Characterization and Properties of Stearic Acid, Titanate and Zirconate Modified Dolomite/Polypropylene Composites

by

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LIST OF ABBREVIATIONS

Al_2O_3	Alumina
C_3H_6	Propene
$C_{18}H_{36}0_2$	Stearic Acid
$CaCO_3$	Calcium Carbonate
$CaMg(CO_3)_2$	Dolomite
CaO	Calcium Oxide
CSW	Calcium Sulfate Whiskers
DOC	Degree of crystallinity
DPC	Dolomite Plastic Composites
DSC	Differential Scanning Calorimetry
Fe2O3	Iron (III) Oxide
FTIR	Fourier Transform Infrared
ICDD	International Center for Diffraction Data
K_2O	Pottasium Oxide
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
LICA12	Neopentyl(diallyl)oxy-tri(dioctyl)phosphate titanate
MgO	Magnesium Oxide
MSW	Municipal Solid Waste
MWCNT	Multi-walled Carbon Nanotube
Na_2O	Sodium Oxide
NZ12	Neopentyl (diallyl) oxy-tri (dioctyl) phosphato zirconate
PBT	Poly (butylene terephtalate)
PE	Polyethylene
PEGDA	Polyethylene Glycol Diacrylate
PE-g-MA	Polyethylene-grafted-maleic anhydride
PP	Polypropylene
PPC	Particulate Polymer Composite

PP-g-MA	Polypropylene-grafted-maleic anhydride
PS	Polystyrene
PSA	Particle Size Analysis
PVC	Polivinylchloride
SEM	Scanning Electron Microscopy
$SiCl_4$	Silicon Tetrachloride
SiO_2	Silicon Oxide
TGA	Thermogravimetric Analysis
TiO2	Titanium Dioxide
TPS	Thermoplastic Starch
TPSS	Thermoplastic Sago Starch
UV	Ultraviolet
XRD	X-ray Diffraction
XRF	X-ray Fluorescent

LIST OF SYMBOLS

wt.%	Weight Percent
µm	micron-meter
°C	degree Celcius
g	gram
ml	mililitre
rpm	rotation per minute
mm	milimetre
Ǻ	Armstrong
kV	kilovolt
mA	miliampere
W_f	Weight of floated sample
W_o	Overall weight of sample
J	Joule
MPa	Megapascal
X_c	Degree of crystallinity
ΔH_f	Enthalpy of fusion
$\Delta H°_f$	Enthalpy of fusion of 100% crystalline material
T_c	Crystallization Temperature
T_m	Melting Temperature

Pencirian dan Sifat-sifat Komposit Dolomit Dirawat Asid Stearik, Titanat dan Zirkonat / Polipropilena

ABSTRAK

Peningkatan permintaan untuk penggunaan komposit polimer berpengisi mineral semulajadi telah menarik perhatian para penyelidik ke arah persekitaran yang lebih hijau di samping mengurangkan kos pemprosesan dan pengeluaran bahan komposit. Dalam kajian ini, kesan kandungan pengisi dolomit dan kesan pengisi yang dirawat pada kelakuan mekanikal, terma dan luluhawa bagi komposit polipropilene/dolomit (PP/dolomit) telah dikaji. Bahagian pertama kajian ini melaporkan mengenai kajian awal ke atas sifat-sifat optimum dolomit. Batuan mentah dolomit dikisar dengan menggunakan masa pengisaran yang berbeza untuk mendapatkan saiz partikel dolomit yang optimum sebelum dimasukkan ke dalam komposit. Proses pengisaran selama 2 jam menghasilkan parameter optimum dengan saiz partikel 8.183μm dan struktur kristal yang dikekalkan walaupun selepas operasi pengisaran intensif menggunakan pengisar planet. Keduanya, komposit PP/dolomit yang mengandungi 0 - 25% berat dolomit telah disediakan menggunakan pengadun dalaman Brabender pada suhu 180 ° C, kelajuan rotor 60 rpm dan kaedah pengacuan mampatan. Penambahan dolomit ke dalam matriks PP menurunkan kekuatan tensil dan pemanjangan pada takat putus komposit. Modulus Young meningkat disebabkan penambahan pengisi dolomit ke dalam komposit PP/dolomit. Analisis termogravimetrik (TGA) menunjukkan bahawa penambahan kandungan dolomit yang rendah telah meningkatkan kestabilan terma komposit. Pada bahagian ketiga, kesan kandungan asid stearik ke atas rawatan kimia komposit PP/dolomit telah dikaji. Didapati bahawa dolomit telah berjaya dirawat oleh asid stearik melalui transformasi fourier inframerah (FTIR) dan menunjukkan bahawa kandungan asid stearik yang optimum telah meningkatkan peratusan hidrofobisiti dan meningkatkan kekuatan tensil, pemanjangan pada takat putus, sifat lenturan dan juga kestabilan terma komposit polimer. Satu interaksi rekatan antaramuka yang lebih baik antara partikel dolomit dan PP juga diperhatikan. Kandungan asid stearik optimum yang diperolehi kemudiannya dikekalkan dalam usaha untuk membandingkan kesan perawat yang lain iaitu titanat (LICA12) dan zirkonat (NZ12) terhadap kelakuan mekanikal, terma dan morfologi komposit. Penambahan perawat-perawat ini telah menunjukkan peningkatan ketara bagi kekuatan tensil dan modulus Young komposit. Komposit PP/dolomit yang telah dirawat menunjukkan sedikit peningkatan pada kekuatan tensil, kekuatan hentaman dan sifat lenturan. Spektrum FTIR membuktikan perubahan kumpulan fungsi dolomit yang dirawat dan peningkatan interaksi rekatan antaramuka. Penambahan nanosilika telah menunjukkan peningkatan pada kekuatan hentaman yang dirawat berbanding dengan yang tidak dirawat, tetapi di sisi lain ia menurunkan kestabilan terma bagi komposit PP/dolomit. Bahagian akhir kajian ini memberi tumpuan kepada kesan luluhawa semula jadi dan dipercepatkan kepada sifat mekanik dan fizik komposit PP/dolomit dan nanokomposit hibridnya. Komposit PP dengan dolomit yang dirawat menunjukkan pengekalan kekuatan tensil bagi komposit PP/dolomit yang melalui proses degradasi secara semulajadi serta dipercepatkan.

