALC AND
CALCIUM CARBONATE FILLED
POLYPROPYLENE HYBRID COMPOSITES**

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CARBONATE FILLED POLYPROPYLENE HYBRID
COMPOSITES**

By

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LIST OF ABBREVIATION

ABS	: Acrylonitrile - Butadiene - Styrene
ALAE	: Active Level of Acoustic Emission
AE	: Acoustic Emission
AO	: Antioxidant
CaCO ₃	: Calcium Carbonate
CH ₃	: Methyl Group
DOC	: Degree of Crystallinity
DSC	: Differential Scanning Calorimetry
EOR	: Ethylene Octene Copolymer
EPCP	: Ethylene-Propylene Block Copolymer
EPDM	: Ethylene-Propylene-Diene Rubber
EVA	: Ethylene Vinyl Acetate
HDPE	: High Density Polyethylene
iPP	: Isotactic Polypropylene
JIS	: Japanese International Standard
LCD	: Liquid Crystal Display
LDPE	: Low density Polyethylene
LLDPE	: Linear Low Density Polyethylene
MFI	: Melt Flow Index
MFR	: Melt Flow Rate
Mg(OH) ₂	: Magnesium Oxide
PE	: Polyethylene
PET	: Polyethylene Terephthalate

PP : Polypropylene
PS : Polystyrene
PVC : Polyvinyl Chloride
SEM : Scanning Electron Microscope
sPP : Syndiotactic Polypropylene
UV : Ultra Violet

LIST OF MAIN SYMBOLS

A	: Area
B	: Extrudate Swell Ratio
δx	: Deformation
d_d	: Die Diameter
d_e	: Equilibrium of Extrudate Diameter
D	: Die Diameter
E	: Activation Energy of Flow
F	: Shear Force
G	: Shear Modulus
ΔH_m	: Heat of Fusion for Sample
ΔH_f	: Heat of Fusion for 100% Crystalline Material
K	: Constant
L	: Die Length
M_c	: Critical Value of Molecular Weight
M_n	: Number-Average Molecular Weight
M_w	: Weight-Average Molecular Weight
n	: Power Law Index
η	: Apparent Viscosity
η_0	: Zero - Shear Viscosity
P	: Pressure
Q	: Flow Rate
\emptyset	: Volume Fraction of Filler
ρ	: Density

R	: Universal Gas Constant
R	: Radius of Die
Re	: Reynold's Number
τ	: Shear Stress
τ_y	: Yield Stress
t	: Measuring Time
T	: Temperature
T_m	: Melting Temperature
T_g	: Glass Transition Temperature
μ	: Coefficient of Viscosity
v	: Volume
V	: Velocity Gradient
γ	: Shear Strain
$\dot{\gamma}$: Shear Rate
V	: Average Velocity
W_f	: Weight Fraction of Fillers
X_{max}	: Measurement of Terminating Point
X_{min}	: Measurement of Starting Point
y	: Original Depth of the Material

KELAKUAN REOLOGI KOMPOSIT HIBRID POLIPROPILENA BERPENGISI TALKUM DAN KALSIUM KARBONAT

ABSTRAK

Kelakuan reologi dan kekenyalan leburan bagi polipropilena isotaktik berpengisi partikel talkum dan CaCO_3 dalam pelbagai amaun (10 hingga 30 % berat) telah dikaji menggunakan reometer kapilari Shimadzu (tegasan ricihan tetap). Pencampuran ini telah disediakan dengan menggunakan pencampur dalaman Brabender. Kelakuan reologi bagi komposit berpengisi tunggal telah dibandingkan bagi mengkaji kesan penambahan pengisi, jenis pengisi dan suhu. Skop kajian reologi ini merangkumi kajian mengenai kelikatan ricihan komposit, pembengkakan ekstrudat dan fenomena rekahan leburan. Kajian awal bagi kelikatan ricihan komposit PP berpengisi talkum menunjukkan kelikatannya lebih tinggi berbanding dengan komposit berpengisi CaCO_3 . Kelikatan komposit bagi kedua-dua jenis pengisi juga telah menunjukkan ianya menurun dengan peningkatan kadar ricihan. Selain daripada itu pengisi talkum juga telah mengurangkan kadar pembengkakan dai dan rekahan leburan berbanding dengan PP berpengisi CaCO_3 dan yang tidak berpengisi. Sifat morfologi antara kedua-dua pengisi dan PP telah dikaji dengan menggunakan mikroskop imbasan elektron (SEM). Kajian analisa terma menggunakan kalorimetri imbasan pembezaan (DSC) telah menunjukkan pengisi talkum berupaya bertindak sebagai agen peneukleusan yang kuat berbanding dengan CaCO_3 . Dalam bahagian kedua kajian ini, 30% jumlah keseluruhan bagi amaun pengisi digunakan sebagai rujukan bagi formulasi komposit hibrid yang optimum. Keputusan menunjukkan bahawa kelikatan ricihan telah meningkat dan kadar pembengkakan dai berkurangan dengan peningkatan penambahan nisbah talkum dalam sistem komposit hibrid PP. Kesan sinergistik hibrid telah dapat dicapai pada nisbah PP:talkum: CaCO_3 – 70:15:15, dengan kelikatan ricihan adalah rendah daripada nisbah talkum yang tinggi manakala nisbah pembengkakan dan rekahan leburan adalah rendah daripada nisbah CaCO_3 yang tinggi. Kesan perawatan asid stearik pada pengisi CaCO_3 telah dikaji dalam bahagian ketiga kajian ini pada sistem komposit hibrid (PP:talkum: CaCO_3 - 70:15:15). Keputusan menunjukkan kelikatan ricihan bagi komposit yang mempunyai perawatan asid stearik adalah lebih rendah daripada CaCO_3 yang tidak dirawat dengan asid stearik. Perawatan CaCO_3 dengan asid sterik juga mempamerkan nisbah pembengkakan ekstrudat dan rekahan leburan yang rendah berbanding CaCO_3 yang tidak dirawat.

