UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PREPARATION AND CHARACTERIZATION OF WASTE FRUIT STARCH FILLED POLYPROPYLENE COMPOSITES

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) with Honours.

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) with Honours. The member of the supervisory committee is as follow:

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ABSTRAK

Tujuan kajian ini dijalankan adalah untuk mengkaji sifat mekanikal dan kebolehupayaan penguraian bahan komposit iaitu sisa buangan buah-buahan yang dicampurkan bersama polipropelina di atas sebab penggunaan komposisi bahan yang berlainan dan kepekatan bahan kimia yang digunakan dengan menggunakan masa yang sesuai. Sebatian polipropelina dan kulit pisang disediakan melalui penggunaan mesin 'internal mixer' dengan penambahan silan sebagai agen percantuman dan pengikatan. Komposisi campuran bahan adalah faktor utama untuk mengkaji nilai kekuatan sesuatu bahan campuran itu. Semua bahan campuran itu tadi disebatikan dalam lima kumpulan berlainan komposisi campuran bahan. Komposisi tersebut adalah 5, 10, 15, 30 peratusan daripada berat kulit pisang yang akan digunakan dalam sesuatu sebatian. Bahan campuran itu kemudiannye dikeluarkan dari mesin 'internal mixer' dan kemudiannya di kisar menjadi ketulan halus dan seterusnya dimasukkan ke dalam mesin 'hot press' untuk dijadikan kepingan-kepingan sampel uji kaji. Kajian terhadap sifat mekanikal dan kebolehupayaan penguraian akan dikemukan melalui ujian penarikan, ujian penyerapan air dan analisis penanaman dalam tanah. Selain itu, penggunaan agen pengikat di dalam sebatian itu akan membolehkan penambahbaikan berlaku kepada pengikatan antara dua bahan. Dengan itu, ia akan menjadikan bahan campuran itu menjadi lebih kuat dari segi kekuatan tarikan. Selain itu, penggunaan komposisi yang menggunakan peratusan kulit pisang yang paling banyak akan mempengaruhi peenguraian bahan campuran itu. Ia boleh dibuktikan dengan pengurangan berat yang berlaku setelah bahan campuran itu ditanam di dalam tanah dan penambahan berat yang berlaku setelah bahan campuran itu direndam di dalam air. Mesin 'FT-IR' digunakan untuk membuktikan kehadiran unsur-unsur organik dan bukan organik di dalam bahan campuran itu.

ABSTRACT

The aim of this study is to study the mechanical properties and degradability of the waste fruit starch filled polypropylene composites as a function of filler loading and chemical treatment in terms of concentration and treatment time. A series of polypropylene (PP)/banana starch compounds with various banana starch contents were prepared by internal mixer with the addition of silane coupling agent as compatibilizer. The filler loading of the composites is the main factor to determine the strength of the composites. The composites were compounded into five compounding. Each compounding has 5, 10, 15 and 30 percent of banana skin filler. The molten composites that taken out from internal mixer was pressed using a hot press machine. Studies on their mechanical properties and biodegradation were carried out by tensile test, water absorption test and soil burial analysis respectively. The presence of high starch contents had an adverse effect on the tensile properties of PP/banana starch blends. However, the addition of silane as compatibilizer to the blends improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the composites. High content of starch also found to increase the rate of biodegradability of PP/banana starch composites. It can be proved by weight loses in soil burial analysis and weight gained in water absorption testing. Fourier Transform Infrared (FT-IR) spectroscopy was used to determine the presence of organic or inorganic element of the composites.

DEDICATION

Special dedication to my mum and family members who always love me,
my supervisor, my beloved friends, my fellow colleague,
and all Faculty members

For all your love, care, support, and believe in me

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LIST OF ABBREVIATIONS

ASTM	-	American Standard Testing Method
BS		Banana starch
CMC	-	Ceramic matrix composites
CO_2	-	Carbon dioxide
FTIR		Fourier Transformed Infrared
H_2O	-	Water
HDPE	-	High density polyethylene
LDPE	-	Low density polyethylene
MMC	-	Metal matrix composites
MI	-	Melt index
MAPP	-	Maleated polypropylene
PE	-	Polyethylene
PP	-	Polypropylene
PS	-	Polystyrene
PET	-	Poly(ethylene terephthalate)
PVC	-	Poly(vinyl chloride)
PMC	-	Polymer matrix composites
PLA	-	Polylactic acid
PHB	-	Polyhydroxy butyrate
PCL	-	Polycaprolactone