Characterization and Properties of Stearic Acid, Titatante and Zirconate Modified Dolomite/Polypropylene Composites

ABSTRACT

An increase in demand for the use of natural mineral filler polymer composites has attracted attention towards a greener environment and in reducing the processing and production cost of composites materials. In this study the effect of dolomite filler content and the effect of filler treatments on the mechanical, thermal and degradation behaviour of modified dolomite/polypropylene (PP/dolomite) composites were investigated. The first part of this study reported on the preliminary study on optimum ground dolomite properties. The raw dolomite was ground using various grinding time in order to obtain the optimum size of dolomite particle to be incorporated into the composites. The grinding process of 2h resulted in optimum grinding parameter with particle size 8.183μm and maintained crystalline structure even after the intensive grinding operation in the planetary mill. Secondly, the PP/dolomite composites containing 0 – 25 wt.% of dolomite was prepared using Brabender internal mixer at temperature 180˚C , rotor speed 60 rpm and compression moulding method. The addition of dolomite into the PP matrix decreased the tensile strength and elongation at break of the composites. The Young's modulus increased due to the addition of dolomite particulate filler into the PP/dolomite composites. Thermogravimetric analysis (TGA) confirms that the addition of lower content of dolomite increased thermal stability of the composites. In the third part, the effect of stearic acid content as modifier on the surface treatment of PP/dolomite composites was studied. It was found that the dolomite has been successfully modified by the stearic acid observed through the fourier transform infrared (FTIR) and exhibited that the optimum stearic acid content has elevated the percentage of hydrophobicity and resulted in highest tensile strength, elongation at break, flexural properties and also thermal stability of the polymer composites. A better interfacial adhesion between the particulate dolomite and PP also was observed. This optimum stearic acid content obtained was then maintained in order to compare the effect of other modifiers which were titanate (LICA12) and zirconate (NZ12) as modifiers towards the mechanical, thermal and morphology behaviour of the composites. The addition of these modifiers has shown a significant improvement the tensile strength and Young's modulus of the composites. The modified PP/dolomite composites showed slight improvement on tensile strength, impact strength and flexural properties. FTIR spectra proved the changes of functional group of modified dolomite and enhancement of interfacial adhesion respectively. The addition of nanosilica has marked an improvement in the impact strength of modified composites compared to unmodified ones, but on the other hands it lowers the thermal stability. The final part of this study focused on the effect of degradation by natural and accelerated weathering to the mechanical and physical properties of PP/dolomite and its hybrid nanocomposites. The composites of PP with modified dolomite sustain the tensile strength for both natural and accelerated weathering.

CHAPTER 1 : INTRODUCTION

1.1 Research background

The demands for plastic materials from synthetic polymers which mainly are derived from non-degradable petroleum based thermoplastic materials are increasing in recent years and being used in various applications. Due to its versatility, in these recent years the current global municipal solid waste (MSW) levels was reported to be approximately 1.3 billion metric tonnes per year and is expected to increase up to relatively 2.2 billion metric tonnes per year by 2025 (Ismail, 2013). Based on that phenomenon, polypropylene (PP) waste becomes seconds of the largest plastic wastes in Malaysia compared to the other commodity plastics such as polyvinylchloride (PVC), polyethylene (PE) and polystyrene (PS) (Jayashree et al., 2012). The drawbacks for these types of plastics such as strong intermolecular bonding, long degradation time and release of toxic substance when incinerated; to name a few, has as well contributed to the environmental issues nowadays (Chuensangjun et al., 2013). The researchers from all over the world have also reported on the shortage of current oil resources worldwide since the production of petroleum crises are getting worse and frightened (Abidin et al., 2012).

Polypropylene (PP) is one of a raw plastic materials derived from petroleum derivatives. It is a versatile polymer with the chemical structure (C_3H_6) and has relatively high melting point of 160°C. It is the lightest thermoplastics among all commodity plastics due to its low density (0.9 g/mL) and offers a lot of benefit in numerous applications such as in food containers, medical and laboratory tools, toys, automotive industry including automobile parts, carpeting and technology by virtue of its cheap price and flexibility for molding (Maddah, 2016). In order to achieve a great material properties with minimum processing cost, the addition of fillers into PP matrix producing PP composites has been widely introduced, used and practiced in most industries (Ammar et al., 2017).

PP composites has developed into an important class of engineering materials of which the incorporation of inorganic mineral fillers into PP has intensify tensile and impact properties of PP, as well as diminished production cost and minimize environmental pollution caused by PP by reducing the amount of thermoplastics used during production. Until today, distinct kinds of inorganic mineral fillers including dolomite (Akanbi et al., 2015), montmorillonite (Gong et al., 2004), silica (Dong & Bok, 2016), calcium carbonate (Lee et al., 2014) and aluminium oxide (Zhi et al., 2016) have been introduced in order to infer an improvement of thermo mechanical properties of PP such as its toughness, rigidity and heat resistance. However the poor interaction between PP matrix and inorganic mineral filler due to its polar and non-polar behaviour has become a greatest challenge in achieving the desired properties. Hence the compatibility strategy between these two materials has turned into one of the significance properties development enhancement studied by researchers. Onuegbu and friends, (2014) reported that filler surface treatments or modifications such as titatante coupling agent can be proposed in contemplation of promoting the surface interaction, compatibility and processing capability between the matrix and the filler by incorporating the coupling agents or compatibilizer.

