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Effects of Natural Sand on the Mechanical Properties of High Density Polyethylene and Polypropylene

By

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A THESIS

SUBMMITED TO THE POSTGRADUATE STUDIES PROGRAMME AS A REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN MECHANICAL ENGINEERING

BANDAR SERI ISKANDAR,

PERAK

JULY, 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature: ______________________________
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TO MY FAMILY

ACKNOWLEDGEMENT

I would like to express my sincerest gratitude and appreciation to my supervisor Associate Professor Dr.Othman Mamat for his invaluable continuous guidance, and understanding during the course of this research work.

I also would like to thank technologists, Mr. Anuar A. Muin, Mr. Omar Ramli, Mr. Faisal Ismail, Mr. Shairul Harun and Mr. Irwan Othman for their help with machines during the experimentation.

Many thanks to my family for their consistent encouragement and support, without their backup, this work cannot be done.

ABSTRACT

Composite materials were manufactured from two semi-crystalline thermoplastic polymers namely, high density polyethylene and polypropylene using Malaysian natural sand as filler. The chemical content and structure of the filler were studied using XRF and XRD respectively. Two different types of natural sand, Silica Sand (SS) and Beach Sand (BS) were used for comparison purpose. Test results from composite containing 10% by weight of each filler show that SS composite is much better than the BS composite. The effects of the natural SS content on the mechanical properties of the composite were investigated too. For the study, the composite was prepared in four different filler concentrations by weight of the polymer matrix, 0%, 5%, 10% and 15% using melt mixing process. A decrease in tensile strength of 10.3% and 9.3%, maximum elongation of 19.18% and 26.41% and a substantial increase in stiffness of around 42.9% and 5.8% were observed for the untreated HDPE/SS and PP/SS composites at 15wt% filler content respectively. Flexural test results for the polymer composites show a maximum modulus at 15wt% of 8.0% and an increasing trend of flexural strength for untreated HDPE/SS composite. On the other hand, for untreated PP/SS composite, a decrease in maximum deflection of 1.5% and an increment in flexural modulus of 19.7% and flexural strength of 3.5% have been observed at 15wt% filler content.

The interfacial interaction between filler and matrix was studied by applying chemical treatment on the SS filler using silane coupling agent (SCA). The two types of SCA, γ-methacryloxypropyltrimethoxysilane (MTS) and vinyltriethoxysilane (VTES) were used for treatment. Samples prepared in the same manner as the untreated samples were tested. The HDPE/SS composites showed a tremendous increment in tensile strength and tensile modulus but a reduction in maximum elongation. Analysis of the treated PP composite showed a slight decrease in tensile strength and maximum deflection but a substantial increase in modulus of elasticity was observed as the percentage of filler was increased. Improvements in the flexural strength and flexural modulus were also recorded. A comparison of mechanical properties between 10wt% HDPE composites produced from MTS and VTES revealed that MTS is better than VTES.

Morphology of the fractured surface from tensile test was analyzed by using Scanning Electron Microscopy (SEM). The microstructure revealed that there is weak interaction between the untreated filler and the matrix. On the other hand, a clear interfacial interaction was observed between the filler and polymer matrix in the case of treated sample.

Thermal properties, mixing torque and rheology of the composite were also studied. It was found that the melting and crystalline temperatures show a slight increment of about 1.14% and 1.40% for 15wt% treated HDPE/SS composite. On the other hand, a decrease in melting and crystalline temperature of 0.74% and 0.04% for treated PP/SS composite respectively. The maximum torque required for mixing and rheological properties such as viscosity and shear rate were also increased with the filler content for the untreated composite sample. In the case of treated composite samples, the viscosity show a decrement compared to the untreated composite with maximum decrement of 35.6% was achieved at 15 wt%.

Since this study is in a laboratory level, the maximum amount of filler is limited 15wt%. Applying a filler content of more than 15wt% can cause severe wear of the machine parts during mixing process.

Key words: Natural sand, micro-composites, high density polyethylene, polypropylene, surface treatment, silane coupling agents, silica sand

ABSTRAK

Bahan komposit dihasilkan daripada campuran polimer-polimer termoplastik, polietilena ketumpatan tinggi dan polipropilena, dengan menggunakan pasir semulajadi Malaysia sebagai pengisi. Kandungan bahan kimia dan struktur pengisi telah analisa dengan menggunakan XRF dan XRD. Dua jenis pasir semula jadi, iaitu Pasir Silika (SS) dan Pasir Pantai (BS) telah digunakan untuk tujuan perbandingan. Keputusan ujian daripada komposit yang mengandungi 10% berat rencam SS adalah lebih baik daripada rencam BS. Kesan kandungan SS pada sifat-sifat mekanikal telah diselidiki terlalu. Dalam kajian ini, komposit dengan rencam dalam empat tahap penumpuan pengisi berbeza oleh berat bagi matriks polimer, 0%, 5%, 10% dan 15% telah disedakan dengan menggunakan proses penyebatian cecair. Satu pengurangan dalam kekuatan tegangan 10.3% dan 9.3%, pemanjangan maksimum 19.18% dan 26.41% dan satu bertambah teguh dalam ketegaran sekitar 42.9% dan 5.8% telah dicerap untuk HDPE yang tidak dirawat / SS dan PP / SS komposit pada 15wt% kandungan pengisi masing-masing. Lenturan keputusan ujian untuk bahan komposit polimer menunjukkan satu modulus maksimum pada 15wt% 8.0% dan satu aliran bertambah lenturan kekuatan untuk HDPE yang tidak dirawat / rencam SS. Sebaliknya, untuk PP yang tidak dirawat / rencam SS, satu pengurangan dalam pesongan maksimum 1.5% dan satu tambahan dalam lenturan modulus 19.7% dan lenturan kekuatan 3.5% telah diperhatikan pada tehap 15wt% pengisi.

Interaksi antara permukaan-permukaan pengisi dan matrik telah dikaji dengan merawat pengisi SS menggunakan silana agen pengupelan (SCA). Dua jenis-jenis SCA, γ-methacryloxypropyltrimethoxysilane (MTS) dan vinyltriethoxysilane (VTES) telah digunakan untuk rawatan. Kadua-dua sampel asal dan dirawat telah dikaji. Komposit HDPE / SS menunjukkan peningkatan dalam kekuatan tegangan dan tegang modulus, namun pengurangan dalam pemanjangan maksimum. Analisis rencam PP menunjukkan sedikit pengurangan dalam kekuatan tegangan dan pesongan maksimum manakala modulus kekenyalan meningkat dengan peratusan penambahan pebgisi. Satu perbandingan ciri-ciri mekanikal bagi 10wt% HDPE komposit menggunakan daripada MTS dan VTES mendedahkan bahawa MTS berpotensi menawarkan hasil yang lebih baik.

Morfologi permukaan pecah daripada ujian tegangan telah dianalisa dengan menggunakan Kemikroskopan Elektron Imbasan (SEM). Mikrostruktur itu menunjukkan bahawa terdapat kesan saling tindakan lemah antara pengisi tidak dirawat dan matrik. Sebaliknya, satu pemerhatian jelas interaksi permukaan telah dapat diperhatikan antara pengisi dan matriks polimer dalam kes SS yang telah dirawat.

Sifat-sifat terma, kilas penyebatian tork dan reologi rencam juga telah dikaji. Komposit HDPE-15wt% SS telah menunjukkan penarunbluran sebanyak 1.14% dan 1.4% dalam takat suhu lelair dan suhu penghabluran manakala komposit PP-15wt% SS menunjukkan pengurangan sebanyak 0.74% dan 0.04%. Tork maksimum yang diperlukan untuk pencampuran dan sifat-sifat reologi meningkat dangan kandungan pengisi. Kelikatan komposit dengan kandungan 15wt% SS yang telah dirawat, menurun sebanyak 35.6%.

Di dalam kajian makmal ini kandungan pengisi telah dihadkan kepada 15wt% maksimum. Penambahan kuantiti pengisi yang lebih tinggi daripada 15wt% akan mendedahkan komponen-komponen mesin kepada kesan haus yang lebihteruk (bahaya).

Kata-kata utama: Pasir semulajadi, mikro-komposit, polietilena ketumpatan tinggi, polipropilena, rawatan permukaan, ejen gandingan silana, pasir silika

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
$BaSO_4$	Barium sulfate
BS	Beach sand
$CaCO_3$	Calcium carbonate
DSC	Differential Scanning Calorimetry
Fe	Iron
HDPE	High Density Polyethylene
HDT	Heat deflection temperature
HPP	Homopolymer polypropylene
ICP	Impact copolymer
ISO	International organization for standardization
LPE	Linear Polyethylene
MFR	Melt Flow Rate
MTS	γ-methacryloxopropyltrimethoxysilane
PE	Polyethylene
PP	Polypropylene
Ppm	Part per million
PS	Polystyrene
PVC	Polyvinylchloride
RCP	Random copolymer
SCA	Silane coupling agent
SEM	Scanning Electron Microscopy
SS	Silica sand
T-HDPE/SS	Treated silica sand-high density polyethylene composite
T-PP/SS	Treated silica sand-high density polypropylene composite
UTM	Universal Tensile Machine
U-HDPE/SS	Untreated silica sand-high density polyethylene composite
U-PP/SS	Untreated silica sand-polypropylene composite

VTES	Vinyltriethoxysilane
XRD	X-ray diffractometer
XRF	X-ray fluorescence

LIST OF SYMBOLS

λ	Wave length
σ	Shielding constant
E	Energy
σ_t	Tensile strength
σ_y	Tensile strength at yield
F	Load
F_{max}	Maximum load
W	Width
T	Thickness
ε	Strain
Δl	Elongation
l_0	Original gauge length
E_t	Tensile modulus of elasticity
σ_f	Flexural strength
L_1	Span length
E_f	Flexural modulus of elasticity
m	Slope of the initial portion of the load deflection curve
τ	shear stress
$\dot{\gamma}$	Shear rate
μ	viscosity
m'	flow consistency index
n	flow behavior index
n’	order of reflection

CHAPTER 1
INTRODUCTION

1.1 GENERAL INTRODUCTION

It is difficult to tell exactly when people start to make use of composite materials. However, as a natural composite, wood and bone have been used for many applications since the creation of mankind. And nowadays man made composites are the most effective materials used for important applications ranging from house hold items to sophisticated aerospace technology.
Organic-inorganic composites with nano and micro scale dimensions are of growing interest because of their unique properties[1], and numerous potential applications such as enhancement of conductivity [2-5], toughness [5], stiffness, heat resistivity [6,7], chemical selectivity [8] and so on. In these materials, inorganic and organic components are mixed in different composition ratio to form a hybrid composite material. The inorganic component can be from one of the main material categories, metals and/or ceramics.

Ceramics and strong minerals are generally known for their hardness and brittleness, along with their resistance to high temperature and severe physical and/or chemical environment [9, 10]. For most applications, the brittleness (lack of impact strength) is the major, sometimes fatal, deficiency of these materials [9]. On the other hand, organic polymers are usually noted for their low density and high toughness (high impact strength such as rubber). However, lack of hardness is one of the most significant flaws of polymers in many applications. Associated with lack of hardness are the problems of low wear and scratch resistance as well as dimensional stability [11]. The development of conventional composite materials with ceramics and strong minerals as fillers and polymers as matrix are being researched extensively. Important examples of these composite materials are the semi-crystalline polymers mixed with inorganic particles [12, 13].

These inorganic filler particles could be in a different size, shape, content etc and accordingly the composite material will have different characteristics.

Minerals in the form of powder have been used as reinforcement materials in composite technology to achieve specific purpose. However, as far as economy is concerned, the availability of the mineral filler is the most important factor which limits its use as composite filler. Mineral silica is the most ubiquitous on the earth, found as a component in almost all other mineral deposits. It is found in natural sand as crystalline silica, in fly ash, attapulgite, bentonite, ceramic beads, clay and so on. There are over 20 crystalline phases of silica, differing only in physical properties. Most of them are found naturally but only a few have a significant use in polymers, notably quartz, novacite and crystobalite. Naturally occurring silica sand minerals are round or angular in shape. However, after mechanical crushing for size reduction, all the particles will have angular shape because of its crystalline nature [14].

The uses of crystalline silica are a result of its high hardness, chemical inertness, heat resistance, low coefficient of thermal expansion and good electrical insulation. These properties make silica a very good functional extender for plastics especially when silane coupling agent is used. The study of the effects of reinforcing particulate natural silica sand in a Semi crystalline polymer and improving the interfacial interaction between the polymer and reinforcement are the motivation of this thesis.

1.2 OVERVIEW OF THE PROJECT

Modern reinforced composites have small particulate filler in the range of nano to micro level. Even though nano particulate reinforced composites are taking attention these days, micro particulates are still used in many composites for several applications.

As a general principle, the reinforcement of nano particles in a polymer matrix has its own advantage. However, it is somehow difficult to go down to nano scale and also have the agglomeration effect. Agglomeration is the phenomena in which the same particles join one another by means of the attraction force between them. This effect also prevails in the case of micro scale particles but in a much less strength than the nano scale particles because of the relatively bigger size and smaller surface area. Moreover, the production of particulate matter in a nano scale is more expensive than that of micro sized particles in the case of rigid mineral fillers.

1.2.2 PROJECT MOTIVATION AND PROBLEM STATEMENT

Though there are many polymer fillers, problem occurs in resisting the stress applied on the composite due to filler cleavage which directly deteriorates the mechanical properties of the composite. This type of failure exists in the case of soft filler composite where failure is from the filler particle instead of the matrix. On the other hand, rigid fillers such as silica and certain silicates have sufficient strength and respond so well to appropriate coupling agents that fracture of their composites is entirely through the resin with practically no failure at the interface or through filler cleavage.

This project is to solve the problem due to filler cleavage on the properties of semi crystalline polymer composites reinforced by soft material filler and to improve the properties by reinforcing rigid inorganic materials to the polymers. In doing so, the mechanism and the effects of filler concentration on the properties of the composite have been also studied.

Thermoplastics such as polypropylene (PP) and polyethylene (PE) have found widespread applications in diverse areas such as households, automotive and electrical industries. These polymers derive their usefulness and versatility from their inherent toughness, chemical resistance, and good mechanical and electrical properties. Recently, interests in rigid particle-strengthened thermoplastics have been developed. Moreover, the study of certain rigid fillers such as alumina, glass, zircon, and certain silicates have made an impressive impact on the study of some other minerals in the range of the same Moh’s hardness, natural Silica sand is the best example of such particulate filler.

Different mineral particulate fillers have been used so far by many researchers (e.g., talc, mica, clay, calcite, alumina trihydrate, dolomite, silica, calcium carbonate, wood, glass etc.). Natural sand as the name implies is found naturally and the most abundant material in the earth’s crust consists of silica as the predominant component. In addition to its applications in rubber tire and coatings, natural silica sand can be used as stiffening filler. Its hardness and heat resistance capacity makes it to be an important material for further investigation as filler in different polymer materials to improve the properties of the polymer matrix.

1.2.3 OBJECTIVES

The main objectives of this research are:

(a) To study the effect of reinforcing natural silica sand and natural beach sand on the thermoplastic polymers polypropylene (PP) and high density polyethylene (HDPE) by focusing on:

- Mechanical properties (tensile and flexural properties)
- Mixing properties (mixing time and torque)
- Rheology and thermal properties
- Interfacial interaction between filler and matrix (microstructure)

(b) To compare the properties of the composite with the corresponding pure thermoplastic polymer.

(c) To compare the properties of composites containing chemically treated filler with the one containing untreated filler material.

1.2.4 SCOPE OF RESEARCH

The study is focused on the properties of natural sand composites and on two semi-crystalline non-polar HDPE and PP matrix. It involves the preparation of micro sized natural sand powder and the characterization of particles and the composites, particularly the mechanical properties of the composite.

The effect of crushing and drying temperature on the particles, mechanical properties (tensile and flexural) of the composite has been investigated based on three filler compositions (0-15wt %). Maximum mixing torque of the composites, thermal properties such as melting and crystallization temperature, as well as rheology of the composites were also investigated.

Chemical Treatments on particulate filler with silane coupling agents were performed to improve the filler-matrix interaction. The effect of treatment on the mechanical properties of the composite was analyzed and compared with the untreated filler matrix composite. Morphology of the fractured surface of the composites from tensile test was also examined to study the micro structure of filler-matrix interaction.

Note that, this research work is limited to a maximum filler content of 15wt% in laboratory scale equipments. Industrially, it is possible to go up to maximum filler content of 30wt% where the end product could be used in construction industry as rural corrugated roofs and exterior walls. Based on this particular work, the composite could be used to replace the pure polymer in high stiffness requiring application.

1.3 STRUCTURE OF THE THESIS

In this thesis the mechanical properties of a reinforced mineral composite is described. The influence of Malaysian natural silica sand on the properties of semi-crystalline high density polyethylene and polypropylene are investigated. A general overview of the theories behind composite materials, types of interfacial bonding, compounding mechanisms, mineral fillers and their effect is given in chapter 2.

Chapter 3 includes the detailed experimental method, materials used, composite preparation and filler characterization. It also includes melt flow characteristics of the composite or rheology, mechanical properties, morphological studies and thermal properties.

In chapter 4 the analysis of the results obtained during the experimentation are presented. The results of the composition and structure of the natural sand analyzed using XRF and XRD and tensile and flexural properties of the composites using UTM are presented. Morphology of the fractures surfaces from tensile test was also studied by means of Scanning Electron Microscope (SEM). This chapter also contains the required mixing torque in an internal mixer during the composite preparation and the rheological properties of the composite using capillary rheometer. Thermal properties of the composite from the analysis of Differential Scanning Calorimetry (DSC) are also given.

Finally, in chapter 5 general conclusion and suggestions for continuation of this research are given.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 INTRODUCTION

Every single thing that has ever been made has been constructed from some material or another. There are many thousands of different engineering materials available today but they can be placed into one or other of the following categories: metals, polymers, ceramics & inorganic glasses and composites. Each of the main categories has different characteristics and these days there is an increasing emphasis on combining materials from different material categories, or even different materials within each category, in such a way as to achieve properties and performance that are unique. Such materials are called composites.

A composite can be different things, depending on the level of definition we use. In the most basic sense, all materials except elements are composites. For instance, a combination of two elements like an alloy can be considered as a composite on an atomic scale. In terms of microstructure, which is larger than the atomic scale, composites are composed of crystals, phases and compounds, for example steel. On the other hand when we consider macro scale structure, we will find materials composed of fibers, matrices, and particulates. Considering only the latter case, composites are defined as materials made of two or more different materials in such a way that the out coming material will have a property that is not possible to attain by any of the constituent materials or a material brought about by combining materials differing in composition or form on a macro-scale for the purpose of obtaining specific characteristics and properties.

Even though there are different types of composite materials, generally, this paper is concerned about polymer-composite; specifically polymer-inorganic particulate filler composite. Here, as the name implies the polymer composite is so called because the major constituent (bulk) of the material is polymer and called matrix. The other constituent is a structural component also called reinforcement or filler. The reinforcements and the matrix are usually very distinct types of materials with widely different properties [15]. Depending on the constituent contained in them, polymer composite materials can be broadly classified into two as polymer-inorganic filler composites and polymer-organic filler composites. Further classification by the type of filler gives us fiber reinforced composites and particulate reinforced composites. Figure 2.1 shows the classification of composite materials.

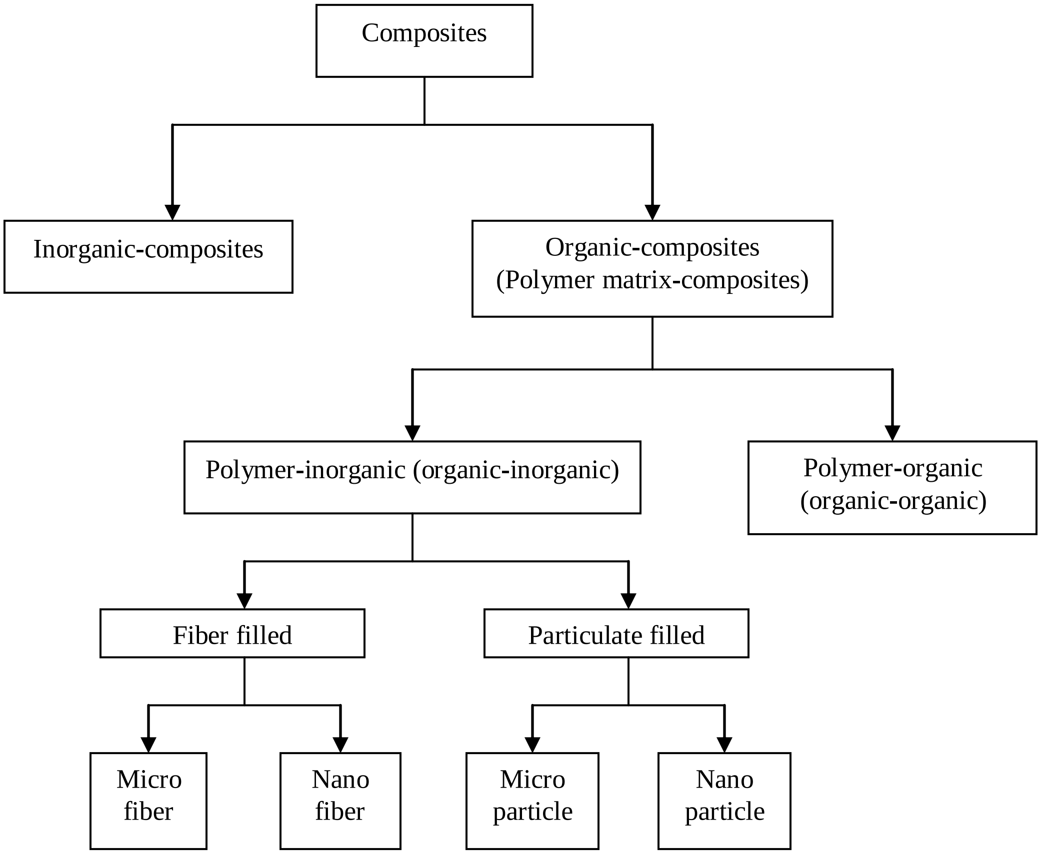

Figure 2.1 Classification of composite materials

There are many reasons for using composite materials instead of homogeneous polymers. Some of these reasons are listed below.

1. Increased in stiffness, strength, and dimensional stability
2. Increased in toughness or impact strength
3. Increased heat distortion temperature
4. Increased mechanical damping
5. Reduced permeability to gases and liquids
6. Modified electrical properties
7. Reduced cost

It is hardly possible to get all the advantages listed above in a single composite. The most important consideration is the composite material could offer a balance against undesirable properties, which includes complex rheological behavior and difficult fabrication techniques as well as reduction in some physical and mechanical properties.

All polymers contain some form of additives ranging from small fractions of catalyst residue to large-scale incorporation of mineral filler. The most important additives are those introduced for some specific purpose and would therefore include fillers, plasticizers, colorants, reinforcing fibers, blowing agents, stabilizers, flame retardants, processing aids, and final group of miscellaneous additives. Sometimes, because of low specific gravities, the strength-to-weight ratio and the modulus-to-weight ratio, and also fatigue strength-to-weight ratio, these materials are superior to those of metallic materials [16].

This study focused on additives that are incorporated in a semi crystalline polymer as a filler to toughen, stiffen and improve the mechanical properties. Description of fillers and their effect on a polymer matrix is presented in the following part.

2.2 FILLERS

Many researchers relate the mechanical, thermal, rheological and physical properties of a polymer composite to the interfacial bonding [17, 18, 19]. The interactions at the filler-matrix interface can be classified into three types: a) interactions due to intermolecular forces between the two phases, b) chemical bonding, and c) physical bonding or mechanical interlocking [20]. The interaction due to intermolecular forces between the filler surface and polymer matrix is a simple case of intermolecular interaction. These forces include dispersion force (van der Waals), hydrogen bonding; dipole –dipole and dipole-induces dipole forces. The degree of intermolecular interaction can be determined by controlling the surface properties of filler particles through either heat or chemical treatment. Then the polymer composites are prepared from these well-designed filler surfaces. The mechanical properties of these polymer composites are related with the strength of interfacial interaction. On the other hand, the effects of the interfacial bonding on the mechanical properties of polymer composites are dependent on the characteristics of the materials and environmental test conditions. Volume or weight fraction of fillers and filler surface area can be considered as an example of materials property. Temperature, humidity and so on are examples of testing conditions.

2.3 EFFECT OF FILLER PARTICLES IN A POLYMER MATRIX

The incorporation of filler particles in a polymer matrix can be used to improve the properties of a polymer matrix [21]. It can benefit the polymer matrix in one or more of the following:
(a) improve the modulus of elasticity, (b) reduce coefficient of thermal expansion, (c) improve heat resistance, (d) higher creep resistance, (e) lower permeability behavior of gases and liquids, (f) increase mechanical strength, (g) improve rheological properties, (h) improve electrical properties, (i) improve flame retardancy, (j) improve wear resistance, (k) modified damping properties, (l) lower curing shrinkage and (m) lower material cost. However most of the above mentioned properties are strongly dependent upon the interfacial bonding strength [22, 23].

2.4 MINERAL FILLERS

A mineral is a naturally occurring material formed through geological processes that has a characteristics chemical composition, a highly ordered atomic structure and specific physical properties. Almost all minerals can be used as filler but their effect in composite depending on their corresponding property. These minerals range from a pure element to very complex silicates with thousands of known forms. Generally, a mineral can be identified or characterized by several physical properties or a more complex chemical or X-ray analysis [24].

2.5 CHARACTERIZING MINERAL FILLERS

Properties of the mineral particle were studied using two X-ray analyzers, XRD and XRF. X-rays are short wavelength form of electromagnetic radiation. This was discovered by Wilhelm Röntgen in 1895. X-ray based techniques are used for many purposes; in medical, in the theoretical physics and in the field of material characterization. Today, the technology has advanced to a high degree of sophistication.

Since every crystalline material subjected to this radiation (in XRD) has its own characteristic diffractive pattern, the crystal structure of the unit cell can easily be identified. In the case of XRF, because the relationship between emission wavelength and atomic number is known, isolation of individual characteristic lines allows the unique identification of an element and elemental concentrations can be estimated from the intensities of those lines. Thus, this technique (XRF) is a means of material characterization in terms of chemical composition.

2.5.1 X-RAY DIFFRACTION

All crystalline materials consist of atoms or molecules arranged in a pattern to make the smallest repeating unit known as unit cell which is identical in orientation and composition. When crystalline materials are subjected to a monochromatic beam of light, they exhibit some degree of regular order and under certain experimental conditions; this order will give rise to an X-ray diffraction pattern. The X-ray pattern is characteristic of material from which it was derived, because each unique compound is made up of a similarly unique combination and arrangement of atoms. X-ray diffraction pattern thus can be used to characterize materials.

X-ray patterns are recorded with an almost monochromatic X-ray source and each diffraction peak angle corresponds to one or more d-spacing [25]. Bragg's law (Equation 2.1) is used to convert each observed peak maximum measured in degrees 2θ to d-spacing.

$$\lambda = \left(\frac{2d}{n'}\right)\sin\theta \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.1)$$

Where n' is order of reflection

d is imaginary inter planar space .

λ is wave length

θ angle of incidence

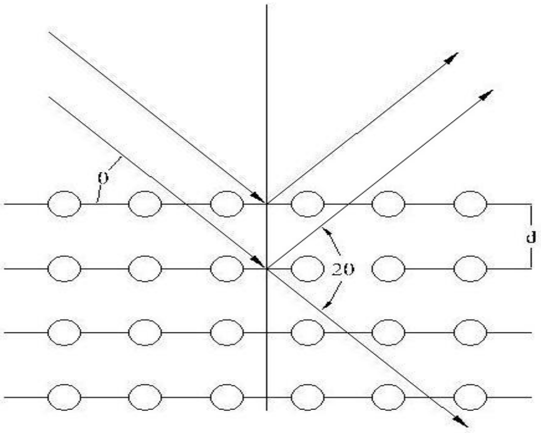

Figure 2.2 Illustration of Brag's law [25]

In addition to determination of crystal structure, X-ray diffraction has variety of other applications. Figure 2.3 shows the use of X-ray diffractometry at non-ambient temperatures. If attachments are provided to the standard diffractometer, it can allow measurements at temperature from ambient up to about 2000 ^{0}C, or down to the temperature of liquid nitrogen [26]. This type of systems allow to study phase transformation of a material in a three dimensional intensity versus 2θ and/or temperature diagrams.

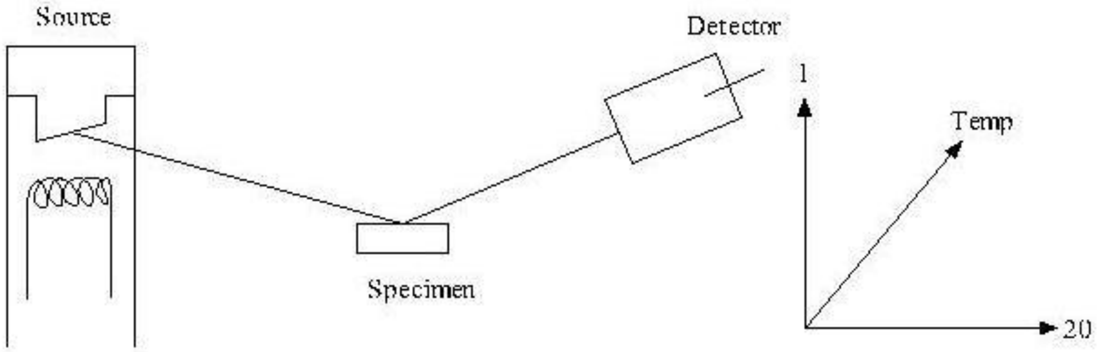

Figure 2.3 Schematic diagram of XRD at non-ambient temperature

Other applications of high temperature diffraction include the study of thermal expansion, crystallization, thermal decomposition, solid state addition and replacement reactions, ore and mineral analysis, determination of air born particles, various thin film applications, study of catalysts, analysis of cement etc.

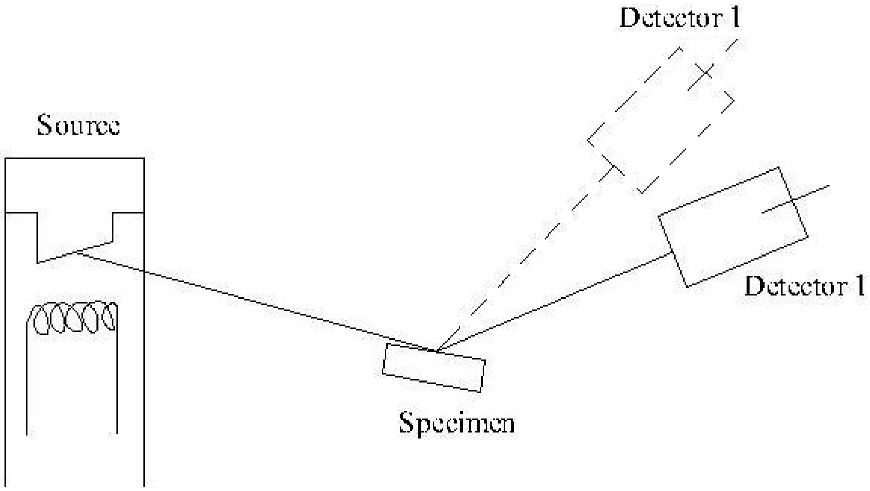

Figure 2.4 Stress measurement using XRD

Another important use of X-ray diffraction is in measuring stress when a metal bar is subjected to stress (tension, bending or compression) Figure 2.4. This is due to the deformation of unit cell crystal structure, which produces different diffraction line profile compared to the pure unstressed sample unit cell crystal structure. Two measurements, one in the Bragg's position and one slightly away from Bragg's will be taken for the unstressed sample to calculate the individual principal stress.