RHEOLOGICAL BEHAVIOR OF TALC AND CALCIUM CARBONATE FILLED POLYPROPYLENE HYBRID COMPOSITES

ABSTRACT

Rheology and melt elasticity behavior of isotactic polypropylene (iPP) filled talc and untreated CaCO_3 particles in various amount of filler (i.e. from 10 to 30 wt %) were investigated using Shimadzu capillary rheometer (constant shear stress). These compounds were prepared in a Brabender internal mixer. The rheological behaviour of single-filler composites were compared to determine the effect of filler loading, type and temperature on the properties studied. The scope of rheological study including apparent shear viscosity, extrudate swell and melt fracture phenomena. Preliminary results show that the shear viscosity of talc filled PP composites is significantly higher compared to CaCO_3 filled PP. It was found that the shear viscosities decrease with increasing shear rate. On the other hand, talc was found to reduce the extrudate swell and melt fracture compared to CaCO_3 and unfilled PP. The morphological study between the fillers and PP was also evaluated using Scanning Electron Microscopy (SEM). A thermal study conducted by Differential Scanning Calorimetry (DSC) was found that talc particle was able to react as a stronger nucleating agent compared to CaCO_3 . In the second part of this study, 30% of base filler loading was used for the determination of the optimum hybrid composite formulation. It was discovered that by incorporation of higher loading of talc filler in the PP hybrid composite had increased the shear viscosity and reduced the extrudate swell ratio. A synergistic hybridization effect was successfully achieved when the weight ratio of PP:talc: CaCO_3 is 70:15:15, which shear viscosity was lower than higher ratio of talc filler while the swelling ratio and melt fracture was lower than higher ratio of CaCO_3 . Effect of commercial stearic-acid treated CaCO_3 in the hybrid composites systems (PP: talc: CaCO_3 is 70:15:15) was conducted in the third part of this research as a comparative study on rheological behavior with non-treated CaCO_3 . The apparent shear viscosity of the composite containing the stearic acid treated is slightly lower than the untreated filler composites. Treated composites also exhibit lower swelling ratio and melt fracture compared to the untreated composite. It is believed that stearic acid coating had improved the filler dispersion and resulted lower filler agglomeration.

CHAPTER 1

INTRODUCTION

1.1 Rheology of Polymer

Rheology is a study of flow and deformation of the matters. It crops up in all aspects of modern life. From squeezing toothpaste tubes, kneaded dough for bread making or applying glue for joining purposes, all involve rheology in one way or another. The subject of rheology is extremely important for polymer research that being an important link in the correlation chain from the catalyst over polymerization and chain structure to processing behavior and final properties (Dealy & Wissburn, 1995; Nielsen, 1977). In all cases, flow is involved in the processing and fabrication of such materials in order to transform them into useful products. The flow occurs when polymer molecules slide past each other and the ease of flow depends on the mobility of the molecular chains and the forces or entanglements holding the molecules together. On the other hand, rheological behavior also influences the mechanical properties of finished product significantly. For example, molecular orientation had dramatic effect on the properties of molded product, films and fibers. The type and degree of orientation is largely determined by the rheological behavior of the polymer and the nature of the flow in the fabrication process. Such studies can lead to many benefits of which the following are probably the most important (Brydson, 1981).

- a. To understand processing faults and defects which are of rheological origin and hence to make logical suggestions for adjusting the processing conditions for either minimizing or completely removing the fault.
- b. To make a prior intelligent selection of the best polymer or polymer compound to use under a given set of circumstances.

- c. They can lead to qualitative and to some extent quantitative, relationships between such factors as output, power consumption, machine dimensions, material properties and operational variables such as temperatures and pressure.

Since there are so many development in polymer types and grades, in addition with the fact that most of the processing occur in the molten state, better understanding of the rheological characteristic of polymer systems is beneficial to the design of polymer processing equipment, with the ability for predicting the energy requirement, optimizing the processing conditions and correlation with the structural development (Hornsby, 1999; Han, 1976).

1.2 Polymer Composites

Composites materials are formed by combining two or more materials that have quite different properties. The different materials work together to give the composite unique properties. Composites represent an important class of engineering material. New requirement and new product has led to drive for more and better polymer composites. Lightweight high performance engineering plastics had replaced metals in many applications as polymers are relatively cheap and large volume structural materials (Sheldon, 1982). The wide application of polymer composites ranges from the manufacturing of high tech engineering structures such as tanks, pipes, aircraft interior furnishings and support beams, to the making of leisure and sporting items such as golf clubs and balls, skis, racquets and boats. Basically, polymer composites may be classified into the following categories (Alger, 1990):

- Polymer-polymer combinations (polymer blends)

- Polymer – gas combinations (expanded, cellular or foamed polymers)
- Polymer – rigid filler combinations of:
 - Polymer-fiber
 - Polymer-particulate filler
 - Polymer-hybrid filler

In these types of composites, the intention is to obtain some enhancement of one or more of the mechanical properties, i.e. reinforcements, although cheap fillers are primarily used as diluents, to reduce cost without much effect on the properties. For polymer-particulate filler, an improvement of stiffness or wear resistance is the main objective. Using the above classification, the present study comes under the polymer hybrid filler category, which the polymer matrix is polypropylene while talc and calcium carbonate is combined in different compositions to form a hybrid fillers systems. A dispersion agent is also added in CaCO_3 to enhance the dispersion of the filler.

