Effects of Coupling Agent on Mechanical Properties of Rice Husk Filled Polyethylene Composite

by

Nur Syuhada Binti Zainol

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Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Dr. Mohamad Zaki Bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
August 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own expect as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR SYUHADA BINTI ZAINOL

ABSTRACT

This project presented the experimental study of the effects of the coupling agents concentration on the mechanical properties of natural fibers reinforced composites such as tensile and flexural properties. The chosen natural fiber used in the project is rice husk flour (RHF), a type of agricultural waste. Based from previous research, RHF has good potential as reinforcement in thermoplastic composite. RHF was combined with high density polyethylene (HDPE) as the matrix to create the composite with the addition of maleic anhydride grafted polyethylene (MAPE) as a coupling agent. The concentration of coupling agent used in the compounding process of RHF and HDPE depended on the pre-determined compositions. The addition of the coupling agents were varied using the percentage varying from 0 wt. % , 2.5 wt. % 5 wt. % , 7.5 wt. % and 10 wt. %. Experiment parameters such as temperature and moisture content affected the results of the composite. The pallets produced from extrusion process below 200°C with screw speed 60rpm. The pallets produced were injection moulded at temperature around 185-200°C to produce specimens for the tensile tests (ASTM D638) and flexural tests (ASTM D790). Five good samples were used for each type of compositions of the composites for the tensile and flexural tests. Based from the conducted tests, it was found that the tensile strength of the composites when using the concentration of 5 wt. % of MAPE is the highest value. The highest value for flexural strength however found using only at 2.5 wt. % of MAPE.

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Mechanical Engineering
Universiti Teknologi PETRONAS

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ABBREVIATIONS AND NOMENCLATURES

RHF – Rice Husk Flour

HDPE – High Density Polyethylene

MAPE – maleic anhydride grafted polyethylene

LDPE – Low Density Polyethylene

PP – Polypropylene

LTC – Lignocellulosic Thermoplastic Composite

PVC – Polyvinyl Chloride

WF – Wood Flour

MaPO – Maleated Polyolefin

CHAPTER 1

INTRODUCTION

1.1 Background of Project

This project evaluates the effects of coupling agent concentration added during the compounding process to the mechanical properties of the rice husk filled polyethylene composites. The mechanical properties of the composite material that were evaluated in this project are tensile and flexural strength. Specimens of the composites were prepared in accordance to ASTM D638 and ASTM D790 Standards using injection moulding process.

1.2 Background of Study

A composite material is a combination of two or more materials of which overall performance characteristics exceed those which are achievable from its individual components [1]. In polymer matrix composites, fibrous materials for example synthetic or natural serve either as filler or as reinforcement by giving strength and stiffness to the structure. While the polymer matrix serves as the adhesive to hold the fibers in place. Natural fibers have been extensively used as reinforcements into polymer matrices as an alternate to the commonly used synthetic fibers such as carbon, glass or aramid because of their low-density good mechanical properties, abundant availability and biodegradability [2]. However, large difference in surface polarity between hydrophilic natural fibers and hydrophobic polyolefin matrix usually leads to poor interfacial adhesion and thus poor mechanical properties of final materials [3].

To promote the interaction between them, various coupling agents or compatibilizers (mainly functionalized polymers) have been used in the literature. Among them, maleic anhydride-grafted PE or PP is the most commonly available because of their ability to effectively enhance mechanical properties of the composites, especially tensile and flexural strengths [3].

The properties of a composite material also are strongly influenced by the properties of its constituents. Various factors that affect the properties of composites are fiber dispersion, orientation and geometry (aspect ratio) of the fibers within the composites, the fibers volume fraction and the quality of interface between the reinforcing fibers and polymer matrices [4]. The use of lignocellulosic natural fibers as fillers or reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in the past few years [5].

These natural fibers can be obtained from several sources, both from forestry and agricultural sources. Wastes from agricultural and forestry industries are renewable abundant natural materials that have been historically in use as fillers for phenolic and ureic resins. The benefits offered by these natural fibers are improved mechanical properties and low cost. Due to low cost and energy saving natural fibers reinforced composites have received increasing attention in automotive and building materials industries [6]. Both these practices contribute to indirectly solving important environmental problems through proper consumption of otherwise agricultural waste. In any commercial development, there must be a long term guaranteed supply of resources as well as readily available raw materials for use as composting fibers.

Fortunately, agricultural fibers such as rice husk flour (RHF) are abundantly available in Malaysia as paddy is a mainstream in agriculture. This composite material made from RHF and HDPE is extruded to profile shape, which looks exactly like a high-strength wood bar in terms of dimension, colour, and hardness [7]. The Fibersit Technology composite (RHF and HDPE) is claimed to have all the structural qualities of wood, handles like wood but yet is stronger and more durable than wood. It can be nailed, screwed, drilled, sawn, milled, processed and finished just like wood [7].

1.3 Problem Statement

The differences in hydrophile characteristics between natural fibers and polymers require the use of coupling agents to improve the interfacial bonding between them, leading to mechanical property improvement. Since natural fibers and polymers have different polar characteristics, the former is polar and the later is non-polar. The most effective concentration for the coupling agent (maleic anhydride grafted polyethylene) that can provide adhesion to the surface of the natural fiber (rice husk flour) and the thermoplastic (high density polyethylene) should be identified.

1.4 Objective

The objective of this project is to investigate the effects of the coupling agent concentration to the mechanical properties of the rice husk flour – high density polyethylene composites. The mechanical properties that were analyzed in this project were tensile and flexural strength.

1.5 Scope of Study

The scopes of study of this project are stated as below:

1. The major materials that were used in this project were rice husk flour (RHF) as the reinforcing filler material, high density polyethylene (HDPE) as the matrix in this project and maleic anhydride grafted polyethylene (MAPE) as coupling agent. The graphic representations of these materials are shown in Figures 1.1, 1.2 and 1.3.

2. RHF was taken industrially from the paddy mill.

3. HDPE in virgin form was obtained from Titan Chemical Corp. Sdn. Bhd (Titanvene™ HD5218EA).
4. The coupling agent was maleic anhydride grafted polyethylene (MAPE), manufactured by Sigma-Aldrich Co.

Figure 1.1: RHF in abundant.

Figure 1.2: Virgin HDPE in pallets form.

Figure 1.3: MAPE in pallets form.

5. Mixture compositions of the reinforcing filler material and matrix polymer were around 70 wt. % HDPE and 30 wt. % of rice husk flour. Filler loading was fixed at 30 wt. %.

6. The coupling agents were varied from 0 wt. %, 2.5 wt. %, 5wt. %, 7.5 wt. % and 10 wt. %.

7. Preparation of natural filler reinforced composites involved the following stages:
    a) Samples preparation of HDPE and RHF
    b) Subsequent mixing of HDPE and RHF with coupling agents using twin screw extrusion process.
    c) Drying of the pallets using dry oven for an overnight.
    d) Injection molding of the mixtures.

8. Samples produce from the injection molding process were used to determine the tensile strength of the composites (ASTM D638 Standard). The mechanism of tensile test is shown in Figure 1.4.

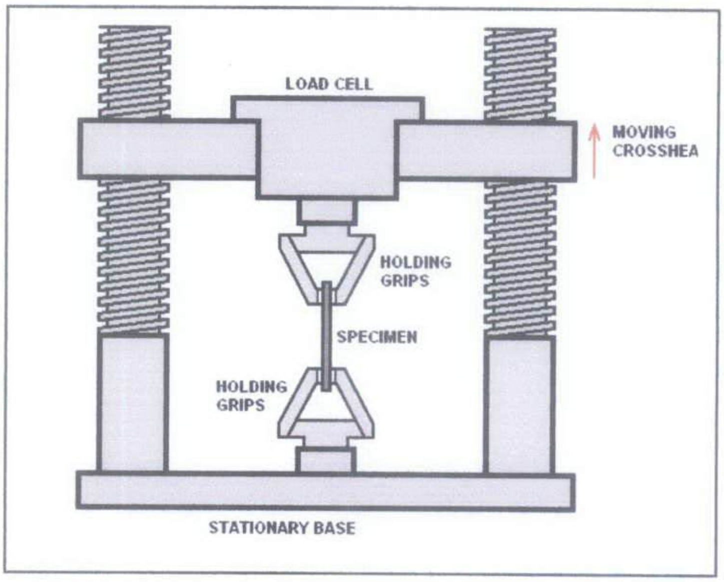


Figure 1.4: Mechanism of tensile test.