Hybrid composites have intrigued interests in the current research trends nowadays as they offer a range of properties that are not able to be attained with a single type of reinforcement be it in mechanical or thermal properties. Hybridization of two different types or sizes of mineral fillers provide advantages over using each filler alone in the single polymer matrix (Sharma, 2012). The improvement in tensile strength and tensile modulus for hybrid fillers composites has been reported by Huang and colleagues (2013). Sadej & Andrzejewska, (2016) carried out a research on silica/aluminium oxide hybrid as fillers for photocurable composites and discussed that the addition of hybrid fillers into polyethylene glycol diacrylate (PEGDA)– based composites enhanced the mechanical properties, polymerization, conversion and detrimental effect at low filler loading (5wt.%).

'Hybrid' is of Greek-Latin origin and can be found in various scientific fields. In polymer composites the hybrid system means one kind of reinforcing materials are incorporated in a mixture of different matrices (blends), or two or more reinforcing and filling materials a mixed in a single matrix to further increase its mechanical and thermal properties (Jawaid & Abdul Khalil, 2011). Recently the hybrid filler fabricated with two geometrically dissimilar nanofiller was found to have significance synergistic effects in reinforcing polymer matrix than single filler (Hu et al., 2016).

Studies regarding incorporation of nanosilica with other inorganic particles as hybrid filler have been carried out (Chieruzzi et al., 2015). Zakaria et al., (2015) have introduced an advanced hybrid filler system in improving flexural properties of multi-walled carbon nanotube-alumina (MWCNT-Al_2O_3)/epoxy nanocomposites. These systems have been reported to significantly improve the flexural strength and flexural modulus of the composites up to 30% and 35% respectively.

Thus this research work presented in this thesis focuses on the study of PP/dolomite composites by modifying the dolomite surface with various types of modifiers as well as the improvement achieved due to the incorporation of nanosilica into the composites system.

1.2 Problem Statements

Nowadays, petroleum based thermoplastic materials are being used increasingly in various applications. The use of petroleum based polymer also may lead to environmental pollution, thus the addition of mineral filler is to reduce the petroleum based material usage and also one of the effort in saving the environment. Furthermore, there is abundance of inorganic mineral filler (dolomite) in Perlis which has not been fully utilized as inorganic filler despite of its good properties. Hence, in this study the dolomite is used as filler for polypropylene composites since dolomite is well known for its hardness and high thermal stability to be applied for outdoor application.

One of the major key challenges of producing an inorganic/organic composite with excellent properties is to overcome unwanted agglomeration of mineral filler particles in the polypropylene matrix (Aguilar et al., 2014). The homogenous dispersion of inorganic particles in organic polymer is difficult to achieve due to the strong tendency of the particles to agglomerate and generate high viscosity during composite processing. Since the inorganic mineral filler is hydrophilic and the organic polymer is hydrophobic, there is an issue regarding the interfacial adhesion between the filler particles and polymer matrix (Müller et al., 2017). This research planned to functionalize mineral filler via coupling approach by using three types of modifiers which are stearic acid, titanate and zirconate. These modifiers will act as an interface between inorganic substrate and an organic material to bond or couple the two dissimilar materials in order to exhibit a polymer composite with great interfacial adhesion and good dispersion of mineral filler in the polymer matrix.

Eventhough the incorporation of single mineral fillers into composites system has been found to promote some of its mechanical properties; it also will affect some other properties like impact strength and thermal stability. This drawback however can be reduced by the embodiment of very fine particles; in this case the nanosilica particles is used (Xingxun et al., 2014). Nanosilica is well known to induce high thermal conductivity and stability of the composites (Klapiszewski et al., 2015).

In addition to the focuses on improving the compatibility and enhancement of mechanical and thermal properties of the composites with single system or hybrid system, another milestone is to study the degradation behaviour of the composites of which outdoor degradation and accelerated degradation conditions were observed for mechanical properties of the composites since this study focused on producing thermoplastics composites for outdoor application.

1.3 Objectives of the Study

The purpose of this work is to develop and fabricate an environmental friendly PP/dolomite composite with excellent mechanical and thermal properties. This research work highlights on the innovation of using a low filler loading of submicron mineral particles in PP matrix by optimizing the amount and varying the types of coupling agents use in filler surface treatment process.

Following are the four objectives of this research work:

(i) To determine the optimum size of dolomite particle to be used as submicron particle for the study

(ii) To determine the optimum filler loading of the unmodified PP/dolomite composites to be used for PP/dolomite modified composites

(iii) To analyze the effect of surface modification using stearic acid, titanate and zirconate coupling agent on the mechanical properties and thermal stability of polymer composites

(iv) To study the effect of natural degradation on the physical and mechanical properties of PP/dolomite composites and its hybrid nanocomposites

1.4 Outline of Thesis Structure

This thesis has been divided into five chapters. Each chapter gives the information about the research interest as mentioned in the objectives part.

Chapter 1 starts with a brief introduction on research background including the thermoplastics composites and its hybrid composites incorporated with mineral fillers and silica inorganic particles. The primary objectives and the general flow of the whole research program are also outlined.

Chapter 2 briefs about fundamental concept of inorganic particulate filled polymer composites and highlights the important concepts for developing polymer composites with inorganic particles.

Chapter 3 explains about the raw materials used in this study and describes the experimental procedures employed throughout the research works as well as the details of lab equipments used in the study.