2.5.2 X-RAY FLUORESCENCE

X-ray fluorescence spectrometry provides a means of identification of an element, by measurement of its characteristic X-ray emission wavelength or energy. The method allows the qualification of a given element by first measuring the emitted characteristic line intensity and then relating this intensity to elemental concentration. The first use of X-ray fluorescence spectrometric method was in 1912 by Henry Moseley and he established a relationship between the wave length λ of the characteristic X-ray photon and the atomic number Z of the exited element by the following equation [26].

$$\frac{1}{\lambda} = K[Z - \sigma]^2 \quad \text{..........} \quad (2.2)$$

And $E = \frac{1.24}{\lambda}$ .... (2.3)

Where

K - A constant that takes different values for each spectral series.

σ - The shielding constant that has a value of just less than unity.

E - Energy in KeV (kinetic energy acquired by an electron losing one volt of potential).

λ - Wave length in nm (nano-meter)

FEATURES OF XRD AND XRF

Like any other analytical techniques, both X-ray diffraction and X-ray fluorescence have their advantage and disadvantages. The features of XRD and XRF are given in table 2.1.

Table 2.1 Features of XRD and XRF [26]

Features	X-ray fluorescence	X-ray diffraction
Range	Z>5	All Ordered Materials
Speed	Sec. to min.	Min. to hours
Precision	0.1%	0.25%
Accuracy	0.1 to 1.0%	0.5 to 5%
Sensitivity	Low part per million(ppm)	0.1 to 2 %

In terms of the range of application, X-ray fluorescence analysis allows the quantification of all elements in the periodic table from carbon ($Z = 6$) and upwards. Accuracies of a few tenths of one percent are possible and elements are detectable, in most cases, to the low ppm level. X-ray diffractometry is applicable to any ordered (crystalline) material and, although much less accurate or sensitive than the fluorescence method, is almost unique in its ability to differentiate phases. The techniques differ widely in terms of speed of analysis. The modern multichannel fluorescence spectrometer is able to produce data from 20 to 30 elements in less than one minute. An energy dispersive spectrometry, or even a relatively simple wavelength dispersive spectrometer, is able to perform a full qualitative analysis on unknown sample in less than 30 minutes. The diffraction technique, on the other hand, can take as much as an order of magnitude longer. Even with the most sophisticated computer control powder diffractometers available today, diffraction techniques are still time consuming.

A similar difference also exists in the sensitivities of the two methods. In terms of precision and accuracy, the spectrometry method out performs the diffraction technique again, perhaps by as much as an order of magnitude. The diffraction technique is, at best, a rather insensitive, slow technique, giving somewhat poor quantitative accuracy. On the other hand, it will be realized that the information given by the X-ray diffraction method is unique and no other technique is able to provide such a data.

2.5.3 PHYSICAL PROPERTIES OF FILLERS

Classifying minerals can range from simple to very difficult. A mineral can be identified by several physical properties, some of them being sufficient for full identification without equivocation. The physical properties of minerals include hardness, luster, color, specific gravity etc. Table 2.2 shows the classification of minerals according to hardness in a Moh's scale. The scale is relative and it ranges from 1 to 10.

Table 2.2 Moh's scale of minerals [24]

Moh's scale	Example	Moh's scale	Example
1	Talc [$Mg_3Si_4O_{10}(OH)_2$]	6	Orthoclase [$KAlSi_3O_8$]
2	Gypsum [$CaSO_4 \cdot 2H_2O$]	7	Quartz [SiO_2]
3	Calcite [$CaCO_3$]	8	Topaz [$Al_2SiO_4(OH,F)_2$]
4	Fluorite [$CaFl_2$]	9	Corundum [Al_2O_3]
5	Apatite [$Ca_5(PO_4)_3(OH,Cl,F)$]	10	Diamond [C] (pure carbon in a cubic crystalline form)

2.5.4 CHEMICAL PROPERTIES OF FILLERS

Though there are currently 4,000 known minerals found in nature, only 100 are called "common" and 50 are "occasional" and the rest are "rare" to "extreme rare". When identification of these minerals by their physical properties becomes difficult, their chemical properties become more helpful. Here are some examples of class of minerals by their chemical composition.

a) Silicates: - e.g. feldspar, quartz, olivine, pyroxene, amphiboles, garnets and mica etc.
b) Carbonates:- e.g. nitrate and borate minerals
c) Sulfates: - e.g. calcium sulfate, barium sulfate, gypsum etc.
d) Halides:- e.g. hematite, magnetite, chromites etc
e) Sulfides: - e.g. iron sulfide, lead sulfide etc.
f) Phosphates: - e.g. apatite, arsenate, antimonite etc.
g) Elements: - e.g. gold, silver, copper etc.
h) Organics: - e.g. whewellite, moolooite, mellite, fichtelite, carpathite etc.

Although there are many minerals as mentioned above, only few have been tried as filler in composite making to increase the mechanical, thermal and/or physical property of the matrix. Among all classes, silicate, carbonate, phosphate and sulfate minerals are the most known types of mineral fillers in composites. Like all other types of fillers, mineral fillers also have their own properties that make them important reinforcing materials for different applications. Talc, a silicate mineral with Moh’s hardness of 1, is used as reinforcing filler in polypropylene and high density polyethylene matrix for automotive and aerospace applications [27]. Calcite, a carbonate mineral with Moh’s hardness of 3, has been used as reinforcing filler in polymers for coating, impact and many other applications [28]. Apatite, a phosphate mineral with Moh’s hardness of 5, is used as a reinforcing material in high density polyethylene as analogue material for bone replacement [29]. In this work, the Malaysian natural silica sand is use as a reinforcing material to improve the mechanical properties of polypropylene and high density polyethylene.

2.6 SILICA

Silica is the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth’s crust. In spite of its simple chemical formula, SiO_2, silica exists in many different forms. Silica is found commonly in the crystalline state but occurs also in an amorphous state resulting from weathering or plankton fossilization. Silica exists in ten different crystalline forms or polymorphs, quartz being by far the most common. It is hard, chemically inert and has a high melting point because of the strength of the bonds between the atoms. These are prized qualities in various industrial uses. The industry mainly uses the crystallite forms of silica, i.e. quartz and crystobalite.

Quartz is the second most common mineral on the earth's surface and it is found in almost every type of rock, i.e. igneous, metamorphic and sedimentary. Since it is so abundant, quartz is present in nearly all-mining operations. It occurs in the host rock, in the ore being mined, as well as in the soil and surface materials above the bedrock, which are called the overburden [24]. Quartz is usually a colorless or white but it can have different color based on the impurities in it. Even a small percentage of impurities in quartz can greatly affect the properties of its composite if they are active enough. Iron can be given as an example of impurity that affects corrosion resistance of the composite when the amount is beyond a certain limit. Depending on how the silica sand was formed, quartz grains may be sharp and angular or rounded however after a mechanical crushing process all the silica particles will have angular shape.

For usage as filler, crystalline silica and crystobalite in their finest form are used as reinforcing filler because of their resistance against abrasive actions and chemical attack. Moreover, silica fillers improve tint retention, durability, and resistance to dirt, mildew, cracking and weathering in architectural paints. In marine and maintenance coatings, the durability of silica imparts excellent abrasion and corrosion resistance [30][1].

In addition to the natural silica, synthetic silica like fumed silica made of thermal process and precipitated silica made of wet process are used as fillers. The following reactions show the process of fumed and precipitated silica formation respectively.

Fumed silica [31]:

$Si + 4HCl\,(g) \rightarrow SiCl_4 + 2H_2$

$2H_2 + 2O \rightarrow 2H_2O$

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[1] The reader can read more on the major applications of silica and other related mineral fillers

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

Precipitated silica [31]:

$3SiO_2 + Na_2CO_3 \rightarrow 3SiO_2.Na_2O + CO_2$

$(SiO_2. Na_2O)_{aq} + H^+SO_4^- \rightarrow SiO_2 + Na_2SO_4 + H_2O$

Another form of silica that can be produced artificially from the naturally existing silica sand is known as the silica gel. The chemical reaction and the block diagram of the process is shown in Figure 2.5.

Silica gel:

$12NaCl + 8NH_3 + 6CO_3 + 3O_2 \rightarrow 6Na_2CO_3 + 12HCl + 4N_2 + 6H_2O$

$SiO_2 + Na_2CO_3 \rightarrow Na_2O.SiO_2 + CO_2$

$Na_2O.SiO_2 + H_2SO_4 \rightarrow SiO_2 + H_2O + Na_2SO_4$

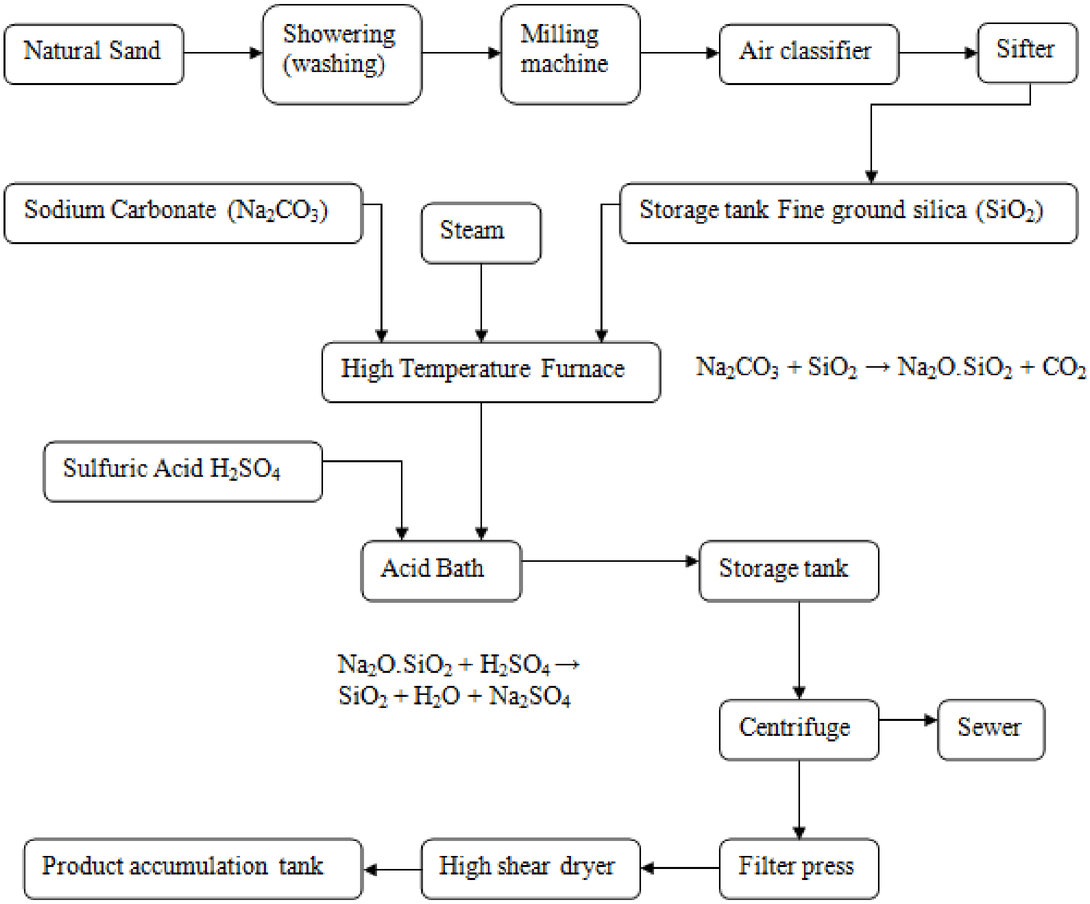


Figure 2.5 A block diagram of Silica gel processing

2.7 REINFORCEMENT-POLYMER MATRIX INTERFACE

The interface in reinforced polymer matrix composite plays an important role in transferring the load applied on the matrix to the reinforcement and vice versa. Therefore, the reinforcement filler must have a strong bonding with the polymer matrix, if high strength and stiffness are desired on the composite. On the contrary, a weak interface results in low stiffness and strength. Interface also has a critical impact on the fracture behavior of composites. Generally, a weak interface results in low stiffness and strength, but high resistance to fracture whereas strong interface produces high strength and stiffness but often low resistance to fracture (brittle behavior).

Interface greatly depends on many factors such as the type of polymer matrix and reinforcement. It can be considered as a thin film or region with only a few atoms in thickness across, in which there is a change in properties from the polymer matrix to the reinforcement. Thus, the interface is usually a discontinuity in chemical, crystal and molecular structure, physical, mechanical and other properties. Because of the discontinuity in properties, further study to improve interfacial bonding has been a focus of many science and engineering researchers since 1960s [32]. Among the factors affecting interface, wettability is considered as crucial.

2.8 WETTABILITY

In studying interface between reinforcement and polymer matrix, an intimate contact between the two surfaces is an important phenomenon to be considered. Thus, for a better interfacial bond to occur the wettability of the reinforcement by the polymer matrix is the crucial criteria. Wettability defines the extent to which a liquid will spread over a solid surface. Covering every bump and dip of the rough surface of the reinforcement and displacing the air will produce good wettability. Another way of defining wettability of a liquid is the contact angle between droplets of the liquid in thermal equilibrium on a horizontal surface. Depending on the type of surface and liquid, the droplet may take a variety of shapes as shown in Figure 2.6. The wetting angle θ is given by the angle between the interface of the droplet and the horizontal surface. The liquid is seemed nonwetting when $90^o < \theta < 180^o$ and wetting when $0^o < \theta < 90^o$. If $\theta = 0$ or 180^o then we call it a perfect wettability and the droplet will spread forming a film on the surface.

Figure 2.6 A liquid droplet in equilibrium with a horizontal surface surrounded by a gas. The angle θ defines the wettability of the liquid. a) Nonwetting fluid b) a wetting fluid

In general, it is the behavior and property of the interface that generally control the properties of a composite [33]. Thus, it is important to study the type of interfacial bond that exist in the interface.

2.9 INTERFACIAL BONDING

Since the interface of a composite is the most critical part of a reinforced composite that determines the property of the composite, an intensive investigation on this part must be undertaken. Once the matrix has wet the reinforcement, therefore in intimate contact with it, bonding will occur. For a given system more than one bonding mechanisms may be operative at the same time. Four different types of bonding mechanisms are discussed in the following sub-sections.

2.9.1 MECHANICAL BONDING

A mechanical interlocking or keying of two surfaces can lead to a reasonable bond. Rough interfaces do have a better mechanical interlocking than any other surfaces. Figure 2.7 shows a typical mechanical bonding between filler and matrix.

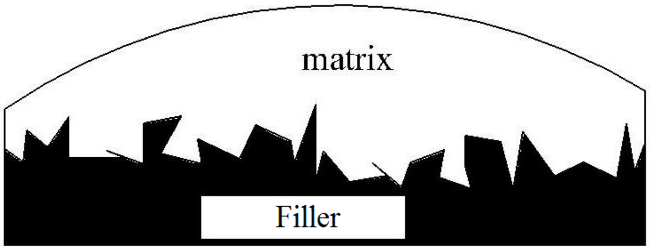


Figure 2.7 Mechanical Bonding

2.9.2 ELECTROSTATIC BONDING

Electrostatic bonding is the bonding due to the difference in charge on the surface of filler and matrix that leads to an electrostatic attraction between the components of the composite. This type of bonding is effective only in a small distance and a short range electrostatic interaction. Figure 2.8 illustrates a typical electrostatic bonding between filler and matrix.

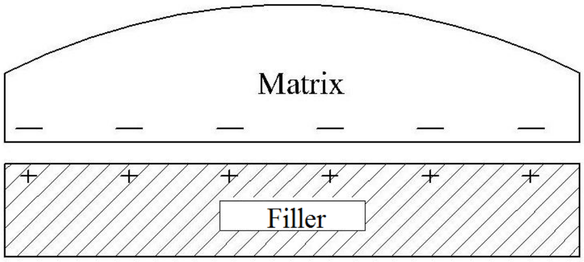


Figure 2.8 Electrostatic bonding

2.9.3 CHEMICAL BONDING

Figure 2.9 shows a typical chemical bonding between filler and matrix. Chemical bonding is the strongest of all interfacial bonding between the reinforcement and polymer matrix which greatly depends on the type and number of bonds. When the chemical groups of the matrix (Y) and that of the substrate on its surface (X) are compatible, a chemical bonding will occur. The interaction of hydroxyl groups on the surface of filler and hydrophilic matrix can be considered as an example of a chemical bonding.

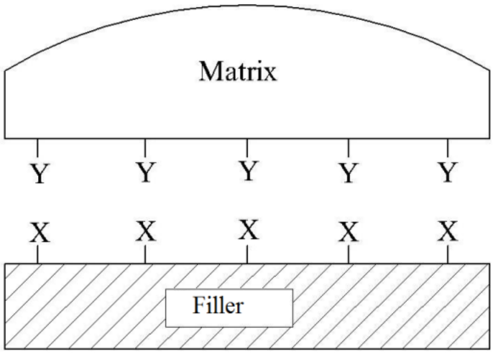


Figure 2.9 Chemical bonding

2.9.4 INTERDIFFUSION BONDING

Interdiffusion of atoms or molecules of two components of a composite at the interface produce a reaction or Interdiffusion bond. Figure 2.10 shows intertwining of molecules among the components of a composite at the interface. The bond strength of this kind of interaction depends on the distance between the molecules which have been entwined and the extent of entanglement. Moreover the number of molecules per unit area of interface affects the strength of the bond. Thus, the higher the number of molecules per unit area of interface the stronger the bond will be.

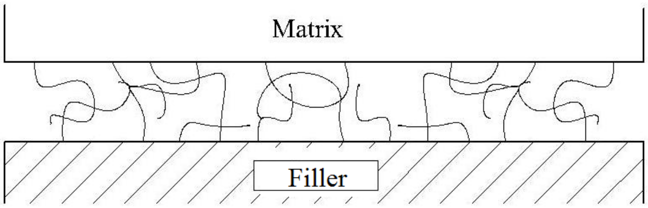


Figure 2.10 Reaction or Interdiffusion bonding

2.10 THE BASICS OF RESINS

The word resin or matrix can be used interchangeably to represent a class of materials called polymers. Polymers are long chain of organic molecules with carbon atom as their back bone. Their chain length determines the characteristics properties such as weight and mechanical properties. Generally as the length of the chain gets larger, the weight increases and improves the mechanical properties such as tensile strength and toughness. This is due to the result of inter-chain forces, including entanglements of chains. Therefore, the entanglement of nearby polymer chains is a key characteristic in determining the nature of polymeric materials. Both polymer molecular weight and crystallinity affect stiffness of the polymer chain. As the chain stiffened, both mechanical and thermal properties increase [34].

Based on its molecular structure, a polymer can be related to its response to mechanical forces at elevated temperature. Thus according to behavior of the polymer with rising temperature, polymers can be classified as thermoplastic and thermosetting. Thermoplastic polymers soften when heated (and eventually liquefy) and harden when cooled, processes that are totally reversible and may be repeated. On the other hand, thermosetting polymers are network polymers, become permanently hard during their formation and do not soften upon heating. Thus, heating this type of polymer may cause degradation. In this particular study, thermoplastic polymers are used as resin and are presented in detail in the succeeding section.

2.11 THERMOPLASTICS RESINS AND PROPERTIES

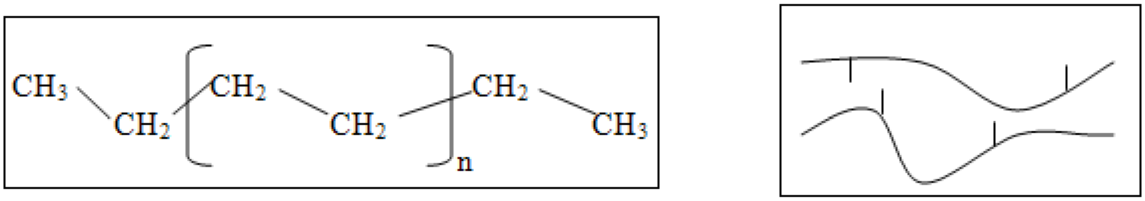
The resin in a particulate reinforced composite plays an important role in transferring the imposed loads to the filler, so it must have a good bond with the reinforcing agents. It is also responsible for providing the shape to the finished product. Thus it must be readily formable, and must retain that shape and mechanical properties throughout the temperature range of use. Moreover, in order to protect the reinforcing agents from environmental damage, the resin should have sufficient toughness [34]. In this study, the thermoplastics High density polyethylene and polypropylene are used as a composite matrix and the properties of both matrices are discussed below.

2.11.1 CHEMICAL STRUCTURE

As it was mentioned in section 2.10, characteristics of a polymer highly depends on its chemical structure. Generally, the structure of the chain determines the polymers chain stiffness that directly affects its mechanical and thermal properties. The chemical structure and general characteristics of the polymers used for this study are given in the subsequent sub-sections.

2.11.1[a] HIGH DENSITY POLYETHYLENE

HDPE is one of the semi crystalline thermoplastic polymer in the polyethylene main group with a general chemical formula $C_{2n}H_{4n+2}$. The general chemical structure of polyethylene is shown in Figure 2.11. Where, n is the degree of polymerization (the number of ethylene monomers polymerized from the chain) and ranges from 100 to 250,000 with their molecular weight ranging from 1400 to more than 3,500,000.



(a) (b)

Figure 2.11 a) Chemical structure of pure PE b) Schematic diagram of HDPE chain

Depending on the defects on the carbon back bone, the polymer PE can be divided into many divisions. Branches and other defects on the regular chain structure limit the crystallinity level. Therefore, chains with fewer defects are more crystalline than others with more defects, and as the crystallinity of the polymer increases the density also increases. Generally, the higher the concentration branches in a polymer chain, the lower the density. Chemically HDPE is close in structure to pure PE with a density ranging from 0.94 – 0.97g/cm^3. HDPE is sometimes known as linear polyethylene (LPE) because of its very low level of branching. See Figure 2.11(b).

Semi crystalline polymers are those that consist of two or more solid phase, in at least one of which molecular chain segments are organized into a regular three dimensional array, and in one or more other phases chains are disordered. In a solid phase PE, there are three phases. These are: a) submicroscopic crystals (crystallites) b) non crystalline phase surrounding the crystallite and comprising a partially ordered layer adjacent to the crystallites and c) disordered material in the intervening space.

Figure 2.12 shows a crystal unit cell of HDPE. The unit cell of most non polymeric compounds contains an integral number of complete molecules. In contrast, polymeric unit cells contain short segments from one or more molecular chains. Generally, PE exhibits three different types of units cells namely, orthorhombic, monoclinic and hexagonal. The type shown in Figure 2.12 is an orthorhombic unit cell of HDPE with a complete ethylene unit from one chain segment and four other from surrounding chain segments for a total of two ethylene per unit cell.

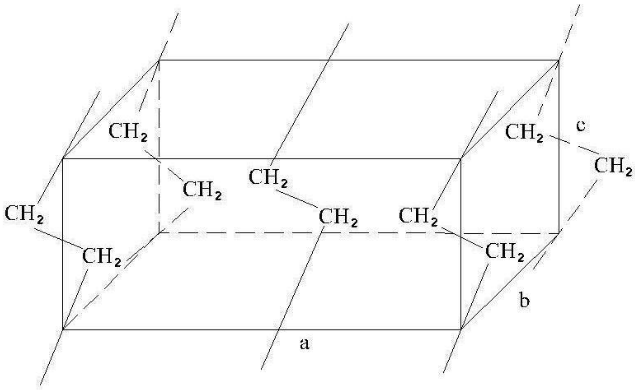


Figure 2.12 HDPE orthorhombic unit cell[2]

2.11.1[b] POLYPROPYLENE

Another semi crystalline polymer with special characteristics to accept many kinds of filler is polypropylene. Currently, it accounts for the largest consumption of PP monomers followed by acrylonitrile, oxo chemicals and propylene oxides. Other competitive plastics in the commodity markets are polystyrene (PS) and polyvinyl chloride (PVC), in addition to HDPE.

PP is a two phase system consisting of crystalline and non crystalline region where the small crystalline part is embedded in the non crystalline region, which adds flexibility and promotes ease of processing below the melting temperature. It is produced by polymerizing propylene molecules, which are the monomer units. There are two forms of PP. One is produced by catalysts that produce crystallizable polymer chains and the other one is produced in a much lower amount as a byproduct of the semi crystalline PP, which is soft and sticky and used in adhesives and sealants. These two products are often referred to as ‘isotactic’ (crystallizable) PP

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[2] The C-axis is always along the chain direction

(i-PP) and ‘atactic’ (noncrystallizable) PP (a-PP), respectively. The chemical structure of PP is shown in the Figure 2.13, where n is the degree of polymerization.

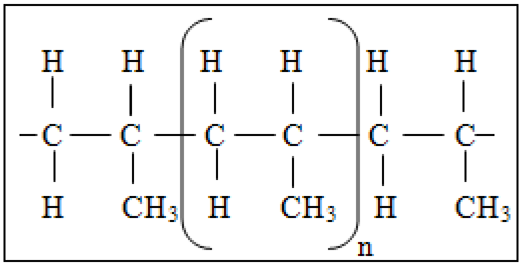


Figure 2.13 Chemical structure of PP

Though there are different types of PP depending on the chemical structure, commercially the different types of PP are known by their thermal property specifically by their melt flow rate (MFR). MFR is an indicator of the weight-average molecular weight as measured by the ASTM D1238 or ISO1133 MFR test method. This helps to determine how easily the melted raw material will flow during processing. Higher MFR PPs fill the plastic mold more easily during the injection or blow moulding production process. As the melt flow increases, however, some physical properties, like impact strength, will decrease.

Generally there are three types of PP, homopolymer polypropylene (HPP), random copolymer (RCP) and impact copolymer (ICP). In this thesis the term PP refers to HPP, containing only pure propylene monomer in the crystalline solid form. Both RCP and ICP are copolymers of ethylene and PP with a percentage of 1-8% and 45-65% ethylene content in RCP and ICP, respectively.

2.11.2 MECHANICAL PROPERTIES

The mechanical properties of resins used for matrix material in reinforced composites must consider the effect of the reinforcement material. Properties of the composite material such as tensile strength and flexural strength are greatly affected by the reinforcing material, and many other factors such as chemical treatment and testing conditions. Therefore, the reinforcing material dominates the mechanical properties of resin composite.

2.11.3 THERMAL PROPERTIES

As the temperature of the composite is increased, more and more energy is imparted to the polymer, thus causing molecular motion. At lower temperatures, the motion is largely vibrational, which is relatively unrestricted. When temperatures become higher, the molecules gain sufficient energy to flex and rotate, and at even higher temperatures they begin to translate. In highly crystalline polymers, the crystal lattice energies are strong resulting in tightly held molecules with very little rotation and almost no translation until the imposed energy is sufficient enough to overcome the lattice energies. This phenomenon is called the crystalline melting point (T_c) for the polymer. In totally amorphous polymers there is no crystalline structure and therefore, no crystal lattice energy. The transition from solid to melt is more gradual with only small indications of the increased mobility of the molecules. The temperature at which this transition occurs is called the glass transition temperature, T_g, for the polymer. The T_g, T_c, melting temperature T_m, and the heat distortion temperature, HDT, the maximum use temperature for the polymer for continuous service, define general thermal characteristics of a given polymer [34, 35].

2.12 COMPOSITE PROCESSING

The process of converting a polymer into its products involves the application of temperature, pressure, shear and other type of mechanical manipulation is referred to as polymer processing. Many types of polymer processes are in use for the manufacturing of polymer matrix based composites. Each process is designed based on the desired end product. Though there are more than twenty major types of polymer processes, not all processes are suitable for thermoplastic processing and not all thermoplastic processes are suitable for reinforced thermoplastic composite production. The following are some of the polymer matrix composite processes which are currently in use: Extrusion (single and twin screw), internal mixer, injection moulding, compression moulding, rotational moulding, blow moulding etc. But the most widely used polymer processes are extrusion and injection moulding [36]. This is because both are suitable for mass production in a short period of time.

Polymer processing involving the production of composites with fillers or reinforcements incorporated in the pure polymer matrix is known as composite processing. The processing of particulate reinforced composites based on thermoplastic polymer matrix involves compounding the small particles and matrix at the matrix melting point in an internal mixer or extruder followed by product shaping in a compression or injection moulding. As is apparent, fillers and reinforcements increase the difficulty of polymer processing as the percentage of filler increases. Therefore, there is a limitation in the amount of reinforcement that can be added to reinforced polymer matrix composite.

2.12.1 MIXING OR COMPOUNDING

Polymer materials are processed through different operations to get the desired end product. Some of the elementary operations involved in a polymer process are handling of particulate solids, melting, pressurizing and pumping, mixing and devolatilization. Among the above mentioned processes, mixing is one of the main elementary polymer processing operations, which is crucial in obtaining high quality products, especially in composite production.

As a simple definition, mixture is a combination of two or more different substances. Therefore, mixing is the rearrangement of components of a mixture to improve the homogeneity of the mixture. There are a number of different mixing operations that occur in polymer processing. When the materials to be mixed are all in solid state, the mixing typically involves particulate solids. This type of mixing is technically called solid-solid mixing. When a polymer has to be mixed with particulate solid filler and both the polymer and filler are in powder form, substantial mixing can take place with the use of solid-solid mixing.

Another type of mixing that is in use in polymer processing is the mixing of two or more polymers. When polymers are mixed in the molten state, the process is referred to as liquid-liquid mixing. The remainder of the mixing then is accomplished by melting the polymer and or filler mix to achieve complete wetting of the filler by the polymer [36]. Here the mixing of the molten polymer with the solid filler is referred to as solid-liquid mixing or solid-liquid compounding. In a typical mixing process, properties of the resulting composite mixture are affected by the mechanism of mixing. Using the same composition but different mixing mechanisms will give different properties of the same material.

There are a number of ways of classifying mixers but one of the best ways to classify them is whether the mixer is batch mixer or a continuous mixer. Batch mixers can be particulate solid mixers or liquid mixers whereas continuous mixers are those mixers with one or many mixing screws or rotors. In this study, internal mixer and twin screw extruder were used for compounding the melted polymer matrix with silica sand filler.