9. The samples also were used in Flexural Testing (ASTM D790) to test the stiffness of the composite material. The mechanism of flexural test is shown in Figure 1.5.

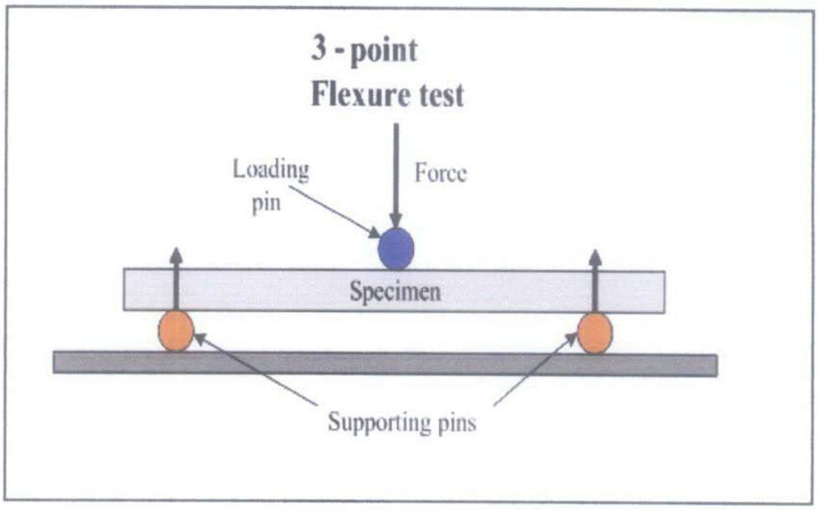


Figure 1.5: Mechanism of flexural test.

CHAPTER 2

LITERATURE REVIEW/THEORY

2.1 Overview

This chapter discusses on the origins and background of the lignocellulosic thermoplastic composites (LTC) and its applications. In this chapter also, lignocellulosic term is used instead of natural fibers to represent any type of filler size for example short fibers, long fibers, and flour. This chapter focuses on the use of rice husk flour (RHF) as the filler in the composites and the use of the high density polyethylene (HDPE) as the matrix material. The significant of RHF is this material can be obtained easily in Malaysia. The use of HDPE in the RHF composites is due to the processing temperature below 200°C which decreases the risk of lignocellulosic degradation. This chapter also focuses on the usage of the coupling agents in the compounding process of the composite materials. Coupling agents are used as the modification of filler surface in order to improve the interfacial adhesion between filler particles (hydrophilic) and polymer macromolecules (generally hydrophobic).

2.2 Lignocellulosic Thermoplastic Composite (LTC)

Composites are important class of engineering materials that have been used in applications ranging from leisure goods to construction Their excellent specific properties make them particularly attractive for applications in which weight saving is advantageous especially for transportation and aerospace [8]. The objective is to produce a product which performance characteristics combine the beneficial aspect of each constituent component.

The use of lignocellulosics with thermoplastics as composite is a more recent innovation after a long history of the use of lignocellulosics with thermosetting polymeric materials. The lignocellulosic thermoplastic composite (LTC) could be from any kind of agricultural residue or by-product that combined to the thermoplastic resin [9].

LTC was first gained recognition in the early 1950s when the automotive industry began adding wood flour to polypropylene to manufacture rear package shelves, spare tire covers and door liners. On 1983, American Woodstock from Wisconsin was producing 50 % wood flour filled in polypropylene as the automotive interior substrates using Italian extrusion technology [10]-[11].

In most applications, the LTCs are reported to have high modulus of elasticity which is 20% greater than polyvinyl chloride (PVC). They also have high impact resistant, outstanding screw and nail retention, low flame spread and excellent thermal properties [12].

The benefits offered by LTC include making the final product lighter and decreasing the wear of the machinery used in the production process. Moreover, LTCs have the advantages of low cost, biodegradability and the absence of residues or toxic by-products, whereas inorganic materials such as glass fibers, carbon fibers, talc, clay and synthetic fibers do not have these benefits. Another attraction of using these materials is it would allow various agro-wastes to be appropriately recycled [13].

As a result, composites using lignocellulosic materials as reinforcing fillers have been used extensively in the automotive and as interior finishing industry. More recently, their utilization has been extended to such areas as flooring, instrument grips, and pallets [8]. LTCs are believed to have low maintenance, lack of cracking and splintering, low thermal expansion and high durability [11]-[12].

2.2.1 Applications of Lignocellulosic-Thermoplastic Composite (LTC)

Based from previous studies, it was observed that LTCs are being developed for applications in automotive, building, furniture and packaging industries [14]. Some of its typical applications in the building industry include decking, skirting boards, porches, verandas, railings, door/window profile, furniture, architraves, fencing, industrial flooring, landscape timbers, and mouldings [11]. It also found that LTC was also used in marine piling, pier and dock surfaces [15]. In Malaysia, the applications include park benches, fencing and small economy house [7]. Example of LTC products are shown in Figures 2.1 and 2.2.

Figure 2.1: Example of LTC composite as wood decks.

Figure 2.2: Example of LTC composite in building materials.

2.3 Cellulose Based Fibers

There is a wide variety of cellulose fibers that can be used to reinforce thermoplastics such as wood fibers, agro based fibers such as stems stalks, bast leaves and seed hairs. Recycling agro based fibers based products such as rice hulls from rice processing plants are one of a large source of natural fibers [16].

Cellulosic fibers, like henequen, sisal, coconut fibers (coir), jute, palm, bamboo, wood, paper in their natural condition, as well as, several waste cellulosic products as shell flour, wood flour and pulp have been used as reinforcing agents of thermosetting and thermoplastic resins [16].

2.3.1 Moisture Absorption of Natural Fibers

All natural fibers derived from plants are based on cellulose, which is hydrophilic and hence absorb moisture. Usually moisture content in natural fibers varies between 5 and 15%. High moisture content can lead to dimensional variation and affects mechanical properties. Therefore, natural fibers must be processed, dried and stored under optimal conditions before impregnating them with polymers during processing of thermoplastic composites. Chemical treatments of natural fibers are believed to improve their mechanical properties, thermal stability and reduce moisture content of natural fibers [17].

The moisture absorption by composites containing natural fibers has several adverse effects on their properties and thus affects their long-term performance. For example, increased moisture content decreases their mechanical properties, provides necessary conditions for bio-degradations and changes their dimensions. To improve the moisture resistance of composites, numerous efforts have been made. Coupling agents and other chemical modifications were used to improve the moisture resistance of composites [17].

2.4 Polymer Matrices in Composites

Matrix plays a significant role in the performance of any composite. The matrix material in composites is load transferring medium between fibers. The ability to transfer load between fibers is mainly characterized by mechanical properties of matrix for example Young's modulus and tensile strength) and the interfacial bond between fibers and matrix [18]. The main limitation in choosing a suitable polymer matrix for natural fibers impregnation is the processing temperature, which is restricted to the temperature below 200°C to avoid thermal degradation of natural fibers.

Both thermosetting and thermoplastic polymers have been used for a long time as attractive polymer matrices for natural fibers reinforced polymer composites. Thermoplastic polymers offer many advantages over thermosetting polymers, one of which is their low processing costs and another is design flexibility and ease of moulding [19].

The lower thermal stability of natural fibers limits the number of thermoplastics to be used as matrix material for natural fibers reinforced thermoplastic composites. Only those thermoplastics can be used whose processing temperature does not exceed 230°C [20].