Chapter 4 reports the results obtained via grinding process of bulky dolomite in order to obtain submicron particles of dolomite. The result is explained with the aid of X-ray diffraction (XRD), X-ray fluorescent (XRF), particle size analysis (PSA), scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR). Second part of this chapter depicts the filler loading effects of dolomite in polypropylene matrix and detailed analysis is explained by tensile and flexural testing for mechanical properties. The morphology of tensile fractured which was studied using SEM supported tensile properties of the composites. Thermogravimetric Analysis (TGA) report is presented to facilitate the thermal properties of the composites. Graphs and tables on the physical, mechanical and thermal properties of this composite are presented here and detailed analysis is made on the data collections. The optimum amount of dolomite loading to be used for the production of modified dolomite in single dolomite filler composites and hybrid composites is also reported in this section. The third section reports the effect of surface treatment on the filler using different amount of stearic acid as reference on the mechanical and thermal properties of PP matrix. A comprehensive work using such as Fourier Transform Infrared Analysis (FTIR), XRD, percentage of hydrophobicity experiment, tensile test and flexural test, TGA and SEM has been carried out to study the effectiveness of the surface treatment process. The optimum amount of stearic acid on the composites that provides the best tensile and flexural properties is reported as well. The next sub-topic in this chapter discusses the effect of modification on the optimum amount of filler loading (5 wt.%) using fixed amount of stearic acid, titanate and zirconate coupling agent (1 wt.%) on the tensile, flexural and impact strength, creep behaviour as well as the thermal properties of PP/dolomite composites and its hybrid composites. The final part reports the effect of natural and accelerated weathering testing on PP/dolomite composites its hybrid composites.

Chapter 5 presents concludes and summarizes the research outputs that have been done in this research and the suggestion for future improvement.

CHAPTER 2 : LITERATURE REVIEW

2.1 Particulate Filled Polyolefins Composites & Its Hybrid Composites

Polyolefins, particularly polypropylene (PP) and polyethylene (PE) are widely chosen to be used in everyday life due to its wide range of applications and these types of polyolefins are far less toxic compared to other type of commodity plastics (Sauter et al., 2017). Significant commercial importance of particulate filled polyolefins composites have been proved in recent years, aligned with industries and technologists desire of seeking new cost effective materials for specific applications. The particulate filler itself suggested that reinforcing phase is often spherical or having dimensions of similar order in all directions and can be divided into different shapes such as block, flake, cube and so on (Kickelbick, 2014). These types of fillers are utilized in order to improve the desired properties of composites such as the stiffness, dimensional stability and most importantly, to reduce the polymers usage hence producing a more economical product (Liang, 2013).

Other than single filler composites system, the hybrid composites have become commercially important in their own right. At first, the hybrid composites were developed not more than just a research tool or model systems for systematic studies of composites structure (Abu Bakar et al., 2007). Nowadays the hybrid composites were introduced to satisfy several purposes in example to meet specific processing and performance requirements which cannot be fulfilled by a single component. A study on particulate filled PP composites has been carried out by Abu Bakar et al., (2007) and they concluded that the hybrid composite of talc and kaolin in PP matrix has given a notable result in enhancing the stiffness and strength properties of the composites compared to single filler composites of talc and kaolin respectively.

2.2 Particulate Mineral Filled Thermoplastic Composites

Thermoplastics pose a disadvantage since they soften appreciably as they are heated thus the modulus decreases and they begins to creep. At higher temperature thermoplastics progressively lose their shape and melt. In order to overcome this limitation, few efforts have been made included addition of mineral filler into thermoplastic composites. The addition of talc into polypropylene has been reported to increase the modulus and heat distortion temperature of thermoplastics (Brydson, 1999). Originally, the main function of adding fillers into thermoplastics is to reduce the cost of the compound. However, for the case of polypropylene (PP) and polyethylene (PE) whereas the costs per unit volume are least expensive compared to other thermoplastics, the addition of fillers was more of the point to increase the properties of composites. Filler that are usually change the properties of polymer and have lots of advantage and disadvantage is called "functional fillers" (Armitt & Handcock, 2003).

Many researches regarding the incorporation and interaction of mineral fillers into thermoplastics has been conducted and reported. Zuirderduin and co-workers have studied that the addition of precipitated calcium carbonate particles into aliphatic polyketone has increased the modulus of the composites and impact resistance, but decreased its yield strength due to the debonding of the particles.

Polyvinyl chloride (PVC) is another type of thermoplastic that is usually used for producing particulate filled composites. A study has been carried out by Ghada and friends on the effects of marble powder and dolomite to the mechanical and thermal stability of PVC. It was observed that the addition of marble powder and dolomite enhanced the mechanical and thermal properties of the composites, and the impact strength of PVC/dolomite composites increased compared to PVC/marble composites (Ghad et al., 2010).

Another research has been carried out by Syed Bakar et al. on incorporation of dolomite into recycled PP and they concluded that the highest tensile strength was observed with the presence of 30 wt.% of 300µm dolomite in recycled PP/dolomite composites (Syed Bakar et al., 2014).

2.3 Filler-matrix Interaction

Mechanical performance of polymer composites is dependent upon the interfacial interaction between the fillers and polymer matrix (Li et al., 2016). This interfacial bonding occurs once the matrix has wet and in intimate contact with the filler, if the interfacial region is stronger than the matrix, the matrix will yield. However, if the interfacial region is weaker than the matrix, de-bonding may initiate along the interface. The extent of interaction would depend on how well the filler is dispersed in the matrix. Because of the strong van der Waals forces and electrostatic interactions, micro/nanofillers tend to aggregate in solvents. Although van der Waals forces are considered to be weak intermolecular forces, they become significant at the micro/nanoscale due to the large surface area per unit mass of the material (Bhattacharya, 2016b). The interaction between filler-matrix is responsible for changes in the physical and mechanical properties of filled materials and usually improves material reinforcement. The interaction process involves chemical reaction between the filler and the matrix materials, physical interaction including Van der Waals or hydrogen bonding, changes in morphology of interactiong components and also mechanical interlocking (Hulugappa et al., 2016).