CHAPTER 1

INTRODUCTION

1.1 Background of study

Synthetic polymers have become technologically significant since the 1940s and packaging is one industry that has been revolutionized by oil-based polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC). Plastics' versatility allows it to be used in everything from the simple part, for example plastic bags, bottles and dolls to the high-technology parts, cars, computer casing, electronic devices casing and many more. The reason behind multiuse of plastics is unique capability to be manufactured to meet very specific functional needs for consumers. Plastics have been found useful in applications ranging from transportation, packaging, building, medical appliances, agricultures and communication (Steve, 2002).

Synthetic plastics such as polyethylene and polypropylene have a very low water vapor transmission rate and most importantly, so that, they are totally non-biodegradable, and therefore lead to environmental pollution, which pose serious ecological problems. Polyolefin are not degraded by microorganisms in the environment, which contributes to their long lifetime of hundred of years. There has been an increased interest in enhancing the biodegradability of synthetic plastics by blending them with low cost natural biopolymers.

The widespread use of plastic materials has created severe environmental, economic, social, and political problems. The availability of landfill space has decreased rapidly and the cost of land filling plastic wastes has increased enormously. To alleviate these problems, plastic recycling is becoming a priority in most waste management program. The other method to tackle this problem is to use natural fillers as the reinforcements in polymers. Since natural fillers are biodegradable, the composites of natural fillers and polymers may offer a new class of materials which can provide environmental protection. In addition, the low cost and high specific properties of natural fillers imply a significant property potential for the commodity synthetic polymer.

Composites are one of materials that have been widely used worldwide as the substitute for the other material such as metal and woods. Composites are the smart materials that combined two or more element of material in one unit to produce the better materials with better properties than the previous materials.

One of natural fillers showing a great promise is starch. Starch, obtained from renewable resources, has many advantages which include low cost, abundant supply, and environmental amity. Therefore, it shows that starch has a great potential to be produced into biodegradable polymer. However, starch properties need to be improved with chemical treatments due to poor mechanical properties, processability, and water sensitivity.

Addition of silane as a compatibilizer will improve the incorporation of starch in PP and also enhancing the biodegradability of the blends. Low molecular weight plastic additives like compatibilizers and fillers are usually susceptible to microbial attack. This leads to physical embrittlement of the polymer, leaving a porous and mechanically weakened the polymer (Sastry, *et al*., 1998).

1.2 Problem statement

Natural filler such as starch are hydrophilic and thermoplastic polymer which is polypropylene are hydrophobic. Due to the inherent poor compatibility between hydrophobic and hydrophilic purpose, there are several treatment available to improve the filler-matrix interfacial bonding. Several researchers have focused their attention on the improvement of the mechanical properties (usually deteriorated after the addition of the starch, particularly the ductility), achieved with the use of small amounts of coupling agents, which improve the interfacial polymer–filler adhesion and the dispersion of the filler within the matrix. The most important chemical treatment involves coupling methods. The coupling agent used contains a chemical group, which can react with the filler and the polymer. Other than that, the concentration that needed in the reaction and duration of treatment will be taken as a main factor.

A polymeric degradation is an irreversible process caused by factors that are answerable for the loss of its properties. In this process, in general, the scission of polymeric chains occurs and structural alterations take place by other mechanisms. The degradation of the majority of synthetic polymers in nature is a very slow process that involves environmental factors and microorganism activities. Addition of starch to conventional synthetic polymers increases the porosity and the surface/content ratio of the blends and provides the waste of this additive for the microorganisms. The problem here are to analyze the duration of the degradation will occur on the waste fruit starch filled polypropylene composites as a function of filler loading due to composition of filler and polypropylene.

1.3 Objectives

The objectives of the project are:

(a) To study the mechanical properties of the silane treated waste fruit starch filled polypropylene composites as a function of filler loading by using tensile test.

(b) To study the degradability of the silane treated waste fruit starch filled polypropylene composites as a function of filler loading by using soil burial and water absorption test.