2.4.1 Polyethylene as the Matrix Based

The use of thermoplastics as the matrix instead of thermosets adds the potential of product recycling [17]. Although thermoplastics have their limitations due to their tendency to creep and therefore limited load bearing ability, they have unique processing advantages and do not have the volatile emissions associated with formaldehyde based adhesives [21].

Table 2.1 shows that the melting temperature of polyethylene is obviously lower as compared to polypropylene. The lower processing temperature of polyethylene permits the composite to be processed at temperature below than 200°C [11]. Since then, polyethylene is the best thermoplastic matrix for the composite processing without lignocellulosic filler degradation.

Table 2.1: The thermal stability polyethylene and polypropylene [22].

	Polyethylene	Polypropylene
Melting temperature (°C)	110-135	130-168
Maximum service temperature, Air (°C)	41-120	44-148
Processing temperature (°C)	190-274	202-252

The thermoplastic is often selected based on its inherent properties, product need, availability, cost, and the manufacturer's familiarity with the material. Due to the limited thermal stability of lignocellulosic, it is suggested that only thermoplastics that melt or can be processed at temperatures below 200°C should be used [11].

2.5 Rice Husk Filled Composites

Development of composites using agro-wastes or lignocellulosic materials as reinforcing fillers with thermoplastic polymers as matrices is currently the focus of attention. Rice husk is of such major agro-waste products and natural filler, which contain cellulose, hemicelluloses, lignin and ash [23]-[24]. This natural filler has been utilized in the manufacture of composite panels.

Polyolefin (HDPE, LDPE and PP) were used as matrix polymer. Thickness swelling and water absorption of bio-composites slightly increase while mechanical properties decrease as filler loading increases, but their values are negligible as compared with those of the wood-based composites and solid woods.

Rice husk powder is one of the favourite filler since paddy is the third most widely planted crop after palm oil and rubber. On average, paddy production in Malaysia is about 2 million tonnes yearly. With residues in the form of rice husk estimated at 22%, a total volume of 0.44 million tonnes of rice husk would theoretically be available.

The rice husks generated become a problem of disposing especially when open burning is no longer permitted due to environmental concerns. There are more than 100 million metric tons of rice husk generated each year throughout the world [19]. This circumstances actually driving the utilization of this agricultural residue into useful value-added product.

Rice husk is unique within nature. The chemical structure of the rice husk, containing amorphous silica bound to water, closely resembles that of the opal, and this gives the rice husk some fairly amazing properties [23]-[24]. Table 2.2 shows a list of rice husk's composition from various sources in percentage.

Table 2.2: Rice Husk's chemical composition from various sources (%).

	Cellulose	**Hemicellulose**	**Lignin**	**Silica**	**Ash**	**Extracts**
Rice husk[a]	35	25	20	16	1	3
Rice husk[b]	38		22	19	20	1

[a] *Source : [23]*
[b] *Source : [24]*

2.6 Chemical Modification and Use of Adhesion Promoters

The most important issue associated with these composites is the interfacial adhesion between the natural reinforcing fillers and matrix polymers. In order to obtain good properties by improving the compatibility between these two materials with their different properties, reinforcing fillers are used after chemical modification. In other words, chemical modification is performed to overcome the incompatibility between the hydrophilic lignocellulosic material and the hydrophobic matrix polymer. The compatibility problem may be due to the fact that the polyolefin is non-polar and hydrophobic, whereas the natural fiber, which is a lignocellulosic material, is polar, due to the –OH groups in the cellulose [13].

Extensive studies are currently being performed on polyolefin (polypropylene and polyethylene) and various natural reinforcing fillers, in conjunction with various chemicals that could affect the interface. The adhesion promoters are mainly based on the same polyolefin modified with maleic anhydride [25].

The results are quite variable, depending on the polymer matrix used, the filler type and quantity, the adhesion promoter used (i.e. the base polymer on which it is prepared, its molecular weight, the modifier percentage, etc.) and its amount, the processing techniques, etc. [25].

In general, it could be that these adhesion promoters, on average, can significantly improve tensile properties and process ability, while water absorption is reduced. However, in some cases, impact strength may not be enhanced; therefore specific elastomeric impact modifiers should be used [25]. An example of the improvements that a maleated adhesion promoter can assure to a green composite based on polypropylene and 30 wt. % wood flour is reported in Table 2.3.

Table 2.3: Main mechanical properties of polypropylene/wood flour green composite without and with the use of a maleated adhesion promoter [25].

Properties	**PP + 30% WF**	**PP + 30% WF + 3% MAPP**
Elastic modulus (MPa)	954	1035
Tensile strength (MPa)	19.5	27.2
Elongation at break (%)	4.2	4.6
Impact strength (unnotched) (J/m)	83	98

2.6.1 Maleic Anhydride Coupling Agent

This results in poor adhesion and prevents the reinforcing filler from acting effectively within the composite. In order to solve these problems, studies have been performed on surface modification or treatment using a coupling agent for the purpose of making the polyolefin chain hydrophilic. The strong interfacial bonding strength obtained by improving the compatibility between the hydrophilic filler and hydrophobic matrix polymer can improve the physical, mechanical and thermal properties of the composite system [13].

Maleated polypropylene has traditionally been used as a coupling agent for various polymeric composites which are filled with lignocellulosic materials, however, when polyethylene composites need to be reinforced, maleated polypropylenes are not recommended, because of the incompatibility between polyethylene and polypropylene. Thus, the use of maleated polyethylene which contains ethylene blocks is a better choice [13].

Interactions between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fibers can overcome the incompatibility problem to increase tensile and flexural strengths of natural fibers thermoplastic composites

[25]. The coupling agent chemically bonded with hydrophilic filler and blended by wetting in the polymer chain. The mechanism of coupling agent is shown in Figures 2.3 and 2.4 [26].

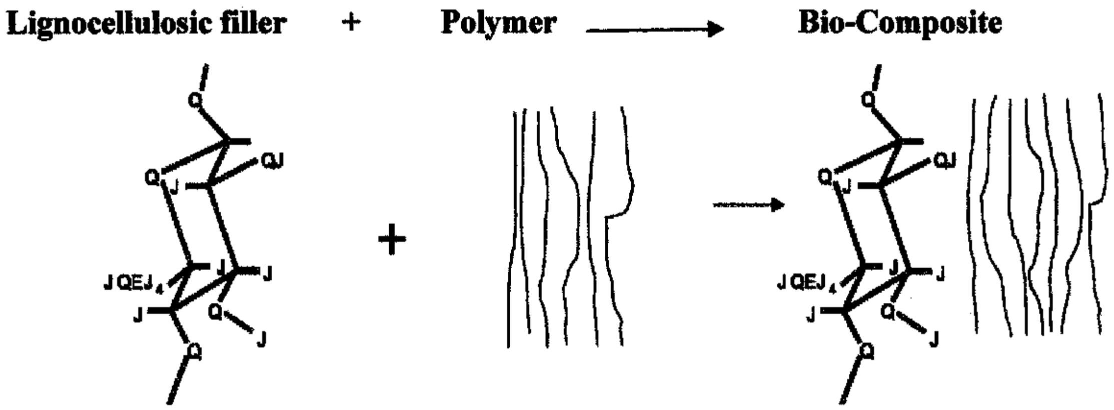


Figure 2.3: Mechanism of coupling agent between hydrophilic filler and hydrophobic matrix polymer [26].