2.12.1[a] INTERNAL MIXER

Internal mixer is one of the mechanisms used in polymer processing technology. Originally it was developed by Thomas Hancock around 1830 with a single rotor inside the mixing chamber for compounding. Then the twin rotor internal mixer was introduced around 1880 by Werner and Pfleider GmbH. An internal mixer can accept large clumps of feed stock that made the method more popular in rubber industry. It can also handle sticky and blocky materials without much trouble.

Figure 2.14 show the schematic diagram of a cross sectional view of typical internal mixer. In the mixing process, the mixture of granulated polymer and filler material fed through the chute into the chamber where the three thermocouple temperatures are adjusted for a specified operation. The polymer started to melt inside the chamber while it is being mixed by the twin rotating rotors. The mixing action of the internal mixer is concentrated in the narrow gaps between rotor and the housing. In these regions, high rates of shearing and elongation occur, resulting in intensive mixing action. The rotor speed, mixing time and the thermocouples temperature can be adjusted by the software which is connected to the machine.

The sequence of ingredients addition is a key to good mixing in internal mixers. A normal mixing process involves loading the polymer and one half of the filler, followed by mixing until the material softens. Then the remaining filler will be added and continue mixing until fully incorporated.

Here are some advantages of the batch internal mixer:

1) It accepts feed stock in various forms.
2) It has intensive mixing action.
3) It has a well defined residence time.
4) Quick material change can be made and
5) A wide range of mixing procedures can be used.

On the other hand, batch internal mixer has a self wiping problem and batch-to-batch variations can affect product quality unless totally cleaned.

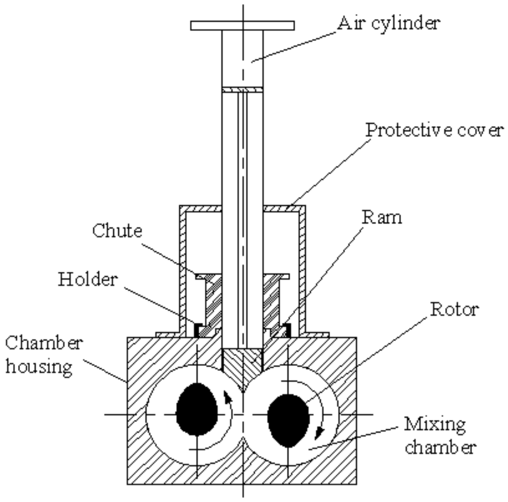


Figure 2.14 Schematic diagram of a typical internal mixer

2.12.1[b] EXTRUDER

Extrusion is a means of producing continuous linear products in steady state fusion. Both single and twin screw extruders are used in mixing or compounding polymer matrix reinforced composite. Extruders are classified by their screw length to diameter ratio, L/D. For a twin screw extruder, L/D ratio range from 12:1 to 30:1. Figure 2.15 shows a schematic diagram of a typical twin screw extruder used in this work. The process is generally characterized by four sequential segments [37], solid conveying, melting, melt pumping and extruding.

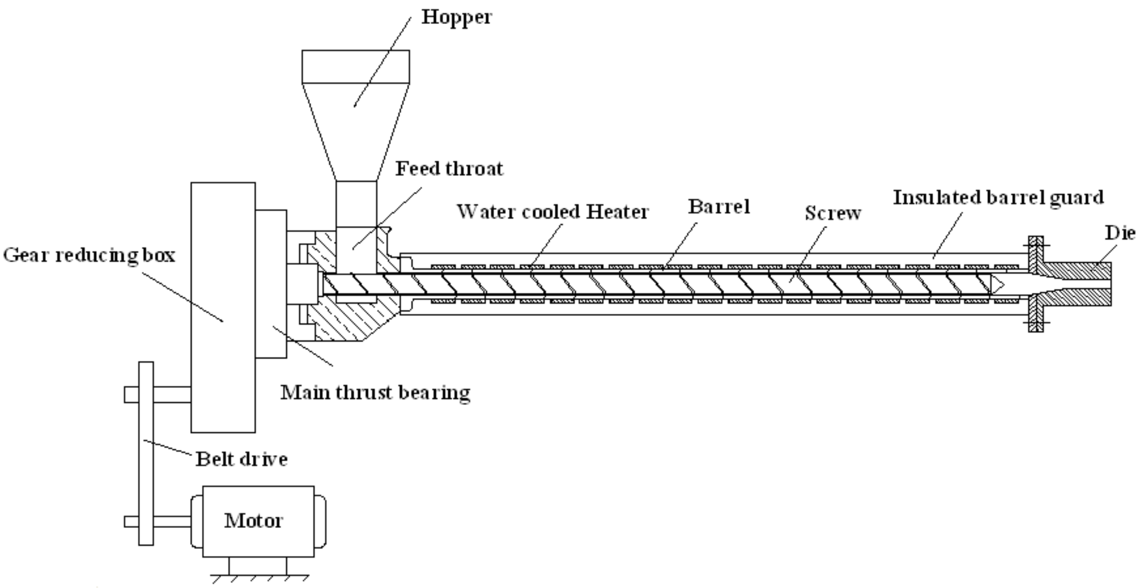


Figure2.15 Schematic diagram of a typical twin screw extruder machine

Granulated polymer and reinforcement fillers are fed to the machine through the hopper and shear force between the screws, and the screws and barrel breaks the agglomerated particles for a uniform compounding. The polymer gets melted by a water cooled heater covering the screw as it is conveyed along the screw. The water cooled heaters are adjusted at different temperature zones for a particular compounding process. The melt polymer becomes a viscous fluid at its melting temperature and the rotational motion of the screw conveys the melt mixture to the die, where the desired shape is obtained.

2.12.2 INJECTION MOULDING

Injection moulding is one of the most widely used polymer processing method in which a complex structural features can be produced with more effective way and in a short period of time. Moreover, the process can be used for mass production and it is a more suitable method for almost all thermoplastic polymers and their composites. A typical schematic diagram of injection moulding is shown in Figure 2.16.

Pellet from extrusion or granulated polymer is fed into the hopper of injection machine, which is then subjected to heating until it melts as it is conveyed by a single screw inside the barrel. This time the melted polymer accumulates in front of the screw and the screw (not rotating) pushes the melt forward into the closed mold cavity. When the mold is completely filled, the screw remains stationary for some time to keep the plastic in the mold under pressure and to prevent back flow of the melt from the mold cavity. It will also inject additional melt into the mold to compensate the decrease in volume due to cooling. After the material in the mold has cooled sufficiently to hold its shape, the mold opens and the product is ejected from the mold, and then close again for the next cycle. The barrel temperatures, pressure and screw speed are the controlling parameters for a particular injection operation [38, 39].

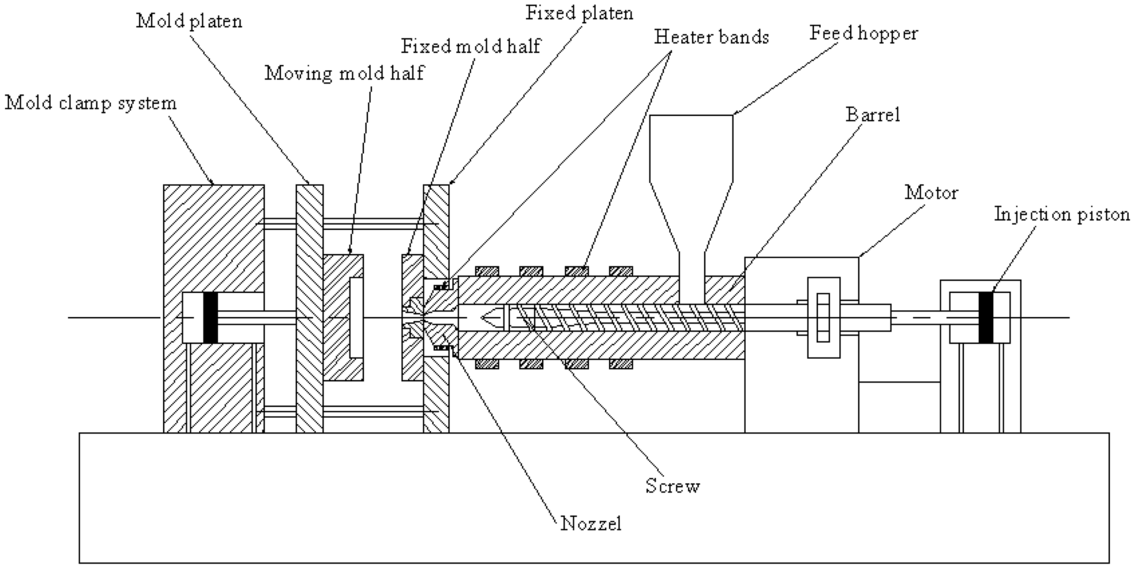


Figure 2.16 Schematic diagram of a typical injection moulding machine

2.13 PARTICLE REINFORCED COMPOSITES

A polymer composite reinforced by a small particles in the range of micro to nano scale are known as particulate filled composites. In these materials the particulate fillers are used as the polymer matrix property modifier and often are in the form of powder. In developing a particulate filled composite, some considerations of the filler concerning its chemical, physical, thermal properties as well as cost should be taken into account.

The cost of any filler should be less than the cost of the pure polymer matrix in order to be economically feasible. Generally, more rare particulate filler is more expensive than common fillers.

Chemistry, composition and impurity: - the chemical nature of a particulate mineral filler has little direct importance to its use in composites, but it plays significant roles in determining the structure of the mineral and the nature of interaction between the polymer and the filler itself. On the other hand for a few fillers, the chemical reactivity of fillers plays a very important role in the properties of a composite. Therefore, we can divide the fillers into two types as reactive such as aluminum hydroxide and inert fillers such as kaolin, mica, talc and quartz. Another important factor to consider in particulate filled composite is impurity of the filler which greatly affect the properties of a composite. Thus, chemically active impurities in small concentration have higher effect on the properties of a composite than chemically nonreactive impurities with higher concentration.

Density is determined by the size of the atoms forming the mineral, the closeness with which they are packed together and by impurities present inside the crystal lattice; the heavier the atoms and the more tightly they are packed together, the higher the density is. All in all, the specific gravity of particulate additives can range from less than one for a hollow glass beads to over six for some metallic fillers. Composites for a light weight application have fillers of low density for example, fly ash.

Hardness is the resistance of a material for scratching and it is measured in a Moh’s hardness scale. Soft mineral fillers such as talc readily delaminate due to weak structural features. Such a soft mineral particles can fracture or cleave when polymer composites are deformed, thus limiting their reinforcing properties.

The main thermal properties of a filler material are specific heat, thermal conductivity and coefficient of thermal expansion. Some mineral filler have low thermal conductivity therefore their composite can be used for insulation purpose. Others have the capacity to be used as fire retardant. Moreover, identifying the thermal property of the filler will help to determine the method of composite process. Thus thermal properties of filler should be considered in development of a particulate filled composite.

Particle shape and size are the most dominant properties of filler that affect powder flow, compounding behavior, composite behavior, mechanical, thermal and optical properties of a composite. In addition, most of the present mathematical models of a particulate filled composite considers a spherical and flake shapes, though these types of particles are rare in the real world.

Spherical shape is an ideal shape for a particle to attain maximum surface area, which determines the interface characteristics. On the other hand, the size of the particle also affects the surface area of filler particles. The smaller the size of a particle is the higher the surface area, which directly affects the properties of particulate filled composite.

2.14 SURFACE TREATMENT

Surface modification of particulate filler improves the properties of a polymer composite and because of this, the science and engineering of surface modification receives enormous attention over the last few decades. However, it is difficult to obtain a fairly uniform distribution of particles in a particulate filled composite by using a conventional mixing process (melt mixing, in situ polymerization or solution blending). This is due to the strong filler-filler interaction which will produce two different kinds of particle collections, agglomerates (collection of particles with weak filler-filler interaction or bond) and aggregates (collection of particles with strong filler-filler interaction or bond).

2.14.1 CHEMICAL TREATMENT

Now a days, different kinds of chemical treatment are in use to modify the surface of filler particles for a better dispersion and therefore, for improved properties. The choice of using a particular chemical modifier depends on the polymer and filler to be used. The most widely used modifiers are organo-silanes and organo-titanates; but other types such as organo-zirconates, organo-borates etc. can also be applied.

2.14.1[a] ORGANO-SILANE

As was mentioned earlier in section 2.4, the interface between filler and polymer matrix greatly affects the properties of composites; and organo-silanes are the most commonly used and commercially available chemicals used in providing an improved surface interactions. Though many in numbers, the general formula for an organo-silane is given by:

X_n - Si - $(RY)_{4-n}$ ………………………………………………..........................….. (2.4)

Where X- Hydrolyzable group

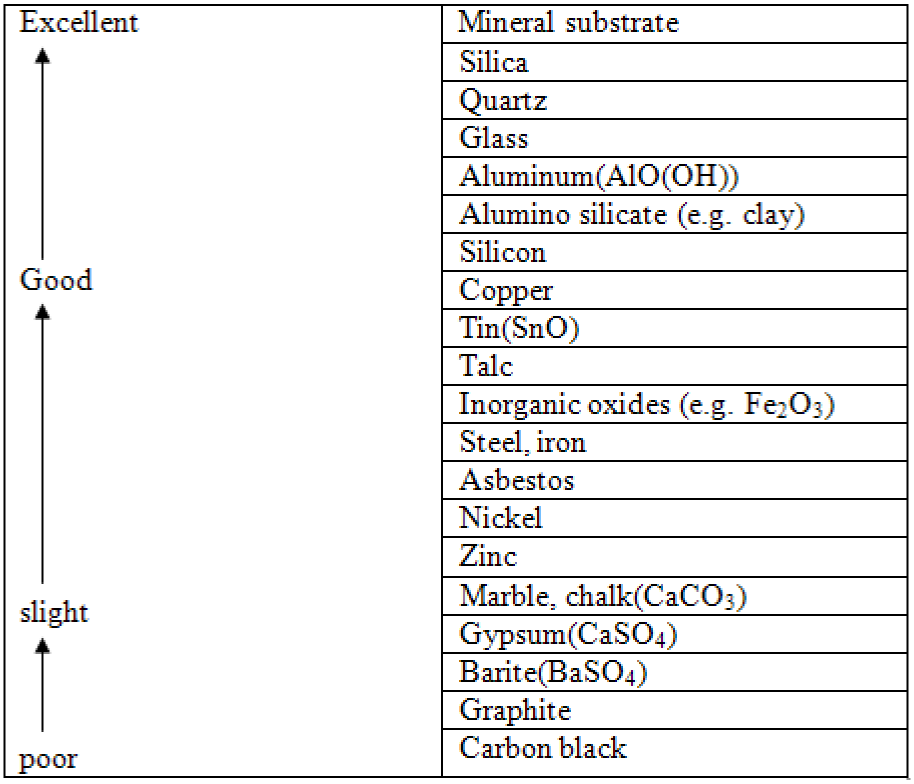
Y- Organofunctional group

R- Hydrocarbon spacer group (linker) and n = 1 to 3

2.14.1[b] SILANE COUPLING AGENTS

Silane coupling agents (SCA) are one of the organo-silicone compounds with the general formula given in equation 2.4 when n = 3. SCA are generally considered to be adhesion promoters between inorganic mineral fillers and organic matrix resins and as such provide improved mechanical strength and chemical resistance to the composite [32]. They rely on reaction with surface hydroxyls to produce a stable layer; therefore, they are more effective in mineral fillers with high concentrations of reactive hydroxyls. Minerals such as silica, silicates like glass, oxides and hydroxides are most receptive. On the other hand, silanes have little effect on carbon black and not effective on surfaces such as sulfates and carbonates. Table 2.3 summarized the effectiveness of silane on different mineral surfaces.

Table 2.3 silane effectiveness on inorganic minerals [40]



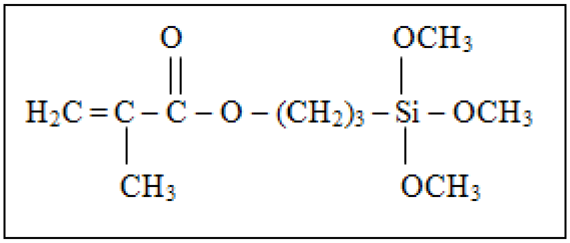
Excellent	Mineral substrate
	Silica
	Quartz
	Glass
	Aluminum(AlO(OH))
	Alumino silicate (e.g. clay)
	Silicon
Good	Copper
	Tin(SnO)
	Talc
	Inorganic oxides (e.g. Fe_2O_3)
	Steel, iron
	Asbestos
	Nickel
	Zinc
slight	Marble, chalk($CaCO_3$)
	Gypsum($CaSO_4$)
	Barite($BaSO_4$)
	Graphite
poor	Carbon black

Based on Table 2.3, it is clear that natural sand having silica quartz as the dominant constituent is excellent silane effective inorganic mineral filler. Hydrolysis of the hydrolysable group in the silane coupling agents produces reaction on the hydroxyl surfaces of the natural sand powder. On the other hand, the organofunctional groups of the silane coupling agent form covalent bond with the matrix. Therefore, a silane coupling agent will act as an interface between an inorganic substrate and organic material (matrix) to bond or couple the two dissimilar materials. Besides the chemical bonding at the interface, it can also polymerize and form a polymer network on a filler surface. This modifies the interface region by forming interpenetrating network, which strengthens the organic and inorganic boundary layers.

This type of chemical treatment is commercially available and is widely used in surface treatment methods for inorganic substrates. Generally, there are many SCA depending on the functional group (amino, sulfur, Epoxy, methacryl, chloro, vinyl functional silane, etc.). The two silanes MTS and VTES were used in this work.

As their name implies, γ-methacryloxypropyltrimethoxysilane (MTS) and vinyltriethoxysilane (VTES) are from the methacryl and vinyl-functional silane, respectively; used as adhesion promoter at organic/inorganic interfaces, as surface modifier and as a coupling agent to improve bonding between filler or reinforcement and resins.

γ-methacryloxypropyltrimethoxysilane (MTS)

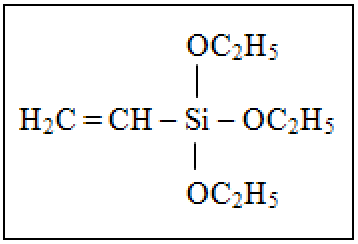


$$H_2C=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{||}}{C}-O-(CH_2)_3-\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{Si}}-OCH_3$$

Figure 2.17 Chemical structure of MTS

MTS: – soluble in methanol, ethanol, isopropanol, acetone, benzene, Toluene and xylene.

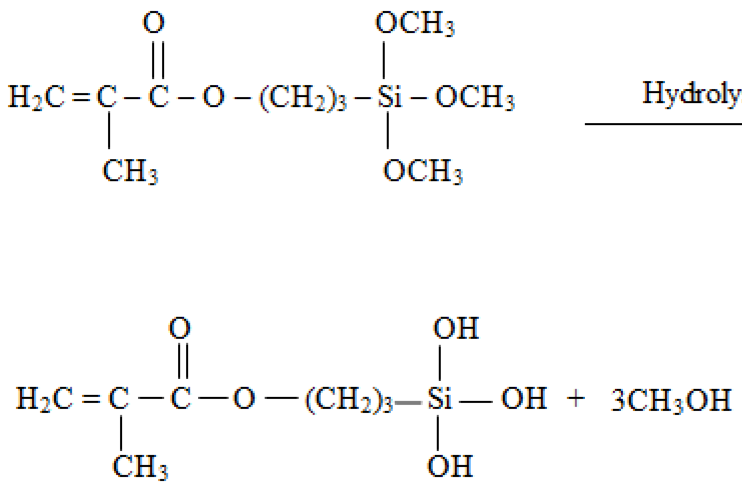
Vinyltriethoxysilane (VTES)



$$H_2C=CH-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OC_2H_5$$

Figure 2.18 Chemical structure of VTES

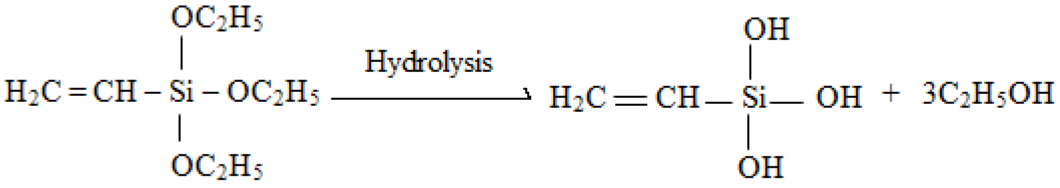
The hydrolysis reactions of MTS and VTES in silane treatment are presented in Equations 2.5 and 2.6 respectively. In the presence of moisture, hydrolysis of the hydrolysable group of the silane leads to formation of silanol.



$$H_2C=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_3-\underset{\displaystyle OCH_3}{\underset{|}{\overset{\displaystyle OCH_3}{\overset{|}{Si}}}}-OCH_3 \xrightarrow{\text{Hydrolysis}}$$

$$H_2C=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{Si}}}}-OH + 3CH_3OH$$

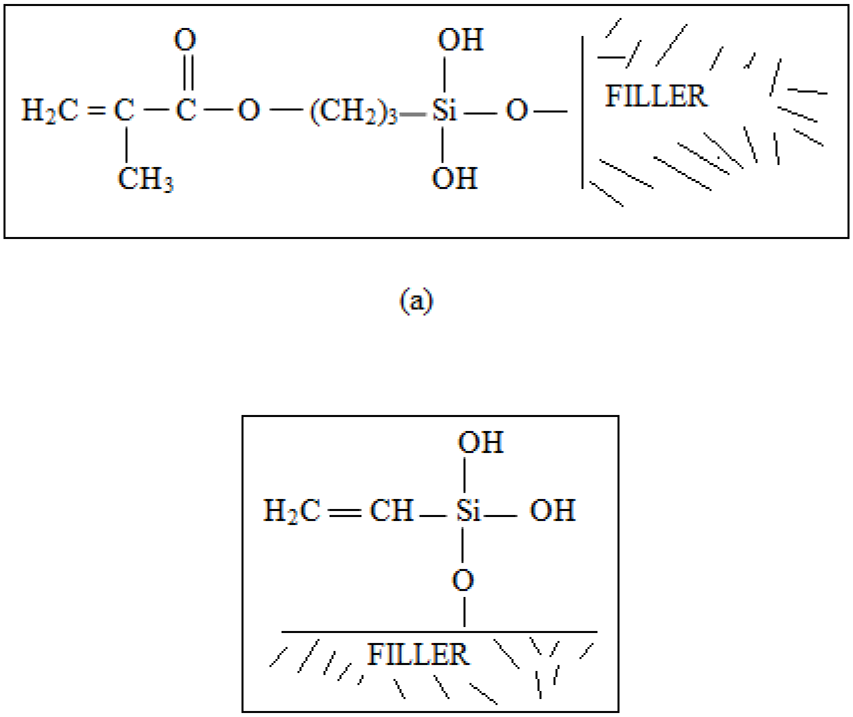
………………... (2.5)



$$H_2C=CH-\underset{\displaystyle OC_2H_5}{\underset{|}{\overset{\displaystyle OC_2H_5}{\overset{|}{Si}}}}-OC_2H_5 \xrightarrow{\text{Hydrolysis}} H_2C=CH-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{Si}}}}-OH + 3C_2H_5OH$$

…… (2.6)

Silanol then react with inorganic filler forming siloxane bond as shown in the Figure 2.19.



(a)

(b)

Figure 2.19 Reaction of hydrolyzed silane with substrate surface (a) MTS (b) VTES

2.15 EFFECT OF ADDITION OF MINERAL FILLERS ON THE MECHANICAL PROPERTIES OF POLYMER COMPOSITES

Since almost all materials are subjected to some kind of stress, it is critical to study their mechanical behavior. In this research work a particular focus is given to the tensile and flexural properties of the composites. Tensile test data are analyzed from the load versus displacement curve using the following equations.

$$\sigma_t = \frac{F}{W \times T} \quad \text{.........} \quad (2.7)$$

$$\sigma_y = \frac{F_{\max}}{W \times T} \qquad (2.8)$$

Where σ_t - tensile strength [MPa], σ_y - tensile strength at yield [MPa], F - the load applied on the specimen [N], $F_{\max}$ -maximum load recorded [N], W - width of the specimen [mm] and T - thickness of specimen [mm]

Strain (ε) is given by

$$\varepsilon = \frac{\Delta l}{l_0} \qquad (2.9)$$

Where Δl - the elongation [mm] and l_0 - the original gauge length [mm]

Tensile modulus of elasticity E_t [MPa] can be determined by extending the initial linear portion of load-elongation curve and dividing the difference in stress obtained from any segment of section on this straight line $\Delta\sigma_t$ [MPa] by the corresponding difference in strain $\Delta\varepsilon$.

$$E_t = \frac{\Delta\sigma_t}{\Delta\varepsilon} \qquad (2.10)$$

And the flexural strength σ_f [MPa] is given by

$$\sigma_f = \frac{3FL_1}{2WT^2} \qquad (2.11)$$

Where L_1 - span length [mm].

The flexural modulus of elasticity E_f [MPa] is determined by Equation 2.12.

$$E_f = \frac{(L_1)^3 m}{4WT^3} \qquad (2.12)$$

Where m - is the slope of the initial straight line portion of load-deflection curve.

Studies on the effect of mineral fillers on the mechanical properties of reinforced composites have been done by many researchers [41 - 45]. It was discovered that the reinforcement enhance the stiffness or rigidity of the resin for almost all mineral particulate reinforced composite without subjecting the minerals to chemical modification.

Ali Gungor [42], studied the influence of Fe powder on the mechanical and physical properties of HDPE by reinforcing three different percentages by volume concentration using a conventional melt mixing process. Fe powder with average particle size of 50µm and 99.75% purity was used as filler. The comparison of physical and mechanical properties of the composite with the unfilled HDPE matrix showed that the yield and tensile strength, percentage elongation, and izod impact of HDPE decreased with increasing filler content. On the other hand, the addition of Fe powder increased the modulus of elasticity, hardness, vicat softening, melt flow index (MFI), and heat deflection temperature (HDT) of HDPE.

B.M. Sole and A. Ball [41], investigated the effect of mineral fillers talc, $CaCO_3$, $BaSO_4$, and fly ash on the mechanical properties of a general homopolymer grade PP. A decrease in tensile strength and percentage elongation was observed as the filler content was increased for all types of mineral fillers. Although all the minerals exhibit the same trend of decreasing yield strength with filler content, there were noticeable differences in their individual behavior. Talc filled composite showed a significant increment over the unfilled PP and the same trend was observed on the other three fillers at small filler concentration. However, a large fall in tensile strength was observed with increasing filler content.

2.16 EFFECT OF CHEMICAL TREATMENT ON MECHANICAL PROPERTIES OF POLYMER COMPOSITES

Fillers are incorporated into polymer matrices to reduce cost, modify the physical, mechanical, rheological as well as thermal properties in order to suit for a wide range of applications [21, 45]. The major constituents of these additives are inorganic particulate minerals such as talc, mica, clay, silica, glass beads, ceramics, etc. But, the uniform distribution and surface interaction of these fillers with the polymer matrix greatly determine the effectiveness of the composite, which could be difficult to attain by conventional mixing methods. Therefore, investigations on the surface treatment (chemical treatment) of filler particles are in progress to reduce the problem. Studies on the effect of chemical treatment of particulate fillers on the mechanical properties of polymer composites have been carried out by many researchers [44- 52].

S.F. XAVIER et al. [46 - 48] studied the dependence of mechanical properties of PP composite on fillers, talc, mica, and $CaCO_3$ at various content and surface treatment using silane and titanate. They found that talc has the highest normalized modulus followed by mica and then $CaCO_3$. As the filler content increased, the modulus also increased behaving similar to the untreated composite. For the treatment, silane gave a higher tensile value than titanates.

S. N. Maiti and K. K. Sharma [49] found that the modulus of elasticity of talc filled PP composites increased with increasing filler content and with increasing surface treatment by titanate, while the tensile strength and elongation at break decreased in both cases.

2.17 RHEOLOGICAL PROPERTIES OF MINERAL PARTICULATE FILLED COMPOSITES

A study of the rheological properties of a composite contributes to an understanding of its behavior for processing by determining the viscosity of the melted composite. There are two different mechanisms for determining the rheological properties of a polymer composite, rotary viscometer and capillary rheometer. This particular study used capillary rheometer to study the flow characteristics of the composite. A schematic diagram of a particular capillary rheometer cylinder is shown in Figure 2.20.

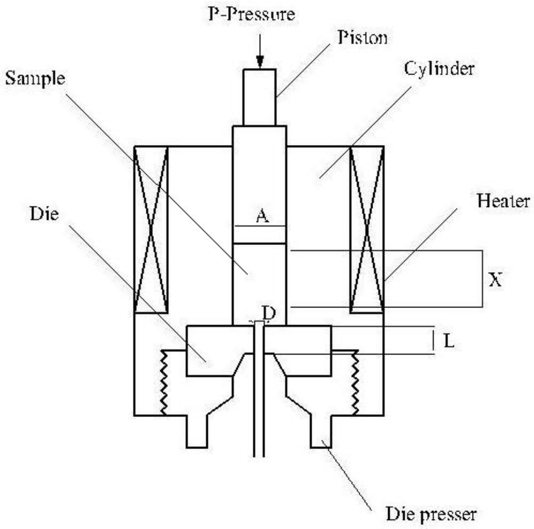


Figure 2.20 Schematic diagram of cylinder unit structure of capillary rheometer

The heater surrounding the cylinder heats and melts the sample inside the cylinder, and the piston with cross sectional area A applies a pressure ΔP on the melt. The melted sample is then extruded through the thin orifice of diameter D of the die of length L. Based on the sample flow rate, the fluidity or the melt viscosity can be obtained. Shear stress (τ), shear rate ($\dot{\gamma}$) and viscosity of the melt (μ) for capillary type of rheometer are given in equations 2.13 to 2.16 respectively.

$$\tau = \frac{\Delta PD}{4 \times L} \quad \text{..........} \quad (2.13)$$

$$\overset{\bullet}{\gamma} = \frac{32Q}{\pi D^3} \quad \text{..........} \quad (2.14)$$

Where Q is volumetric flow rate

For a Newtonian fluid, the slope of shear stress versus shear rate curve produces the viscosity of the flow as in Equation 2.15.

$$\mu = \frac{\tau}{\overset{\bullet}{\gamma}} \quad \text{..........} \quad (2.15)$$

But for a non Newtonian fluid the shear stress is expressed as

$$\tau = m'\left(\overset{\bullet}{\gamma}\right)^n \quad \text{..........} \quad (2.16)$$

Where m' is flow consistency index

m'=μ viscosity for Newtonian fluid

n = flow behavior index

n = 1 Newtonian fluid

n > 1 Dilatant (shear thickening)

n < 1 Psedoplastic (shear thinning)

Many of the researches concerning filled polymer composite have mostly focused on the mechanical properties, while a few reports have been related to rheological behavior of their melts. It is well known that knowledge of the rheology of melt not only gives useful information for material moulding and processing, but also is an important way to characterize the structure and properties of polymer materials [52]. On the other hand, the characteristics of polymer matrix and filler, as well as the interaction of polymer - filler influence the rheological behavior of filled polymer system.