1.3 Thermoplastic Hybrid Composites

Historically, thermoplastic polymers have been used extensively as matrix material for injection molded and short fiber reinforced composites. In the early 1980's, polymer chemist developed advanced thermoplastic matrices suitable for higher performance composites. The result is a new class of composites with short processing time, damage tolerance superior to that of traditional thermosetting polymer matrix composites and an adequate solvent resistance (Miller, 1996).

At this moment, using of this mixed fiber and particulate composites has been recognized for many years. Growth of hybrid systems has been particularly rapid in the last decade or so, encouraged by the demand for high performance engineering materials,

especially where low weights is great importance. Although individual classes of fillers or fibers can contribute some desirable properties, the real interest in composites is in optimizing the different contributions from different types of fillers. In this study, fillers i.e. talc and calcium carbonates were used, whereby the desirable properties contributed by each filler were optimized while at the same time keeping an eye in reducing cost. One of the main factors, which contribute to the current emphasis on composites, is the reduced cost of hybridizing, whereby part of the more expensive talc was replaced by with calcium carbonate (talc is five times more expensive than calcium carbonate). Although, one can predict the mechanical behaviour of hybrid composites using the Rule of Mixtures, it should be mentioned that there is a possible extent of synergistic behavior arising from the use of hybrids, for example Gan *et al.* (2001) have successfully developed poly (ether ketone ketone) filled with hybrid filler consisting mica and glass fibers, which showed improved tensile strength and ultimate elongation compared to single-filler composites containing either mica or glass fiber.

Turning to specific applications, polypropylene hybrid composites has the potential to be used in automotive applications such as door trims, bumpers, panels and interior furnishings. Other types of thermoplastic hybrids include the use of nylon and carbon in fishing rods, whilst boron has also been used with carbon in sports equipment and aerospace parts (Sheldon, 1982).

1.4 Problem statement

For years, fillers have been used extensively to improve the mechanical properties of polymeric material. Besides the increment obtained in stiffness, hardness, abrasion resistance, and reduced cost of the filled material, the addition of filler to polymer also modify their flow behavior and consequently their processability. The use of talc as filler in

PP composites by manufacturers has been growing since the 1980's and today talc plays a dominant role as the most widely used filler in PP composites. However, the use of talc has a trade off, in that talc is getting more costly, especially for importing countries such as Malaysia, which is lacking of its source. The vast resources of CaCO_3 in Malaysia have driven Malaysia Plastic Manufacturers to switch to use CaCO_3 as a cheaper alternative to fill PP composites. In fact, CaCO_3 is five times cheaper than talc and it takes an overwhelming proportion of the filler market in plastics, although in PP it occupies second place behind talc. Study on the hybrid filled PP composites of talc and CaCO_3 had been conducted by [Leong *et al.* \(2001\)](#) in order to get a balance material properties and cost. He found that a synergistic effect can be achieved at filler ratio of PP: talc: CaCO_3 ; 70:15:15 by an improvement on the tensile and impact properties of the composites.

It has been well documented that the general behavior of adding fillers to polymers will increase the viscosity and decrease melt elasticity of the polymer. Hence the study of the melt rheological behavior will be important in controlling the filled polymer in processing operation in order to know how the flow behave under different conditions of temperatures, pressure, etc. Furthermore, availability of talc and CaCO_3 with variation in size, shape and chemical structure will greatly influence the flow of the composites systems. Another important thing of the rheological study is helping one to carry out theoretical analysis of the mechanics of flow for rheologically complex polymeric material in various kind of processing equipment. Such a theoretical study will be useful for designing better processing equipment and determining optimal processing conditions. Thus, the effect of filler loading, type and treatment of the filler will be investigated with regards to the flow behavior and as well the extrudate swell and melt fracture phenomena of the composites.

1.5 Objectives of Study

The primary objective of this study is:

- To investigate the effect of different filler loading/ratio, temperature and pressure on the melt flow system of the single filler and hybrid filler composites, which able to eliminate processing fault and defect.
- To study effect of talc and CaCO₃ filler incorporation on the melt elasticity behaviour of PP. This study then can be utilized to establish better processing conditions and to develop optimum morphology to maximize products performance.
- To observe the effect of stearic acid treated CaCO₃ on the flow behaviors and melt elasticity of the PP hybrid composites.

1.6 Outline of Thesis Structure

Chapter 1: Begins with definition and application of the rheology, particularly in the polymer area, followed by a brief introduction on the composites and thermoplastic hybrid composites. The importance of this study, which generated the ideas and energies to this research work, is also stated. The primary objectives and the general flow of the whole research program are also specifically outlined.

Chapter 2: Relates the polypropylene composites, filler and extenders with particular interest focused on the flow behavior and melt elasticity phenomena of the composites systems. A literature survey from various published works, which closely related with this work was also carried out and reviewed.

Chapter 3 : Describes step by step the experimental procedures employed, details of laboratory equipment used as well as any other processing techniques involves in generating any data that were used and presented in the course of study.

Chapter 4: Discusses on the melt rheological behavior of filled polymer composites which has been divided into three sections based on the three main variables of interest. Section 4.1 discusses the rheological behavior of single filler composite Talc and CaCO_3 , while, Section 4.2 discusses the rheological behavior of the hybrid composite with the ratio 15T:15UCC, and Section 4.3 discusses the effect of filler treatment on the rheological behavior of hybrid composite 15T:15UCC. Each section will report on the effect of temperature, filler concentration on the shear viscosity and also melts elasticity phenomena of the composite.

