TESTING AND CHARACTERIZATION OF DURIAN SEED FLOUR FILLED POLYPROPYLENE OR HIGH DENSITY POLYETHYLENE COMPOSITES

by

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APPROVAL AND DECLARATION SHEET

This thesis titled Testing and Characterization of Durian Seed Flour Filled PP or HDPE Composites was prepared and submitted by Muhammad Haniff bin Zakaria (Matrix Number: 0931620405) and has been found satisfactory in terms of scope, quality and presentation as partial fulfillment of the requirement for the award of degree of Master of Science (Polymer Engineering) in University Malaysia Perlis (UniMAP).

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile-Butadiene-Styrene
ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
DSF	Durian Seed Flour
DTG	Derivative thermogravimetry
E_B	Elongation at break
FTIR	Fourier Transform Infra-Red
GPC	Gel Permeation Chromatography
HCl	Hydrochloric Acid
HDPE	High Density Polyethylene
HF	Hydrofluoric Acid
iPP	isotactic polypropylene
MAPP	Maleic Anhydride Grafted Polypropylene
MW	Molecular Weight
OSHA	Occupational Safety and Health Administration
PE	Polyethylene
php	Parts per hundred polymer
PP	Polypropylene
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscopy
sPP	Syndiotactic Polypropylene
TGA	Thermogravimetric analysis
TEM	Transmission electron microscopy
TPE	Thermoplastic Elastomer
UV	Ultra-Violet
XPS	X-ray photoelectron

LIST OF SYMBOLS

μm	Micrometer
$Al(OH)_3$	Aluminum hydroxide
Al_2O_3	Aluminum oxide
BaSO4	Barium sulphate
$C_6H_{12}O$	Glucose
$CaCO_3$	Calcium carbonate
CH_2O	Formaldehyde
HNO_3	Nitric acid
KBr	Potassium bromide
kg	Kilogram
$Mg(OH)_2$	Magnesium hydroxide
MgO	Magnesium oxide
OH	Hydroxide
Sb_2O_3	Antimony trioxide
Si	Silica
SiO_2	Silicon dioxide
T_0	Initial degradation temperature
T_{deg}	Final degradation temperature
wt	Weight

UJIAN DAN PENCIRIAN KOMPOSIT POLIPROPILENA ATAU POLIETILENA BERKETUMPATAN TINGGI TERISI TEPUNG BIJI DURIAN

ABSTRAK

Komposit polipropilena (PP) dan polietilena berketumpatan tinggi (HDPE) terisi tepung biji durian (DSF) telah dikaji. Kesemua sampel ujian disediakan menggunakan pencampur dalaman Brabender Plastograph EC pada suhu 180°C, dan diacuan menggunakan pengacuanan mampatan pada suhu 180°C. Keputusan menunjukkan bahawa keliatan komposit PP dan HDPE terisi DSF meningkat dengan peningkatan jumlah pengisi, walaupun pengurangan pada kekuatan regangan dapat dilihat. Berdasarkan kepada keputusan, komposit PP terisi DSF didapati dapat memberi sifat-sifat regangan yang lebih baik berbanding komposit HDPE terisi DSF, maka PP telah dipilih sebagai matriks utama untuk keseluruhan kajian berikutnya. Sifat-sifat komposit diperkuatkan lagi dengan penggunaan kalsium karbonat ($CaCO_3$) dan kanji jagung sebagai pengisi kacuk kepada DSF. Nisbah untuk kacukan DSF/$CaCO_3$ dan DSF/kanji jagung yang dikaji adalah gabungan 0/40, 10/30, 20/20, 30/10 dan 40/0. Kedua-dua pengisi kacukan tersebut didapati dapat memberi kesan penguatan bantuan terhadapt DSF. Pelekatan di antara pengisi dan matriks telah ditingkatkan dengan menggunakan MAPP sebagai agen pengserasi. Kedua-dua penambahan pengisi kacukan dan pengserasi telah meningkatkan sifat-sifat regangan beserta sifat-sifat pelupusan terma komposit-komposit tersebut. Pencirian mikroskop pengimbas elektron (SEM) telah dijalankan untuk mengkaji sifat permukaan rekahan. Ujian pelupusan semulajadi yang ringkas telah dijalankan untuk setiap siri daripada komposit-komposit, dimana analisa FTIR telah dijalankan untuk mengkaji kebolehlupusan secara

