INJECTION MOLDED SILANE CROSSLINKABLE RICE STRAW/HIGH DENSITY POLYETHYLENE BIOCOMPOSITE

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"Dedicated to my beloved husband Haritz Khan, parents, brothers and sister for all their love, encouragement and support..."

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ABSTRACT

A formulation was designed to produce silane crosslinked rice straw/High Density Polyethylene (RSPE) compound suitable for injection molding process. The formulation consist of HDPE as the base polymer, rice straw as the filler, processing aids and a mixture of crosslink chemicals. Crosslink chemicals consist of vinyltrimethoxysilane (VTMO) as crosslinking agent, dicumyl peroxide (DCP) as the initiator and dibutyltin dilaurate (DBTL) as the condensation catalyst. The rice straw was oven dried at 70ºC for 24 hours, grinded and followed by sieved. A counter rotating twin shaft high speed mixer was utilized to mix the rice straw, HDPE and the processing aids. The blends were then compounded on twin screw extruder. Test specimens were prepared via injection molding process followed by oven cured at 90ºC. Fourier Transform Infra Red (FTIR) was used to determine the chemical functional group involved in the crosslinking reaction. Degree of crosslinking in the silane crosslinked compounds was measured by determining the gel content. Thermal properties were analyzed on the Differential Scanning Calorimetry (DSC) for the melt temperature whereas Thermogravimetry Analysis (TGA) for its thermal stability behavior. The degree of crosslinking in RSPE increased with an increased in VTMO and DCP concentration. The results from FTIR showed the presence of Si-O-Si bond and Si-O-C indicative of crosslinks formation. Thermal stability of the compound illustrated that the crosslinked RSPE was more stable than the uncrosslinked RSPE while the melting point was unchanged. Tensile strength and flexural strength improved after crosslinking and increased with the amount of VTMO and DCP, whilst impact strength showed an optimum value with respect to crosslink chemicals composition. The concentration of 3 phr VTMO, 0.5 PHR dcp AND 0.015 phr DBTL was the optimum crosslinked chemical composition to produce the crosslinked RSPE, significant properties enhancement.

ABSTRAK

Formulasi telah direkabentuk untuk menghasilkan sebatian silane terpaut silang jerami padi/Polietilina berketumpatan tinggi (RSPE) yang sesuai untuk proses pengacuan suntikan. Formulasi ini mengandungi HDPE sebagai polimer asas, pengisi jerami padi, bahan bantu pemprosesan dan campuran kimia pemaut silang. Campuran kimia pemaut silang terdiri daripada vinyltrimethoxysilane (VTMO) sebagai agen pemaut silangan, dicumyl peroxide (DCP) sebagai bahan pemula dan dibutyltin dilaurate (DBTL) sebagai pemangkin kondensasi. Jerami padi dikeringkan pada suhu 70ºC selama 24 jam dan seterusnya dihancurkan dan diayak. Pencampur berkelajuan tinggi digunakan untuk mencampurkan jerami padi, HDPE, bahan penyuai dan bahan bantu pemprosesan. Campuran kemudian disebatikan menggunakan penyemperitan skru berkembar. Spesimen-spesimen ujian disediakan melalui proses pengacuan suntikan dan seterusnya dimasukkan ke dalam ketuhar pada suhu 90ºC untuk diawet. Fourier Transform Infra Red (FTIR) digunakan untuk mengenal pasti kumpulan berfungsi yang terlibat dalam tindakbalas pemaut silangan. Darjah pemaut silangan pada sebatian silane terpaut silang dapat diukur berdasarkan kandungan gel. Sifat haba bagi sampel berangkai silang dianalisa menggunakan Differential Scanning Calorimetry (DSC) untuk menguji takat lebur sebaliknya Thermogravimetry Analysis (TGA) untuk kelakuan kestabilan haba. Darjah pemaut silangan RSPE meningkat dengan pertambahan kepekatan VTMO, DBTL dan DCP. Keputusan FTIR menunjukkan kehadiran ikatan Si-O-Si dan Si-O-C membuktikan berlakunya pembentukan pemaut silang. Kestabilan sebatian menggambarkan terpaut silang RSPE yang telah berangkai silang lebih stabil daripada tidak terpaut silang RSPE manakala takat lebur tidak menunjukkan perubahan yang ketara. Kekuatan regangan dan kekuatan lenturan menunjukkan peningkatan selepas pemaut silangan dan semakin meningkat dengan pertambahan VTMO dan DCP manakala kekuatan hentaman menunjukkan nilai optimum dengan pertambahan komposisi kimia pemaut silang. Kepekatan yang bersesuaian, berdasarkan 100 bahagian polimer asas, untuk VTMO ialah 3.0 phr , DCP ialah 0.5 dan DBTL 0.015 untuk menjadikan terpaut silang RSPE mempunyai sifat yang baik.