The shear viscosity and shear rate for treated and untreated PS/$CaCO_3$ composites were investigated by Clegg et al. [52]. They found that the shear viscosity of the composite decreased with the shear rate. For a constant shear rate the order of shear viscosity was such that shear viscosity of PS was less than treated PS/$CaCO_3$ composite, which was again less than untreated PS/$CaCO_3$ composite.

CHAPTER 3

EXPERIMENTAL

3.1. MATERIAL

This study is based on experimental investigations. The materials and equipments that have been used for the study are mentioned in the following sub-sections.

3.1.1 NATURAL SAND

The experiments were carried out using two different types of natural sand with a mean size in the range of 0.25 to 2 mm, which can be said medium to very coarse grain size in Wentworth class scale. The two natural sands are named as silica sand (SS) and beach sand (BS) according to the composition and the origin of sample.

3.1.1[a] SILICA SAND

Naturally existing sand is called silica sand or industrial sand if the percentage composition of silica (SiO_2) in the sand is greater than 95% [24]. In this particular research project, sand sample from Tronoh was taken with a size ranging from coarse to very- coarse (diameter of 0.5 to 2 mm).

3.1.1[b] BEACH SAND

As the name implies, this sand is naturally existing beach sand from Lumut. The size of this sample is in the range of medium to coarse in a Wentworth class scale (diameter of 0.25 to 1 mm).

3.1.2 POLYMERS

In this experimental study, the two semi crystalline thermoplastics polymers HDPE and PP are used as a resin. In order to be consistent, both polymers were provided by the same supplier.

3.1.2[a] HIGH DENSITY POLYETHYLENE

The HDPE was provided by Titan Petchem (M) Sdn. Bhd. TITANZEX chemicals having a density of 0.961g/cm^3 and melt flow index of 7g/10min.

3.1.2[b] POLYPROPYLENE

The PP was provided by Titan Petchem (M) Sdn. Bhd. TITANZEX chemicals having a density of 0.950g/cm^3 and melt flow index of 75g/10min.

3.1.3 CHEMICALS

Two chemicals were used for surface modification or surface treatment of the particles. The SCA γ-methacryloxypropyltrimethoxysilane (MTS) and Vinyltriethoxysilane (VTES) from Dow Corning Corporation, acetic acid and ethanol with water were used for the process of surface treatment.

3.2 PARTICLE CHARACTERIZATION

Characterization of particle has been studied using XRD and XRF analysis. Sample was taken to the XRD and XRF machines as a dry powder form and the structure and composition was determined. As mentioned in section 2.10 studying the characteristics of the filler is necessary to determine its chemical composition, chemical reactivity and crystal structure and impurity. In the XRD test, five different batches of the natural sand sample were prepared from the screened powder and have been subjected to gradual heating inside furnace from 200 to 1000^{0}C.

3.3 METHODOLOGY FOR PREPARATION OF COMPOSITES

The composite materials; silica sand reinforced high density polyethylene (HDPE/SS) and silica sand reinforced polypropylene (PP/SS), were prepared according to the steps shown in Figure 3.1 below. The process was started by washing the natural sand sample in pure water to remove all soluble salt and other organic remnants. The wet natural sand was then dried in the oven for 24 hours at 55°C.

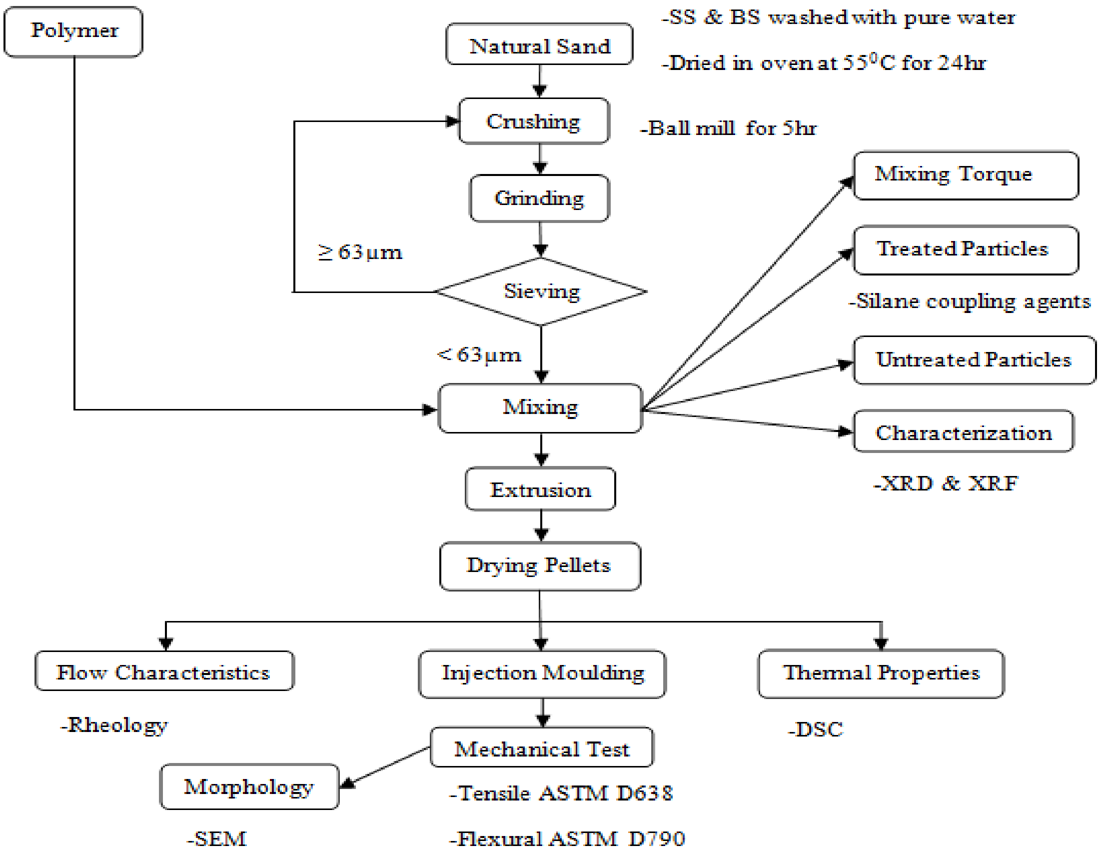


Figure 3.1 Flowchart of composite specimen preparation, and types of characterization methods used

3.3.1 CRUSHING

As the size of the sand is on the range of medium to very coarse, it must be subjected to crushing in order to be used for the composite production as filler. A ball mill with ceramic balls of diameter 9.3 mm was used for the process. Then the characteristic of the sand after mill was studied. It was discovered that an intensive mechanical ball milling for more than 5 hrs will crush the natural sand into fine sand. Further crushing should be done at this stage to reduce the size into a very fine size.

3.3.2 GRINDING

Though crushing in a mechanical ball mill reduces the size of the particles, but as the milling time increases the small particles will start to agglomerate, forming flake like structure that would be difficult in the screening process. A small motor grinding machine plays an important role in bringing the flake into powder. Grinding process was carried out from 1.5 to 3 minutes for each grinding steps.

3.3.3 SIEVING

The sieving process was done in such a way that the different mesh size sieves were ordered one on the top of another in ascending order, with the collecting pan at the bottom and the cover at the top. A shaking machine was fitted with a clamping device to ensure that the nest of sieves was held firmly without over tightening. Over sized particles were collected and returned to crushing and grinding. Standard sieves of mesh size 150 µm, 100 µm and 63 µm were used for the process one on the top of another. Then size distribution of the particle was analyzed by particle size analyzer. Figure 3.2 shows the particle size distribution of natural sand after sieving process.

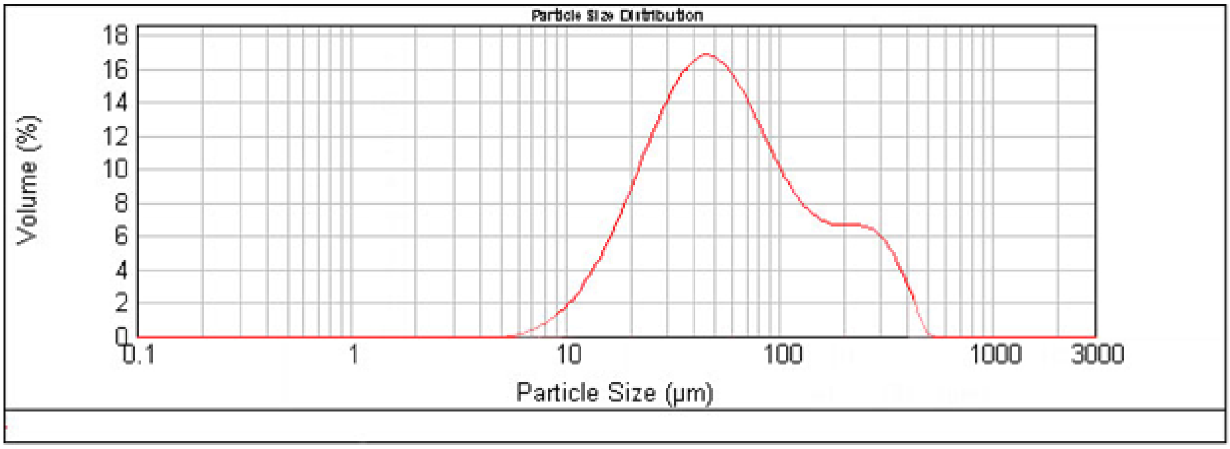


Figure 3.2 Particle size distribution of natural sand after sieving

3.3.4 CHEMICAL TREATMENT

Two batches of the filler were prepared at this point after sieving. One batch was used for untreated filler preparation while the other was for chemically treated filler composite. SCA γ-methacryloxypropyltrimethoxysilane (MTS) and vinyltriethoxysilane (VTES) were used for treating the filler particles. The particle was treated with 1% SCA in ethanol/water solution. Ethanol/water solution was first prepared in a 60/40 proportion and stirred for 10 to 20 minutes before adding the SCA. Then SCA was added to the mixture and mixed together for 1 hour. The pH of the solution was controlled by acetic acid to be in the range of 3-4. After uniformly mixing using a hot plate magnetic mixer, the treated particles were dried in an oven at 60^0C for 24 hour.

3.3.5 MIXING OR COMPOUNDING

A typical polymer process consists of several elementary operations, namely 1) handling of particulate, 2) melting, 3) pressurizing and pumping, 4) mixing and 5) devolatizing. Among all, mixing is the most important step in most polymer processing operations to obtain high-quality products [52].

(i) INTERNAL MIXER

First, the natural sand sample (the filler) without treatment was prepared in three different percentages by weight of the polymer as 5wt%, 10wt% and 15wt%. Each mixture was then mixed by direct melt mixing method using THERMO HAAKE polylab system internal mixer. The mixing temperature and time were set to be 180^{o}C and 15 min respectively at 50 rpm rotor speed. The shear force in the mixing chamber breaks the cohesive force between powder particles of the filler. It was discovered that the mixing torque for all samples attained a constant value approximately after 10 min mixing time.

(ii) EXTRUSION

The mixed material from the internal mixer now becomes a composite but there is an important step (extrusion) to follow in order to produce pellets of the composite for injection moulding. Moreover, extrusion improves the dispersion of fillers in the composite by the shear force developed between the screws. LEISTRITZ Mio27/Gl-32D, GERMANY twin screw extruder with 50 rpm mixing speed was used for this purpose. The extrusion temperature was adjusted at different zones as160 ^{0}C at zone 1 and 2, 170^{0}C from zone 3 to 7 and 180^{0}C at the flange and die. The mixture from the twin extruder was extruded through a 4mm die to water bath, pulled and pelletized. Then the pelletized composite was kept at room temperature for 24 hrs before moving to the injection moulding. At this stage, some of the sample was kept for the flow characterization to determine the rheological properties of the pelletized composite.

3.3.6 FLOW CHARACTERISTICS

As mentioned before in the previous sub section, this test is for flow characterization because of at least two important reasons:

1) Many fabrication techniques for composite involve the flow suspensions of liquids or molten polymers.

2) Most of the theories of moduli of composites have their origin in the theory of viscosity.

Here the viscosity, flow rate and shear rate of the composites have been determined by using capillary rheometer.

3.3.7 RHEOLOGY

In this particular experiment, FLOWMETER CFT-D capillary rheometer was used. Pelletized sample composite from the twin extruder with 0wt%, 5wt%, 10wt% and 15wt% particulate filled composite were used to study the effect of filler content on melt flow characteristics. A constant temperature of 180^{o}C and load of 5N, 10N, 15N, 20N, 25N, 30N, 35N and 40N were used for this purpose. A 0.5 mm diameter with 1 mm length die was used for studying the rheological behaviors of both the chemically treated and untreated composite samples.

3.3.8 INJECTION MOULDING

Specimens for mechanical test were prepared by transferring the pelletized composites into Tat Ming ME20 III injection moulding machine with a screw speed of 50 rpm and the temperatures at different zones set to 110^{o}C, 190^{o}C, and 210^{o}C at zone 1, 2 and 3 respectively. Two different types of specimens one with treated particulate filled composite and another with treated particulate filled composite were prepared according to the standard test specimen size. The samples obtained at the end of these production steps were analyzed and tested according to ASTM Standards [54], focusing on three different aspects in material properties: namely mechanical, thermal, and morphological properties.

3.3.9 MECHANICAL TESTING

The mechanical properties, among all the properties of materials, are often the most important properties because virtually all service conditions and the majority of end-use applications involve some degree of mechanical loading. The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, flexural strength and impact strength. However, the application of mechanical testing was not that much understood and emphasized by designers especially for plastics and their composites. In this study, tensile and flexural properties of the composite were tested on a universal tensile testing machine and are presented as in the following subsections.

(i) TENSILE TESTING

In the tensile testing of any material using universal testing machine, the machine applies tensile load when one end of the test specimen is attached to a movable cross head and the other end to a stationary member. The cross head is then positioned in such a manner as to pull the sample apart. In this particular experiment, standard tensile specimens were prepared according to ASTM D 638 (standard test method for tensile properties of plastics) [54] by using a 5KN LLOYD instruments LTD, SEGENSWORTH FAREHAM, ENGLAND, Universal Tensile Test machine (UTM). The properties, namely tensile strength, tensile modulus and maximum elongation were analyzed at an extension rate (cross head speed) of 5mm/min. All specimens were kept at room temperature for 24 hrs before the test. The tensile specimen may have different shapes but usually made in a dog-bone shape. The dog-bone shape ensures that the sample will break in the center and not in the grip area. The shape and dimensions of the tensile specimen is shown in Figure 3.3 where, the overall length L_O = 190mm, the distance between grips D = 115mm, the width of narrow section W = 10mm and thickness T = 4mm.

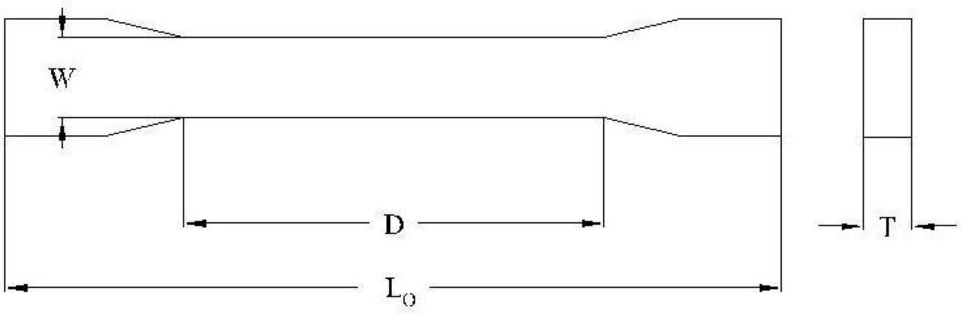


Figure 3.3 Schematic diagram of tensile test specimen, ASTM D638 dimensions

(ii) FLEXURAL TESTING

The main standard referred for this test is ASTM D790-30 [56]. Sample was prepared according to the standard with different filler content similar to those for tensile test namely as 0wt% (pure matrix), 5wt%, 10wt% and 15wt%. The specimens were then kept at room temperature for 24 hrs before the test. The 5KN UTM machine with a cross head speed 2 mm/min was used for this test. Pelletized samples from the twin screw extruder were transferred into the injection moulding to produce flexural samples of dimensions shown in Figure 3.4 where, the overall length L = 120mm, the width W = 10mm and thickness T = 4mm.

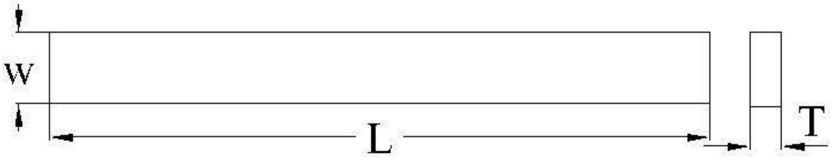


Figure 3.4 Schematic diagram of flexural test specimen, ASTM D790 dimensions

3.3.10 MORPHOLOGY

In order to examine the relationship between the morphological structure and the mechanical behaviour of the samples, fracture surfaces of specimens from tensile test were analyzed by Scanning Electron Microscopy (SEM). Small sliced sample from the fracture surfaces of tensile test specimen were taken and subjected to coating process for about four to five minutes. Coating was necessary because of the non conductive properties of the composite material. All samples were coated with Gold (Au) and Palladium (Pd) with a SPUTTER COATER in vacuum.

3.3.11 THERMAL PROPERTIES

(i) DIFFERENTIAL SCANNING CALORIMETER (DSC)

The thermal properties of the composite, melting temperature T_m, crystalline temperature T_c and enthalpy of transition were analyzed by using DSC. A typical schematic diagram of DSC set up is shown in Figure 3.5.

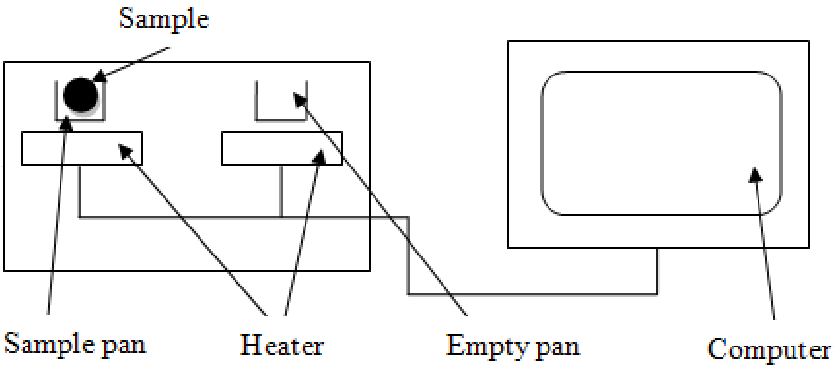


Figure 3.5 Schematic diagram of DSC experimental setup

In DSC, an average temperature circuit measures and controls the temperature of the sample and the reference holders to conform to predetermined time-temperature program. This temperature is plotted on one axis of an x-y recorder. During the experiment, the sample undergoes a thermal transition, the power supply to the two heaters is adjusted to maintain their temperatures, and a signal proportional to the power difference is plotted on the second axis of the recorder. The area under the resulting curve is a direct measure of the heat of transition. The test has been conducted according to the ASTM D 3418 (determination of transition temperatures for plastics) with a sample of 5-10 mg and a heating rate of 10^0C/min.

CHAPTER 4

RESULTS AND DISCUSSION

4. 1 COMPOSITION AND STRUCTURE

4.1.1 X-RAY FLUORESCENCE (XRF)

A sample of powdered natural sand was subjected to XRF test to determine the composition. Table 4.1 shows the compositions of both silica sand (SS) and beach sand (BS).

Table 4.1 Chemical composition of natural sand (SS-silica sand, BS-beach sand)

Compound (element)	Beach Sand		Silica Sand	
	KCps (kilo count/sec.)	%	KCps (kilo count/sec.)	%
SiO_2	823.6	91.30	961	97.40
CaO	147.0	5.940	0.8	0.0228
Al_2O_3	9.80	1.040	1.6	1.60
Fe_2O_3	81.90	0.570	50.8	0.443
K_2O	12.60	0.455	2.4	0.084
MgO	2.40	0.188	-	
Na_2O	0.90	0.178	-	
SO_3	0.80	0.0731	0.7	0.0228
Cr_2O_3	4.20	0.0486	3.9	0.0731
TiO_2	1.10	0.0401	1.4	0.0433
SrO	33.10	0.0302	-	
ZrO_2	34.60	0.0266	34.6	0.0313
Re	-	-	18.2	0.140

In both cases, SS and BS, the composition of silica (SiO_2) is high, 97.4% in SS and 91.3% in BS. As mentioned in chapter 2, section 2.9, a small amount of active impurity in filler affects the property of the composite. Therefore, based on the result on Table 4.1, SS has got less amount of impurity with higher percentage composition of silica than BS.

4.1.2 X-RAY DIFFRACTION (XRD)

The characteristics of the natural sand were studied by subjecting the powder for different milling time and heating it at different temperature. X-rays are usually obtained by bombarding a material target with a beam of high-voltage electrons inside a vacuum tube. Choice of the material target and the applied voltage determines the output wavelength. X-rays of a given wavelength are diffracted only for certain orientations of the sample. If the structures are arranged in an orderly array or lattice, the interference effects with structures are sharpened. The information obtained from scattering at wide angles describes the spatial arrangements of the atoms, while low angle X-ray scattering is useful in detecting larger periodicities. The XRD curves for different milling time and heating temperature are given in Figure 4.1, 4.2 and Appendix B.

From the Figure 4.1 and 4.2 it can be observed that maximum intensity was recorded around $2\theta = 27^0$, hexagonal structure with unit cell dimensional parameters:

Lattice constants: - a = b= 4.91410, c = 5.40600

Inter axial angles: - $\alpha = \beta = 90^0$, $\gamma = 120^0$

Then XRD analysis was taken for samples of silica sand heated at 200°C, 400°C, 600°C and 800°C and results are given in Appendix B. Even though there are slight changes in the maximum intensity about $2\theta = 27^0$, the samples revealed the same unit cell structure.

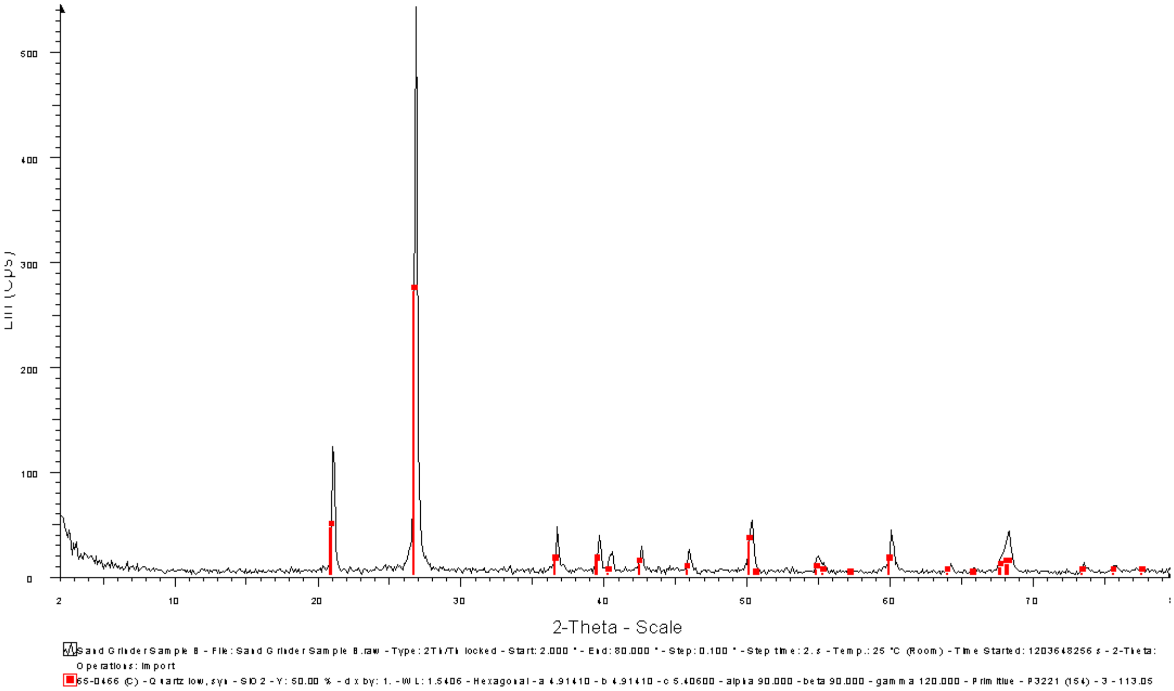


Figure 4.1 XRD curve for silica sand with 5 hrs ball mill and 15-20 min grinding before screening.

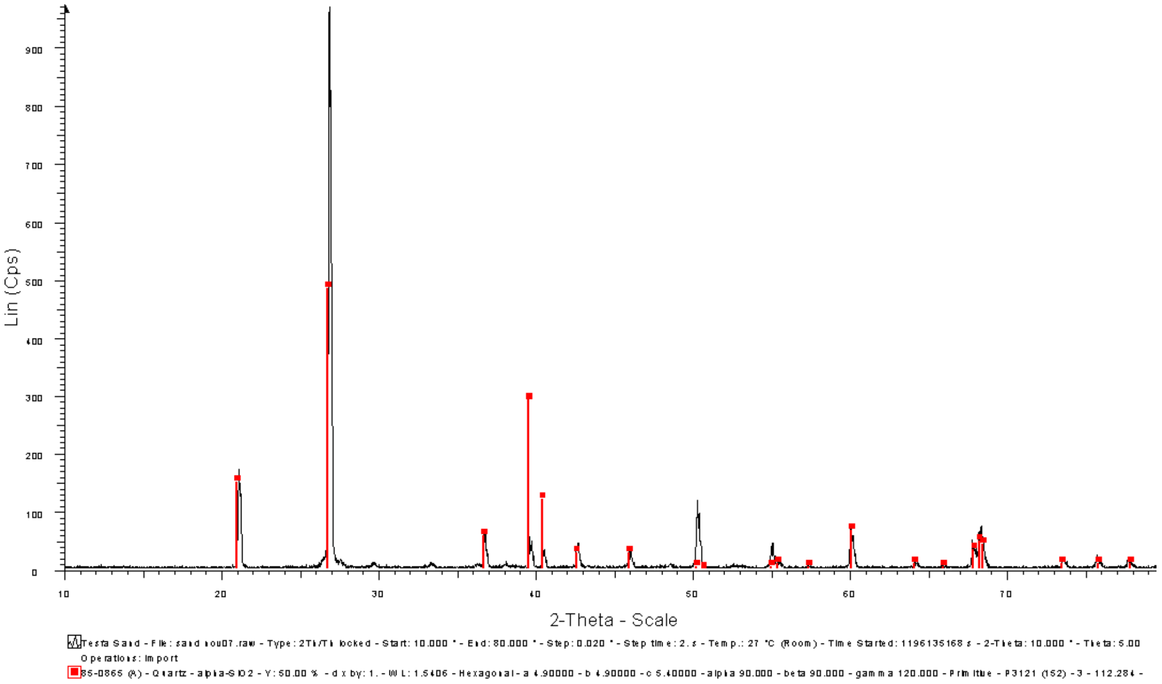


Figure 4.2 XRD curve for beach sand with 5 hrs ball mill and 15-20 min grinding before screening.

The characteristics change of structure with milling time was also studied for the natural sand. It was found that as the milling time increases the maximum intensity increases with out changing the diffraction angle 2θ.

Applying Bragg’s law (Equation 2.1):

$$\lambda = 2d\sin\theta \Rightarrow d = \frac{\lambda}{2\sin\theta} \quad \text{..} (4.1)$$

Equation 4.1 describes the relationship between wavelength λ, d-spacing (the distance between imaginary planes in the atomic lattice) and the diffracted angle 2θ. Based on the experimental result, mechanical milling only increases the intensity which by the above equation has no effect on the d-spacing. The change in d-spacing in a unit cell results in deformation of the structure.

4.2 CHARACTERIZATION OF THE COMPOSITE

As mentioned in chapter 3, all tests follow ASTM standard and the mechanical property, morphology of fractured surface, mixing torque, thermal properties and rheology of the composite are presented in the preceding sections.

4.2.1 MECHANICAL PROPERTIES

Mechanical test of all composites were performed and the average results and the standard deviations were calculated and reported. Accordingly, the effect of filler (natural sand) and filler concentration on tensile properties of the composite are illustrated in Figure 4.3 to 4.6.

(i) TENSILE STRENGTH

Figure 4.3 illustrates the tensile strength behavior of both untreated HDPE/SS (U-HDPE/SS) and PP/SS (U-PP/SS) composites with the variation in filler content.

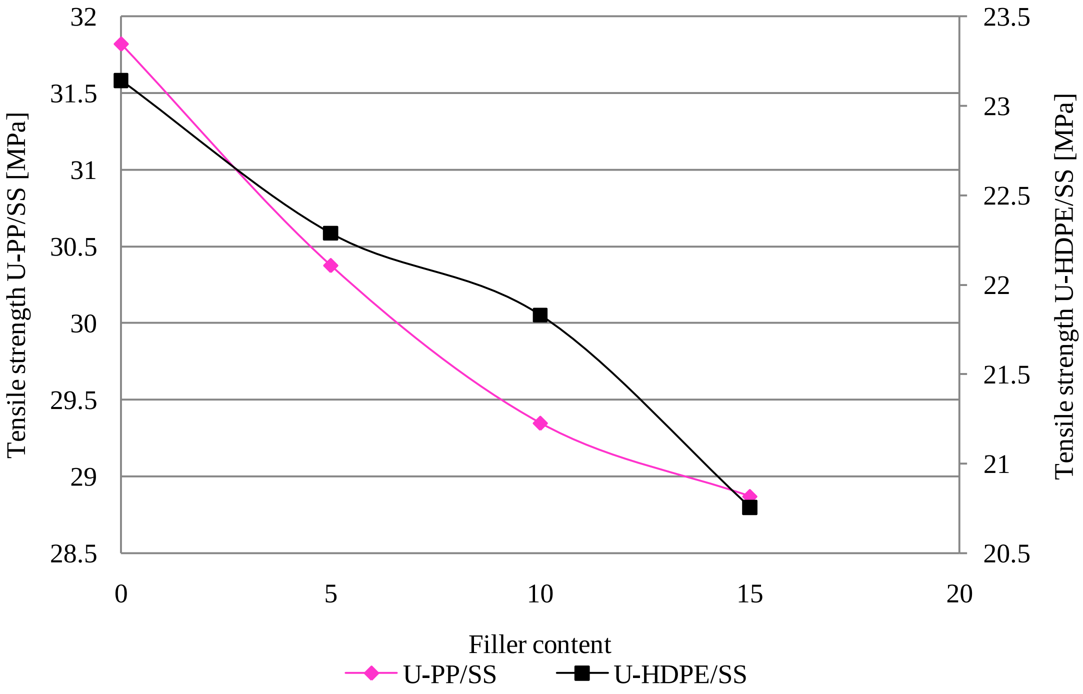


Figure 4.3 Tensile strength of U-HDPE/SS and U-PP/SS composites

It was discovered that the tensile strength of both composites decreases when the content of the filler increases. The decrease in the tensile strength at 15 wt% filler content was 10.30% and 9.30% for U-HDPE/SS and U-PP/SS composites, respectively. The decrease in the tensile strength is probably due to the weak interfacial bond strength between the filler and the matrix, which leads to the formation of micro crack at the interface when the composites are subjected to load. Moreover, as the filler content increases the formation of agglomerates increases, which aggravate the weak filler matrix interaction. The weak interaction form discontinuity thus, reduces stress transfer within the components of the composite. All of these possibilities lead to lower strength values as the filler content increases. The actual values of mechanical properties of the pure polymer as well as the composite are given in Table A-1to A-10 of appendix A.

