TITLE

PRODUCTION AND CHARACTERIZATION OF PLASTIC FROM MARINE ALGAE

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ABSTRACT

The two main objective of this research is to test the viability of using marine algae as a profound bio-filler for the production of plastic where the plastic produce will have the tendency to reduce usage of non-renewable recourse which contributes to severe ecological problems. The second objective is to characterize the plastic blend produced using marine algae via physical, mechanical and thermal testing. In this study, Marine algae and Low density polyethylene is used as raw material and blended to produce plastic sample which later on was characterized using Differential Scanning Calorimeter (DSC), Thermogravimetry Analyzer (TGA), and tensile tester as well as water absorption tests. The results concluded that these red marine algae are not suitable for plastic production without any modification. This is due to the fact that it have weak mechanical properties and also very high water absorbance level which contributes mechanical failure under moist conditions.

PENGHASILAN DAN PENCIRIAN PLASTIK DARIPADA PLASTIC ALGA MARIN

ABSTRAK

Dua objektif utama kajian ini adalah untuk menguji kebolehan menggunakan alga marin sebagai bio-pengisi yang berkemampuan tinggi untuk penghasilan plastik di mana plastic and dihasilkan akan mempunyai kecenderungan untuk mengurangkan penggunaan sumber tidak boleh diperbaharui seperti petroleum yang menyumbang kepada masalah ekologi yg membimbangkan. Satu lagi objektif adalah untuk mencirikan campuran plastik dihasilkan menggunakan alga marin melalui ujian fizikal, mekanikal dan degredasi haba. Dalam kajian ini, alga Marin dan polietilena berketumpatan rendah digunakan sebagai bahan mentah dan dicampur untuk menghasilkan sampel plastik yang kemudian dicirikan menggunakan kalorimetri pengimbas pembezaan (DSC), Analyzer termogravimetri (TGA), dan penguji tegangan serta ujian penyerapan air. Keputusan menyimpulkan bahawa alga marin merah tidak sesuai untuk pengeluaran plastik tanpa sebarang pengubahsuaian struktur molekulnya. Ini adalah disebabkan oleh ia mempunyai sifat-sifat mekanikal yang lemah dan juga tahap penyerapan air yang sangat tinggi yang menyumbang kepada kegagalan mekanikal di bawah situasi yang berkelembapan tinggi.

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LIST OF ABBREVIATIONS

DSC	Differential Screening Calorimeter
EVA	Ethylene Vinyl Acetate
FE	Formaldehyde Emission
FTIR	Fourier Transform Infrared spectroscopic
HDPE	High Density Poly Ethylene
LDPE	Low Density Poly Ethylene
NP	Natural Pigment
OSB	Oriented Strand Board
PP	Polypropylene
RTV	Room Temperature Vulcanizing
SEM	Scanning Electron Microscopic
TGA	Thermo-gravimetric Analyser
UV/V	Ultra-violet Visible Spectrophotometer

LIST OF SYMBOLS

˚C	Degree Celsius
%	Percentage
MPa	Mega Pascal
USD	United States Dollar
RM	Ringgit Malaysia
Tons	Tonnes
$	Dollar
pH	Power of Hydrogen
˚F	Degree Fahrenheit
g/cm^3	Gram per centimeter cube
µm	Micro meter
mm	Millimeter
M	Molarity
V	Volume
mL	Milli-Liter
g	Gram
h	Hour
cP	Centipoises
wt.	Weight
s	Second

CHAPTER 1

Introduction

1.1 Background of study

A brief history of plastics predates back to middle ages. During these times, plastics were mostly   naturally occurring polymeric compounds which were used to derive product of daily use. One of the examples would be the usage of animal horns in building window frames and lantern heads. As time progressed, substitute polymeric materials were made from lye treated milk protein-solids (casein). It was a breakthrough when Charles Goodyear's discovery of vulcanization as a route to create sulphur chains in materials derived from natural rubber was commercialized. Thus from then till today the polymeric industry have underwent continuous revolution in search of alternative and more suitable materials for various purposes.