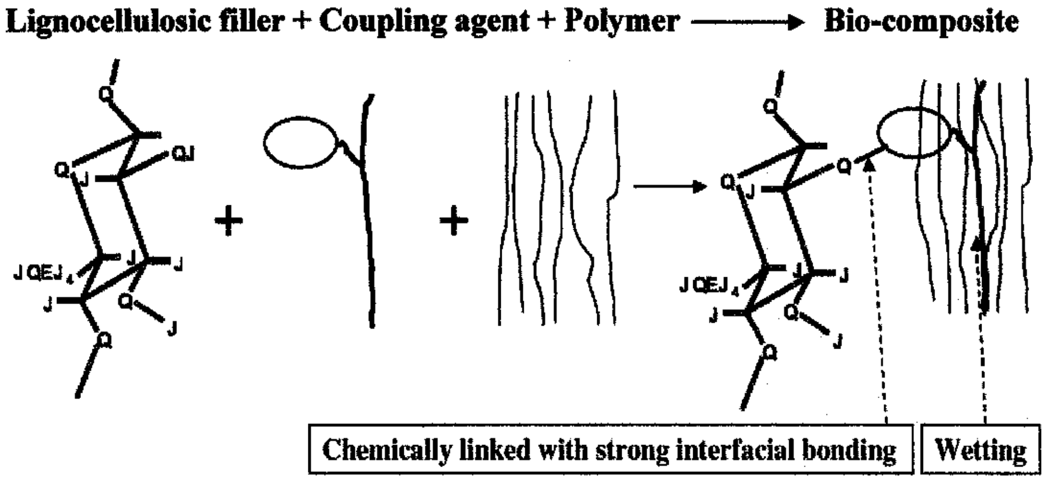


Figure 2.4: Mechanism of coupling agent between hydrophilic filler and hydrophobic matrix polymer with coupling agents [26].

2.6.2 Grafting Mechanisms

Previous Structural studies suggested that the grafting utilizes the carbon–carbon unsaturation of the maleic anhydride group to form the bond to the polymer chain thus leaving the anhydride group free to react as an anhydride in the newly formed polymer [25]. The presence of the relatively polar anhydride groups on the olefin imparts the unique set of properties to the graft polymer that makes these polymers good couplers for natural fibers in polyolefin [27].

Another reason for success of maleated polyolefin (MaPO) couplers pertains to their excellent balance of properties to bridge the interface between polar and non-polar species. A coupler holds dissimilar materials together. In the case of a MaPO, the coupler may co-crystallize with the continuous polyolefin while the maleic anhydride portion of the molecule can interact with the more polar natural fibers surface [27]. Evidence suggests the interaction between the coupler and wood may be of a covalent nature consisting of covalent bonds, secondary bonding (such as hydrogen bonding and Van der Waals' forces) [28].

CHAPTER 3

METHODOLOGY

3.1 Experimental Procedures

3.1.1 Materials

3.1.1.1 Matrix Polymer

The matrix polymer is high density polyethylene (HDPE). The manufacturer is Titan Chemical Corp. Sdn. Bhd (Titanvene™ HD5218EA). Below is the specification of this material as stated as below in Tables 3.1 and 3.2 (refer APPENDIX 3-1 for more details):

Table 3.1: General Properties of HDPE (HD5218EA).

General Properties	Value	Unit
Melt Flow Rate (190°C/2.16 kg)	18	g/10 min
Nominal Density	950	kg/m^3
Melting Point	130	°C

Table 3.2: Mechanical Properties of HDPE (HD5218EA).

Mechanical Properties	Value	Unit
Tensile Stress at Yield	23	MPa
Elongation at Break	250	%
Charpy Impact Strength	5	kJ/m^2
Flexural Modulus	1300	MPa

The main materials used in this project were rice husk flour (RHF) as the reinforcing filler material, high density polyethylene (HDPE) as the matrix in this project while the HDPE was obtained from Titan Chemical Corp. Sdn. Bhd (Titanvene™ HD5218EA). The coupling agent was maleic anhydride grafted polyethylene (MAPE).

3.1.1.2 Reinforcing Filler

The lignocellulosic material that was used as the reinforcing filler in the composite, in order to obtain the comparative data, was rice-husk flour (RHF). Rice Husk flour was taken industrially from the paddy mill.

3.1.1.3 Coupling Agents

Coupling agent was maleated polyethylene (MAPE), obtained from the manufacturer for MAPE is Sigma-Aldrich Co. Below is the specifications of the product as stated in Table 3.3.

Table 3.3: Properties of MAPE (456624 - viscosity 500 cP (140°C)(lit.)).

Composition	maleic anhydride, ~0.5 wt. %
Viscosity	500 cP (140°C) (lit.)
Saponification value	6 mg KOH/g
Transition temp	T_m (DSC) 107°C (at peak)
Solubility	H_2O: insoluble toluene and xylene: soluble
Density	0.92 g/mL at 25°C

3.1.2 Materials Composition

The composites were prepared based on ratio by weight percentage as stated in Table 3.4.

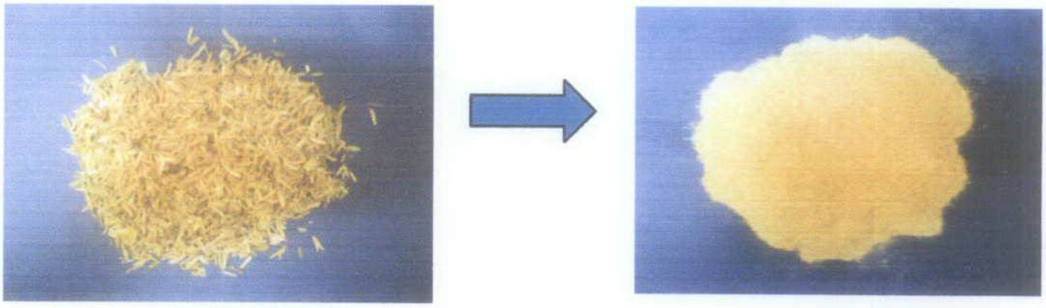
Table 3.4: Composite composition fixed at 30 wt. % filler loading.

HDPE (wt. %)	**RHF (wt. %)**	**MAPE (wt. %)**
70	30	0
67.5	30	2.5
65	30	5
62.5	30	7.5
60	30	10

3.1.3 Sample Preparation

The samples of the experiments were prepared according to these methods:

1. The reinforcing fillers, RHF were ground to 500 μm using the lab scale grinder as shown in Figure 3.1.



(a) (b)

Figure 3.1: Rice husk flour conditions (a) before grinding and (b) after grinding.

2. The reinforcing filler, RHF was oven dried to 1–3% moisture content using an air dryer oven at 100°C for 24 hours.

3. The materials were stored over a desiccant in sealed containers in an environmental controller prior to compounding.

4. RHF, HDPE and MAPE were mixed together according to the pre-determined compositions as shown in Figure 3.2.

Figure 3.2: Mixtures of RHF + HDPE + MAPE.

5. A laboratory scale twin-screw extruder was employed to compound the RHF with the HDPE, the latter being used as a matrix polymer, using three general processes; melt blending, extrusion and pelletizing.

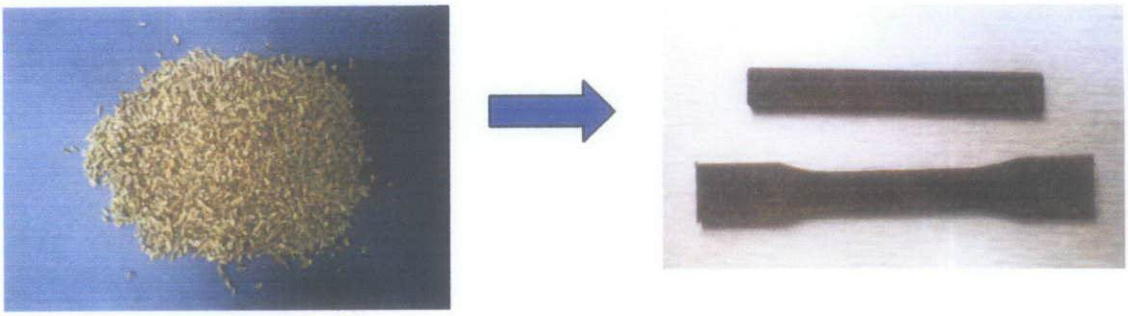
6. Compounding was performed at an average temperature 180°C with a screw speed of 60 rpm. The temperature profile at the twin screw extruder zones are as stated in Table 3.5.

Table 3.5: Temperature Profile at the Twin Screw Extruder.

Barrel Temperature Settings (°C)									
Zone	1	2	3	4	5	6	7	Flange	Die
Temp (°C)	165	170	175	180	180	180	180	175	170

7. The extruded strand was quenched in a water bath and then pelletized and stored in sealed packs containing a desiccant to avoid unexpected moisture.