Several approaches has been explored and studied in order to reduce the aggregation between filler particles as well as to promote the adhesion and incompatibility between filler and most matrices including chemical modification, using compatibilizing agent and surface treatment of the filler prior to composite manufacture (Saba et al., 2014). Interfacial interactions play an important role in the determination of the properties of composites materials as it leads to the formation of an interphase with specific properties, determine the amount of filler to be added into the polymer, resulted in the particle size dependence of properties and determine the prevailing micromechanical deformation mechanism of the composite (Moczo, 2004).

2.4 Filler

Filler is a strong material that is equipped for changing the physical and substance properties of materials by surface association or its inadequacy in that area and by its own particular physical attributes. The fundamental purpose of including fillers into matrix was presumably the aim for lower costs in view of its reasonableness and usually the concentrations of 10% to 50% were used; consequently would make the materials less expensive (Vasudeo et al., 2016). Currently low cost fillers are added to polyolefin and to most polymers without decreasing the profile or hindering melt flow (Ram, 2013).

2.5 Classification of Filler

Filler term is very broad and it encompasses a very wide range of materials used. Usually filler is defined as varieties of solid particulate materials (organic & inorganic) that comes in various shapes such as irregular, acicular, fibrous or plate-like and are used in reasonably large volume loadings in plastics. The organic and inorganic compounds that are used as fillers may come in significant diversity in the chemical structures, forms, shapes, sizes and inherent properties. Those compounds normally in a form of rigid materials, immiscible with the matrix in both molten and solid states, thus forms distinct disperse morphologies (Xanthos, 2010). Fillers can be subdivided according to types, shape and size or aspect ratio (Figure 2.1 & Table 2.1).

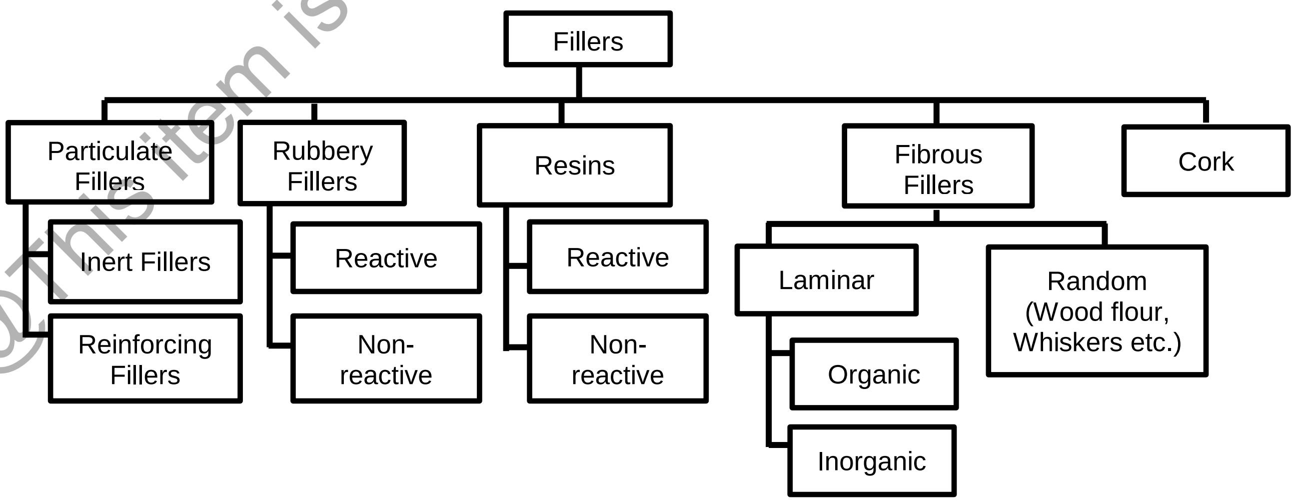
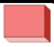


Figure 2.1: Classification of Filler in Polymer (Brydson, 1999).

Table 2.1: Classification of filler according to shape and size (Xanthos, 2010).

Shape		Aspect Ratio	Example
Cube		1	Fledspar, Calcite
Sphere		1	Glass spheres
Block		1 - 4	Quartz, Calcite, Silica, Barite, Dolomite
Plate		4 - 30	Kaolin, Talc, Hydrous Alumina
Flake		50 - 200 ++	Mica, Graphite, Montmorillonite nanoclays
Fiber		20 - 200 ++	Wollastonite, Glass fibers, Carbon nanotubes, Wood fibers, Asbestos fibers, Carbon fibers

The classification of fillers as organic and inorganic substances can be divided according to its chemical family as illustrated in Figure 2.2. There are more than 70 types of particulates/flakes and more than 15 types of fibers of natural or synthetic origin that has been used or evaluated as fillers in thermoplastics and thermosets (Yit, 2016).