(ii) MAXIMUM ELONGATION AND ELONGATION AT YIELD

Figure 4.4 and 4.5 show the maximum elongation and elongation at yield of the two composites, U-HDPE/SS and U-PP/SS when subjected to tensile load.

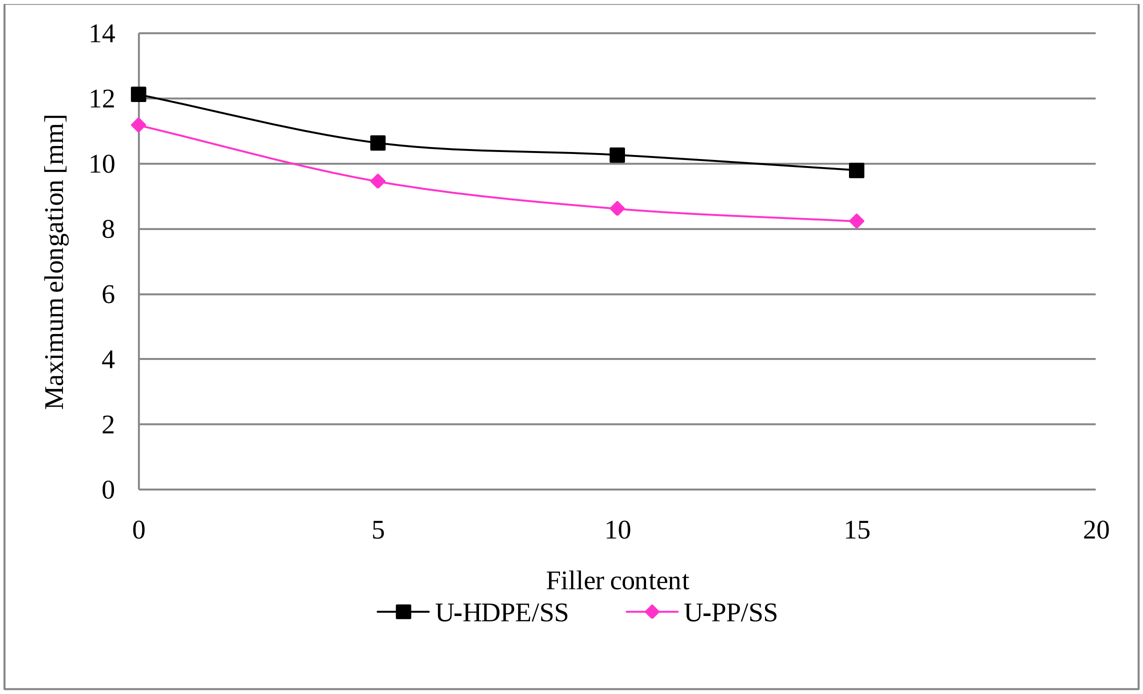


Figure 4.4 Maximum elongations in tension of U-HDPE/SS and U-PP/SS composites

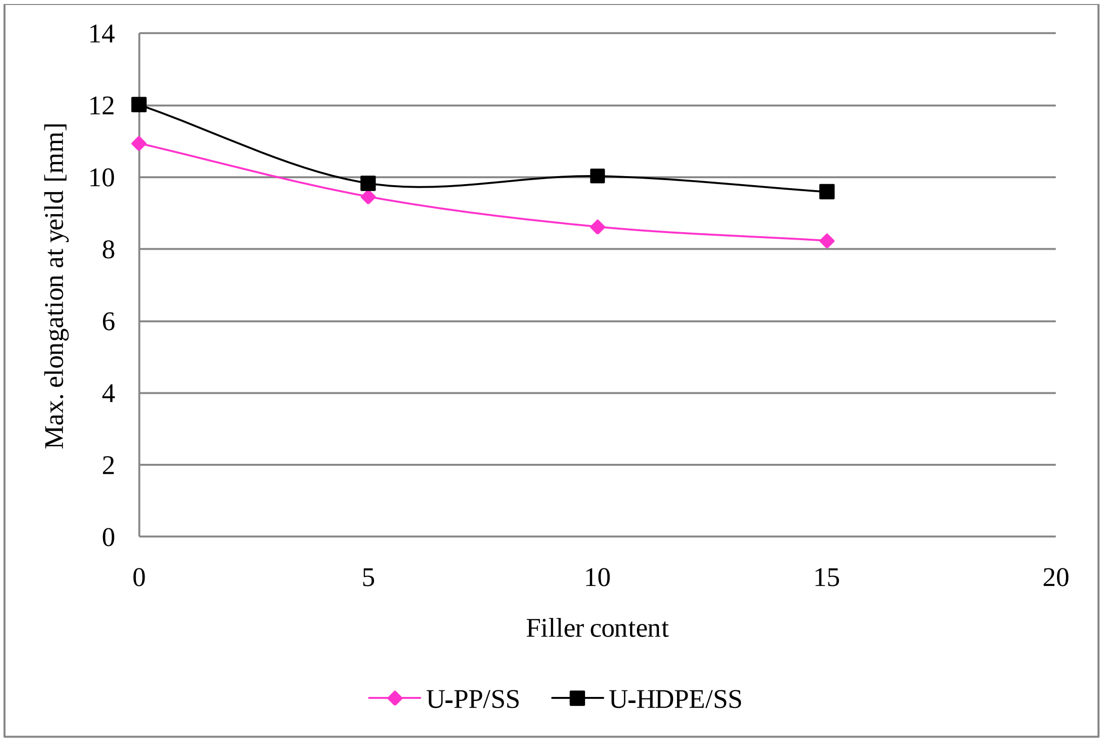


Figure 4.5 Elongation at yield in tension of U- HDPE/SS and U-PP/SS composites

It can be clearly seen from the figures that, both maximum elongation and elongation at yield decreased as the percentage of filler increased. The lowest maximum elongation was recorded at 15 wt% filler content and it is 19.18% and 26.41% for U-HDPE/SS and U-PP/SS composites respectively. And the lowest elongation at yield for U-HDPE/SS composite was 20.15% while for U-PP/SS composite it was around 24.75% at 15wt% filler content. This may be due to the weak interfacial bond strength between the filler and the polymer matrix.

(iii) MODULUS OF ELASTICITY

The slope in the initial portion of the stress strain curve reflects modulus of elasticity of the material. It is a measure of rigidity or stiffness of a material. Figure 4.6 shows the modulus elasticity of the two composites, U-HDPE/SS and U-PP/SS and the effect of filler concentration from tensile test.

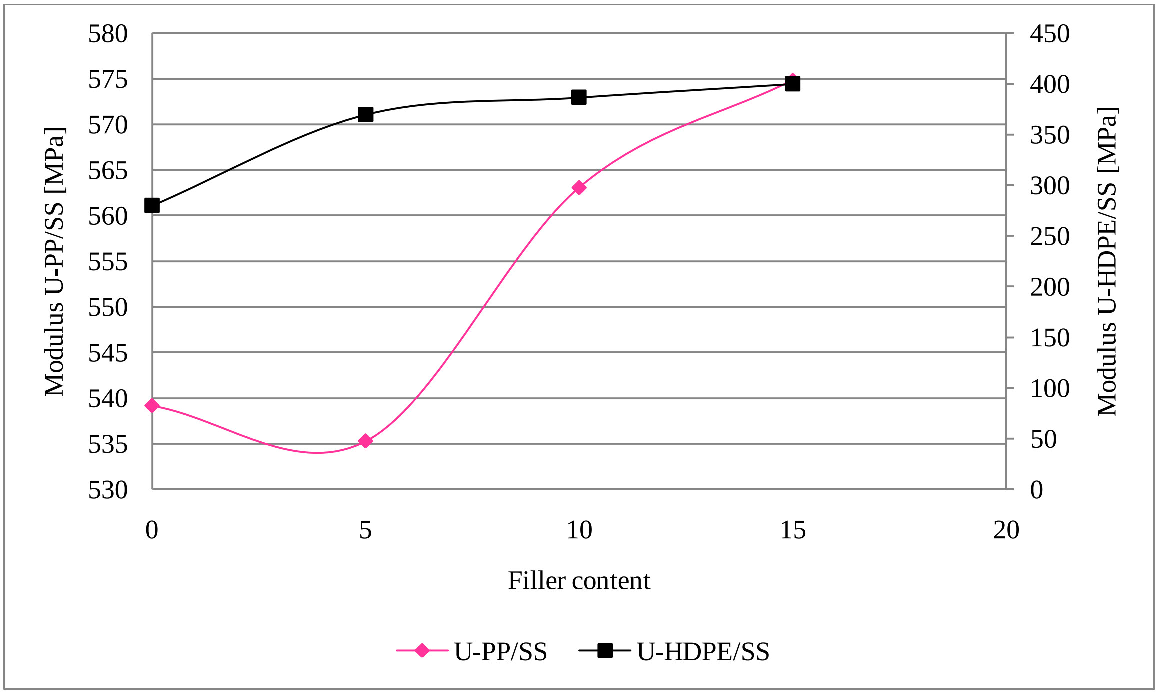


Figure 4.6 Effect of filler concentration on modulus of elasticity of U- HDPE/SS and U-PP/SS composites

As can be seen from the above figure, the tensile modulus of elasticity for U-HDPE/SS composite increases and an increment of 42.9% at 15wt% were recorded. On the other hand, for U- PP/SS composite the trend is somehow decreasing at the beginning until 5wt% filler concentration and starts to increase afterwards. In a general case from the experimental investigation for U-PP/SS composite, an increase of about 5.8% at 15wt% filler content has been observed.

(iv) FLEXURAL TEST

Results of the test, flexural strength, flexural modulus and maximum deflection are illustrated in the figures 4.7, 4.8 and 4.9 respectively.

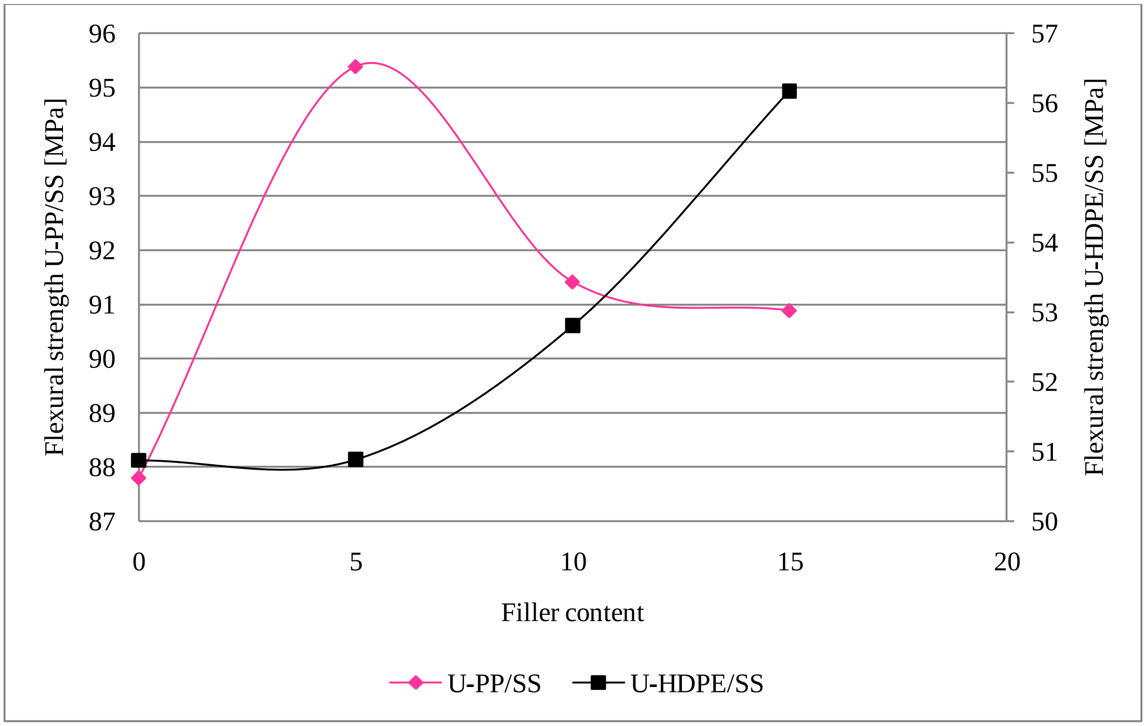


Figure 4.7 Effect of filler concentration on the flexural strength

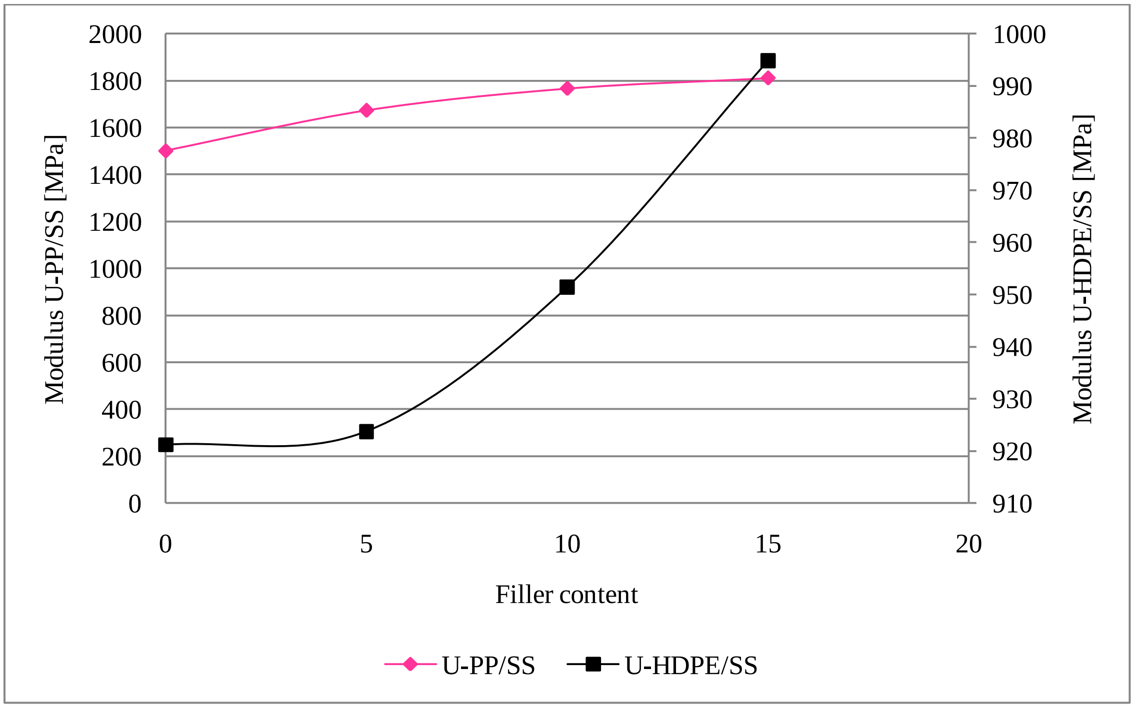


Figure 4.8 Effect of filler concentration on flexural modulus

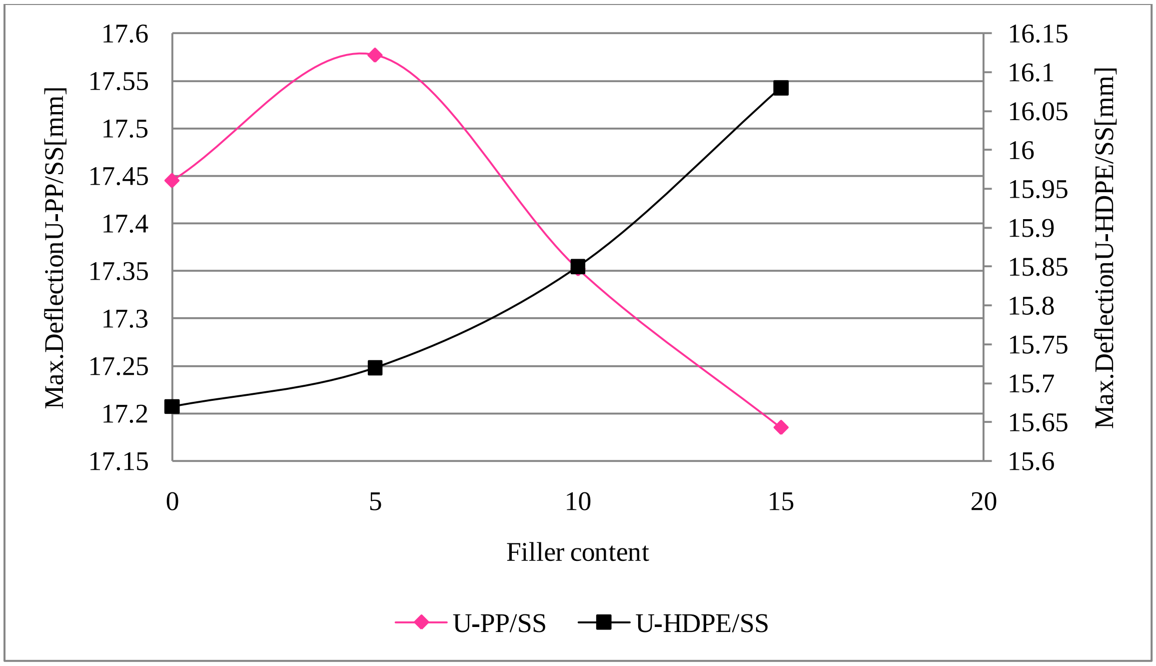


Figure 4.9 Effect of filler concentration on maximum deflection

The results of the flexural test for U-HDPE/SS composite revealed that an increment in flexural modulus, maximum deflection and flexural strength of about 8.0%, 2.62% and 10.42% respectively, were observed. On the other hand, the PP/SS composite show a significant increment in flexural modulus and improvement in flexural strength of about 19.70% and 3.50% respectively with lowest maximum deflection of 1.50% at 15wt% filler concentration. The result shows that the HDPE/SS composite has better flexural properties than its tensile properties. Because of the weak interfacial bond between the filler and the polymer matrix, stress will not be transferred from the polymer to the filler and vice versa if load is applied on the composite. Thus, the weak interfacial bonding between the matrix and the filler caused the properties of the polymer matrix to decrease by inducing micro crack at the interface.

4.3 EFFECT OF CHEMICAL TREATMENT

Effect of chemically treated filler on the mechanical properties of the composite has been studied and the results are presented as follows. The two silanes, MTS and VTES were first used for treating 10wt% of the filler and samples were prepared and tested. Table 4.2 shows the comparison of mechanical properties between MTS and VTES treated samples.

Table 4.2 Comparison between MTS and VTES treatment at 10wt% filler content

		Tensile properties		Flexural properties	
		strength[MPa]	Modulus [MPa]	Strength [MPa]	Modulus [MPa]
MTS treated	HDPE/SS	23.396	401.13	27.847	972.87
	PP/SS	31.025	563.06	47.429	1683.7
VTES treated	HDPE/SS	23.273	397.42	25.739	943.624
	PP/SS	30.926	558.67	46.307	1651.7

From Table 4.2, it can be said that MTS is somehow better than the VTES treatment even though the results from mechanical tests of both treated samples are quite close. Therefore, MTS has been chosen as the treating chemical of the filler. A comparison of mechanical properties between MTS treated and untreated filler composites revealed that the treatment improved the mechanical properties of composites produced from both HDPE and PP matrix. As far as the same size and shape of the filler is concerned, the interfacial bond between the filler and matrix improved somehow by treating the filler with MTS.

4.3.1 EFFECT OF CHEMICAL TREATMENT ON TENSILE PROPERTIES

Samples were prepared in the same method and standard as the untreated samples. The results of the experiment are compared and presented as follows. Figure 4.10 to 4.15 show the comparison of tensile strength, modulus of elasticity and maximum elongation of treated and untreated HDPE/SS and PP/SS composites.

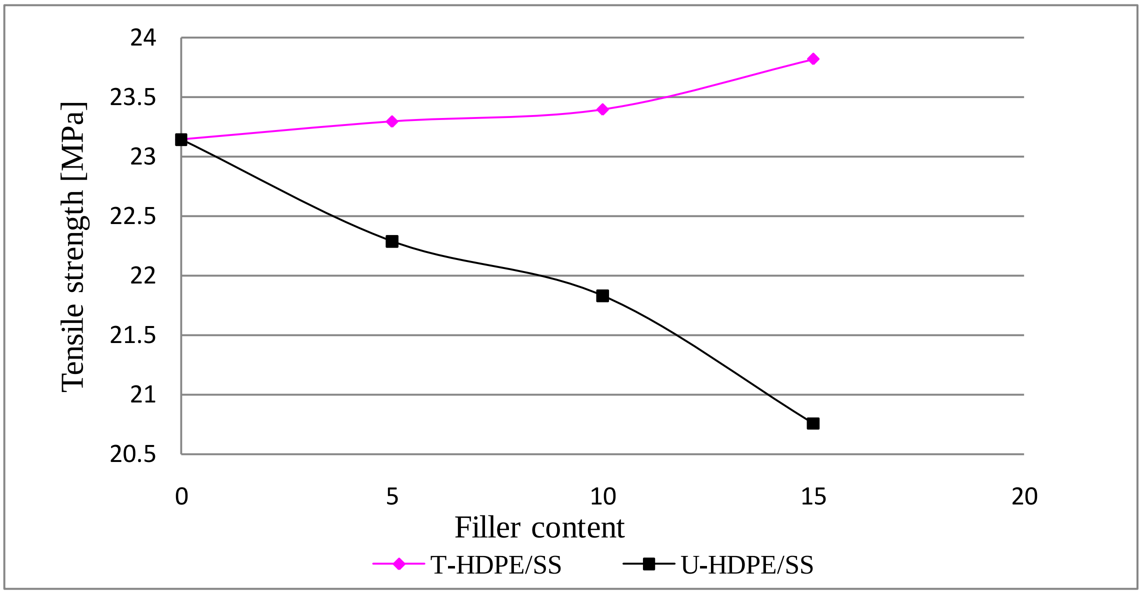


Figure 4.10 Comparison of tensile strength between treated and untreated HDPE/SS composite samples

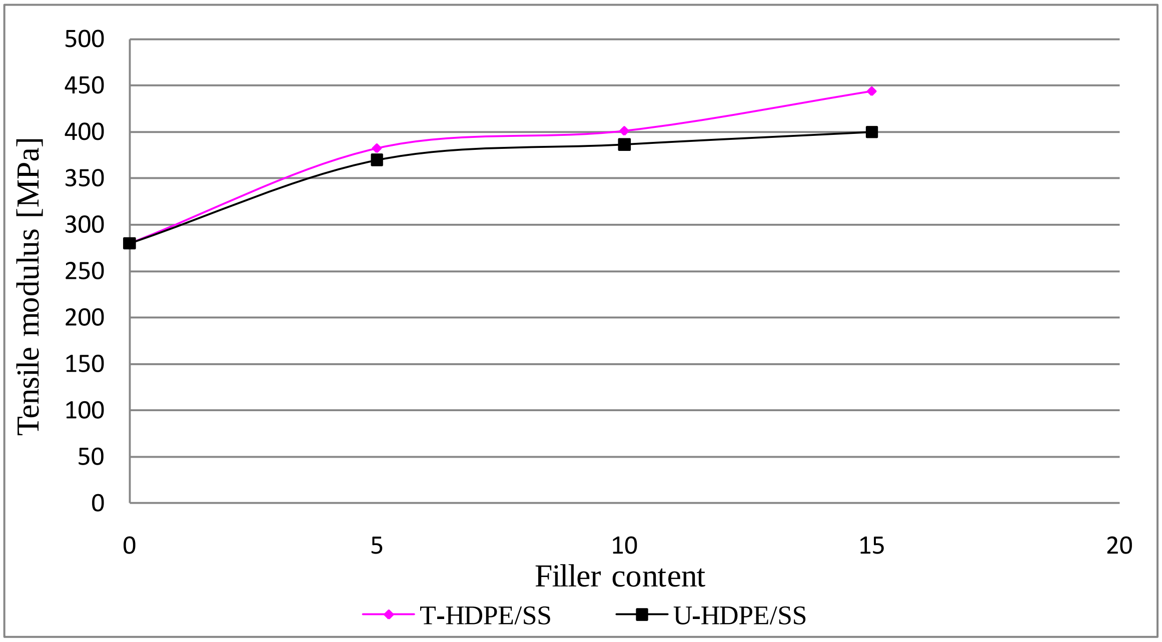


Figure 4.11 Comparison of tensile modulus between treated and untreated HDPE/SS composite samples

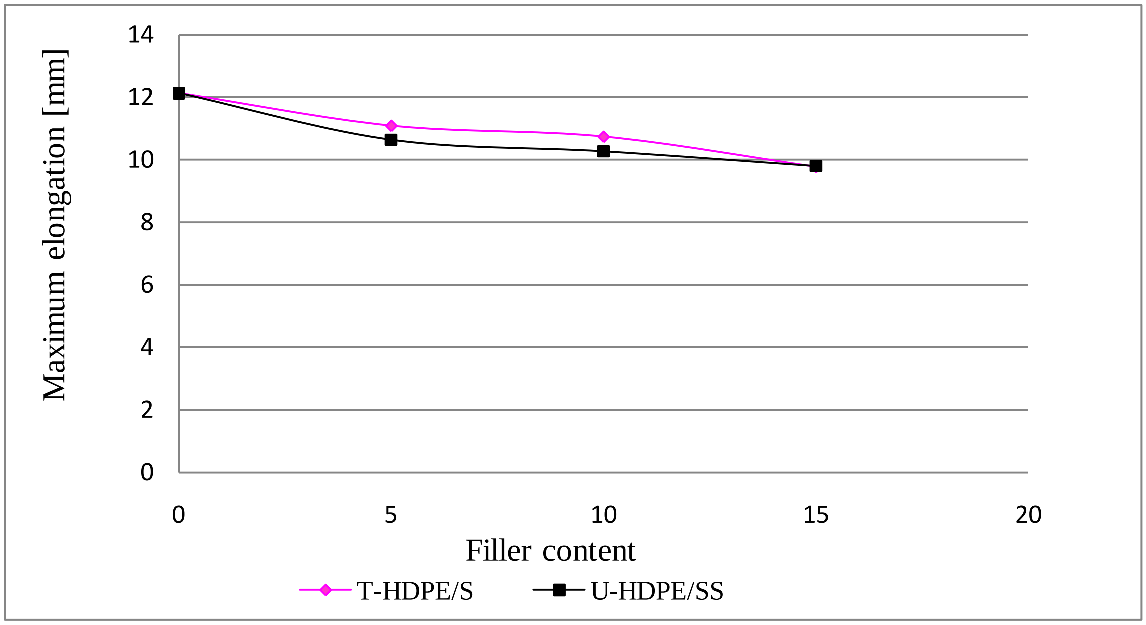


Figure 4.12 Comparison of maximum elongation between treated and untreated HDPE/SS composite samples

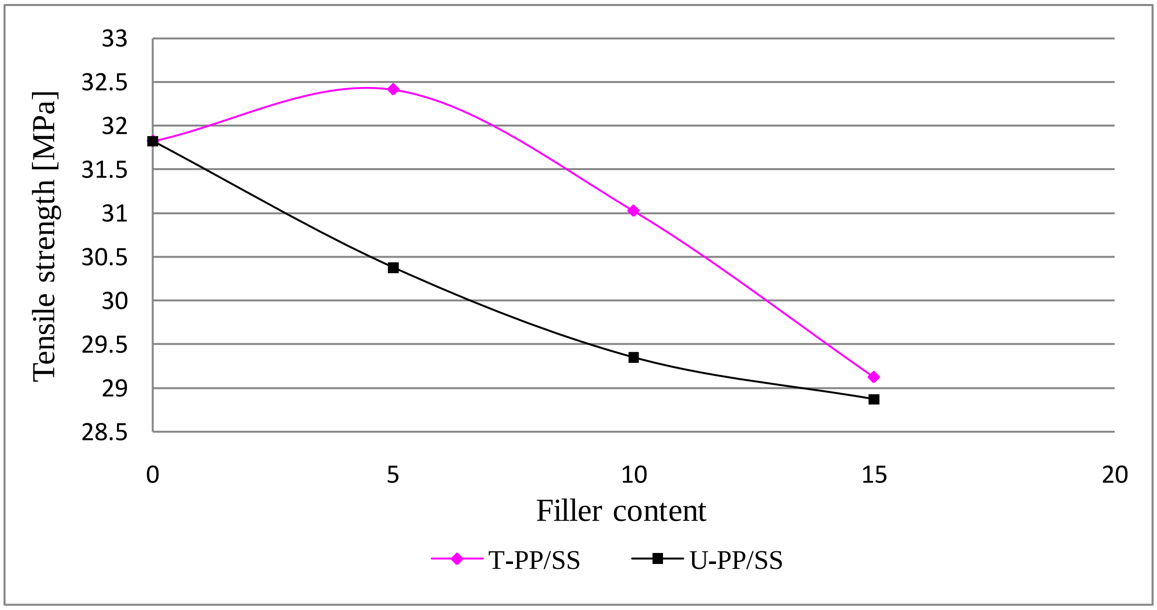


Figure 4.13 Comparison of tensile strength between treated and untreated PP/SS composite samples