semulajadi komposit-komposit tersebut. Keputusan menunjukkan kesemua komposit menunjukkan tanda-tanda kebolehlupusan secara semulajadi.

TESTING AND CHARACTERIZATION OF DURIAN SEED FLOUR FILLED POLYPROPYLNE OR HIGH DENSITY POLYETHYLENE COMPOSITES

ABSTRACT

Composite of polypropylene (PP) and high density polyethylene (HDPE) filled with durian seed flour (DSF) was investigated. All of the test samples (10-40 wt% filler loadings) were prepared using Brabender Plastograph EC internal mixer at temperature of 180°C, and moulded using compression moulding at temperature of 180°C. Results show that the toughness of DSF filled PP and HDPE composites increases with increasing filler loading, although the decrease in strength of the composite was evident. Based on the result, DSF filled PP composites was found to give better tensile properties compared to DSF filled HDPE composites, hence PP was chosen as the main matrix for the rest of the study. The composites properties were further enhanced with incorporation of calcium carbonate ($CaCO_3$) or corn starch, as hybrid filler to the DSF. The DSF/$CaCO_3$ and DSF/corn starch hybrid ratio is studied at 0/40, 10/30, 20/20, 30/10 and 40/0 blend ratio. Both hybrid fillers were found to act as reinforcing fillers to the DSF. The adhesion of the filler and matrix was improved by using MAPP as a compatibilizer. Both addition of hybrid fillers and compatibilizer has improved the tensile properties as well as the thermal degradation properties of the composites. Scanning electron microscopy (SEM) characterization was also done to investigate the fracture surface behavior. Simple biodegradability test was conducted on each series of the composites, where FTIR analysis was done to determine the biodegradability of the composites. Results showed that all composites are subjected to biodegradation.

CHAPTER 1
INTRODUCTION

1.1 Starch Reinforced Polymer Composites Using Biomass

Petroleum is a versatile material, a key ingredient in the production of thousands of everyday products including the plastic found in garbage and grocery bags, computers, telephones, cars, and furniture. Unfortunately, some petroleum-based products can be hazardous. Phenolic resins and urea formaldehyde resins, for example, emit formaldehyde during production creating a dangerous work environment for employees and for the consumers of these products. Formaldehyde, a suspected carcinogen in humans, has been associated with Sick Office Syndrome. As a result, the Occupational Safety and Health Administration (OSHA) has established exposure limits to protect workers from the effects of formaldehyde. The production of petroleum-based products also contributes to pollution, emitting greenhouse gases into the air. Other disadvantages of petroleum are its durability (heat and sunlight cause it to diminish its properties) and flammability (Kurple, 1999).

The increase in environmental concern has pointed out how it is also necessary to reduce and rationalize the use of petroleum based polymeric materials, not only due to their non-biodegradability, but also because their production requires large amount of oil as raw material which is notoriously not renewable. In addition, the price for crude oil continues to rise over time, consequently causing the cost of producing petroleum-based plastic products continues to rise with it. Also, the need for materials that are non-toxic to the human body and have appropriate characteristics for specific purposes is ever increasing due to the lack of resources and increasing levels of environmental pollution. All these issues have induced mankind to look for alternatives (La Mantia & Morreale, 2006), including the use of biomass, i.e. starch as the reinforcing filler in polymeric materials. Starch is the major form of carbohydrate in plants (Zeppa et al., 2009). In packaging applications, starch based materials have received great attention. The convenience of these composites lies in the fact that the ingredients are obtained easily from natural wastes and hence the composites can be made relatively easily. They can be used to resolve environmental problems and to produce products with various physical properties and effective functions.