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LIST OF ABBREVIATIONS AND SYMBOLS

NFRC	-	Natural Fiber Reinforce Composite
WPC		Wood/Natural Fiber Plastic Composites
HDPE	-	High Density Polyethylene
VTMO	-	Vinyltrimethoxysilane
DCP	-	Dicumyl Peroxide
DBTL	-	Dibutyltin Dilaurate
PE	-	Polyethylene
PP	-	Polypropylene
ASTM	-	American Standard Testing Method
RSPE	-	Rice Straw Polyethylene
phr	-	Parts per hundred
DSC	-	Differential Scanning Calorimetry
MFI	-	Melt Flow Index
TGA	-	Thermogravimetry Analysis
FTIR	-	Fourier Transform Infra-Red
ρ	-	Density
m	-	Mass

CHAPTER 1

INTRODUCTION

1.1 Introduction of study

Polymer composite have been subjected to increasing interest, study, and utilization for some decades. The depletion of petroleum resources coupled with increasing environmental regulations are acting synergistically to provide the impetus for new materials and products that are compatible with the environment and independent of fossil fuels. Waste minimization is one of the problems that we need to overcome. All these issues have induced to look for alternatives. Recent advances in genetic engineering, natural fiber development, and composite science offer significant opportunities for new, improved materials from renewable resources, which can biodegradable and recyclable but also obtained from sustainable sources at the same time as reported by Amar *et al.,* (2005) and Hoi-Yan Cheung *et al.,* (2009). Composite materials are attractive because they combine material properties in ways not found in nature.

Recently, natural fibers have been investigated as filler materials capable of serving as localized tensile reinforcement and volume fillers within several types of polymer matrices. Current conventional fillers include wood flour, talc, calcium carbonate, fiberglass and nylon. Natural fillers have several advantages over conventional fillers in improving the general characteristics of plastics for example polyethylene. Natural fillers- plastic composite have several advantages include reduce processing temperatures thereby which is less than 200°C thus reducing energy costs during production. In comparison to other mineral filled plastics, natural filler have a lower specific gravity resulting in both material savings during production and shipping costs after production and increased life span of the molds and extruder due to abrasion by the filler as report by Johnson *et al*., (1997). A number of natural fillers have been under continued investigation for use in natural filler reinforced polymer composites (NFRC); including wood fiber, jute, sisal, kenaf, flax, wheat straw and bamboo. These natural fillers are especially being sought since the production of composites using natural substances as reinforcing fillers is not only inexpensive but also able to minimize the environmental pollution caused by the characteristic biodegradability, enabling these composites to play an important role in resolving future environmental problems (Hang-Seung Yang *et al*., 2004a). More than that, these fillers often contribute greatly to the structural performance when used in plastic composites.

Increased technical innovations, identifications of new applications, continuing political and environmental pressures, and government investment in new methods for fiber harvesting and processing are leading to projections of continued growth in the use of natural fillers in composite. One of the largest areas of recent growth in natural filler composites is the automotive industry, where natural fillers are advantageously used as a result of their low density and increasing environmental pressures. Most of the composites currently made with natural fillers are press molded, although a wide range of processes have been investigated (Craig and Danial, 2005). The automobile industry has begun to apply NFRC in a variety of exterior and interior panel applications. The significant weight savings and the ease and low cost of the raw constituent materials have made NFRC an attractive alternative material compare to glass and carbon fiber reinforced polymer composites. However, further research needs to address significant material and production obstacles before commercially available NFRC are widely used in architectural and civil works.

An increasing amount of interest has developed over the past few years for NFRC because of their ease of production, subsequent increase in productivity, cost reduction, lower density and weight, enhanced biodegradability, combustibility, ease of recyclability, non toxic and use of renewable resources. Composite materials (or composites for short) are engineered materials made from two or more constituent materials with significantly different physical or chemical properties and which remain separate and distinct on a macroscopic level within the finished structure. Recently, these natural fillers especially plant fibers have been coupled in a matrix primarily composed of two commodity thermoplastic matrix materials such as polyethylene (PE) and polypropylene (PP) which melt or soften relatively at low temperatures (Prachayawarakorn and Yaembunying, 2005). Natural fillers have gained their importance especially for load bearing application while specific mechanical properties of natural fillers vary according to the particular filler, the overall performance of natural fillers lies within a relatively tight range as a result of similar molecular composition. These advantages place the natural fillers composites among high performance composites having economical and environmental advantages, with good physical properties (Mehta and Parsania, 2006). Wood-plastic composites are currently one of the dominating natural filler composite markets in North America, as these composite materials are being accepted widely in to the building and construction industry (Suhara and Mohini, 2007). The composite industry always looks into alternative low cost lignocellulosic sources, which can decrease overall manufacturing costs and increase stiffness of the materials.

1.2 Problem Statement

Industries are developing and manufacturing “greener” materials; government is encouraging biobased product research while the academicians are searching for eco-friendly materials; and the public is coming to value the benefit of environment friendly products and processes, but at affordable prices. Previously, most researchers have used wheat straw, wood flour, rice husk and empty fruit bunch as reinforcement in the various polymers such as polyethylene, polyvinyl chloride and polypropylene for making a new type of environmentally-friendly composites (Bakar *et al*., 2005; Nak *et al.,* 2006; Cheng *et al.,* 2009; Ming Zhu *et al*., 2009). The use of natural fillers in polymer matrix is highly beneficial because the strength and toughness of resulting composites are greater than those of unreinforced materials.