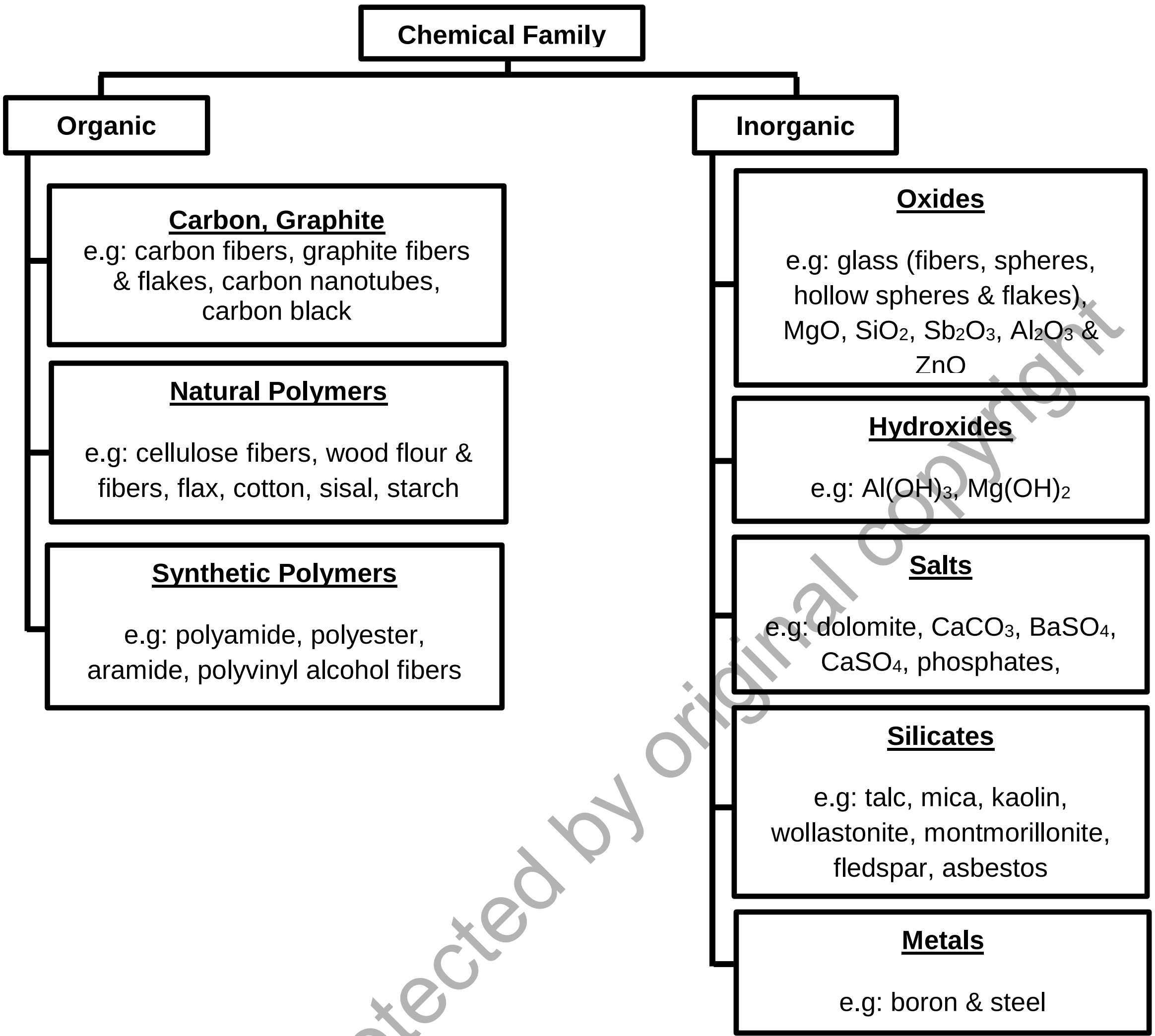


Figure 2.2: Chemical families of filler for plastics (Xanthos, 2010).

Inorganic fillers that are most commonly used nowadays are low cost, natural origin mineral fillers including talc and calcite that are abundantly available in nature. The most important mineral fillers used are from the groups of carbonates (calcite and dolomite), clays (kaolin, montmorilonite and chlorite) and talcs. There is also synthetic mineral filler for instance hollow glass microsphere and solid glass microsphere, however this type of filler is notably expensive compared to those naturally occurring mineral fillers (Kumar et al., 2016).

2.6 Types of Particulate Fillers

From earlier days, particulate fillers have played a significant role in the development of commercial uses for polymers due to its ability to profitably modify many properties of polymer composites and have been used in multiple purposes nowadays. Particulate polymer composites (PPCs) usually consists of micro- or nano-fillers of different sizes and shapes randomly dispersed in polymer matrices (Jajam & Tippur, 2012). Polymer composites based on natural particulate fillers are currently receiving great attention as innovative materials for industrial applications in myriad sectors such as automotive, construction, outdoor appliances, packaging and biomaterials. The use of particulate filled polyolefin in these sectors is presently to increase its mechanical and thermal properties. In order to enhance these properties, they are often compounded with natural minerals that served as fillers (Igwe & Onuegbu, 2012).

In comparison to microscale particles, submicron particles have some unique features. Higher surface area of submicron particles is able to promote stress transfer from the matrix to submicron particles. The required amounts of submicron particles to be filled in polymer matrix composites are usually much lower than of those microparticles (Chauhan & Thakur, 2013). There are numerous types of particulate filled polymer composites from relatively simple chalks and limestones to complex rare-earth magnetic powders. Rothon, 2002 had classified particulate fillers into two major groups which are particulate fillers from natural origin (mineral fillers) and synthetic particulate fillers. The most important used mineral fillers are carbonates, clays, talcs and also silica. Calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate) are the main carbonate fillers that were used widely all across the world other than the mixture of two carbonate such as hydromagnesite and huntite (Phipps, 2014). Clay minerals are aluminium silicates of either the two-layered kaolinite type or three-layered montmorillonite type. The most commonly used clay minerals in polymer industries are kaolinite, motmorillonite and chlorite (Uddin, 2008). Talc is a plate-like layered structured that acts as a good nucleating agent for thermoplastics and has proved to give positive impact on mechanical properties and macromolecular orientation of thermoplastics composites (Ammar et al., 2017). Other inorganic filler that is usually preferred is silica as it promotes better uniform dispersion and offers high interfacial interaction leading to thermally and chemically stable micro and nanocomposites, and it also serves as nucleating agent in thermoplastic composites (Meer et. Al, 2015).