1.4 Scope of Study

The scope of this project was mainly focused on how the waste fruit starch filled polypropylene composites degrade. It was to study the degradability of the composites as a function of filler loading that treated using silane. The waste fruit starch is biodegradable natural fillers while the polypropylene is recyclable. The waste fruit starch that used in this project was banana skin. The filler loading of the composites is the main factor that influenced the strength of the composites. The composites were compounded into five compounding. Each compounding has 5, 10, 15 and 30 percent of banana skin filler. Silane was used as compatibilizers in this compound to improve the interfacial adhesion between filler and matrix so as to improve the mechanical properties. The composites compound were compounded in internal mixer and later pressed by hot pressing machine. The degradability was conducted by determining the weight loss after the soil burial and weight gain after water absorption test. Optical microscope was used to determine physical change of the all specimen including the specimens that undergo soil burial and water absorption test. The project was also used to determine the mechanical properties which were tensile test of the finished product. Fourier Transform Infrared (FT-IR) spectroscopy was used to determine the reaction occurred between the banana starch with the chemical that had been used.

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composite materials are created by combining two or more components to achieve desired properties which could not be obtained with the separate components. Composites are important class of engineering materials that are finding increasing use in applications ranging from leisure goods to construction, their excellent specific properties make them particularly attractive for application in which weight saving is advantageous (Bledzki *et al.*,1999).

In composite materials the idea of using cellulose fillers as reinforcement is not new and recent one but man had used this idea for a long time, since the beginning of civilization when straw and grass were used to reinforce mud to make bricks (Marion *et al.*,2003). Meanwhile, the history of natural filler reinforced polymer composites can be traced back to the advent to synthetic polymers in the early part of twentieth century (Mwaikambo *et al.*,2003). Before this even, examples of the use of natural fillers with natural or semi-synthetic polymer exist. They also carried out pioneering work on natural filler reinforced composites for lighter materials to be used in aircraft primary structures.

Composites can be divided into three group based on the matrix materials which are polymer matrix composites (PMC), metal matrix composites (MMC) and ceramic matrix composites (CMC). The matrix is the component that holds the filler together to form the bulk of the material. It usually consists of various epoxy type polymers but other materials may be used. Composites generally have good resistance to corrosion and increase mechanical damping.

2.2 Polymer Matrix Composites

Polymer matrix composites (PMC) are considered to be a more prominent class of composites when compared to ceramic or metal matrix composites once in commercial applications. For engineering application, the PMC comprises of a matrix from thermosetting (unsaturated polyester, epoxy) or thermoplastic (nylon, polystyrene) and embedded glass carbon, steel or Kevlar fibers (dispersed phase). The industries supporting reinforced polymer markets include transportation, marine accessories, electronic products etc.

Matrix plays a significant role in the performance of any composite. The matrix material in composites in load-transferring medium between fillers. The ability to transfer load between fillers is mainly characterized by mechanical properties of matrix and the interfacial bond between fillers and matrices (Raczs *et al*., 2000). The main limitation in choosing a suitable polymer matrix for natural filler impregnation is the processing temperature, which restricted to the temperature below 170-260℃ to avoid thermal degradation of natural fillers.

Both thermosetting and thermoplastic polymers have been used for a long time as attractive polymer matrices for natural filler 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 molding (Joseph *et al*., 1999).

2.2.1 Thermoplastic

The mostly used thermoplastic polymers as a matrix are Polyethylene (PE), Polypropylene (PP), Polystyrene (PS) and Polyvinyl chloride (PVC). Other thermoplastic such as polyamides, polyesters and polycarbonates require processing temperature greater than 250℃ are therefore not used for processing of natural filler composites (Patil *et al*.,2000). Thermoplastics composites are flexible and tough and exhibit good mechanical properties. However, the percentage loading of filler in comparison to thermosetting polymers is limited. Properties of composites are mainly governed by the properties of fillers, their aspect ratio and fiber-matrix interface (Carvalho *et al.*,2001).

Environmental as well as economic factors are now deriving the trend toward greater utilization of bio-based polymer composites such as polylactic acid (PLA), polyhydroxy butyrate (PHB), cellulose esters, soy based plastic, starch plastic and materials (Vazguez *et al*.,1999).

2.2.2 Thermoset

Thermosetting plastic are not as widely used as the thermoplastics, perhaps because of the added processing complications involved in curing the thermosetting polymer. Thermosetting polymer is distinguished by their highly cross-linked structure. In effect, the formed part (e.g., the port handle or electrical switch cover) becomes one large macromolecule. Thermosets are always amorphous and exhibit no glass transition temperature (Groover *et al*., 2006).