Chapter 5: Presents some concluding remarks on the present work as well as some suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

Introduction

Filled polymer composites have continued to attract interest from researchers due to inherent benefits from working with polymers, which are ease of process ability and productivity, combined with the addition of filler, which from the reinforcement it supplies, can significantly alter the base polymer properties resulting in a low-cost composite material with potentially very useful properties (Thio *et al.* 2002; Da Silva *et al.* 2002). Nevertheless, incorporation of filler in a polymer will affect the melt rheological behavior of this filled composites systems and it is noted that this behavior will be critically important in defining the processability of the composite. The importance of identifying the melt rheological behavior is noted by Rietveld and Al-Ramahi (1992), and claimed that it is important to define the pressure and energy required for flow in processing. Furthermore, this behavior important to study the mechanism by which addition of filler influences the original polymer and to determine those combination in which such effect occur (Babbar and Mathur, 1994). Hence for this literature review chapter an overview on the research done on polypropylene filled composites with particular attention made to research on rheological behavior will be presented.

2.1 Polypropylene Composites.

Polypropylene (PP) composites have been used in large quantities in numerous fields of applications for many years (Pukanzsky, 1995). The success of PP composites lies in its extremely advantageous price/volume/performance relations, with the result that PP composites successfully penetrate fields traditionally occupied by other engineering plastic material such as ABS and nylon. Considerable efforts have been made to extend the

application of PP composites to fields where engineering thermoplastic have been used up to now. Today, particulate filled PP composites such as talc-filled PP is still widely used. Particularly in the automotive industry for the production of bumpers, heater housings, door pockets and trimmings, timing belt covers cladding. Other common fillers include CaCO_3 kaolin, mica and carbon black, while glass fiber is still one of the most commonly used fibrous reinforcements in PP.

2.1.1 Polypropylene

Polypropylene (PP) is a versatile thermoplastics offering a useful balance of heat (160°C) and chemical resistance, good mechanical and electrical properties, and processing ease. Besides PE and PVC, PP is the third commodity polymer produced and applied in large quantities. Crystalline polymers of propylene were first described in the literature in 1954 by G. Natta and his associates at the Chimica Industriale del Politecnico di Milano ([Hanna, 1990](#)). Earlier efforts to initiate propylene polymerization had only resulted in non-crystalline polymers of little or no importance. With the introduction of heterogenous, stereospecific catalyst discovered by K. Ziegler for the low-pressure polymerization of ethylene, the scene suddenly changed. These reactions are products of transition metal compounds with selected organometallic compounds contained active sites for polymerization, such that each new propylene molecule was incorporated in the polymer chain in a regular, geometric manner identical to all preceding methyl groups. Three geometric forms of the polymer chain can be obtained (Figure 2.1). Natta classified them as:

- Isotactic
All methyl groups aligned on one side of the chain
- Syndiotactic

Methyl groups alternating

- Atactic

Methyl groups randomly positioned

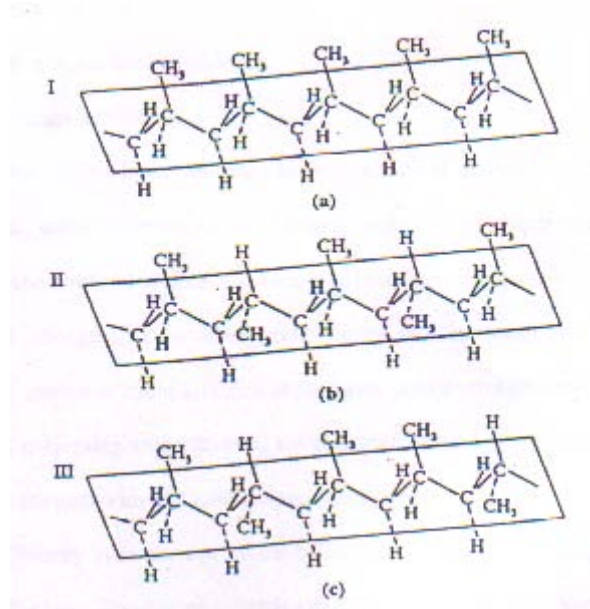


Figure 2.1: Polypropylene structures (a) Isotactic, (b) Syndiotactic, (c) Atactic.

Both isotactic and syndiotactic forms will crystallize when there are cooled from molten states. Commercial injection molding and extrusion grade PP are generally 94 to 97% isotactic. Fabricated parts are typically 60% crystalline, with a range of polyhedral spherulite forms and sizes, depending on the particular mode of crystallization from the melt. Atactic PP, though is not suited to structural plastic uses, have been developed as modifiers in hot melt adhesives, roofing compounds, and communications cable- filler gels. PP can be made into a multidimensional range of products with properties and characteristics interdependent on the

- Type of polymer: homopolymer, random, or block copolymer
- Molecular weight and molecular weight distribution
- Morphology and crystalline structure.

- Additives
- Fillers and reinforcing materials
- Fabrication techniques

Homopolymer have resistance to deformation at elevated temperatures, while high stiffness, tensile strength, surface hardness and good toughness can be observed at ambient temperatures. Random ethylene-propylene copolymers are characterized by higher melt strengths. They have good clarity and resistance to impact at low temperature, gained at some sacrifice in stiffness, tensile strength and hardness. Block copolymers, preferably with ethylene, are classified as having medium, high, or extra-high impact strength with particular respect to sub-zero temperatures. Some properties that are usually considered inherent advantages of PP are (Hanna, 1990):

- Low specific gravity (density)
- Excellent chemical resistance
- High melting point (relative to volume plastics)
- Good stiffness/toughness balance
- Adaptability to many converting methods
- Great range of special purpose grades
- Excellent dielectric properties
- Low cost (per unit volume)

Properties usually considered being disadvantages of PP are

- Flammability
- Low temperatures brittleness
- Moderate stiffness
- Dificult printing, painting and gluing

- Low UV resistance
- Reduced extruder output
- Haziness
- Low melt strength

2.1.2 Filled Polypropylene

Throughout the years, research has been intensively going on which various publications on the use of PP as the main matrix, coupled with various types of modified as well as unmodified fillers and reinforcements could be found in abundance in almost every polymer and composite journal. Comprehensive studies, which concentrate on a particular property of filled PP, have been done. For example, Wang & Wang (1999) have carried out some works on the shear yield behaviour of CaCO₃-filled PP, which involved conducting steady shear test, a transient stress growth test, and a dynamic oscillatory shear flow. The magnitude of the yield stress of polymer melts, which is defined as any critical stress below which no flow can be observed under the condition of experimentation, was found to be closely associated with the thixotropy breakdown and recovery of the microstructure inside the compounds, thus the characteristic time of this transient process plays a part in yield stress measurement. In other words, yield behavior in highly filled (thixotropic) materials has been determined to be a function of structure and hence time.