8. The pallets then were injection moulded to produce specimens for tensile test and flexural test using melt temperature around 185-200°C with screw speed 600 mm/s and pressure at 800 bar. Figure 3.3 shows the pallets and specimens produced from injection moulding process. Figure 3.4 shows the typical injection moulding process.



(a) (b)

Figure 3.3: (a) is the pallets from extrusion process while (b) is the specimens.

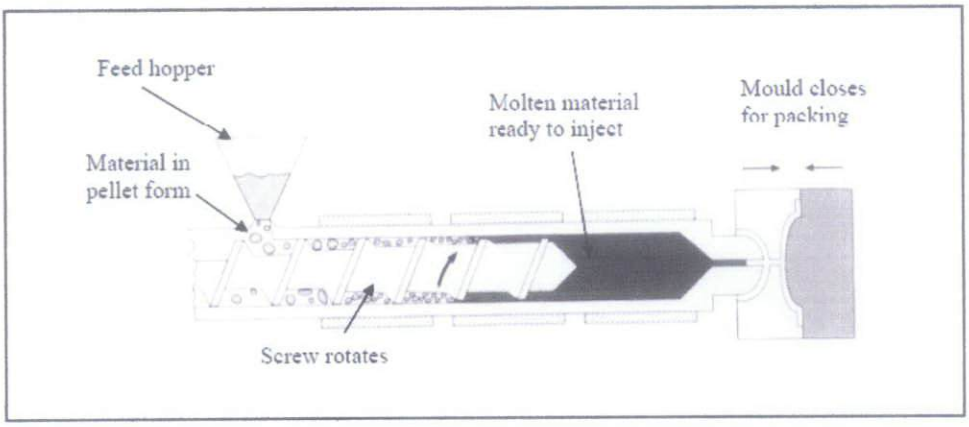


Figure 3.4: A typical injection moulding process.

3.2 Tensile Testing

The tensile tests were conducted according to ASTM D638 using Universal Testing Machine. The scope of the tensile test measures the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. Since the physical properties of many materials (especially thermoplastics) can vary depending on ambient temperature, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment [26].

Five good samples were used for the tests for each of the compositions of the composites. The tests were done using dog bone Type I at a crosshead speed of 5 mm/min and at room temperature. The gauge length used during the test was 50 mm while distance between grips was set at 115 mm. The specimens used in the tensile tests were from Type I as shown in Figure 3.5. The tensile testing was carried out in the lab using the Universal Testing Machine as shown in Figure 3.6.

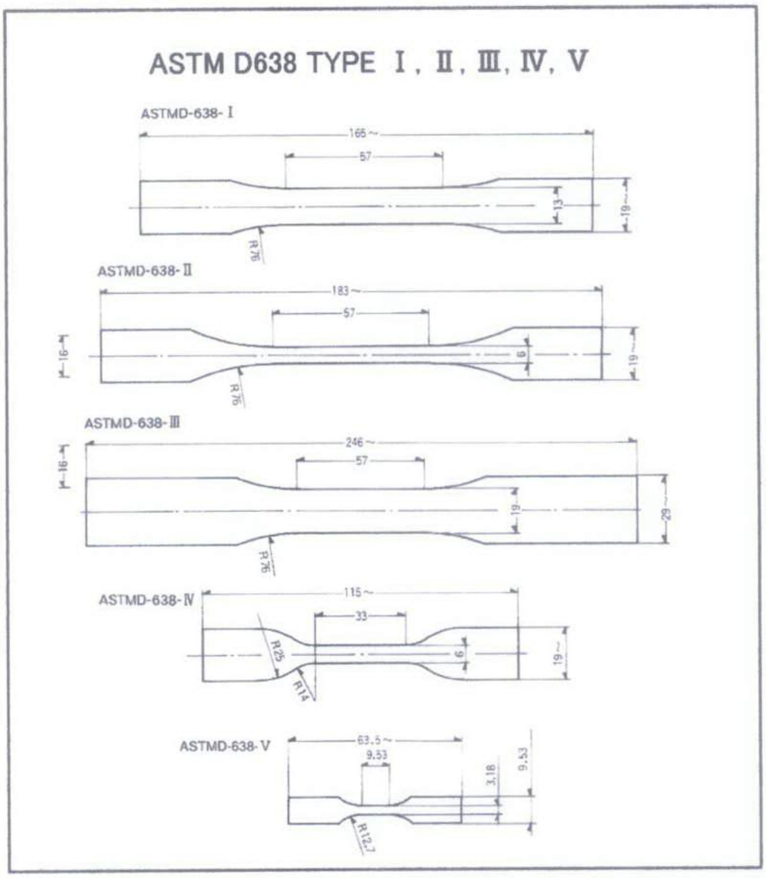


Figure 3.5: Examples of Specimens type for ASTM D638 Standard [29].

Figure 3.6: Tensile testing of the specimens at the lab using Universal Testing Machine.

3.3 Flexural Testing

The flexural tests were conducted in accordance to ASTM D790 using Universal Testing Machine. The scope of the flexural test covers the determination of flexural properties of unreinforced plastics, including high-modulus composites and electrical insulating materials in the form of rectangular bars moulded directly or cut from sheets, plates or moulded shapes. The tests utilize a three point loading system applied to a simply supported beam [29].

Five good samples were used for the tests for each of the compositions of the composites. The specimens having a typical dimension of 125 mm x 12.7 mm x 3.2 mm were measured under three-point bending using the same Universal Testing Machine in accordance with ASTM D790. A crosshead speed of 1.5 mm/min and a span length of 51.2 mm were used for the test. The flexural testing was carried out in the lab using the Ultimate Tensile Testing Machine as shown in Figure 3.7.

Figure 3.7: Flexural testing of the specimens at the lab using Universal Testing Machine.

3.4 Tools and Equipments

Figure 3.8 shows the lab scale grinder that was used to grind the rice husk to 500 μm. Lab scale oven used to dry the rice husk and the pallets produced in twin screw extrusion process is shown in Figure 3.9. The mixtures of HDPE + RHF and MAPE were compounded using the twin screw extruder shown in Figure 3.10. The pallets produced from the compounding process were later injection moulded using the injection moulding machine shown in Figure 3.11. In Figure 3.12, shows the Universal Testing Machine that was used in tensile and flexural tests.

Figure 3.8: Lab Scale Grinder with particles size >500 μm.

Figure 3.9: Lab Scale Dry Oven.

Figure 3.10: Lab Scale Twin Screw Extruder Machine.

Figure 3.11: Lab Scale Injection Moulding Machine.

Figure 3.12: Universal Testing Machine.

3.5 Gantt Chart

This project was done within the period of 14 weeks starting from preparation of materials until the documentation of the findings as shown in Table 3.6:

Table 3.6: Gantt chart.

No	Details	Week														
		1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Preparation of the materials (Grinding, baking)	🟨	🟨	🟨	🟨	🟨	🟨	🟨	MID SEMESTER BREAK							
2	Initial set of experiments without using coupling agents.	🟨	🟨													
3	Identifying the best parameters for twin screw extrusion process and injection molding process		🟨	🟨												
4	Experiments are carried out at twin screw extruder				🟨	🟨	🟨	🟨								
5	Finding alternatives for injection moulding machine									🟨	🟨	🟨				
	Injection Molding of the pellet from twin screw extrusion process											🟨	🟨			
7	Collection and analyzing of the data (Tensile testing and Flexural Testing)											🟨	🟨	🟨		
8	Compilation of all the data and final analysis													🟨		
9	Final documentation of all aspects of the project													🟨	🟨	🟨

CHAPTER 4

RESULTS AND DISCUSSIONS

Tensile strength and flexural properties were determined according to ASTM D638 and D790, respectively. This chapter presents the results and discusses the findings of HDPE/RHF without MAPE and with MAPE ranging from 2.5 wt. % to 10 wt. %. For this purpose, RHF was kept constant at 30 wt. % while HDPE content changes according to the content of MAPE.