Polymeric materials derived from renewable sources, i.e. biomass, are considered as the most promising materials because of their easy availability and cost effectiveness. Manufacturing of high performance engineering materials from renewable resources is one of ambitious goals currently being pursued by researchers all over the world. Extensive effort has been devoted to starch and polymer composites due to many emerging applications, such as decking, building materials, automobile components, and infrastructure. Compared with traditional glass fiber and mineral fillers, starch-based fillers are less-expensive, low density, sustainable, renewable, biodegradable, less abrasive to processing machinery, which makes them able to minimize the environmental pollution caused by the characteristic biodegradability (Premalal et al., 2002), enabling the bio-filler filled composites to play an important role in resolving future environmental problems. Natural fillers have already established a track record as reinforcing material in automotive parts and spreading up with high growth rate to packaging, construction and household utility based small industries because of their light weight, low cost, and environmental friendly nature (Suddel et al., 2005; Bledzki et al., 2008).

Many researches have been done and still ongoing regarding the use of starch-based fillers in polymer composites. For example, the production of polymer composites reinforced with wood flour is an established technology today. Other natural sources of fillers such as bamboo flour (Kitagawa et al., 2002), wheat flour (Le Digabel et al., 2004), rice-husk flour (Yang et al., 2004) and so on are proven to have positive impacts on the properties of respective composites. Very few researches are being done regarding the usage of durian seed flour as the natural reinforcement filler.

Durian (*Durio zibethinus Murr.*) is a seasonal fruit grown in South East Asia. Durian is normally eaten fresh. Only one-third of durian is edible, whereas the seeds (20–25%) and the shell are usually thrown away. Previous studies had shown that durian seed is very nutritious and has high fibre content (Amiza et al., 2004a). Durian seed flour could be incorporated into various food products including cake, cookies, soup, tempura, etc either as a substitute for wheat flour or as thickening agent (Amiza et al., 2004b).

Despite numerous researches worldwide regarding starch as natural fillers, the use of durian seed flour as filler in composite has not yet been extensively studied. Therefore, the focus of this research is to study about the properties of plastic composite, using durian seed flour as the main reinforcement material, combined with selected thermoplastic matrix resins. Within a short period, this area of research has ranges from the use of the durian seed flour on different thermoplastic resins, at different filler content, hybrid fillers and also the addition of compatibilizer to study their effects on durian seed flour reinforced polymer composites.

1.2 Applications and Future Trends

Thermoplasticized starch is mainly used in soluble compostable foams, such as loose fillers, expanded trays, shape molded parts and expanded layers, as a replacement for polystyrene. The use of starch in the textile industries, principally in wrap sizing, finishing, thread glazing and printing, has been well studied and developed (Compton & Martin, 1967).

Extensive study also has been contributed in exploring the use of starch in packaging industries. Starch based polymer composite product is used to package dry and wet foods and meets required food packaging standards. Stilwell et al. (1991) describe the motivation within the packaging industry to consider useful alternatives over the last four decades. Evolution trends in the packaging industry indicate convenience as the market pull in the 1960's, moving to energy crisis in the 1970's, safety and quality in the 1980's, and the changes expected in the 1990's onwards being attributed to environmental issues. The market pull for the present development was based on the need for environmentally improved packaging in the food industry. This pull is generated from the need to reduce energy consumed and waste generated from packaging and other solid materials. Public perception of manufacturing processes also provides impetus for "greener" technologies that are less polluting to the environment.

At this moment, usage of mixed fiber and particulate composites has been recognized for many years. Growth of hybrid systems has been particularly rapid in the last decade or so, encouraged by the demand for high performance engineering materials, especially where low weights is great importance. Although individual classes of fillers or fibers can contribute some desirable properties, the real interest in composites is in optimizing the different contributions from different types of fillers.