In this research, the compounding of plastic blends with structurally modified marine algae culture is to be studied as a new and profound way to progress towards an environmental friendly production of plastics. Thus, we will discuss the two major elements which is the core of this research, first being the study of the algae and next the blending of plastics itself.

1.1.1 Marine Algae

Marine algae, more commonly known as seaweeds, come in various shapes and sizes. Algae are not plants, even though they sometimes look like them. Algae are relatively undifferentiated organisms which, unlike plants, have no true roots, leaves, flowers or seeds. Algae do not have water-conducting tissues, as they are, at some stage, surrounded by water, which is also important for reproduction by spores. The spores may be motile or non-motile. Most of the algae are photosynthetic organisms that have chlorophyll. Apart from chlorophyll, they contain additional pigments, which are the basis of classification. Most of the seaweeds are red (6000 species) and the rest known are brown (2000 species) or green (1200 species).

Seaweeds are used in many maritime countries as a source of food, for industrial applications and as a fertilizer. Nori, a type of Japanese red seaweed has a high protein content (25-35% of dry weight), vitamins (e.g. vitamin C) and mineral salts, especially iodine. Industrial utilization is at present largely confined to extraction for phycocolloid, industrial gums classified as agars, carrageenan and alginates. Agars, extracted from red seaweeds such as *Gracilaria* , are used in the food industry and in laboratory media culture. Carrageenan, extracted from red seaweeds are used to provide particular gel qualities. Alginates are derivatives of alginic acid extracted from large brown algae, are commonly used as They are used in printers' inks, paints, cosmetics, insecticides, and pharmaceutical preparations. Alginates are used as stabilizers in ice cream.

In recent studies, there are an increasing number of researchers done which are looking to get plastics from the sea by using marine life forms as a raw material to make polymers. Algae are the most promising area of research right now. It is already widely used as a raw material for biofuels, but this is increasingly extending to plastics. The theory behind biopolymers is that they use sustainable resources, rather than petrochemicals. The usage of naturally occurring sulphated polysaccharide and phenolic polysaccharide which can be derived from these marine algae is largely used as blending material for bio plastics. According to Frederic Scheer, CEO, Cereplast one of the bio-plastic producing company, resin is to be extracted from this crop to produce bio-adhesives which can be used to make polymeric compounds. It is similar of how starch from corns and other commercialized crops were used in obtaining polymers which will acts various additives and matrix components in plastic production.

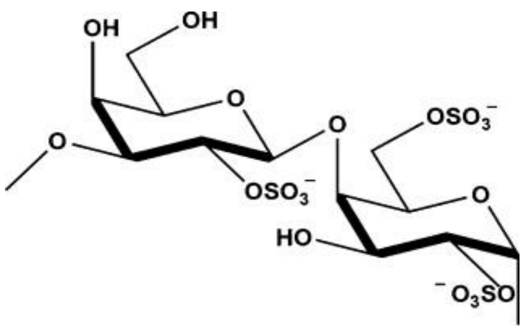

Figure 1.1: Chemical structure of the repeating dimeric units of λ-carrageenan

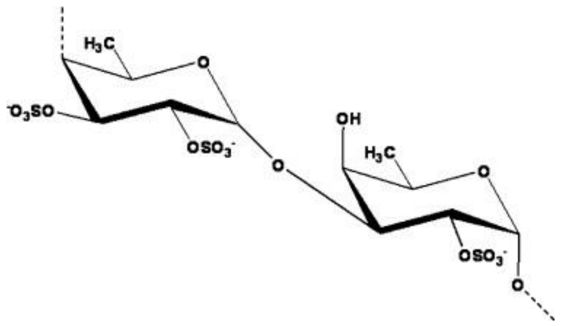

Figure 1.2: Chemical structure of the repeating dimeric units of fucoidal

1.1.2 Plastic and Plastic Blending

Plastic materials are range of products which are blended from synthetic or semi synthetic organic solids that are moldable. Plastics have high average molecular weight compared to other types of polymers and also contain other substance. These plastics are most commonly synthesized from petrochemicals and are often are derived with various characteristics and functions. The vast majority of these polymers are based on chains of carbon atoms alone or with oxygen, sulphur, or nitrogen. Plastics consists of carbon repeating unit which is linked together to form a polymeric chain which is also known as the back bone. To customize the properties of a plastic, different molecular groups attached to the backbone, as the side chains influences the properties of the side chains.