4.1 Tensile Strength

Table 4.1 shows the results of tensile strengths for the composites. Data from Table 4.1 were used to create tensile strength graph against concentration of MAPE shown in Figure 4.1. The results suggest that tensile strength increases with the increase of MAPE until 5 wt. %. Beyond 5 wt. % of MAPE descending trend of tensile strength was observed. At 5 wt. % of MAPE, the highest tensile strength was 16.68 MPa, which was equivalent to 4.97% tensile strength improvement compared to the composites without MAPE. At this point, the standard deviation was the smallest, providing the confidence to the data.

Table 4.1: Tensile strength of the compositions according to according to wt. % of the composites.

	Tensile Strength (MPa) of the compositions according to wt. % (HDPE/RHF/MAPE)				
Sample Reference	70/30/0	67.5/30/2.5	65/30/5	62.5/30/7.5	60/30/10
1	15.93	16.59	16.60	15.59	16.13
2	15.93	16.00	16.58	16.45	16.18
3	16.22	16.20	16.68	15.53	16.18
4	15.91	16.16	16.71	16.20	15.86
5	15.47	15.92	16.82	16.30	16.17
Average	15.89	16.17	16.68	16.01	16.11
Standard Deviation	0.27	0.26	0.09	0.43	0.14

This small value of increment of the tensile strength with only 4.97% may affect from the moisture absorption from the environment. The moisture absorption of the composites having filler type from natural fibers in this case RHF can have several adverse effects on their properties. The excessive moisture can change the dimensions of RHF particle size and provides conditions for bio-degradations [17]. However, the improvement achieved using coupling agent as similar to previous study as stated by Kenner *et al.* (2004) [25].

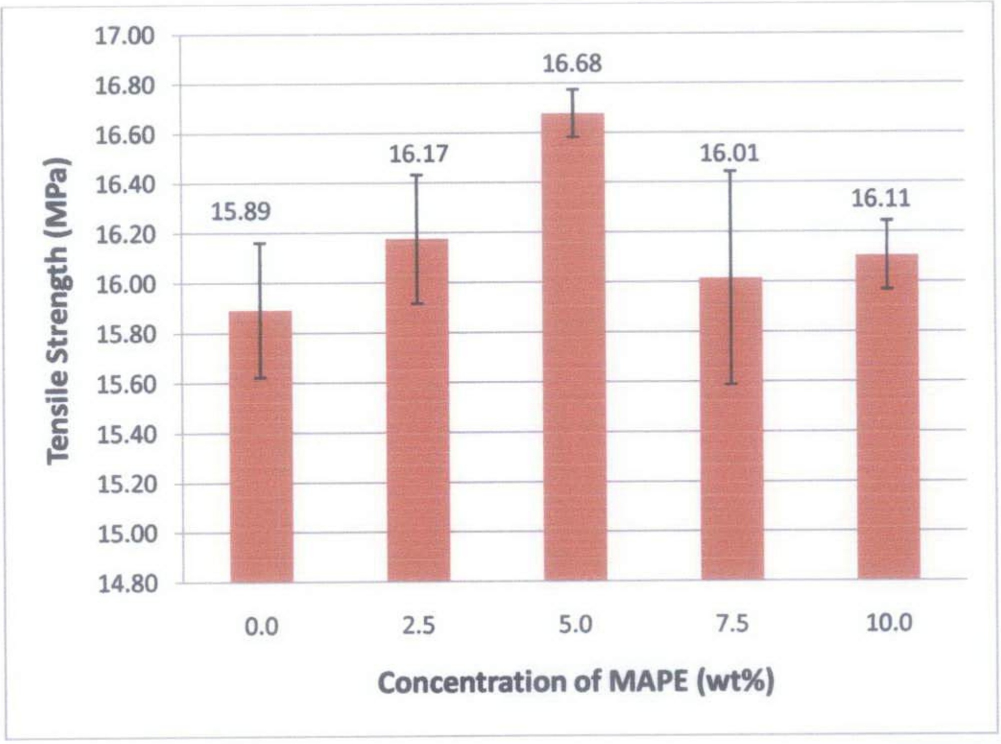


Figure 4.1: Average tensile strength of the composites using different concentrations of the coupling agent.

Thus, it shows that coupling agent help to improve the tensile properties of the composite as it can strengthen the interfacial bonding between the filler material and matrix polymer, in this case RHF and HDPE [13]. The coupling agent is believed to improve the surface functionality of the natural fibers, in this case RHF to bond chemically with HDPE. Addition of the MAPE also can be attributed to better wetting and dispersion of RHF in the HDPE matrix [33]. This mechanism can be simplified as shown in Figure 4.3.

The values of tensile strength reduce as the concentration of MAPE is higher than 5 wt. %. This may be due to the excess wetting provided by the coupling agent (MAPE) to the filler material (RHF) that could reduce the filler–matrix interaction. The decrease of tensile strength observed at high MAPE concentration cause from the occurrence of self- entanglements among coupling agents. This result may indicate that there seemingly exists a critical concentration of coupling agent, beyond which the wetting saturation of the filler is achieved at 5 wt. %. Thus, a higher concentration may be not necessary to improve interface quality. Similar findings were discussed elsewhere [30]-[32].