Even though a very large quantity of work has been published on various natural fillers and its composites, an effort has been made in the present work to introduce new filler which is rice straw in the development of new composite materials for lightweight structures. Some studies were already reported on the exploration and extraction of rice straw which is also comparable with established filler as reported by Kiran *et al.,* (2000), Mohammad *et al.,* (2004) and Fei *et al.,* (2008). Previous work on rice husk polyolefin biocomposite has been done and shows that these filler posses good mechanical properties that make them suitable to compound with plastics (Naurah, 2005; Han-Seung Yang *et al.,* 2004b). Nowadays, rice straw is abundantly available and renewable in nature. As open-field burning of rice straw is being phased out in Malaysia, rice growers and government agencies are looking for new rice straw uses. This economical source compared to other natural sources is still underutilized and not yet established especially in Malaysia.

In spite of all the advantages mentioned about natural filler, there are also drawbacks in using natural filler as reinforcement in thermoplastics. One difficulty that has prevented the use of natural filler is the lack of good adhesion between the hydrophilic filler and the hydrophobic polymer (Magnus and Kristina, 2006). The adhesion between the reinforcement fillers and the composite and the matrix in composite plays an important role in the final mechanical properties since the stress transfer between matrix and fillers determines reinforcement efficiency (Ahmad *et al.,* 2009). It is well known that chemical treatments applied onto filler surface may affect the mechanical properties of the final material as reported by Kostic *et al.,* (2008) who did chemical treatment on hemp fibers. The surface of fillers is usually modified using various types of chemical modification and has been carried out previously by using maleic anhydride, maleated polypropylene and titanate treatments in order to improve the filler surface wettability with the matrix and to create a strong bond at the filler-matrix interface (Han-Seung Yang *et al.,* 2007; Byung Dae *et al.,* 2004; Ferran *et al.,* 2007). Poor adhesion leads to composites with rather poor durability and toughness.

This is the main reason of using silane technology in crosslinking polyethylene-rice straw composites. Silane was used as coupling agents to adhere fillers to a polymer matrix, stabilizing the composite material. In general, the use of this coupling agent significantly improves the mechanical properties of the composites (Soo Jin *et al.,* 2009). Previous research by Magnus and Kristina (2005) has succesfully produced silane crosslinked polyethylene/wood flour composites in a one step process via extrusion. The crosslinked biocomposites showed significantly higher impact strength compared to uncrosslinked. This study was carried out to develop an optimum formulation for the silane crosslinkable rice straw/HDPE compound grade for injection molding. By doing so, the production of the biocomposites is more economical and also believed to be more industrially friendly.

List of problems statement:

(i) Which size of rice straw is suitable for the rice straw/HDPE biocomposite manufacturing on injection molding process?

ii) What is the optimum composition of rice straw as filler for the HDPE biocomposite with respect to strength and processability for injection molding?

iii) Is silane able to crosslink HDPE with rice straw biocomposite for properties improvement and still processable by injection moulding technique?

1.3 Objectives of the Study

The main objective of this study is to develop crosslinkable rice straw/HDPE compound formulation that are processable by injection molding technique. This main objective is further subdivided into:

i) To categorize the appropriate size of rice straw suitable as a filler in HDPE with respect to tensile strength.

ii) To study the effect of rice straw composition based on mechanical properties and flowability of uncrosslinked rice straw/HDPE biocomposite on the injection molding process.

iii) To investigate the potential of silane as crosslinker in injection molded rice straw/HDPE biocomposite.

iv) To determine the characteristics and properties of crosslinkable rice straw/HDPE biocomposite and analyze its suitability for injection molding process.

1.4 Scope of the study

The scope of study involved the following stages:

(i) Filler preparation.

- Rice straw used as filler undergoes preparatory stages prior to compounding. The rice straw was grinded and sieved into three ranges of sizes. The rice straw powder was dried before compounding.

ii) Formulation development of unrosslinked rice straw/HDPE biocomposite.

- HDPE resin was used as base polymer fill with grinded rice straw as filler. Compounding of rice straw with HDPE and standard additive on twin screw extruder. Injection molding process was used to prepared the test specimen
- Tensile test was used as the basic test for following investigations:
    a) Effect of rice straw particle size on uncrosslinked rice straw/HDPE.
    b) Effect of rice straw composition uncrosslinked rice straw/HDPE.
    c) Crosslinking of rice straw/HDPE biocomposite with silane chemicals.
- Silane chemicals formulation

a) Premixing of silane chemicals with rice straw/HDPE biocomposite in the high speed mixer for preparing the crosslinked rice straw/HDPE.

b) Injection molding processability study.

c) Curing

(iii) Rice Straw/HDPE characterizations.

d) FTIR, to analyze the crosslink.

e) Thermal analysis for thermal properties determination.

f) Water absorption test

g) MFI, to determine its injection molding processability.

h) Gel content test to determine the degree of crosslinking.

(iv) Mechanical properties determination

i) Flexural Test

j) Izod Impact Test

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