Compounding consists of preparing plastic formulations by mixing and blending polymers and additives in a molten state. There are different critical criteria to achieve a homogenous blend of the different raw material. There are multiple additives that is being used in plastic blending and formulation.

Fillers are mainly particles which are added to plastic compounding in order to lower the consumption of more expensive binder material or to better some properties of the mixture material. Formerly, fillers were used predominantly to cheapen end products, in which case they are called extenders.

Coupling agents or better a polymeric coupling agent is a polymer that attaches inorganic filler to the polymer matrix. Coupling agents have to be added in order to reduce the repellence of the polymers and fillers respectively. This is because fillers are largely added to polymer matrix in order to reduce the cost and so on.

Plasticizers or dispersants are additives that increase the plasticity or fluidity of a material. The most commonly used plasticizer is phthalate ester. It is used to upgrade or improve the flexibility and durability of plastic materials.

Flame retardant is chemicals used in thermoplastics, thermosets, textiles and coatings that inhibit or resist the spread of fire. There additives are often added to make the product more resistive towards thermal decomposition with different mechanisms.

Colorant is another additive which is used to give the produced plastic material a suited colour. There are 2 methods of colour addition, first is the pigment addition. This mainly involves addition of metallic colour pigment to provide the colour and the next method is to use azonium dye.

1.2 Problem Statement

As there is an increasing awareness on environmental issues, the producing of traditional petro-chemically derived plastics is not favorable. This is due to the fact that synthetic plastics have high resistance towards environmental degradation which takes up to thousands of years to decompose. The only way to dispose is through land fill. Due to this, bio plastics are becoming a new replacement for synthetic compounds as it is more prone to environmental attack and decomposition.

Not only that, certain qualities can also be reinforcing i.e. mechanical strengths via using natural additives or adhesives. In this study, the usage of marine algae as a filler in polymer blending is tested to produce notable bio-plastic with elevated properties and water resistance.

1.3 Objectives

There are two main objectives in this research of producing plastic from marine algae. The first objective to investigate if marine algae are a viable source of bio filler to produce plastic that is environmentally friendly whereby the plastic produced will be biodegradable and slightly decomposed to smaller substances by living organisms from marine algae.

The second objective is to characterize the algae plastic produced via TGA (thermal gravimetric analysis), DSC (differential scanning calorimeter), FTIR (Fourier Transformed Infrared Spectrometer), and water absorption testing.

1.4 Scope of study

The scope of this research includes the description and characterization of the marine algae that will help in the plastic production process. Besides that the blending of marine algae using different percentage of matrix and fillers (marine algae) is also to be studied. The blended plastic is characterized according to the objective of the research.

1.5 Significance of study

The result of this study will be a breakthrough in producing commercial grade of bio-plastic as a substitution for existing synthetic plastic. Furthermore, the enhanced properties and water resistive adaptation will be also promise a better material production proposes.

1.6 Conclusion

As conclusion, the purpose of this study is to find out a new material which can be synthesized to obtain a notable plastic blend to cope with the environmental problem. This research will also benefit other researchers by providing information of characteristics of marine algae plastic for further findings and modifications.