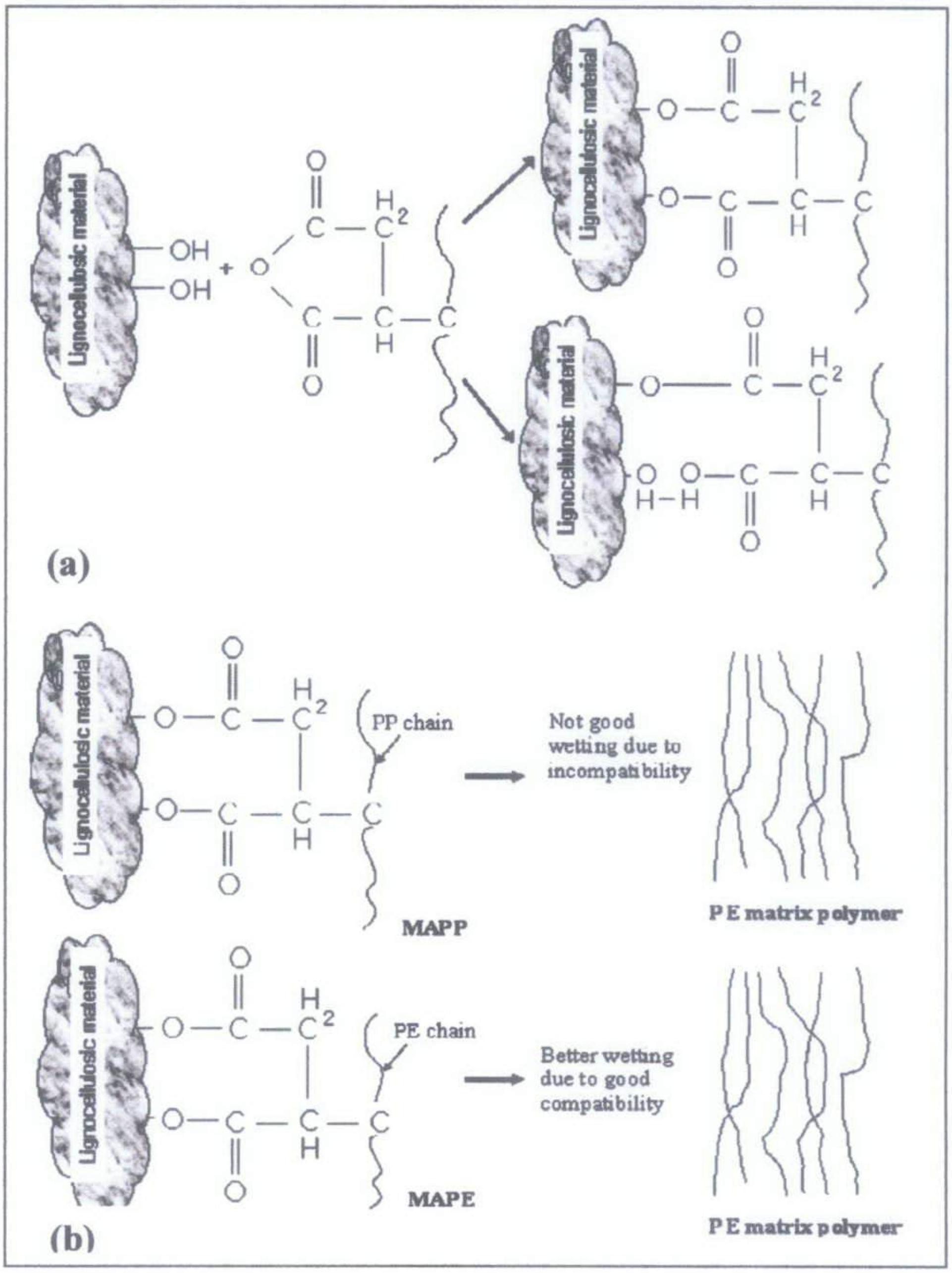


Figure 4.2: Role of coupling agent at the interface between natural filler and matrix polymer: (a) esterification of lignocellulosic material with coupling agent; (b) wetting of coupling agent treated natural filler [13].

4.2. Flexural Properties

Tables 4.2 and 4.3 show the results of flexural strengths and moduli of the composites, respectively. Data from Tables 4.2 and 4.3 were used to create flexural strength and modulus graphs against concentration of MAPE shown in Figures 4.3 and 4.4, respectively. The results suggest that flexural strength peaks at 2.5 wt. % MAPE, stables at 5 wt. % of MAPE (similar value to the one without MAPE), and decreases beyond that point. Flexural modulus also peaks at 2.5 wt. % of MAPE. Beyond that point, decreasing trend of flexural moduli was observed with the increase of MAPE. At 2.5 wt. % of MAPE, the highest flexural strength and modulus were 25.64 MPa and 1.55 GPa, respectively. These improvements were equivalent to 5.69 % and 7.64 %, respectively.

Table 4.2: Flexural strength of the compositions according to according to wt. % of the composites.

	Flexural Strength (MPa) of the compositions according to wt. % (HDPE/RHF/MAPE)				
Sample Reference	70/30/0	67.5/30/2.5	65/30/5	62.5/30/7.5	60/30/10
1	23.39	25.13	25.94	22.34	22.07
2	24.86	25.26	23.69	22.65	22.11
3	24.77	24.82	23.78	21.98	22.17
4	24.43	26.18	23.35	22.35	21.62
5	23.86	26.80	23.42	22.50	21.80
Average	24.26	25.64	24.04	22.36	21.95
Standard Deviation	0.62	0.82	1.08	0.25	0.23

Table 4.3: Flexural modulus of the compositions according to according to wt. % of the composites.

	Flexural modulus (GPa) of the compositions according to wt. % (HDPE/RHF/MAPE)				
Sample Reference	70/30/0	67.5/30/2.5	65/30/5	62.5/30/7.5	60/30/10
1	1.33	1.53	1.59	1.20	1.16
2	1.45	1.52	1.27	1.21	1.16
3	1.43	1.49	1.25	1.16	1.19
4	1.51	1.58	1.24	1.19	1.15
5	1.47	1.61	1.25	1.20	1.15
Average	1.44	1.55	1.32	1.19	1.16
Standard Deviation	0.07	0.05	0.15	0.02	0.02

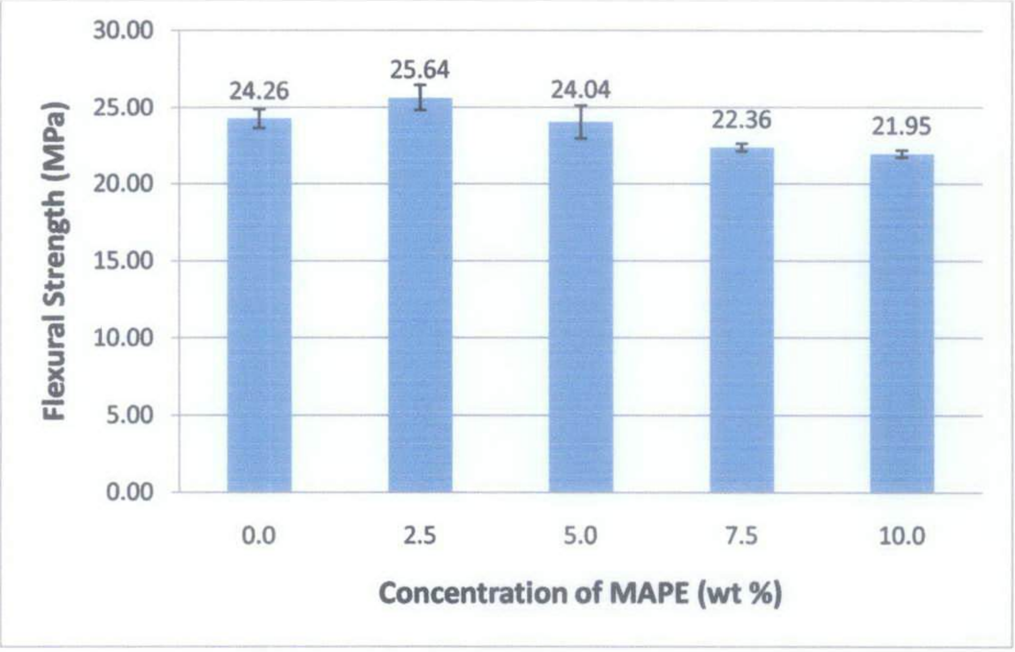


Figure 4.3: Average of the flexural strength from different composites using different concentration of the coupling agent.

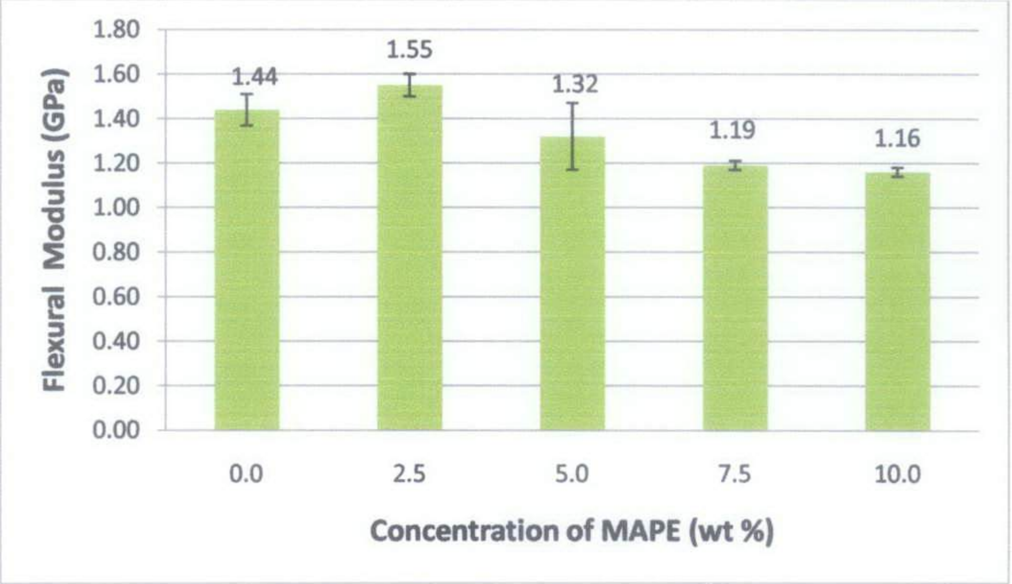


Figure 4.4: Average of the flexural modulus from different composites using different concentration of the coupling agent.

The stiffness can have an adverse effect when higher concentration than 5 wt. % of MAPE is used. As discussed earlier, self-entanglements among coupling agents cause the filler and matrix interfacial bonding to be weak as the coupling agent unable to provide proper adhesion between these two materials [28].