As discussed in the research work done by Hemmasi et al., (2013), the addition of 2 wt% nanoclay into recycled polyethylene composites has shown a significant increment on the tensile and flexural strength, as well as tensile and flexural modulus of the composites. Other than that, the aspect ratio of the particles plays an important role whereas the smaller particle size exhibited a higher tensile and flexural strength of the composites compared to the higher particle size of the filler. Sirin, Balcan, & Dogan, (2012) discussed on the effects of calcium carbonate ($CaCO_3$) particulate filler component on mechanical and thermal properties of PP-LDPE blends. The mechanical properties (tensile strength, elongation at break) of the composites showed high peaks with the addition of $CaCO_3$ into the PP-LDPE blends.

As mentioned earlier, dolomite is one of the crystalline natural mineral filler that received wide attention in improving the desired properties of the polymer composites for instance the tensile and flexural strength, stiffness and thermal stability. It is a solid mineral of a great importance. To date, it is found to be a good additives in paper, plastic, tiles and cheap filler manufacturing (Adesakin et al., 2013). Eventhough it is similar to the properties of calcite, dolomite is actually slightly harder (mohs hardness: 3.5 compared to calcite's mohs hardness 3.0), denser (specific gravity of dolomite 2.85, calcite 2.70) and more resistance to acid. A study on the effect of dolomite powder on combustion and technical properties of wood plastic composites (WPC) and PP has been carried out by Özdemir and colleague, (2017) and they discussed that the incorporation of dolomite has enhanced the tensile and flexural modulus of the hybrid composites. Dolomite filler has also increased the tensile and flexural strength of dolomite plastic composites (DPC) single filler system in PP matrix.

2.7 Mineral Filler

According to Rothon (2002), a mineral is a pure, crystalline, naturally occurring material with a definite chemical composition. They are usually found in nature as rocks or ores, which can vary from relatively pure minerals to complex mixture and are then undergo various processes such as mining, crushing and grinding, comminution, purification, classification, calcination and drying (Balasubramanian, 2015). The use of minerals as fillers in composites has been increasingly used as its properties fulfill the requirements for use in polymer applications such as abundantly available, low cost, and inert. Some of them are readily produce with desired particle sizes and shapes. The main mineral fillers that are widely used in the industries include calcium carbonate, dolomite, clay, mica, talc, wollastonite, silica and huntite to name a few.

2.7.1 Dolomite

Dolomite is one of the most common carbonate minerals in the geologic record built up of anhydrous carbonate minerals composed of calcium, magnesium and carbonate (Rodriguez-Blanco et al., 2015). Dolomite is a double carbonate mineral that is having an alternating structural arrangement of calcium and magnesium ions (Figure 2.3). It does not rapidly dissolve in dilute hydrochloric acid as calcite does (Azimi et al., 2016). Dolomite is commonly used as fillers in concrete and cement industries, and the reason that making dolomite a bit less popular filler than calcium carbonate is generally they are harder to grind/mill and tend to be less white. However, dolomite offers advantages and benefits over calcium carbonate in term of its low-cost and abundantly available, other than it has high hardness due to its rock characteristics that serves it as suitable filler in polymer material with low hardness value. It also may increase the stiffness of composites (Adesakin et al., 2013).

As presented in Table 2.2, commonly used dolomite contains small amount of alumina oxide (Al_2O_3) and silicon dioxide (SiO_2) composition, other than having a high amount of calcium oxide (CaO) and magnesium oxide (MgO) compositions (Rodriguez-Blanco et al., 2015). Salt type minerals including dolomite are characterized by high solubility compared to the other oxide-type minerals.

Table 2.2: Chemical composition of dolomite (Rodriquez-Blanco et al., 2015).

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O
33.4	17.1	2.5	0.7	0.3	0.1	0.1

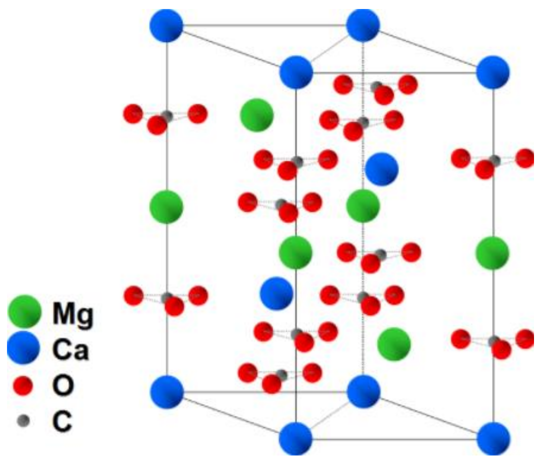


Figure 2.3: Structure of dolomite (Mehmood et.al, 2018).

2.7.2 Silica

In general there are two types of silica namely natural silica and synthetic silica that are available in the market. Natural silica or crystalline silica is the most ubiquitous mineral being found as a component in most other mineral deposits while synthetic silica are divided into two types according to its production methods that are pyrogenic or thermal (known as fumed silica) and wet process (known as precipitated silica). It is a very fine amorphous white powder with primary particle sizes range from 7 nm to 100 nm. In this content we focused on the synthetic fumed silica.

2.7.2.1 Fumed Nanosilica

Fumed nanosilica is one of the most preferable filler by researchers due to its ability to give effective reinforced to the composites with a very low filler loading (Ching & Syamimie, 2013). The term fumed silica was obtained from the smoke/fume like particles resulted from the vapour process. It is represented by a fluffy, white, amorphous powder product with a very low apparent density. The molecular reaction of silicon tetrachloride ($SiCl_4$) vapor in a flame of oxygen and hydrogen leads to the formation of an amorphous form of silicon dioxide (SiO_2) through the reaction:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl \qquad (2.1)$$

The spherical particles of diameter approximately 7 to 14 nm are initially produces from flame hydrolysis process which collide while hot and fuse into aggregate of 0.1 µm that are branched, chain-like structures and can be considered as fumed silica primary structure since the fusion process is irreversible.