Goel (1980) have conducted an in depth study on the effect of polymeric additives on the rheological properties of talc filled PP. It was found that talc does not influence the viscosity of PP but decreases the elasticity of the system. Addition of polypropylene oxide as an oligomer had not only decreased the viscosity but also further decreased the elasticity of the filled polymer composite considerably. The impact properties of filled PP composites

were also tackled by several workers such as Jilken (1991) and Wang and Huang (1996) they have investigated the effect of filler particle size, and had concluded that an increase in impact strength for mineral-filled PP can be obtained by decreasing the particle size of the filler particles. Wang and Huang (1996) on the other hand, had considered processing factors that could influence the state of particle dispersion and hence the impact properties of PP. The experimental results have indicated that good dispersion of filler particle would improve the impact properties of the polymer matrix, but this only occur at moderate filler loading.

Investigation conducted by Pukanszky *et al.* (1994) have suggested that orientation of anisotropic filler particle occurs even under mild shearing condition and the degree of orientation depends on the filler content of the composite. Particle orientation decreases with increasing filler content due to hindrance of rotation caused by particles interfering with each other. A comparison of nucleating ability between talc and CaCO₃ has also been done, which resulted in talc being a stronger nucleator. However, it was found that the effect of nucleation on the mechanical properties of the composites is minimal as compared to the effect of filler particle orientation. In failure of particulate-filled composites, the main energy-consuming process is plastic deformation of the matrix, which is modified by the presence of fillers (Pukanszky *et al.* 1994).

2.1.3 Fillers, Extenders and Reinforcements

Fillers, as the name implies, have commonly been employed to cheapen or extend a product with an evident change or modification of the properties of the unfilled materials such as hardness, rigidity, viscosity or colour. Their use has grown dramatically in recent years, encouraged by the growing demand for high performance plastics and increasing polymer prices. Gradually, the realization grew that by the selective use of fillers. Certain

properties of the unfilled material could be enhanced or even exceeded and reinforcement of properties was possible. Hence fillers are today employed to obtain any, poor combination, of the following effects (Whission, 1971):

- Add rigidity, stiffness and hardness.
- Regulate thermal expansion and shrinkage
- Improve heat resistance.
- Improve or regulate electrical characteristics.
- Increase strength and reduce creep.
- Modify rheological properties
- Aid processability (lubrication, flow, mixing and dispersion)
- Modify appearance (opacity, colour, texture)
- Alter density and bulk

As mentioned above, the term 'filler' is used to carry with it the implication of a cheap additive to an expensive material but it must be emphasized that nowadays, it is not the case with plastic materials. The filler is incorporated with the polymer to give a plastic material in which both the polymer and the filler contribute to the desirable properties of the plastic material. Often, as for example in CaCO_3 filled polypropylene, the filler is much cheaper than the polymer, but fillers such as nano-particulate clays, are much more expensive than the polymer with which it is incorporated. Naturally enough, factors such as particle size will play an important role, since these influence the ease with which it will be bound in the mix together with other components. There is often a 'trade off' between the uses of particular filler and its side effect on other properties. There is a movement towards development of multifunctional fillers, which will make useful contribution to performance in other directions as well as lowering cost (Murphy, 1996).

2.2 Mineral Fillers

Nowadays, fillers play an important role in the plastic industry. In the course of time, these basic raw materials have been refined and purified and today, it becomes the source from which most of the so-called inorganic fillers are derived. The purpose of their use is not confined to cost reduction but also to improve mechanical performance such as rigidity, dimensional stability toughness and as well also change the viscosity of the filled material. The level of such improvement or changing depends significantly upon type, size and shape, content and surface treatment of the fillers (Tebtiang & Venables, 2000; Gonzalez *et al.*, 2002). Gradually, it was realized that the use of different fillers could yield different properties, some of which could even reinforce the properties of the neat polymer. Mineral fillers are used extensively due to their availability, ease of processing, and cost. These fillers consist mainly of carbonates, oxides, clays, alumina silicate, silica and silicates. Examples of some of these mineral fillers commonly used are talc, calcium carbonate, kaolin, magnesium carbonate, silica, alumina, titanium dioxide and mica.

2.2.1 Talc

Hydrated magnesium silicate [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], or better known as talc occurs as the alteration products of magnesium carbonate rock by the natural action of hydrothermal solutions. These purer forms are called steatite talcs. Commercially important deposits are also found in altered ultra basic igneous rocks. After purification, the material is ground and screened about 200 to 300 meshes. Finer grindings are possible; however, the finest particle size achievable for talc will still be considerably larger than the coarsest clays (Wake, 1971). Talc consists of a lamellar structure of thin sheets of magnesium hydroxide sandwiched between layers of silica, as can be seen from Figure 2.2. The layers are held

together by weak bonding forces and are the major reason for the platy shape of particles when they are properly processed in grinding equipment. In Figure 2.3, the thin platelet structure can be readily observed from a scanning electron micrograph of the talc used in this study.