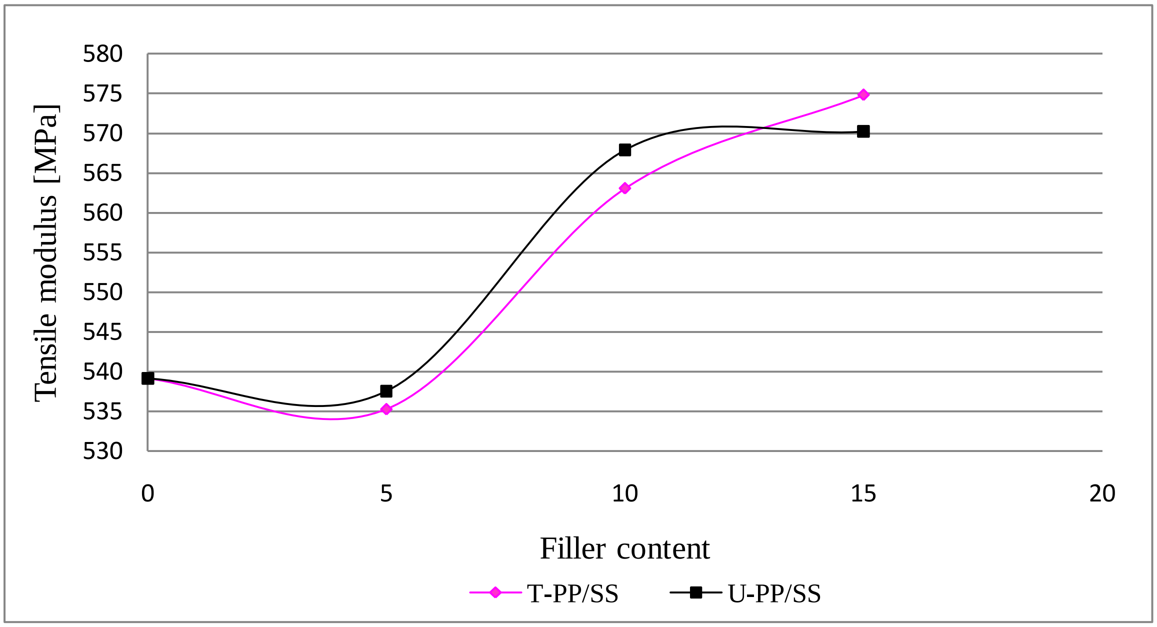


Figure 4.14 Comparison of tensile modulus between treated and untreated PP/SS composite samples

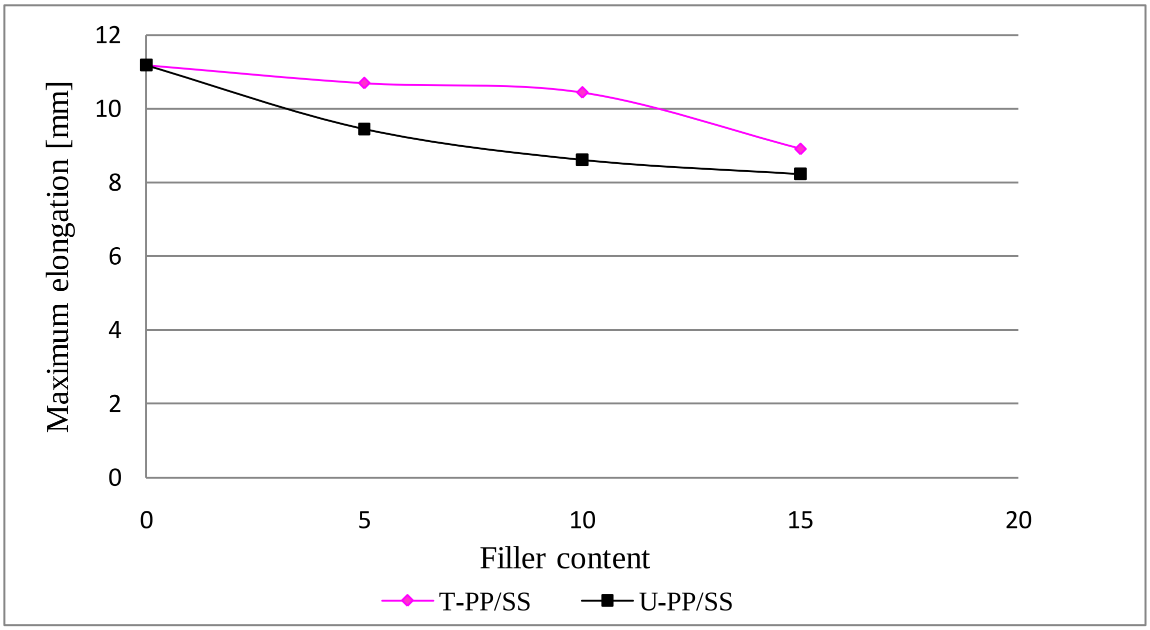


Figure 4.15 Comparison of maximum elongation between treated and untreated PP/SS composite samples

The test results show that the tensile properties at 15wt% filler content for T- HDPE/SS composite improved in such a way that there is an increment of about 2.9% in tensile strength, 58.6% in tensile modulus while a decrease in maximum elongation of 19.4% was investigated. This increment is possibly due to the treatment of filler sample with MTS, which consequently improved the interfacial bond between the filler and the matrix by forming a thin layer of functional group on the surface of the filler. As compared to the pure matrix, the maximum elongation decreases due to the difference in rigidity between the filler and matrix. But the elastic nature of the thin interfacial layer improved a little compared to the untreated samples. On the other hand, test results from T-PP/SS composite revealed improvement in tensile modulus of about 6.6% but a decrease in both tensile strength and maximum elongation of 8.5% and 18.7% respectively, which is much better compared to the untreated sample.

4.3.2 EFFECT OF CHEMICAL TREATMENT ON FLEXURAL TEST

Figure 4.16 to 4.18 show the flexural test results from MTS treated composite compared to the untreated samples. It was discovered that the flexural strength, modulus and maximum deflection improved by 16.8%, 20.0% and 6.2% respectively for T-HDPE/SS sample at 15wt% filler content. As it is mentioned in the tensile test result, the reason might be because of the improvement of interfacial bond due to the chemical treatment. The treatment gives the rigid mineral filler to improve the wettability and functionality and therefore the compatibility of bonding with the matrix as a consequence, this gives better mechanical properties.

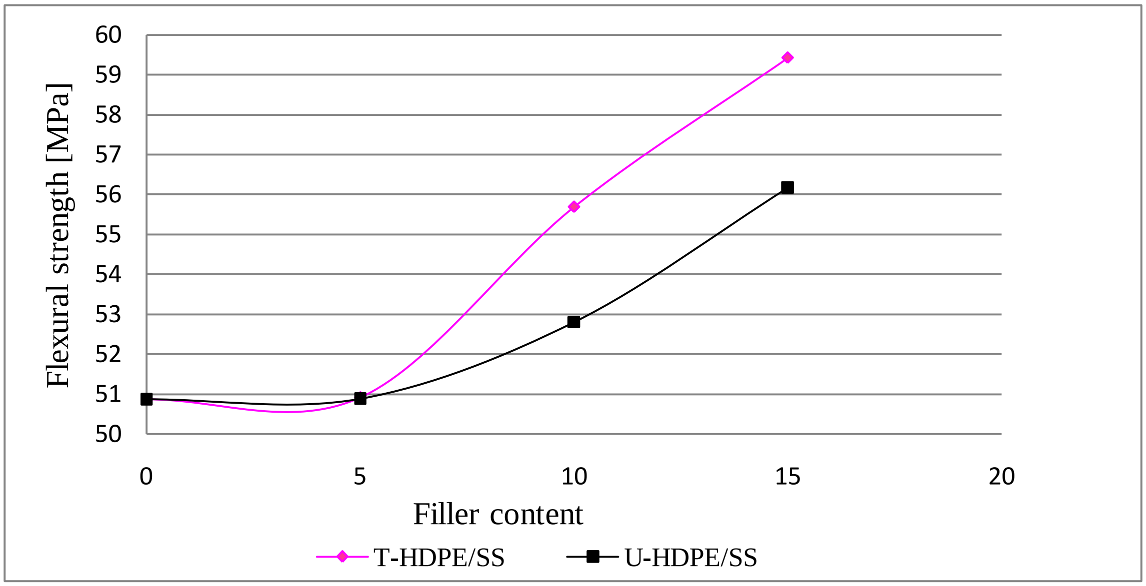


Figure 4.16 Comparison of flexural strength between treated and untreated HDPE/SS composite samples

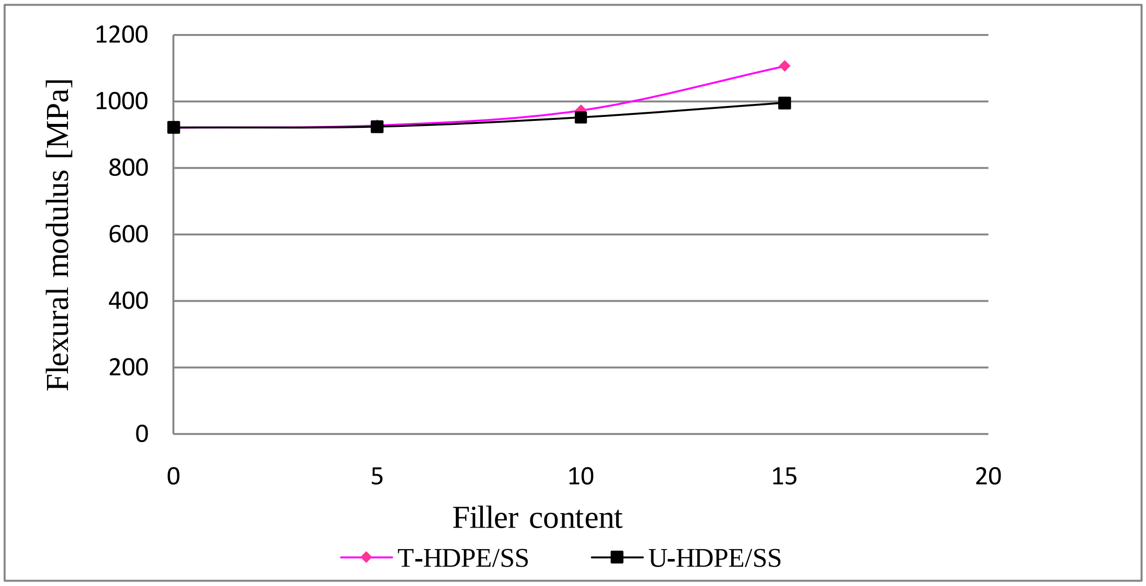


Figure 4.17 Comparison of flexural modulus between treated and untreated HDPE/SS composite samples

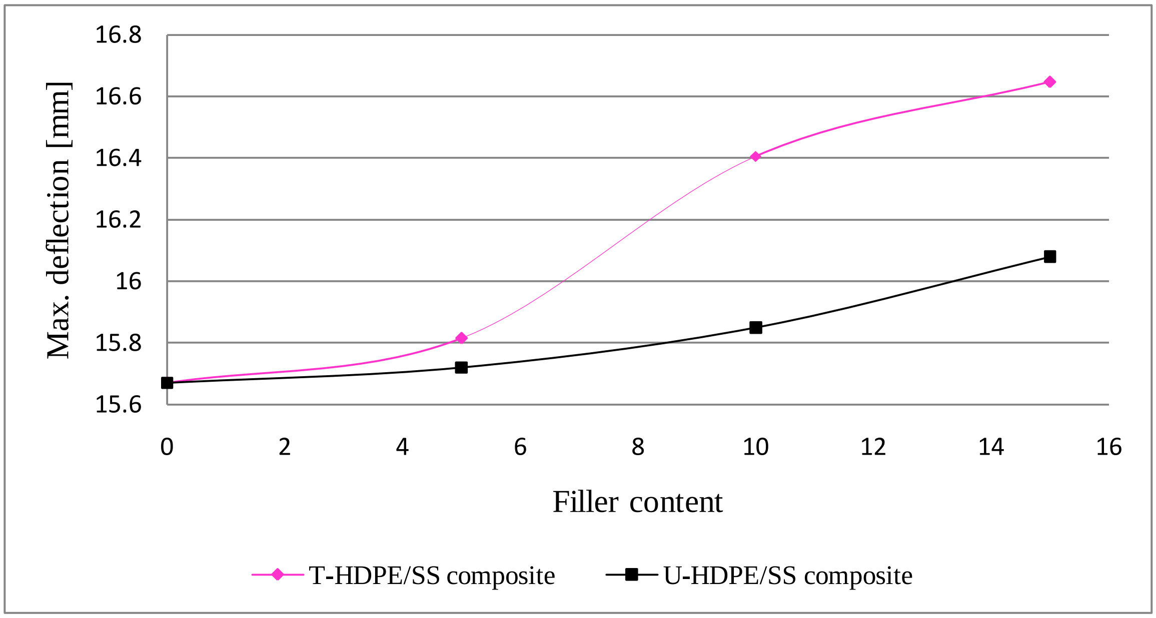


Figure 4.18 Comparison of maximum deflection between treated and untreated HDPE/SS composite samples

Figure 4.19 to 4.21 revealed the flexural test results of T-PP/SS composite and comparison with U-PP/SS.

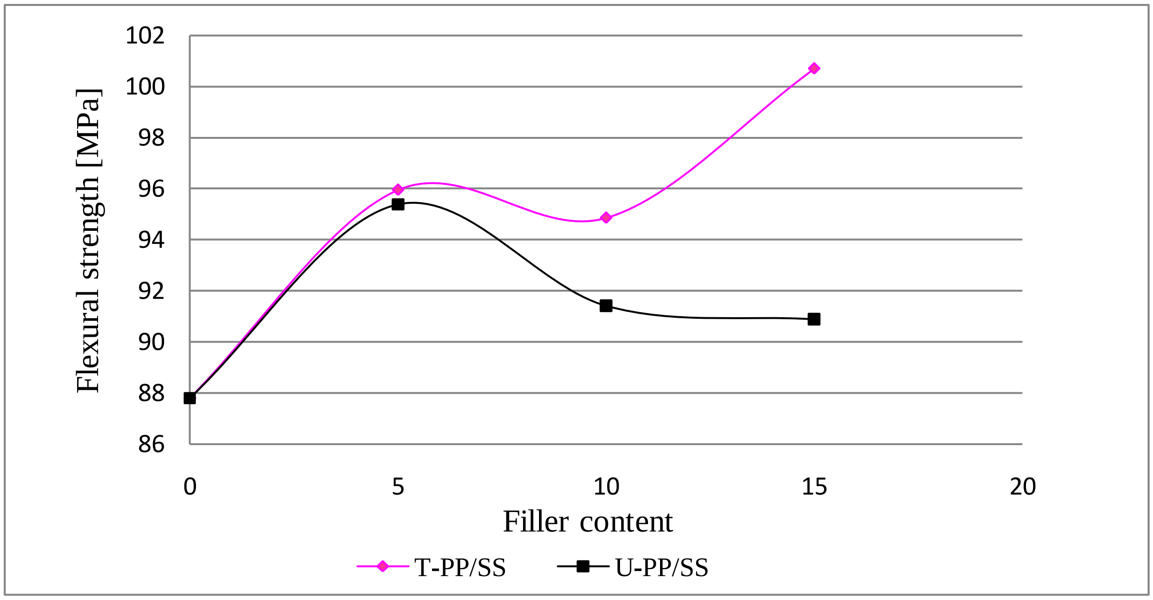


Figure 4.19 Comparison of flexural strength between treated and untreated PP/SS composite samples

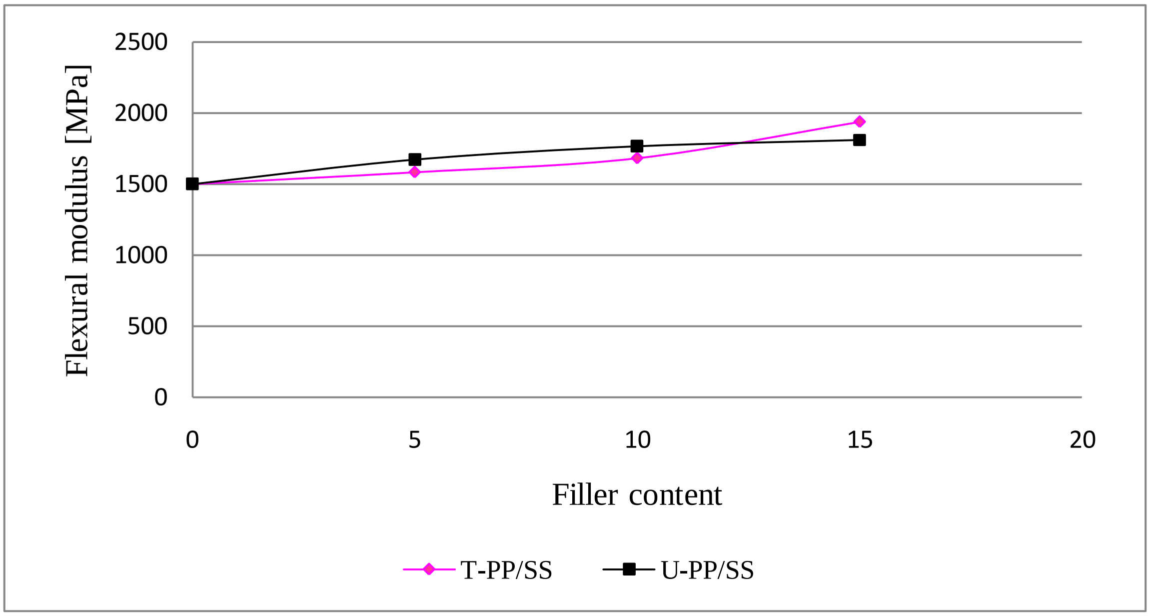


Figure 4.20 Comparison of flexural modulus between treated and untreated PP/SS composite samples

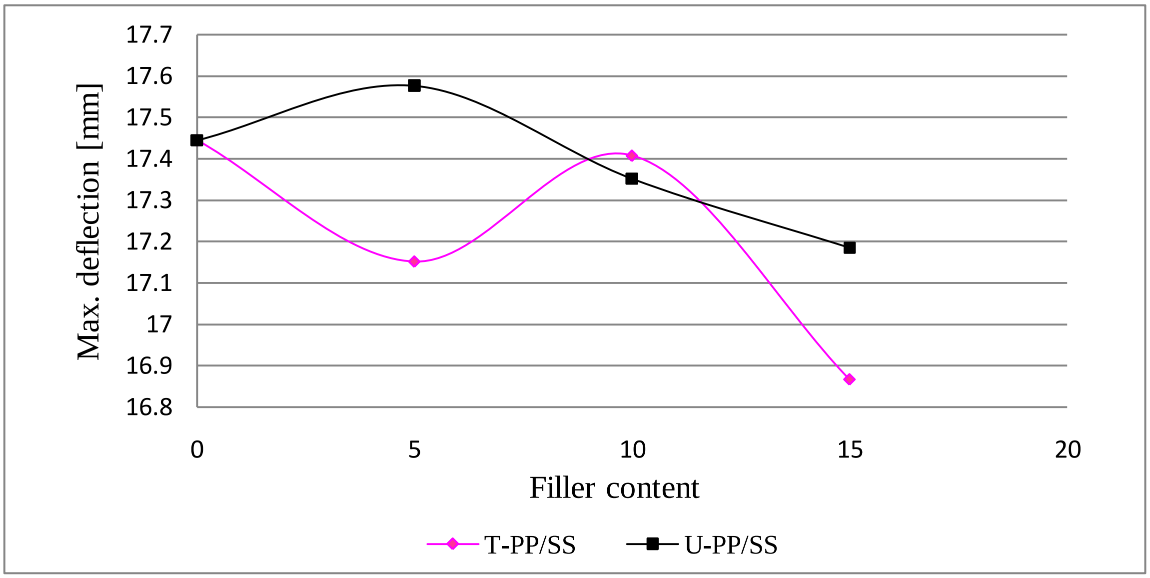


Figure 4.21 Comparison of maximum deflection between treated and untreated PP/SS composite samples

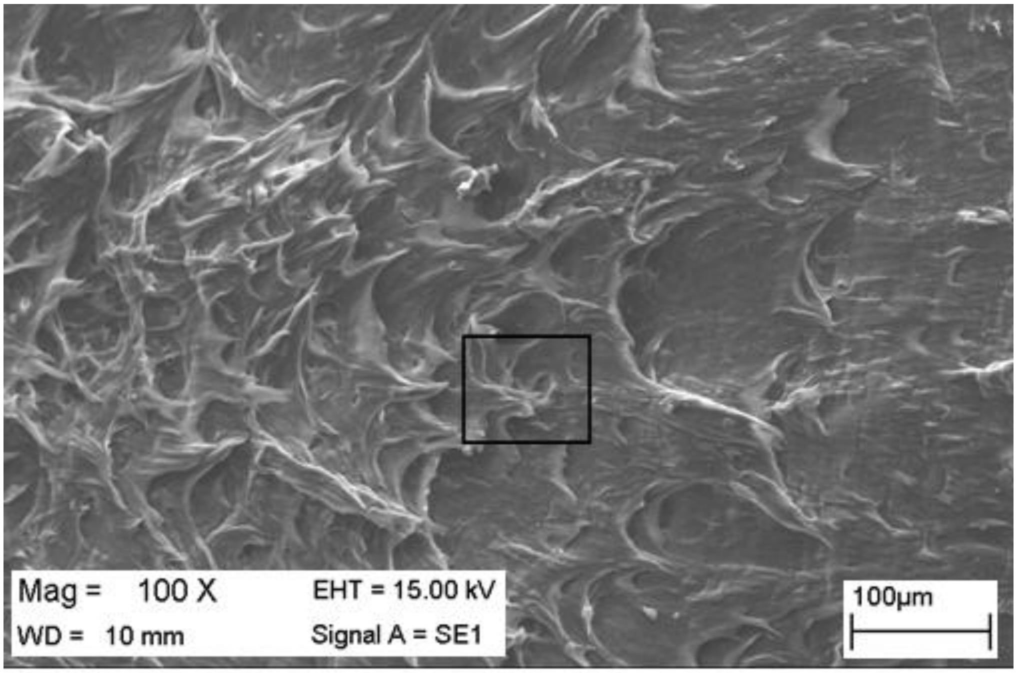
It can be said from Figures 4.19 to 4.21 that the flexural strength and modulus of PP/SS composite improved by 14.7% and 29.1% respectively while the deflection decreased by 3.3% at 15wt% filler content.

The improved in mechanical properties due to filler addition and chemical treatment from mechanical test is supported by the microstructure of fractured surface from tensile test and presented in the following section.

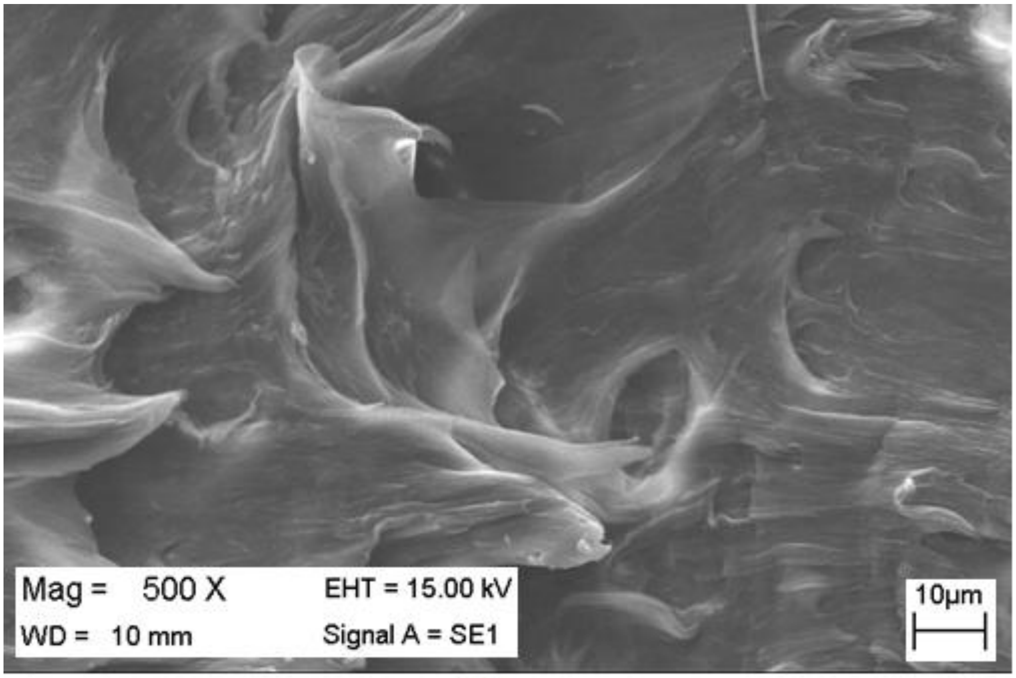
4.4 MORPHOLOGY: MICROSTRUCTURE AND FRACTURE SURFACE

Figures 4.22 to 4.25 show the SEM morphological microstructure of the fracture surfaces from the tensile test specimen. To understand the micro structure of the fractured surface in a more detailed manner, morphology of each sample was taken in two different magnifications.

Figure 4.22(a) and (b) show the morphology of the fractured surface from a pure PP polymer sample. The SEM micrographs show evidence of uniform structure in the matrix since the breaking occurred in the same direction as stretched.

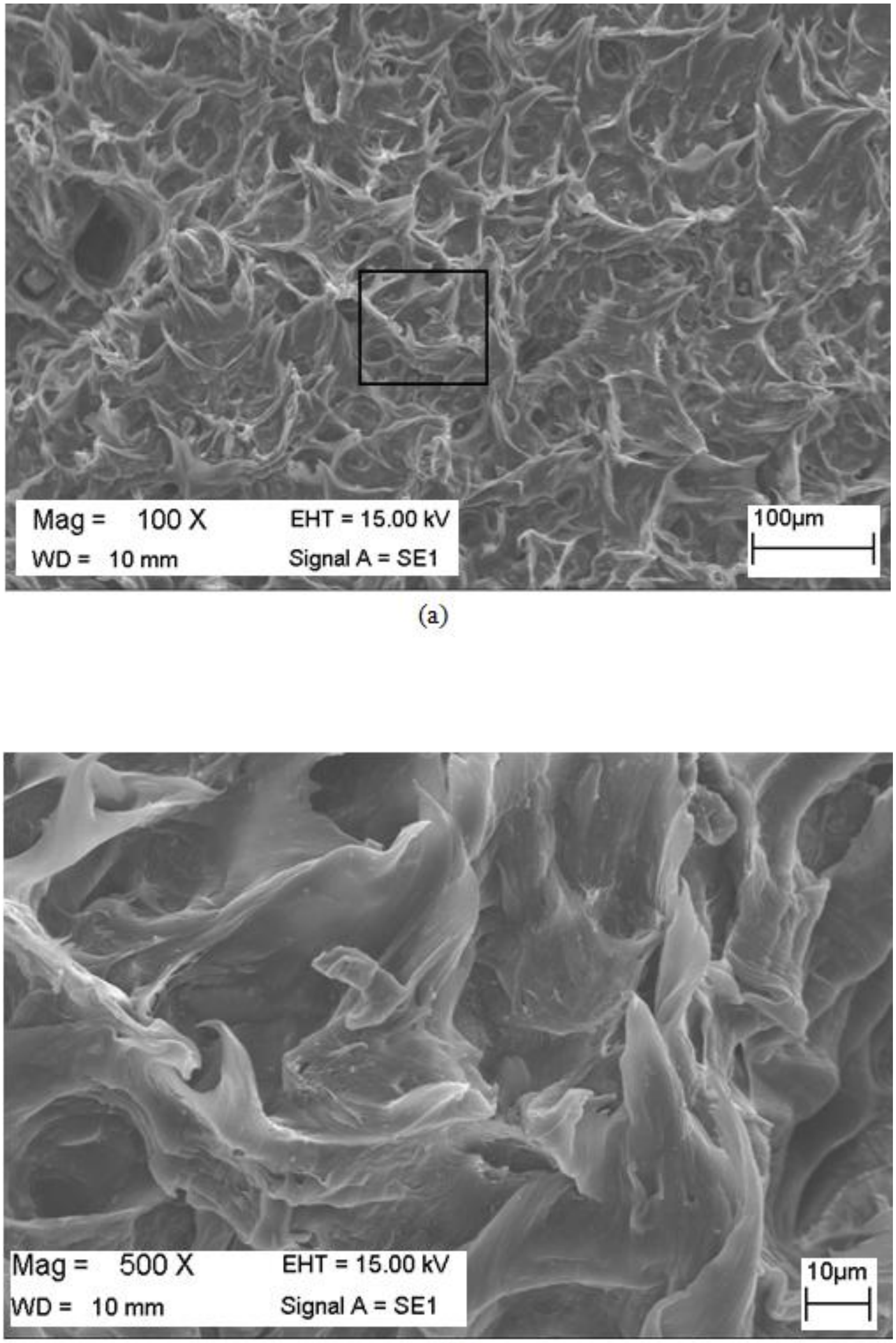


(a)



(b)

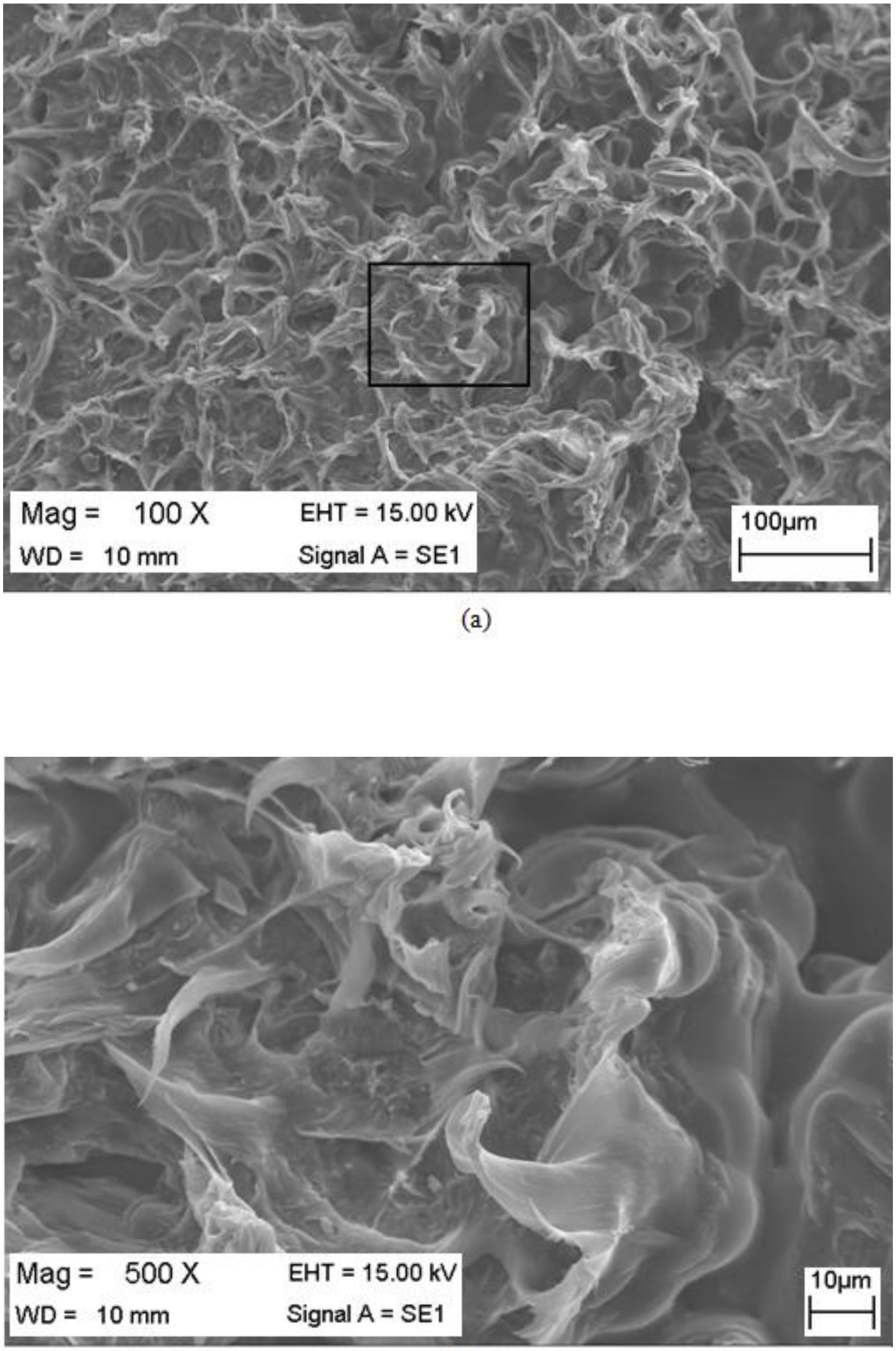
Figure 4.22 SEM micrographs of the tensile fracture surface of pure PP