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The objective of this study is achieved as the mechanical properties such as tensile and flexural properties of HDPE/RHF with and without MAPE were determined and analyzed.

From the tensile test results, it was proven that the coupling agent (MAPE) gave positive effects to the tensile strength. Tensile strength increased with the increase of MAPE and it peaked at 5 wt. % of MAPE. The highest tensile strength was 16.68 MPa, which was equivalent to 4.97% tensile strength improvement compared to the composites without MAPE.

From the flexural test results, it was proven that coupling agent also provided positive effects to the flexural properties of the composites. . The results showed that flexural strength peaked at 2.5 wt. % MAPE and decreased beyond 5 wt. % of MAPE. Flexural modulus also peaked at 2.5 wt. % of MAPE and decreased beyond that point. The highest flexural strength and modulus were 25.64 MPa and 1.55 GPa, which were equivalent to 5.69 % and 7.64 % improvements, respectively.

5.2 Recommendations

This study was done based on the equipment and resources available at Universiti Teknologi PETRONAS. This project was carried out for one year. However, this study can be further improved by using some of following alternative recommendations.

a) Using other types of natural fibers such as bamboo, jute, wood as the filler material to combine with HDPE to see if the results using the coupling agent could be significant or vice versa [3], [4], [25].

b) Using other type of matrix material such as high density polypropylene as the matrix material to see if the results using the coupling agent could be significant or vice versa [18]. In this study virgin type of HDPE is used, for variations using recycled HDPE can be done to see the effects of coupling agent to the mechanical properties of the resulting composite materials.

c) Using other types of coupling agent from different manufacturers to see the effects to the mechanical properties of the composites.

d) Ranging the value of the particles size of RHF from 500 μm to smaller or bigger particle sizes to see the effect of dispersion of RHF inside the matrix material.

e) Ranging the filler loading in the composite other than 30 wt. % for example 10 wt. % , 20 wt. % , 40 wt. % , 50 wt. % to see the effect of the coupling agent towards the bonding of the fibers and matrix material.

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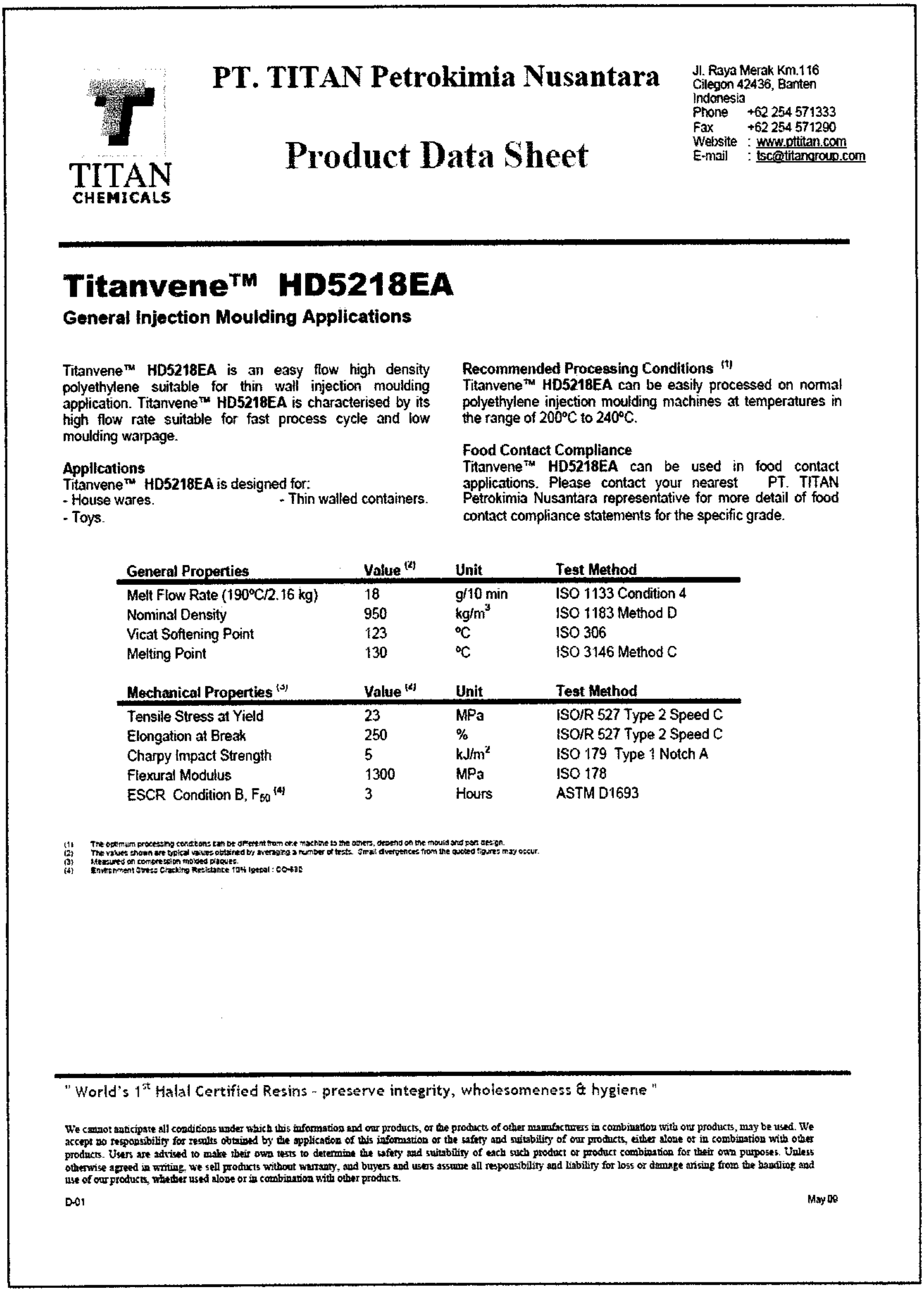
APPENDICES

APPENDIX 3-1



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Product Data Sheet

Jl. Raya Merak Km.116
Cilegon 42436, Banten
Indonesia
Phone +62 254 571333
Fax +62 254 571290
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E-mail : tsc@titangroup.com

Titanvene™ HD5218EA

General Injection Moulding Applications

Titanvene™ **HD5218EA** is an easy flow high density polyethylene suitable for thin wall injection moulding application. Titanvene™ **HD5218EA** is characterised by its high flow rate suitable for fast process cycle and low moulding warpage.

Applications
Titanvene™ **HD5218EA** is designed for:

- House wares.
- Thin walled containers.
- Toys.

Recommended Processing Conditions (1)
Titanvene™ **HD5218EA** can be easily processed on normal polyethylene injection moulding machines at temperatures in the range of 200°C to 240°C.

Food Contact Compliance
Titanvene™ **HD5218EA** can be used in food contact applications. Please contact your nearest PT. TITAN Petrokimia Nusantara representative for more detail of food contact compliance statements for the specific grade.

General Properties	Value (2)	Unit	Test Method
Melt Flow Rate (190°C/2.16 kg)	18	g/10 min	ISO 1133 Condition 4
Nominal Density	950	kg/m^3	ISO 1183 Method D
Vicat Softening Point	123	°C	ISO 306
Melting Point	130	°C	ISO 3146 Method C

Mechanical Properties (3)	Value (4)	Unit	Test Method
Tensile Stress at Yield	23	MPa	ISO/R 527 Type 2 Speed C
Elongation at Break	250	%	ISO/R 527 Type 2 Speed C
Charpy Impact Strength	5	kJ/m^2	ISO 179 Type 1 Notch A
Flexural Modulus	1300	MPa	ISO 178
ESCR Condition B, F_{50} (4)	3	Hours	ASTM D1693

(1) The optimum processing conditions can be different from one machine to the others, depend on the mould and part design.
(2) The values shown are typical values obtained by averaging a number of tests. Small divergences from the quoted figures may occur.
(3) Measured on compression molded plaques.
(4) Environment Stress Cracking Resistance 10% Igepal : CO-630

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