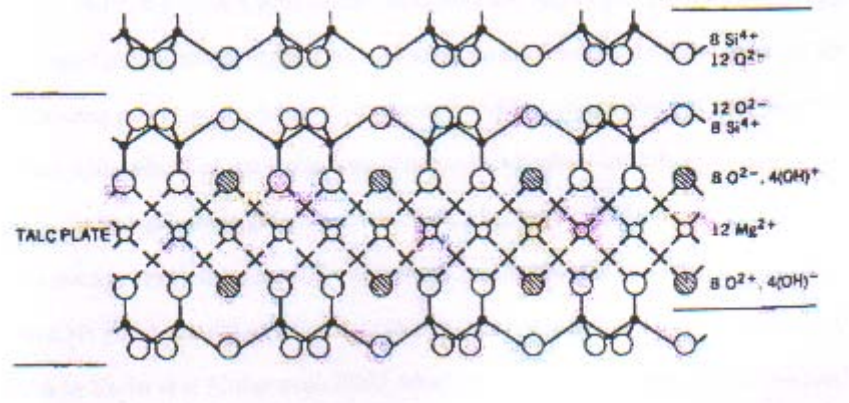


Figure 2.2: Theoretical structure of talc (Riposte and Taper, 1990).

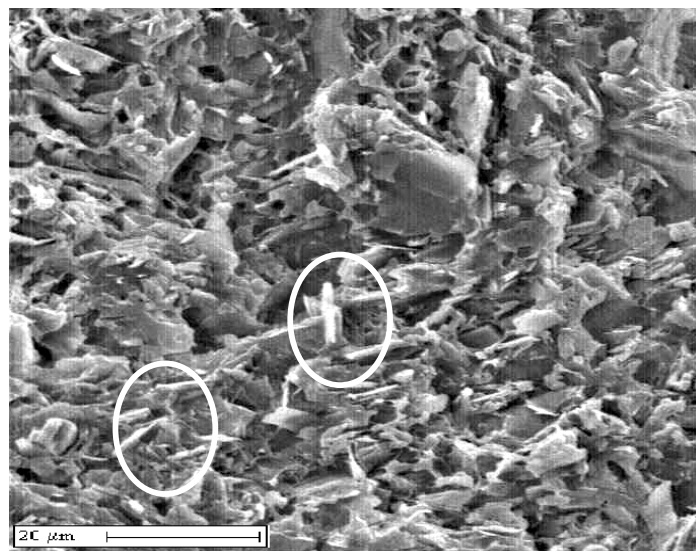


Figure 2.3: Thin platelet structure of talc as seen using Scanning Electron Microscope.

It is water repellent and very soft. In fact, talc is the softest material according to Mohs' hardness scale (Murphy, 1996). It can resist temperature up to 900°C , is unaffected by chemicals and will not harm living tissue. Talc can be utilized as a medium filler of average

whiteness in thermosetting as well as thermoplastic resins where improvements in electrical insulation, heat, and moisture resistance, chemical inertness and good machinability are needed. Talc has low absorption rate and because of its plate like structure, certain grades can improve flexural properties of mouldings.

The aspect ratio (ratio of average platelet diameter to thickness) of talc can vary from 20:1 to 5:1 (Radosta and Taper, 1990). The greater the aspect ratio of the platelet, the greater is the restraint imposed upon the polymer matrix by the talc and, consequently, the greater its reinforcing properties. In PP, talc gives a good balance of rigidity and impact strength (Murphy, 1996). Advanced milling technology can be used to obtain the finest talcs without reducing the reinforcing power of the lamellar structure. Talc filled composites are also easier to colour with reduced pigment requirement due to its whiteness and low yellow index.

Although investigation on talc-filled PP have been done since the 1981, there are still many works that involve the characterization of talc filled PP, which are still on going until today (Pukanzsky, 1995). The most recent publication on talc filled PP is by Collar *et al.* (2003), which involves the grafting of PP with succinyl fluorescence in that acts as an interface modifier to enhance the interface activity of the PP/talc systems. An extensive study on particle orientation and rheological properties of talc-filled PP systems has also been done by Chang & White (1996). A wide-angle X-ray diffraction (WAXD) technique was used to determine the filler orientation in the matrix. It was found that at low filler loadings (~20 wt %), the talc particles tend to orient with the talc-disc normal perpendicular to the direction of flow. Rheological tests showed an increase in viscosity with increasing filler loading and decreasing particle size. Xu *et al.* (2002) have concentrated their efforts on investigating the impact fracture process of talc-filled PP using the acoustic emission (AE) technique. The active level of AE (ALAE) can be used to evaluate the filler particle size as well as the quantity of fillers in the systems. Increasing both filler particle size and

filler quantity will increase the ALAE. Similarly, the ALAE can also be used to determine the filler dispersion, whereby an increase in the maximum of ALAE was recorded with better filler dispersion. Guerrica-Echevarria *et al.* (1998) explored the influence of moulding conditions and filler content on the properties of PP/talc composites. Although the nucleating ability of talc on PP has been well known, it has been proven in the study that the nucleation effect is independent on the talc content or processing conditions. An increase in melt flow index (MFI) was also observed with the increase in melt temperature and screw rotation rate during processing, which was attributed to degradation by chain scission of the PP matrix.

The effect of nucleation, filler anisotropy and particle orientation on the properties of PP/talc composites was further investigated by Pukanszky *et al.* (1994). The workers have concluded that particle anisotropy and orientation have a more pronounced effect on the mechanical properties of PP than nucleation itself. Orientation of the anisotropic fillers particles was reported to be occurred even under low shear stresses and its degree depends on the composition. In tension, the composition dependence of yield and tensile strengths are determined by the decrease of effective load-bearing cross section and interaction between the filler and matrix. In impact, crack initiation plays a vital role, and stress concentrators are definitely considered a nuisance to the systems. In failure of particulate-filled composites, the main energy-consuming process was reported to be the plastic deformation of the matrix, which could be modified with the presence of fillers. As reported by Fujiyama & Wakino (1991), talc and CaCO₃ are the fillers used most often and in the largest quantities in PP. They claimed that talc almost has a plate like structure and nucleates PP crystallization, while CaCO₃ has isotropic particle structure and small nucleation effect.