Turning to specific applications, polypropylene hybrid composites has the potential to be used in automotive applications such as door trims, bumpers, panels and interior furnishings. This is mainly due to the automotive industry interest in biocomposites because of environmental legislation, light weight and low cost. In a vehicle, around 75% of the energy consumption is associated with weight, and therefore natural fillers such as starch and fibers, with their light weight will impart strong potential for automotive components (Powers, 2000). Other types of thermoplastic hybrids include the use of nylon and carbon in fishing rods, whilst boron has also been used with carbon in sports equipment and aerospace parts (Sheldon, 1982).

1.3 Problem Statements

PP and HDPE are so widely used because of their wide range of physical properties and suitability to most of the commercial thermoplastics fabrication process. The most important properties found in HDPE resin is because of the high strength and stiffness, high surface hardness and high heat distortion temperature, while PP provides higher impact resistance and low brittle temperature (Billmeyer, 1971). However, the incorporation of starch might give different outcome on the properties, depending on their compatibility when mixed together. The comparison of their mechanical properties when incorporated with durian seed flour (DSF) will be further studied in this research.

The use of DSF as reinforcement filler has not yet been widely used nor commercialized. The incorporation of DSF alone might not give the best result in improving the characteristics and performance of its reinforced composite. However better results might be obtained if the properties of the DSF are combined with the properties of well known and commercialized fillers to give a combined effect of both fillers when filled into a composite.

The vast resources of $CaCO_3$ in Malaysia have spurred Malaysian manufacturers to switch to using $CaCO_3$ as filler in PP composites, as $CaCO_3$ is considerably cheap. However, the incorporation of $CaCO_3$ in PP led to poor tensile properties if compared to PP composites with expensive fillers; although impact properties of $CaCO_3$ filled PP composites are considerably high. Therefore, in order to reach a balance between cost and material properties, it is reasonably viable to mix both DSF and $CaCO_3$ and incorporate them into PP in order to obtain the best of both worlds. The same reason goes to the idea of mixing DSF with corn starch, one of the widely commercialized and emerging filler in Malaysia, to obtain the combined properties of both worlds. Thus the idea of introducing PP/DSF/$CaCO_3$ and PP/DSF/corn starch was born.

Large difference in surface polarity between hydrophilic starch and hydrophobic thermoplastic matrix usually leads to poor interfacial adhesion and thus poor mechanical properties of final materials. This problem can be alleviated by the use of compatibilizing agents (maleated polypropylene: MAPP).

1.4 Objectives of Study

The aim of this research is to develop starch based polymer composites namely durian seed flour (DSF) filled polypropylene (PP) and high density polyethylene (HDPE) composites. The primary objectives of the study are listed as:

1. To investigate the physical properties of the DSF regarding particle size, surface area, density and thermal analysis;

2. To determine optimum filler content of durian seed flour in PP or HDPE composites. The filler content variability was chosen as 0, 10, 20, 30 and 40 php;

3. To study the effects of compatibilizer in the durian seed flour filled PP/HDPE composites using maleic anhydride polypropylene (MAPP);

4. To investigate the ability of durian seed flour to be hybrid with other reinforcing fillers such as $CaCO_3$ and corn starch. This evaluation is to achieve a superior balance of the composites properties and to minimize the use of more expensive fillers;

5. To characterize the processing torque, FTIR, mechanical, thermal, morphological properties of the durian seed flour filled PP or HDPE composites. The importance/ objective to measure the above properties are:

    a. The processing torque provides information on efficiency of the mixing and process development of the composites;

b. The mechanical properties evaluate the performance of the DSF as a filler in the PP or HDPE composites. This properties associates with composites morphological properties;

c. The thermal degradation properties provide information on service life temperature of the final product. The properties is very important since degradation is the major problem in the composites applications;

d. The morphological properties correlate the mechanical properties explanation through tensile failure mode mechanism of the composites;

e. The FTIR properties identify the chemical groups of the DSF and DSF filled composites.