Jauregui-Beloqui and colleagues, (1999) studied the influence of the specific surface area of fumed silica on the viscoelastic and adhesion properties of thermoplastics polyurethane-fumed silica composites and reported that the viscoelastic properties as well as the crystallization rate of the composites was improved by adding fumed silica and explained that the improvement were obtained by specific surface area lower than $200m^2/g$.

A study on the effect of filler surface area and treatment to the thermo-mechanical properties of high density polyethylene-fumed silica nanocomposites has been reported by Dorigato et al., (2012). They explained that the addition of fumed silica into the polymer matrix had shown an interesting enhancement on both of the thermal degradation resistance and dimensional stability of the nanocomposites.

2.7.3 Ultra-fine Grinding of Mineral Filler

In order to obtain the required particle fineness of mineral fillers according to the needs by the industries, the grinding process is required. Ultra-fine grinding is a unit operation process of which particles were ground to a fine size where 80% of the particles are smaller than 10µm (Pease et al., 2004). Planetary mill has been known to possess higher energy density and provide mechanical impact on materials other than milling devices (Huller et al., 2008). It has been the most commonly used ball mills in preparing samples ranging from soft to hard to brittle and fibrous materials (Radhip et al., 2015).

There are a lot of parameters need to be considered in milling process and the parameters that have been tested most are the rotation speed and milling/grinding time. These two parameters play an important role in determining the effectiveness of the milling process and the products obtained from the process. Another important parameter in milling process that needs to be taken into account is the ball-to-powder weight ratio. Even though majority of the researchers used the range of 10:1 or 20:1 ratio, there are works that used higher ratio up to 100:1. This ratio helps to increase the particle size reduction rate, but it may also resulting in contamination from the collision of grinding balls and inner wall of milling vial thus it is important to choose the milling jar from the uncontaminated material such as zirconia (Rizlan & Mamat, 2014). The schematic diagram of planetary ball mill is shown in Figure 2.4. The processes inside planetary ball mill are complex and strongly depended on the materials, thus the optimum milling condition has to be assessed (Burmister & Kwade, 2013).

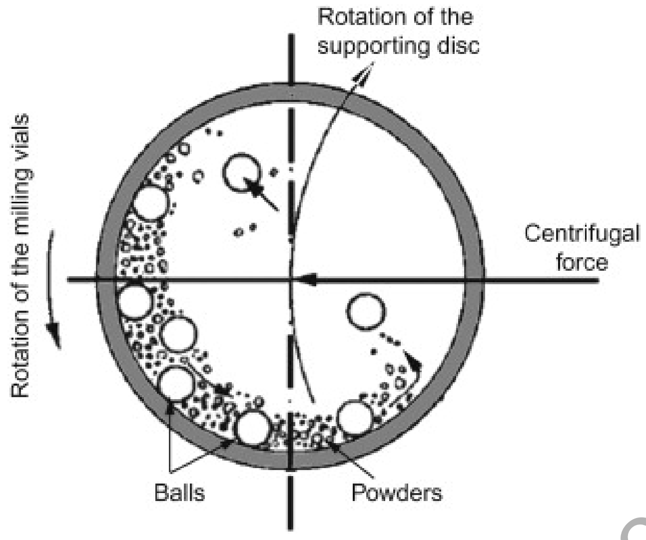


Figure 2.4: Schematic diagram of planetary ball mill (Burmister & Kwade, 2013).

2.8 Matrix

The matrix properties in thermoplastic composites influences composite's overall transverse modulus, shear properties and compression properties and significantly limits a composite's maximum permissible operating temperature. It can be broadly classified on the basis of their usable temperature ranges as mentioned in Table 2.3 (Zweben, 2015).

Table 2.3: Classes of Materials and Usable Temperature Ranges (Zweben, 2015).

Different Classes of Materials and Usable Temperature Ranges	
Matrix Material	Usable Temperature Range (°C)
Polymers	< 260
Metals	260 - 750
Glass	750 - 1150
Ceramic and Carbon	1150 - 1400

There are several considerations have to be factored in while selecting matrix material for composites system such as specific gravity, mechanical properties, melting of curing temperature, viscosity, reactivity with fillers as well as cost. Polymers are the most widely used matrix materials including polyesters, vinylesters, nylon, polycarbonate, epoxies, ureas, melamines and silicones because of its advantages such as low cost, easy processing, low density and superior chemical resistance. However these polymer are limited by a few drawbacks such as low strength and modulus, has limited range for operating temperature and it is sensitive to UV radiation, specific solvents and occasionally humidity. In matrix-based structural composites, the matrix serves two predominant purposes which are binding the filler/reinforcement phases in place and deforming to distribute the stresses among the constituent filler/reinforcement materials under an applied force.

2.8.1 Polypropylene (PP)

Polypropylene (PP) is being used for various applications ranging from single use disposables to long lasting durables due to its excellent physical, mechanical, thermal and dielectric properties, relatively low in weight, resistance to impact and good processability together with price competitiveness (Jeon & Kim, 2016). It is a semi-crystalline polymer that consists of both crystalline and amorphous phase with high level of stiffness and high melting point compared to other commercial thermoplastics materials. PP was produced and applied in a large scale other than polyethylene (PE) and polyvinyl chloride (PVC) (Burmistrov et al., 2016). It gained a strong popularity rapidly since the discovery of it in 1954 due to the fact that PP has the lowest density