Da Silva *et al.* (2002) had made torque studies of filled PP with talc at different filler content. They found that when low filler content was added a decrease in torque values in

relation to PP was observed. The result can be related to the fact that at low filler content a good dispersion in the PP matrix can be achieved resulting in a better interfacial interaction between PP and filler. At high filler content (15 wt %) an increase in torque value in relation to PP was observed which resulted from filler agglomeration.

2.2.2 Calcium Carbonate

Among the various mineral fillers, calcium carbonate (CaCO_3) is one of the most important and widely used filler for plastics in term of weight (Murphy, 1996; Pukanszky, 1995). CaCO_3 is the next most abundant naturally occurring element to silicon (Wake, 1971), which is the reason why it is deemed very cost effective to be made into fillers in plastics. CaCO_3 occurs naturally in two crystalline forms, calcite and aragonite, the former being the more stable and abundant form. Calcite is rhombohedral, has a specific gravity of 2.71 and a hardness of 32.0 on the Moh's Scale. Argonite is the orthorhombic form and occurs naturally as needle-shaped prisms or spherulites in thermal springs. It has a specific gravity of 2.93 and a hardness of 3.5 on the Moh's Scale. When heated, aragonite transforms into calcite.

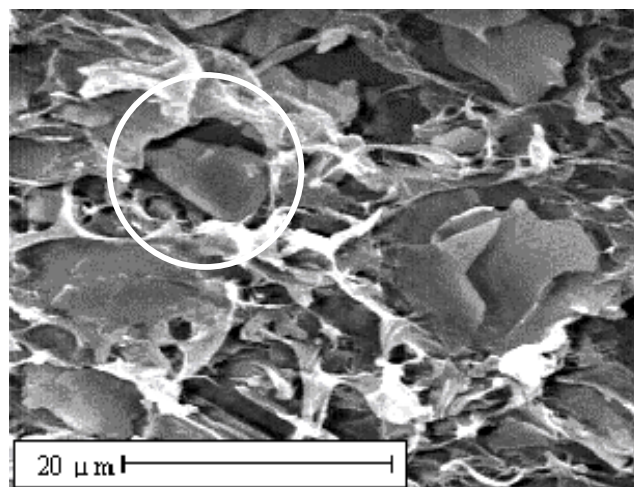


Figure 2.4: Isometric CaCO_3 particles as seen in Scanning Electron Microscope.

CaCO₃ is sometimes coated with stearic acid to reduce particle agglomeration; hence improvements to processability, wet strength and surface finish are conferred. Commercial CaCO₃ fillers come in various sizes, which range from 8 μm to nanometer sizes. The particle shape is generally isometric as displayed in Figure 2.4 hence the aspect ratio of CaCO₃ is fairly low. Generally, the incorporation of rigid particulate fillers to a polymer matrix will have an embrittling effect, which results in a decrease in impact strength of the system. In fact, most of the studies on modification of semi-crystalline polymers with rigid particle reported a significant loss of toughness compared to the neat polymer. Through further investigations, however, the usage of CaCO₃ as a toughening agent is a new concept, which is relatively well known to impart high impact properties and deformability, though at the cost of the strength of PP.

There are a few works that have reported regarding the ability of CaCO₃ to act as toughening agent, the most recent one being Zuiderduin *et al.* (2003), which confirmed that CaCO₃ has indeed the ability to not only increase the stiffness but also the toughness of PP. Furthermore, their work has also reinforced the findings of Pukanszky (1995), which claimed that CaCO₃ is a very weak nucleating agent and has no influence on the melting temperature and the crystallinity of PP. Thio *et al.* (2002) had attempted to study the effect of CaCO₃ filler particle size as well as varying notch depths on the fracture resistance of CaCO₃ filled composites. Smaller filler particles and higher volume fractions of filler were said to induce early fractures and also lead to decreased yield stress. Impact toughness of the filled composites that uses either very large or very small particles was observed to unchange from the unfilled PP value. The failure of both particle sizes to toughen the matrix was said to arise due to the presence of agglomerates and/or individual particles with dimensions larger than the critical flaw size to initiate brittle behavior. The usage of a moderate sized particle, however, was claimed to have resulted in an increased toughness of

the composite due to combined mechanisms of crack deflection toughening and local plastic deformation of interparticle-ligaments following particle matrix debonding.

CaCO₃ is also considered to be inactive filler due to its nearly spherical shape and to the lack of active –OH sites on its surface (Pukanszky, 1995). The reactivity of PP is also low since its carbon chain is a polar, which does not contain reactive groups. When CaCO₃ is introduced into the PP matrix, the tensile properties of the composites usually become poorer than to those of virgin PP. Mechanical properties cannot be improved by the surface treatment of the filler because of the inactivity of the two components. Nevertheless, there have been a great number of compounds such as silanes, titanates, stearic acid, elastomers, and oligomers, which are used as coupling agents to treat CaCO₃ in the hope of obtaining some degree of enhancement in strength of the composite. However, more often than not, this is seldom achieved. While some publications claimed to have observed improvement in the mechanical properties of the composites with treated fillers, the published data could hardly be interpreted and the mechanism of increased component interaction was not known.

Other interesting works using CaCO₃ was done by Badran *et al.* (1982), who have used various concentrations of ethylene oxide oligomer modified CaCO₃ to investigate its effect on the mechanical properties of HDPE. Impact strength as well as deformability of the polymer was found to increase tremendously, while the tensile strength and modulus values were very near to that of pure HDPE.