(a)

(b)

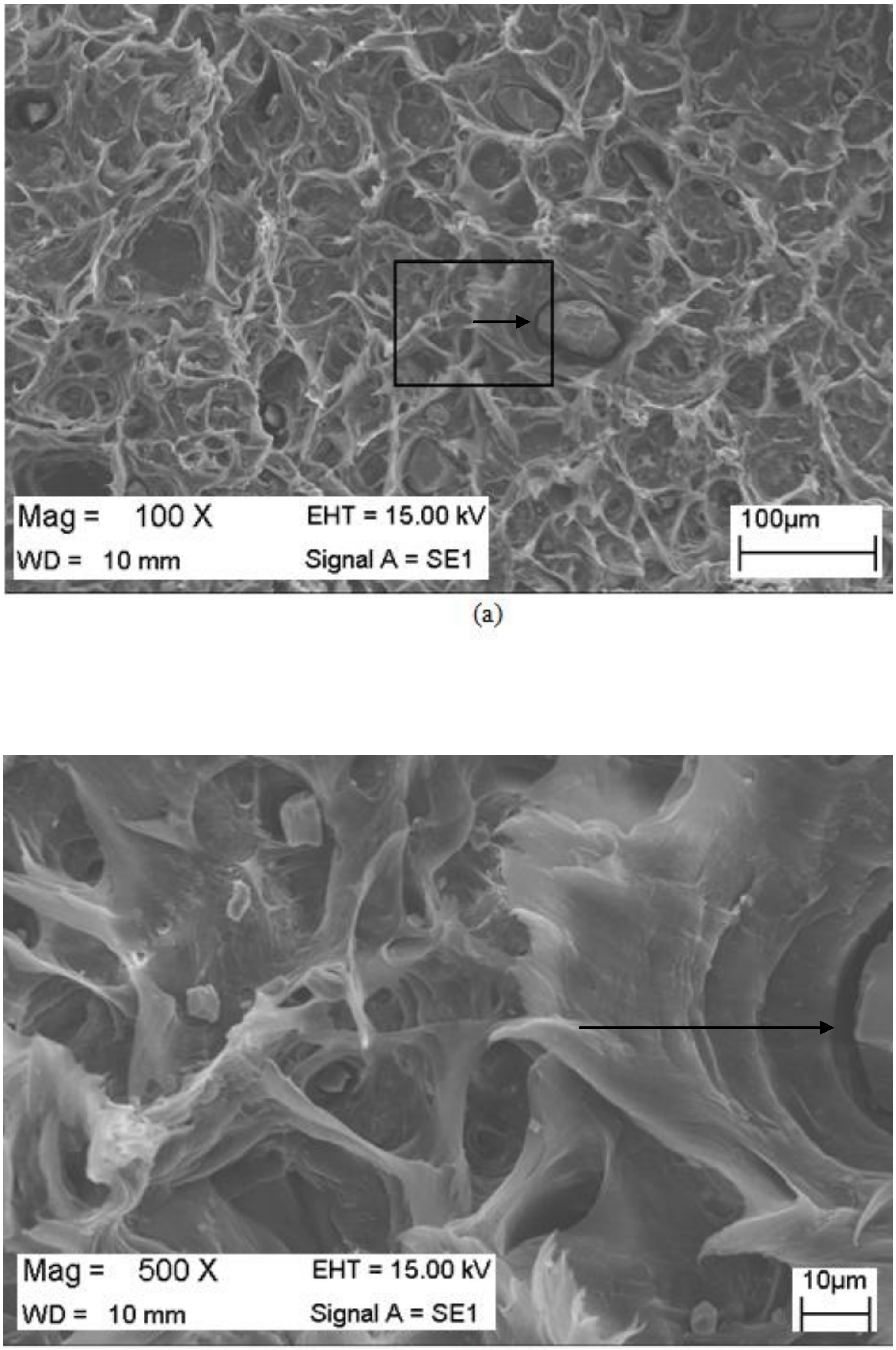
Figure 4.23 SEM micrograph of the tensile fracture surface of 5 % PP/SS composite



(a)

(b)

Figure 4.24 SEM micrograph of the tensile fracture surface of 10% PP/SS composite



(a)

(b)

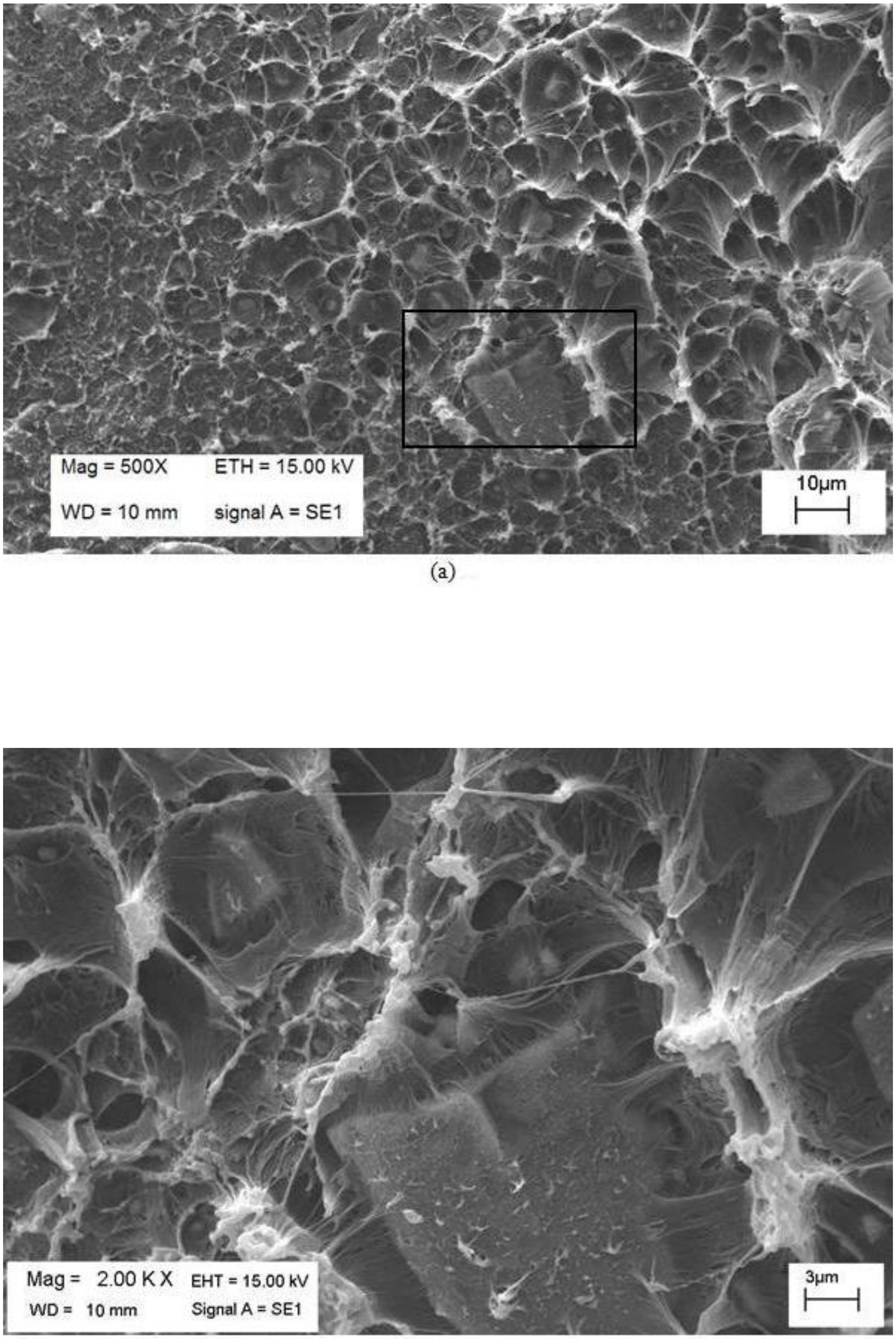
Figure 4.25 SEM micrograph of the tensile fracture surface of 15% PP/SS composite

Figures 4.23 to 4.25 illustrate the fractured structural surface of particulate filled composite with 5wt%, 10wt% and 15wt% respectively. It can be easily said that the fractured surface show a non uniform structure because of the space left by the filler, which has been pulled out from the matrix when subjected to tensile load. The size of the space left by the filler increased with increasing filler content. This is the space taken by the agglomerated particles due to an increase in agglomeration as the concentration of filler increases.

The arrow in Figure 4.25(a) shows the interface of filler and matrix. The magnified image of the structure is shown in Figure 4.25(b). It is shown that there exist a space between the filler and the matrix which is the cause of failure when the material is subjected to stress. This gap limits the transfer of stress from the matrix to the filler and vice versa, and becomes an area of stress concentration that causes the material to reduce its mechanical properties as was explained in the mechanical test analysis, section 4.2.1.

Figure 4.26 (a) and (b) show the SEM microstructure of the tensile fractured surface of treated PP/SS composite. It can be clearly seen that there exists an interfacial interaction between the filler and the polymer matrix. Unlike the untreated composite samples where the particles left a hole behind after fracture, in this case the treatment strengthen the interaction between the filler and polymer matrix by forming a thin interfacial layer. Thus stress can transfer from the matrix to the filler or vice versa leading to the improvement of mechanical properties as mentioned in the mechanical test result section 4.2.

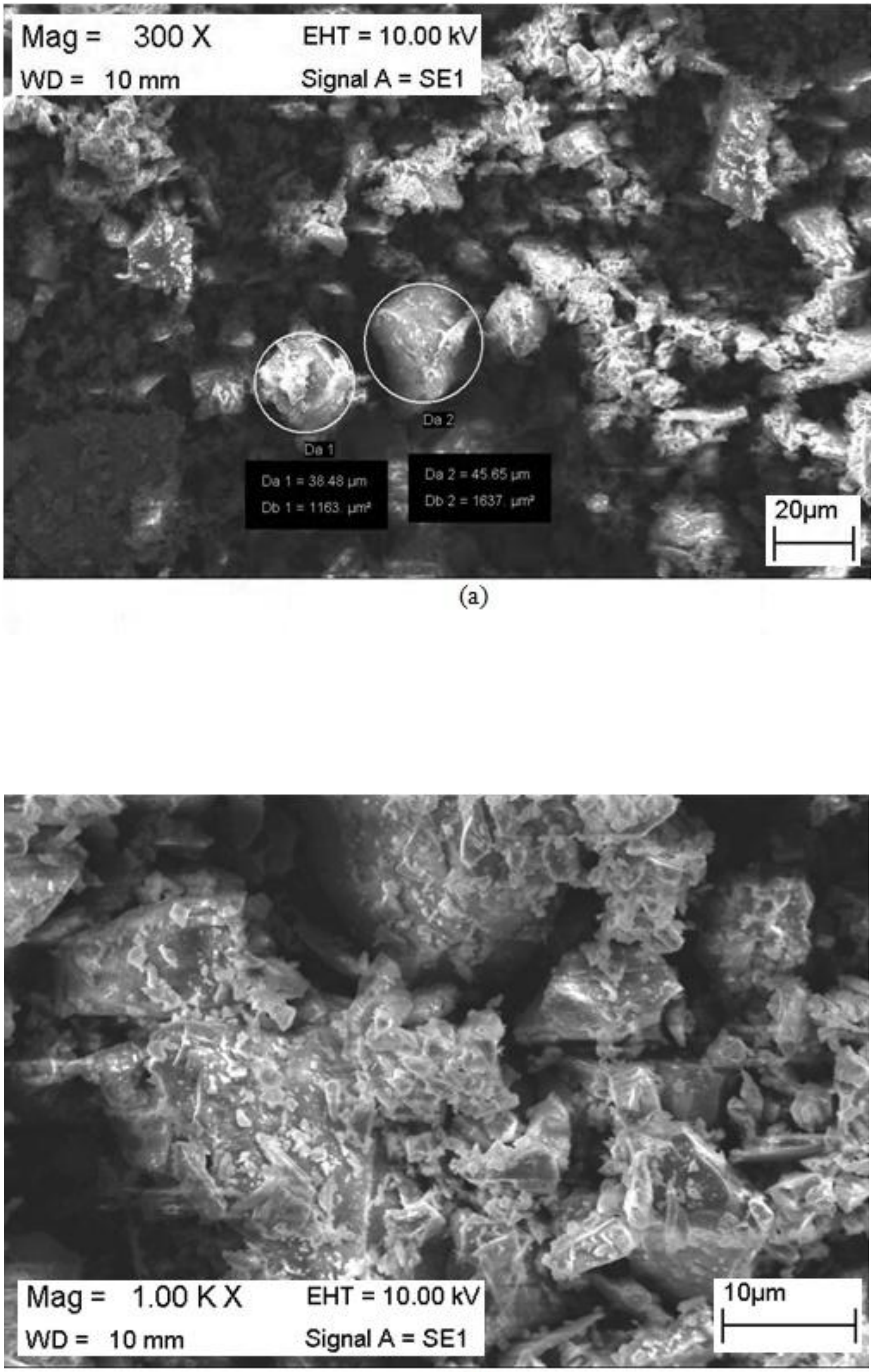
Figures 4.27(a) and (b) show the microstructure of the filler silica sand. The size and shape of the natural sand particle was determined using SEM. It is clear from the figures that the particles have an irregular shape with an approximate diameter of a single particle about 45.65 μm. The area of the particle was calculated to be 1637 μm^2 by assuming a spherical particle of the same size.



(a)

(b)

Figure 4.26 SEM micrographs of the tensile fracture surface of treated 15% PP/SS composite



(a)

(b)

Figure 4.27 SEM micrographs of natural silica sand

4.5 MIXING TORQUE AND TIME

During the mixing stage in the internal mixer, the torque required for mixing and time at which the machine acquires a constant torque has been identified by a remote controlling computer connected to the mixing machine. It was discovered that approximately after ten minutes the torque required to mix the compound became constant as shown in Figure 4.28.

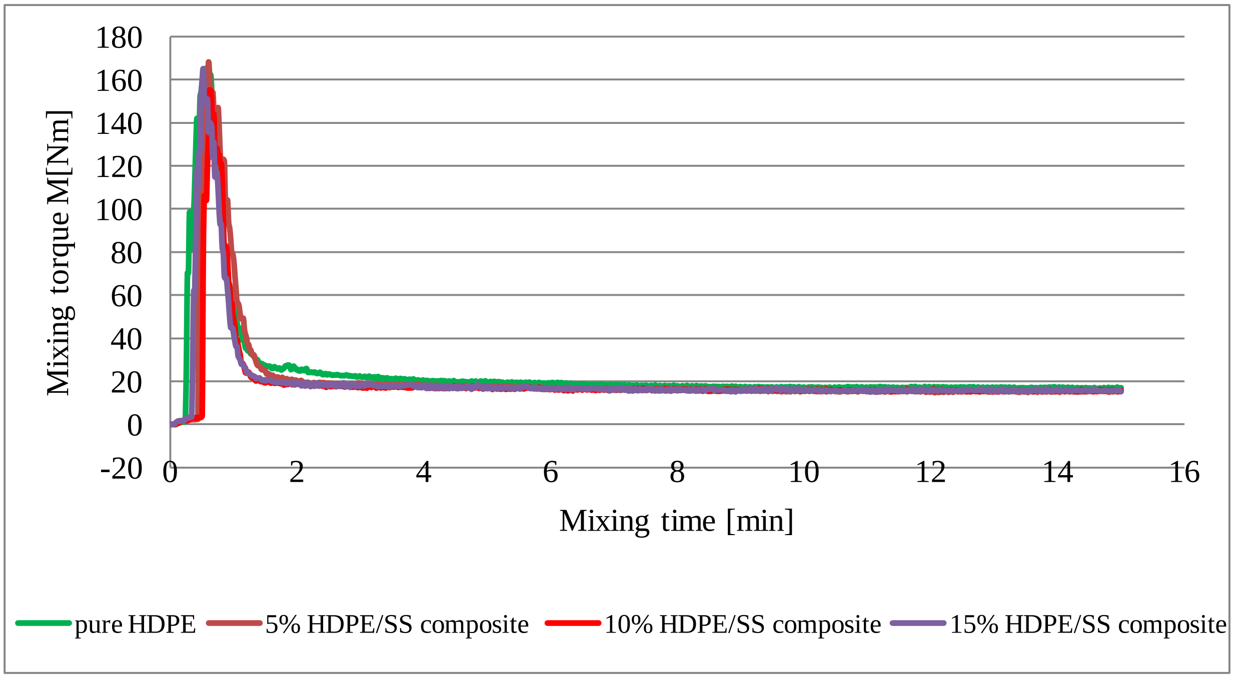


Figure 4.28 Effect of filler concentration on mixing torque and time

As shown in Figure 4.28, the mixing torque attains its maximum value at the beginning when the mixture of filler particles and polymer matrix was charged into the mixing chamber. As the mixing time increases the polymer will start to melt and causes the required mixing torque to decrease. After a few minutes, the mixture becomes uniform as the polymer matrix totally melted, which causes the mixing torque to attain a constant torque value. It was also discovered that the mixing torque increases as the concentration of filler increases. This could be due to an increase in the density of the mixture. The same result was found for both types of composites HDPE/SS and PP/SS composite.

4.6 THERMAL PROPERTIES

4.6.1 DIFFERENTIAL SCANNING CALORIMETER (DSC) ANALYSIS

DSC analysis was conducted to study the trend in the effect of filler concentration on the thermal properties of the composites. Table 4.3 shows the relation between filler concentration and thermal parameters, crystalline temperature (T_c) and melting temperature (T_m).

Table 4.3 Effect of filler concentration on thermal properties of PP/SS and HDPE/SS

Composite	Filler content (weight %)				
		0	5	10	15
PP/SS	T_c(^{0}C)	124.081	122.024	123.189	124.034
	T_m(^{0}C)	164.358	163.633	163.13	163.141
HDPE/SS	T_c(^{0}C)	116.939	117.601	117.923	118.582
	T_m(^{0}C)	131.449	132.616	132.940	132.944

It was discovered that the increase in filler concentration slightly increases the crystalline temperature (T_c) and melting temperature (T_m) of HDPE/SS composite. On the other hand for PP/SS composite, the increase in filler concentration decreases both the crystalline and melting temperature until 5wt% and starts to increase in the case of composite containing 10wt% and 15wt%.

The thermal test in DSC were performed in four steps; holding at -50^{0}C for 1min, heating at 10^{0}C/min from -50^{0}C to 200^{0}C, holding at 200^{0}C for 5min and cooling from 200^{0}C to 25^{0}C. A sample DSC curve of pure PP is shown in Figure 4.29 below.

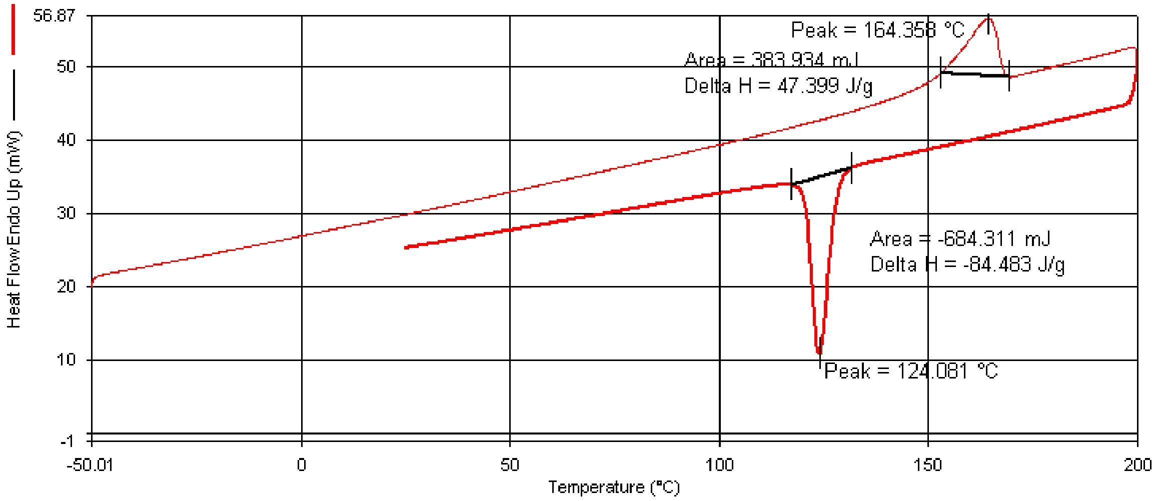


Figure 4.29 Thermal transition temperatures of pure PP from DSC test

The area under the curve is a direct measure of the heat of (change in enthalpy) transition. The heat flow versus temperature curves in Figure 4.29 used to calculate the heat of transition in such a way that positive enthalpy for an endothermic reaction and negative for an exothermic reaction. The upper peak represents the melting temperature whereas the lower peak is for crystalline temperature.

4.7 RHEOLOGY

Shear stress, Shear rate and viscosity of the composite were studied by a capillary rheometer at a constant temperature of 180^0C and presented in Figures 4.30 to 4.35. Load was varied from 5N to 40N with a die of 0.5 mm diameter and length of 1mm.

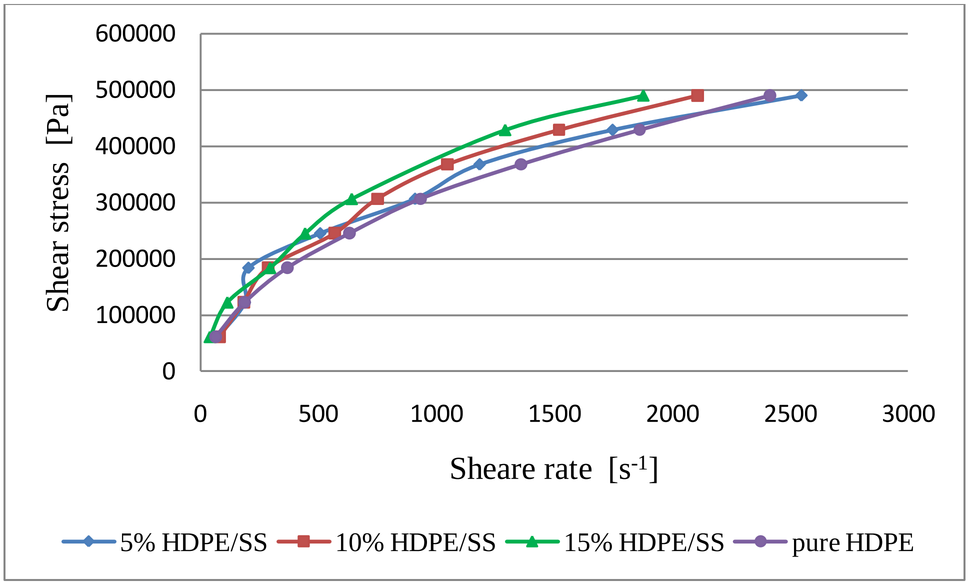


Figure 4.30 Variation of Shear stress with shear rate for U-HDPE/SS composite

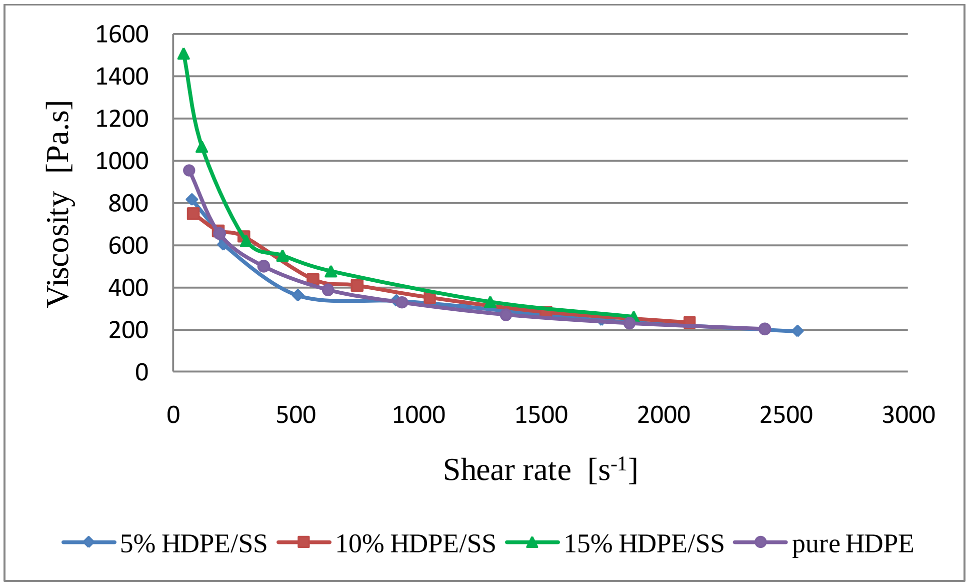


Figure 4.31 Varietion of viscosity with shear rate for U-HDPE/SS composite

The result shows that the rheological properties of the composite, shear stress and viscosity increased with increasing filler content. This is possibly due to hindered movement of polymer strands by the filler particles. On the other hand, the lubrication effect of silane treatment reduces the viscosity of the composite. Figure 4.32 and 4.33 show the comparison of shear viscosity and shear stress with shear rate between treated and untreated samples at 15wt% filler content.

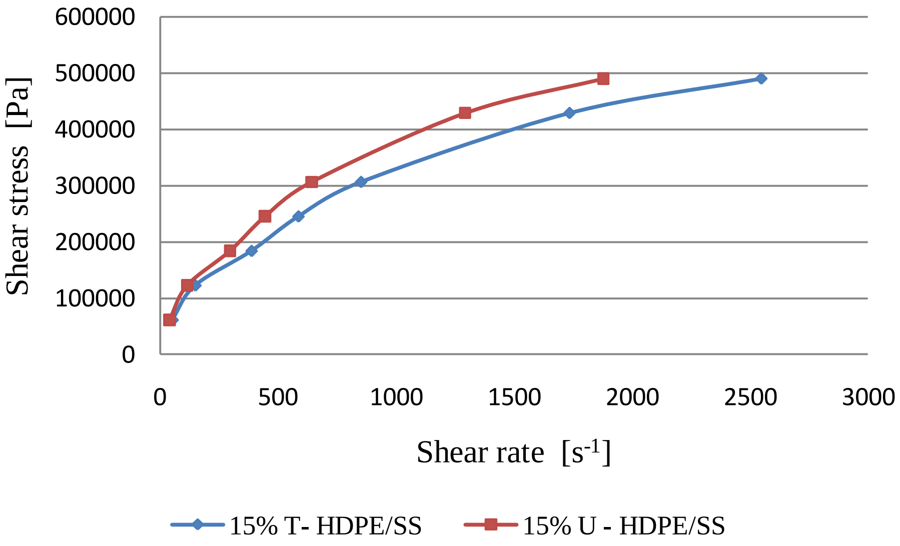


Figure 4.32 Comparison of shear stress between treated and untreated samples

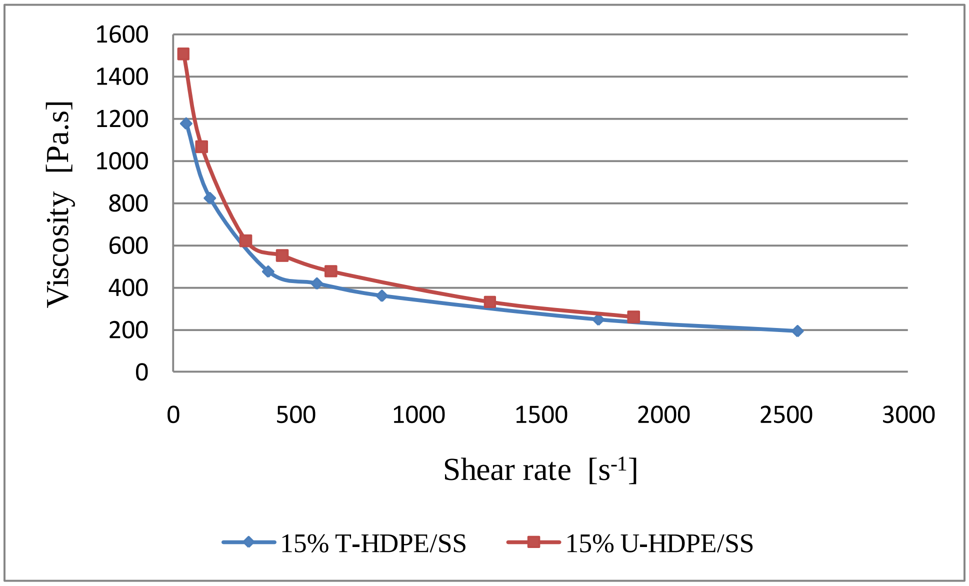


Figure 4.33 Comparison of shear viscosity between treated and untreated samples

It was found that the viscosity of the composite decrease after treatment and a maximum decrement of 35.6% at 15wt% have been recorded. The reduction in viscosity is due to the lubricating effect of chemical treatment.