2.2.3 Biodegradable Polymer

The ASTM defines 'biodegradable' as:

"capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal condition (ASTM Standard D-5488-84d)*."*

The biodegradability of polymers is dependent on the chemical structure of the material and on the constitution of the final product, not just on the raw materials used for its production. Therefore, biodegradable polymers can be based on natural or synthetic resins. Natural biodegradable polymers are based primarily on renewable resources (such as starch) and can be either naturally produced or synthesized from renewable resources. Non-renewable synthetic biodegradable polymers are petroleum-based. As any marketable polymer product must meet the performance requirements of its intended function, many natural biodegradable polymers are blended with synthetic polymers to produce plastics which meet the functional requirements.

Biodegradation is degradation caused by biological activity, particularly by enzyme action leading to significant changes in the materials chemical structure. In essence, biodegradable polymers should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water.

Biodegradable polymers is defined as polymers with similar properties to conventional polymers, but it can be decomposed after disposal to the environment by the activity of microorganisms to produce end products of carbon dioxide (CO_2) and water (H_2O) (Tharanathan, 2003). It has widely become an alternative to the petroleum based non-biodegradable polymers.

Biodegradable polymers can be further categorized into two main areas; renewable and nonrenewable biodegradable polymers. Essentially renewable biodegradable polymers utilize a renewable resource, for example, a plant by-product, in development of the polymer, rather than a non-renewable, for example, petroleum based resource (Halley, 2005).

Polymeric materials are generally durable and inert towards microbes, thus offering long term performance. According to the emphasis on environmental pollution problems and land shortage problem for solid waste management, such as non-availability of landfills, public perception, and reduction of fertility of lands by accumulation of surface litter, environmentally degradable and 'environmentally friendly' polymers are of interest (Arvanitoyannis *et al*., 1998).

Research on biodegradable polymer based on starch filler began in the 1970s and continues today at various laboratories all over the world. Technologies have been developed for continuous production of extrusion films and injection-moulded plastics containing 50% or more of starch (Tharanathan, 2003). Starch satisfies the requirements of adequate thermal stability, minimum interference with melt properties and disturbance of product quality (Shah *et al*., 1995).

2.3 Filler

The filler is generally responsible for strengthening the composite and improves its mechanical properties. During the last few years, a series of works have been done to replace the conventional synthetic filler with natural filler composites. For instant, hemp, sisal, jute, cotton, flax and broom are the most commonly fillers used to reinforce polymers. In addition, fillers like sisal, jute, coir, oil palm, bamboo, wheat and flax straw, waste silk and banana have proved to be good and effective reinforcement in the thermoset and thermoplastic matrices (Suharty *et al*.,2008). All of the different fillers used in composites have different properties and so affect the properties of the composite in different ways. It also provides stiffness to the composites. They are divided to two types of filler which is synthetic filler and natural filler.

2.3.1 Synthetic Filler

These are man made fillers which are a result of research by scientists to improve natural occurring plant and animal fillers. Before synthetic fillers were developed artificially manufactured fillers were from cellulose which comes from plants. Several synthetic fillers are produced by chemical synthesis. This is generally used where the desired mineral is not readily available in nature when high purity, special shapes, or finer sizes than obtainable from comminution are required. The main synthetic processes used involve precipitation from a solution or gas phase. In a few cases the filler may be a by-product from another process (Rothon, 2001).

2.3.2 Natural Filler

Natural fillers have been extensively used as reinforcements into polymer matrices as an alternative to the commonly used synthetic fillers because of their low-density good mechanical properties, abundant availability and biodegradability (Amar *et al*.,2005). Many studies were carried out on the utilization of natural filler in thermoplastic composites. Wood-flour, jute, flax, corn starch, tapioca starch and cereal straw are some of the fillers that received increased attention as a reinforcing component in polymer composites. Most of these studies focused on the effect of filler loadings and filler particle size distribution on mechanical properties of the composites (Lee *et al.*,2001).

Researches carried out on thermoplastic composites using natural fillers have shown that stiffness, hardness and dimensional stability of plastic could be improved by incorporating natural filler. Meanwhile polymers employing these fillers have exhibited certain adverse effects such as toughness and ultimate elongation. The addition of filler to polyolefins seeks to reduce production costs with the subsequent change in tensile and impact properties (Chou *et al.*,1998).