Chacko *et al.* (1983) made use of CaCO₃ to study its effect on the tensile properties of PE with differing molecular weight. It was found that the tensile stress-strain behaviour was dependant upon the filler content, polymer-filler interface, and polymer molecular weight. Further investigation using scanning electron microscopy revealed the presence of a craze type deformation in the composites.

Jancar and Kucera (1990) described the performance of both CaCO_3 and $\text{Mg}(\text{OH})_2$ as fillers for PP and observed that the tensile yield stress of PP filled with CaCO_3 decreased drastically with filler loading, which was blamed on poor filler adhesion to the matrix. However, the tensile yield strength of PP filled with $\text{Mg}(\text{OH})_2$ either decreased slowly or remained constant up to a certain filler loading, although the filler was dubbed to have poor adhesion to the matrix as well.

Supaphol *et al.* (2004) investigated the effects of CaCO_3 of varying particle size (i.e. 1.9, 2.8, and 10.5 μm), content and type of surface modification on crystallization and melting behaviour, mechanical properties, and processability of CaCO_3 -filled syndiotactic polypropylene (sPP). It was found that CaCO_3 was a good nucleating agent for sPP. The nucleating efficiency of CaCO_3 for sPP depended strongly on its purity, type of surface treatment, and average particle size. Tensile strength was found to decrease, while Young's modulus was found to increase, with increasing CaCO_3 content. Shear viscosity of CaCO_3 filled sPP was found to increase with increasing CaCO_3 content and decreasing particle size.

Study on the melt rheology and extrudate swell of CaCO_3 nanoparticle filled isotactic PP (iPP) had been carried out by Rapeephun *et al.* (2005) With increasing of filler content the apparent shear viscosity was noticeable increased and percentage of extrudate swell was found to decrease. Comparison between uncoated and coated CaCO_3 was also conducted and found that addition of stearic acid coated had decreased the apparent shear viscosity compared to the untreated CaCO_3 . Decreasing in shear viscosity was due to good dispersion of the CaCO_3 nano-particles and poor interfacial adhesion between coated CaCO_3 surface and iPP matrix.

2.2.3 Application of Filler Treatments.

Particulate filled polymers must be continuously upgraded in order to meet specific requirements of various new applications. One of the possible ways to do this is by modification of filler surface to alter the filler matrix interfacial interaction (Demjen, 1997). Although changing particle size can be done to modify interaction, the range is still narrow. Thus, the incorporation of coupling agents onto the filler surface is an obvious way to modify interaction by either changing the size of the interface or altering the strength of the interaction.

The influence of stearic acid treated CaCO_3 on the morphology and mechanical properties of PP containing ethylene-octene copolymer (EOR) were thoroughly investigated by Premhet and Horanont (1999). It was observed that there was separate dispersion between the filler and elastomer. The use of surface treatment did not improve this condition; however, it was found that stearic acid promotes hexagonal crystallization of PP and gave a composite with lower onset crystallization temperature, $T_{C \text{ Onset}}$, as well as crystallization temperature, T_C . As a consequence, composite with treated fillers possessed greater impact strength in comparison with composites containing uncoated fillers.

Generally, distribution or dispersion of the filler will affects a great deal to the viscoelasticity of the polymer matrix. According to Thio *et al.* (2002) and Nowaczyk *et al.* (2004) the distribution of the filler within the polymer matrix can be improved by surface treatment with a dispersant, e.g. stearic acid, which helps reduce the viscosity of the matrix and to some extent, prevent the fillers from forming network.

Study conducted by Ou and Yu (1994), on rheological behavior of glass bead filled –nylon 6 in a shear rate range of $10^{-1} - 10^2 \text{ s}^{-1}$ and results shown that the interfacial adhesion strength affected the rheological behavior of the melt systems significantly. In addition it was reported that the melt shear viscosity of the nylon treated glass bead filled system was

obviously higher than that of the unfilled nylon and nylon raw glass bead system at lower shear rates.

Supaphol *et al.* (2004) had carried out a study on the effect of surface modification type (stearic acid coated and paraffin-coated) on the flow behaviour of CaCO_3 filled syndiotactic polypropylene (sPP). He found that both type of surface treatment had reduced the shear viscosity of filled system compared with untreated CaCO_3 and this trend elucidates an improvement of filler distribution in the sPP matrix.

2.3 Fundamental of Rheology

Rheology embodies three main concepts such as forces, deformation and time. Among all forces, shear forces are the most important type of force in rheology. When a material is subjected to a force it tends to deform, this deformation is known as strain. Deformation can be divided into two types, they are viscous and elastic. Viscous and elastic properties are the two fundamental of rheological properties that are of primary concern in polymer processing.

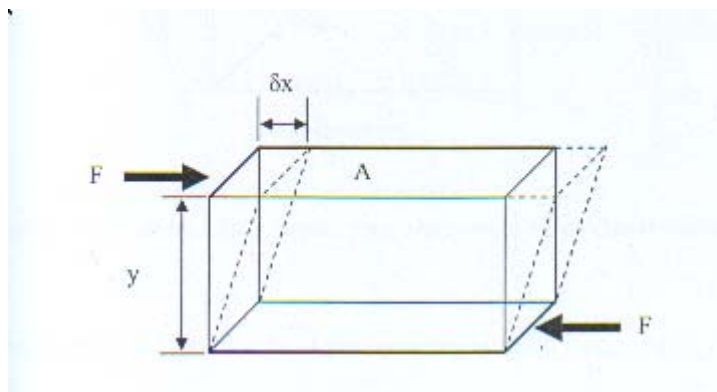


Figure 2.5: Shear deformation of an elastic material (Rauwendaal, 2002)