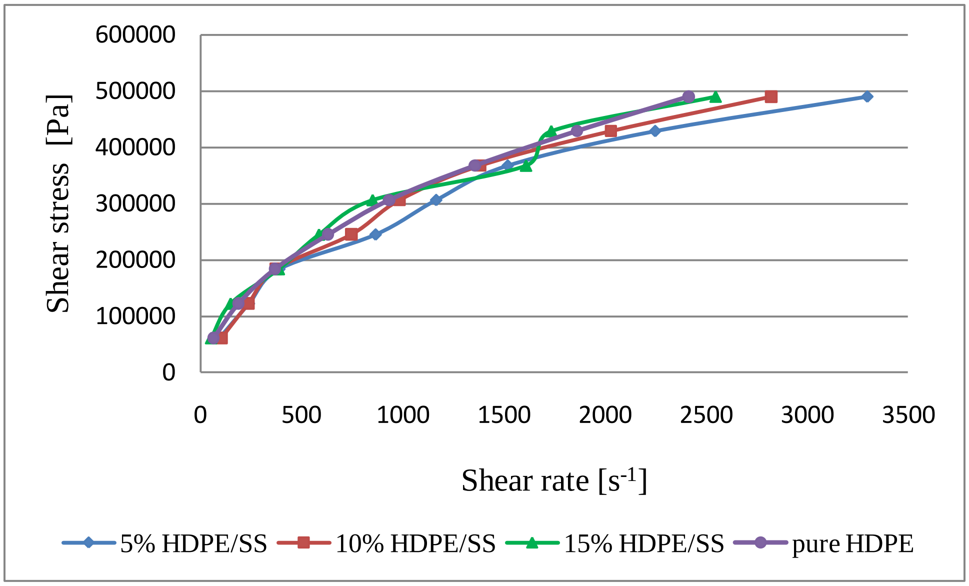


Figure 4.34 Variation of Shear stress with shear rate for T-HDPE/SS composite

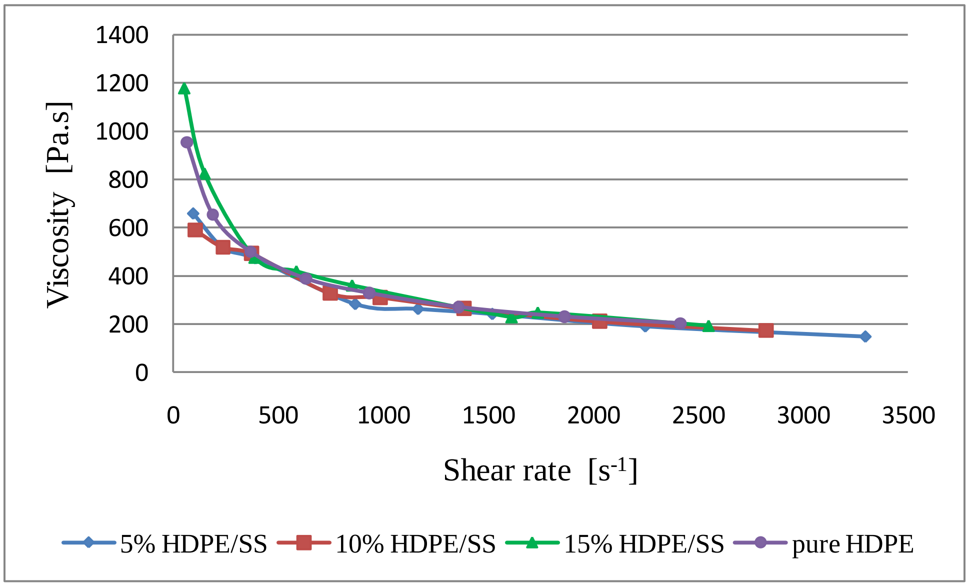


Figure 4.34 Varietion of viscosity with shear rate for T-HDPE/SS composite

From the rheological results it can be said that the chemical treatment reduced the viscosity of the composite. Moreover, the increased in viscosity with the filler content shows a significant difference in the case of the untreated composite and minimal difference in the case of treated composite. Using 40 N weights the maximum decrement in shear viscosity were recorded as 29.4%, 33.9% and 35.6% at 5 wt%, 10 wt% and 15 wt% respectively compared to the untreated composite.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The results of the mechanical test show that there is a decrease in tensile strength, maximum elongation and a significant increment in tensile modulus of elasticity, a slight increment in flexural strength and flexural modulus with reduced maximum deflection for both U-HDPE/SS and U-PP/SS composites. This is probably due to the weak interfacial interaction between filler and the matrix as a result of weak interfacial bonding, less surface energy of the particles due to its size and shape and probably the size reduce the amount of functional group on the surface of filler particles.

The test results based on chemically treated filler show that mechanical properties of the composite have been enhanced as a consequence of improved interfacial interaction. Comparison of composite materials prepared by using two silane coupling agents, MTS and VTES revealed that MTS composite is better than VTES. This may be due to the length of carbon-carbon chain in the back bone of MTS which can improve the interfacial bond as compared to VTES. Hence, MTS has been chosen for treating the whole sample. It was found that increment in tensile strength, modulus of elasticity and much better maximum elongation than U-HDPE/SS for MTS treated HDPE/SS (T-HDPE/SS) composite this might be because of the elastic this interfacial layer between the filler and the polymer matrix. The SEM morphological figures taken from the fractured surface of tensile test also strengthen the conclusion of the mechanical test results.

The mixing torque required and time taken for the process in the internal mixer was also studied. It was found that the maximum torque required for mixing operation increased with the filler content and attained a constant value after 10 min for all mixtures.

From the study of thermal properties, the test results from DSC show that there is a small increment in the melting temperature of the composite as the filler content increases. This may be due to the high heat resistive nature of the filler material. Since the test specimens are small in amount, the probability of having the filler inside the DSC sample is minimal unless otherwise an ideal uniform distribution of the filler in the matrix is attained.

Shear stress, shear rate and viscosity of the composite were studied by a capillary rheometer and it was found that an increment in Shear viscosity and a decrement in shear rate were recorded at a constant shear stress for all filler composition. Moreover, the treated composites show decrement in shear viscosity compared to the untreated sample composites. Maximum decrement of shear viscosity was recorded at 15wt% with 40N load and it was 35.6% compared to the untreated sample. This is possibly due to the restricted movement of the polymer strands by the filler particles in the case of untreated sample. While the effect of chemical treatment adds lubrication and thus reduction in shear viscosity to the composite.

Since this study is based on a micro scaled powdered particle, it is recommended that a better result can be found using a nano-sized particle. By doing so, the surface area and surface energy of the particle increases and therefore, result in better wettability of filler by the matrix. Increasing the wettability of the filler improves the interfacial strength between the filler and matrix as a consequence improves mechanical, thermal as well as rheological properties.

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APPENDIX A

MECHANICAL PROPERTIES

TableA-1 Tensile and Flexural properties of pure HDPE

	Tensile properties		Flexural properties	
Test no.	Strength [MPa]	Modulus [MPa]	Strength [MPa]	Modulus [MPa]
1	22.81	281.83	25.469	916.323
2	23.98	269.74	24.924	902.335
3	22.8	282.52	25.918	944.895
4	22.97	285.84	25.038	910.880
5	-	-	25.836	931.467
Mean	23.143	279.98	25.437	921.18
STD	0.490	6.105	0.403	15.186

TableA-2 Tensile properties of untreated HDPE composite

Filler content	Strength [MPa]	Modulus [MPa]	Elongation at yield [mm]	Maximum elongation[mm]
0wt%	23.143	279.98	12.019	12.128
5wt%	22.288	369.72	9.8357	10.64
10wt%	21.83	386.57	10.035	10.271
15wt%	20.756	399.97	9.5969	9.8015

TableA-3 Tensile properties of MTS treated HDPE composite

Filler content	Strength [MPa]	Modulus [MPa]	Elongation at yield [mm]	Maximum elongation[mm]
5wt%	23.295	382.39	10.705	11.085
10wt%	23.396	401.13	10.338	10.736
15wt%	23.819	443.94	9.197	9.770

TableA-4 Flexural properties of untreated HDPE composite

Filler content	Maximum load[N]	Strength [MPa]	Modulus [MPa]	Deflection[mm]
0wt%	41.743	25.437	921.18	15.67
5wt%	41.752	25.443	923.74	15.72
10wt%	43.327	26.403	951.39	15.85
15wt%	46.091	28.087	994.78	16.08

TableA-5 Flexural properties of MTS treated HDPE composite

Filler content	Maximum load[N]	Strength[MPa]	Modulus[MPa]	Deflection[mm]
5wt%	41.781	25.461	928.05	15.815
10wt%	45.697	27.847	972.87	16.406
15wt%	48.76	29.713	1105.7	16.648

TableA-6 Tensile and Flexural properties of pure PP

	Tensile properties		Flexural properties	
Test no.	Strength[MPa]	Modulus[MPa]	Strength[MPa]	Modulus[MPa]
1	32.159	508.592	45.440	1549.129
2	31.303	533.600	44.269	1642.310
3	32.354	556.478	43.035	1362.621
4	32.241	547.834	44.230	1488.455
5	31.533	540.757	42.53	1466.956
6	31.343	547.631	-	-
Mean	31.822	539.15	43.901	1501.900
STD	0.438	15.356	1.681	92.461

TableA-7 Tensile properties of untreated PP composite

Filler content	Strength [MPa]	Modulus [MPa]	Elongation at yield [mm]	Maximum elongation[mm]
0wt%	31.822	539.15	10.941	11.186
5wt%	30.377	537.55	9.458	9.458
10wt%	29.348	567.90	8.620	8.620
15wt%	28.870	570.22	8.232	8.232

TableA-8 Tensile properties of MTS treated PP composite

Filler content	Strength [MPa]	Modulus [MPa]	Elongation at yield [mm]	Maximum elongation[mm]
5wt%	32.413	535.27	10.696	10.696
10wt%	31.025	563.06	10.411	10.443
15wt%	29.123	574.82	8.916	8.916

TableA-9 Flexural properties of untreated PP composite

Filler content	Maximum load[N]	Strength[MPa]	Modulus[MPa]	Deflection[mm]
0wt%	72.0043	43.901	1501.9	17.445
5wt%	78.267	47.694	1673.8	17.577
10wt%	75.008	45.708	1766.9	17.352
15wt%	74.574	1811.2	1811.2	17.185

TableA-10 Flexural properties of treated PP composite

Filler content	Maximum load[N]	Strength[MPa]	Modulus[MPa]	Deflection[mm]
5wt%	78.729	47.976	1585.2	17.152
10wt%	77.831	47.429	1683.7	17408
15wt%	82.626	50.350	1938.4	16.867

APPENDIX B

X-RAY DIFFRACTION

EFFECT OF MILLING TIME AND TEMPERATURE

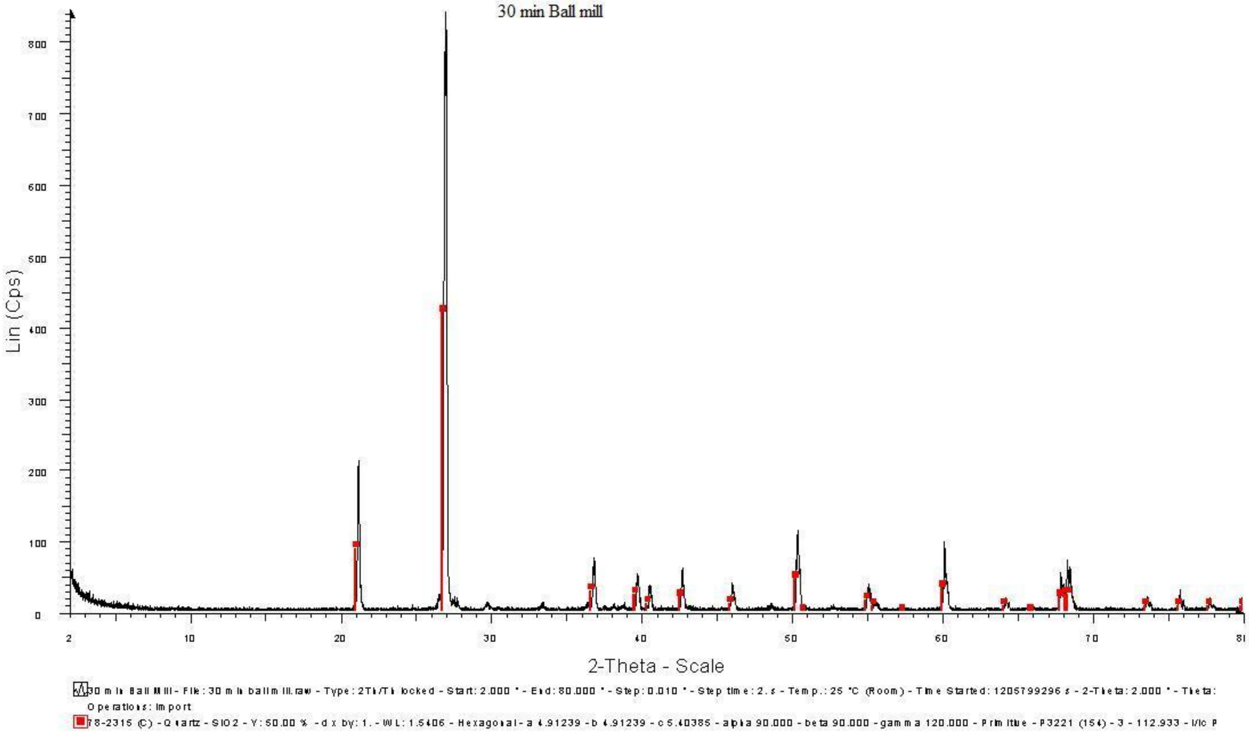

Figure B-1 XRD curve for silica sand with 30 min ball mill and 15-20 min grinding before screening.

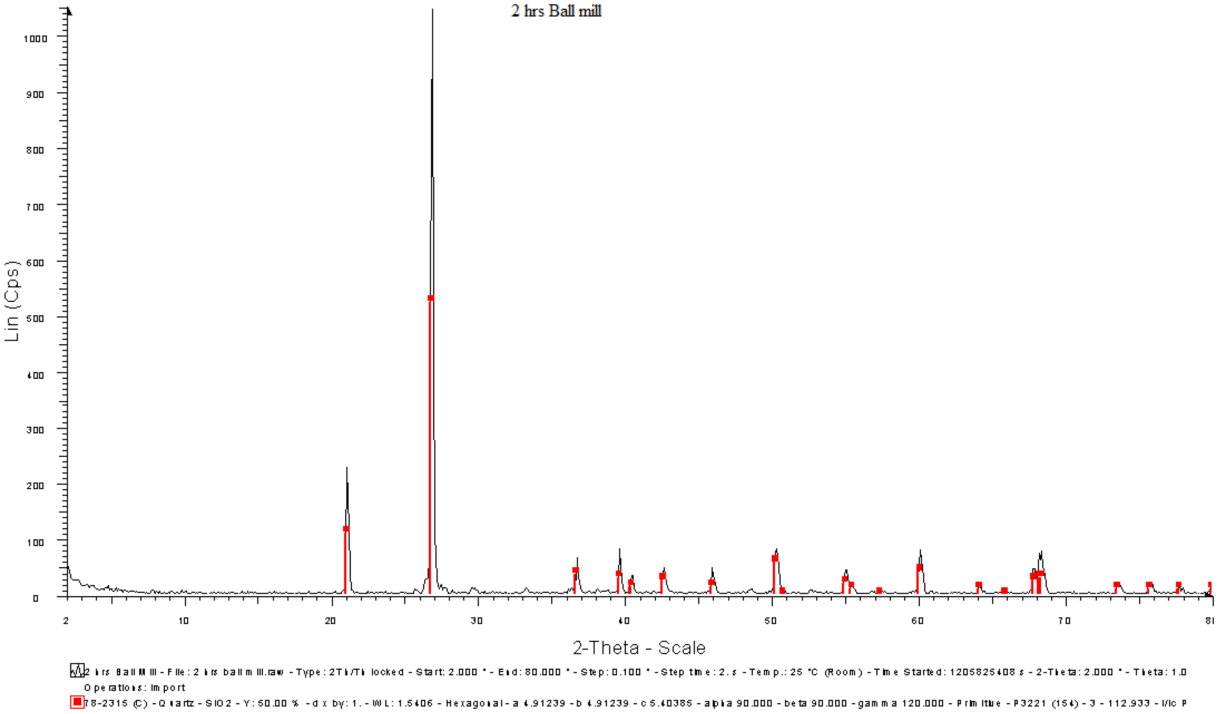

Figure B-2 XRD curve for silica sand with 2 hrs ball mill and 15-20 min grinding before screening.

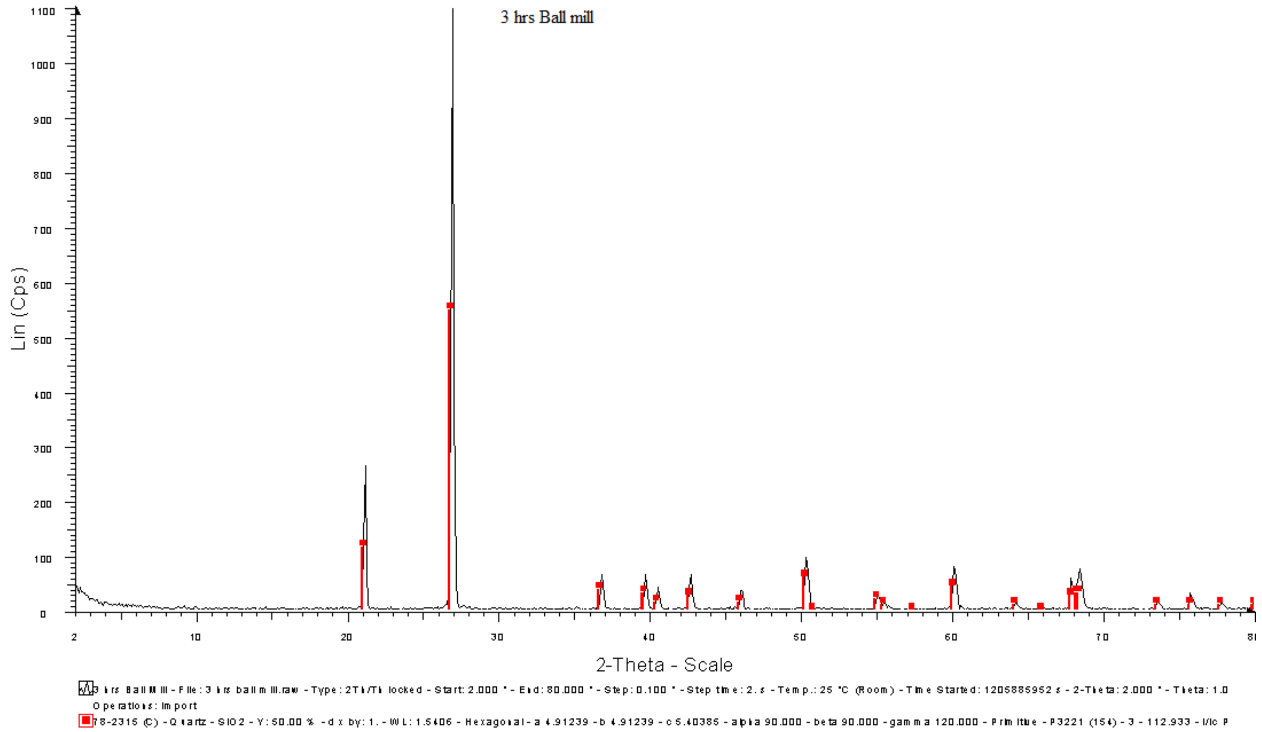

Figure B-3 XRD curve for silica sand with 3 hrs ball mill and 15-20 min grinding before screening.

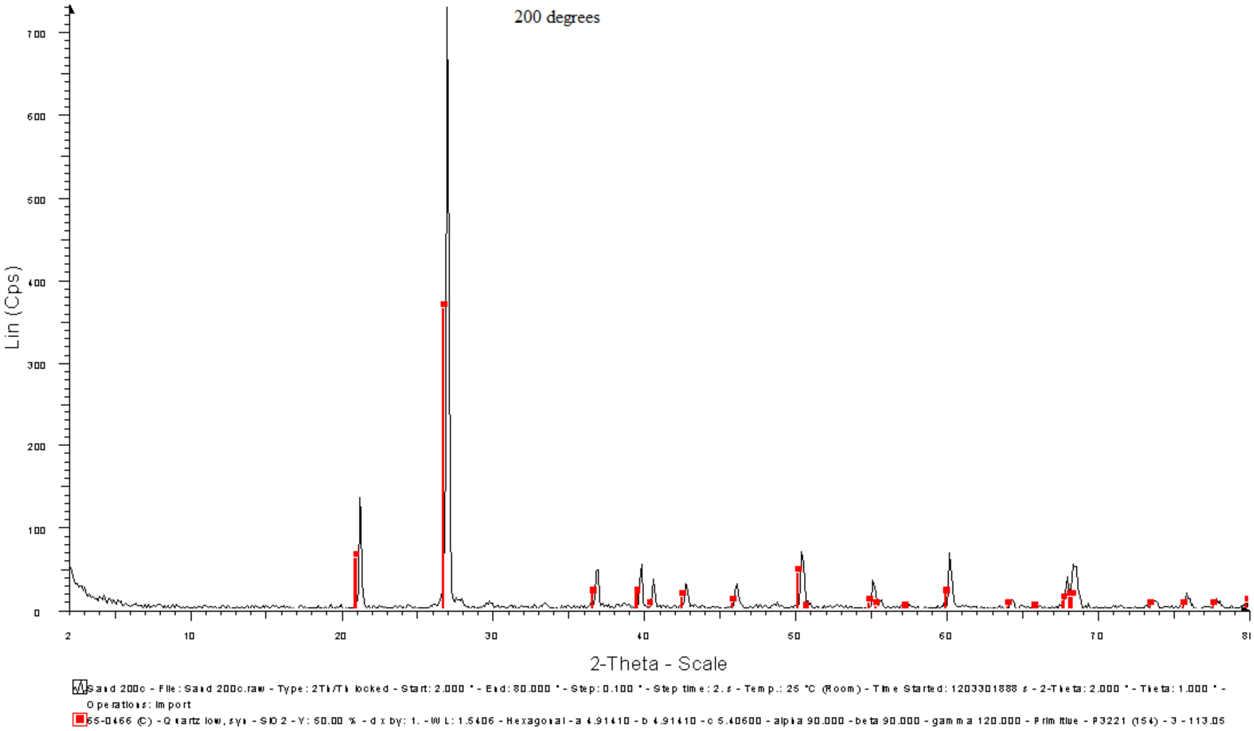

Figure B-4 XRD curve for silica sand with 5 hrs ball mill, heating at 200°C and 15-20 min grinding before screening.

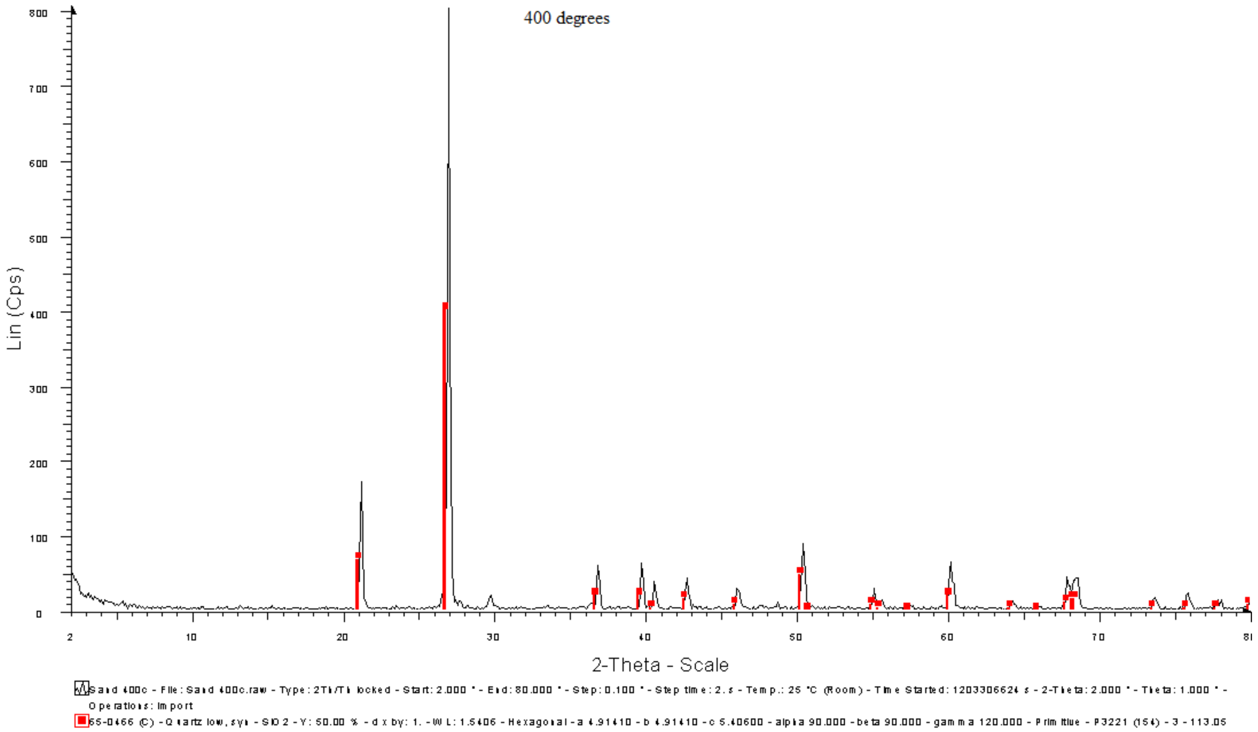

Figure B-5 XRD curve for silica sand with 5 hrs ball mill, heating at 400°C and 15-20 min grinding before screening.

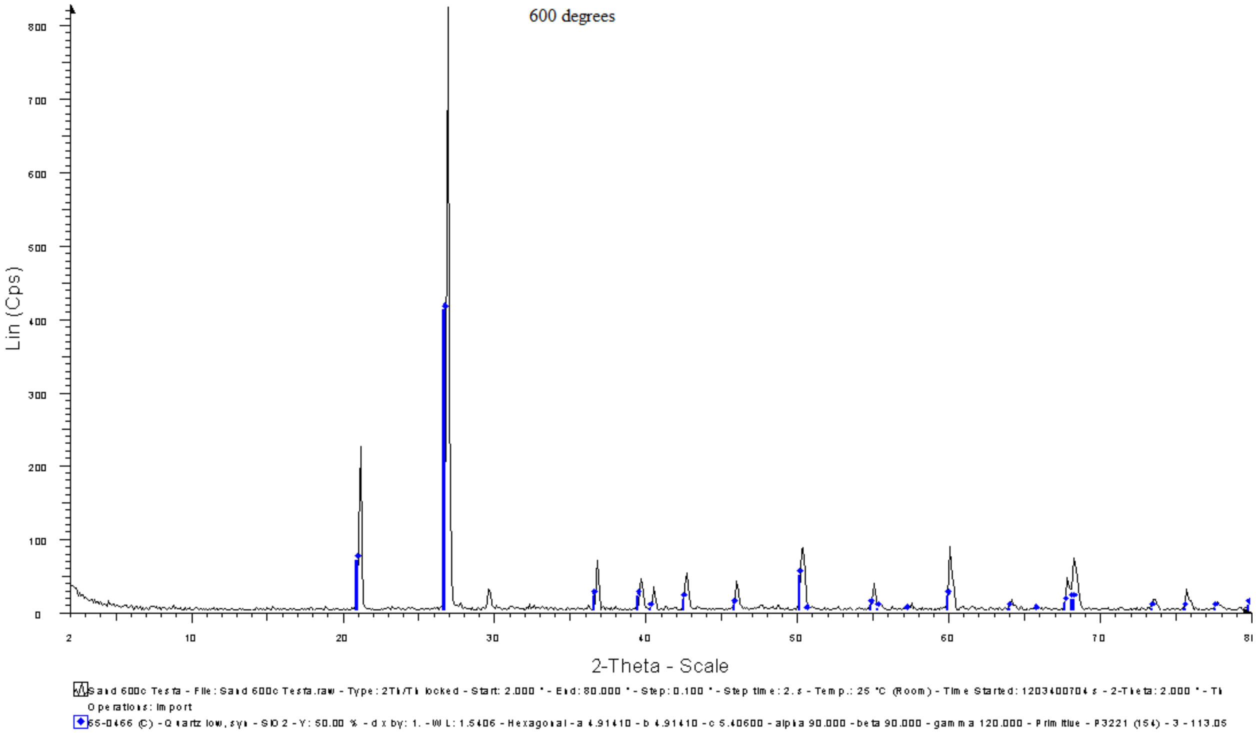

Figure B-4 XRD curve for silica sand with 5 hrs ball mill, heating at 600°C and 15-20 min grinding before screening.

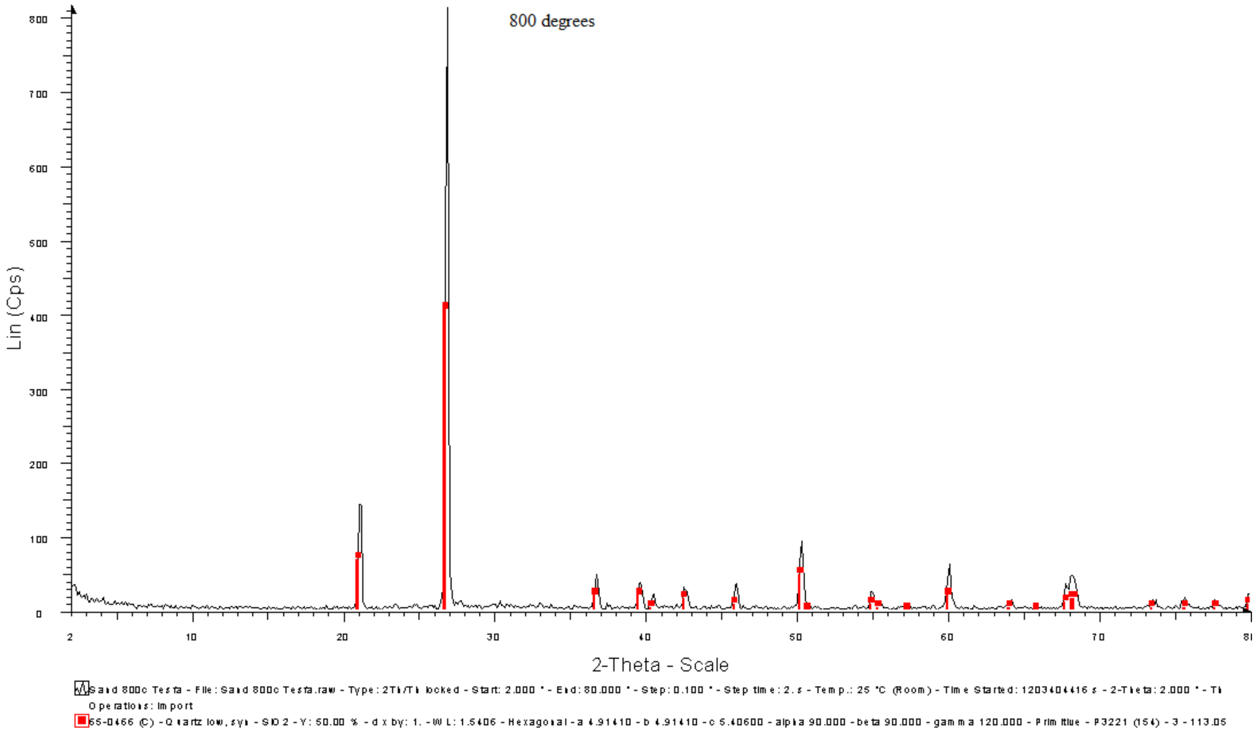

Figure B-4 XRD curve for silica sand with 5 hrs ball mill, heating at 800°C and 15-20 min grinding before screening.