CHAPTER 2

Literature review

2. 1 Introduction

Formulating bio-based plastic blend is a relatively an unchartered scope of study as it has not been commercialized yet. Despite this, there were many researchers have been done where algae extract is used for multiple other factions. In this chapter, commercialized study which has been done with marine algae will be reviewed. Other than that, significant studies using Low Density Poly Ethylene (LDPE) as a blending matrix will also be reviewed. In this research, LDPE is chosen due to its usage in industry as a primary packaging material. It is the major source of plastic which cannot be biologically degraded. Thus making it bio-degradable will provide this research with a strong commercializing value. Also in this research, we will review the process of structural modification which will be done to the towards the algae extract. This step is under taken to modify the physical properties of the polymer blend which will be created. Generally, it is presumed that bio-plastics have a much lower mechanical properties compared to synthetic plastic, thus to overcome this problem, this step is proposed.

2.2 Marine Algae

Seaweed can be classified into three bigger groups according to their pigmentation or in laymen term colour which are brown, green, and red. In this research we are using the red algae which have a vibrant colour due to the presence of phycoerythrin. In most algae, the primary pigment is chlorophyll which is present in most of the green plant. This algae also contains carotenoids, which are brown or yellow,and phycobilins which are either red or blue. This accounts for the colourful hues according to Khaled (1999). The red algae are multicellular which are characterized by a great deal of branching presence in its molecular structure and complex tissue where most of the algae belong to this group. The red algae are commonly found in warm water regions and tropical climates and can grow in great depts. compared to other species of algae. The red algae are a traditional part of oriental cuisine.

The importance of marine algae as sources of functional ingredients has been well recognized due to their diverse usage in multiple fields of studies. It is mainly utilized in the pharmaceutical industry for is multi-vitamin possessing quality. According to Ratih Pangestutia, Se-Kwon Kima,b,* on their paper on Biological activities and health benefit effects from marine algae, the neutral pigment (NP) has great deal of benefits. These NPs exhibit various beneficial biological activities such as antioxidant, anticancer, anti-inflammatory, anti-obesity, anti-antigenic and neuroprotective activities. This contribution focuses on biological activities of marine algae-derived NPs and emphasizing their potential applications in foods as well as pharmaceuticals areas. It was concluded that these NPs are an alternative source for synthetic ingredients that can contribute to consumer's well-being, by being a part of new functional foods and pharmaceuticals.

In another research done by Ali A. El Gamal on biological importance of marine algae, The microalgae phyla have been recognized to provide chemical and pharmacological novelty and diversity. Hence, microalgae are considered as the actual producers of some highly bioactive compounds found in marine resources. The principal use of seaweeds as a source of human food and as a source of gums (phycocollides). Phycocolloides like agar agar, alginic acid and carrageenan are primarily constituents of brown and red algal cell walls and are widely used in industry. Such property of algae exhibits an adhesive character due to the present of lignin which can be utilised as a polymeric additive.

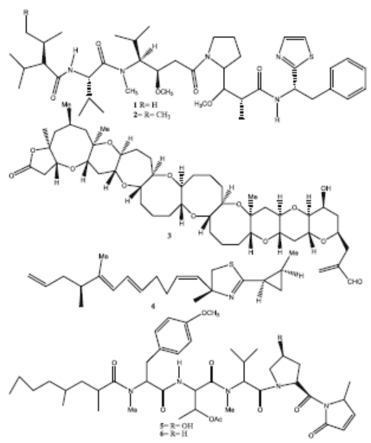

Figure 2.1: A few molecular structure of marine algae extract

This proves significance to our research that since its considered a pharmaceutical product, it is vitally human friendly in addition to environmentally green material. Obtaining the saccharine which also acts as an adhesive for our polymer blend is justified as we can draw parallel and state that the material will undergo environmental degradation. Thus it is a valid source for bio-plastic production alternative.

Other than pharmaceutical usage, marine algae is also used to conduct chemical bio-sorption.This is a process where heavy metal ions such as cobalt and copper ions are bio-sorped onto the marine algae. According to K. Vijayaraghavan a, J. Jegan b, K. Palanivelu c, M. Velan a,* on their paper on Biosorption of copper, cobalt and nickel by marine green alga Ulva reticulata in a packed column, it is stated that marine algae offer advantages for biosorption because their macroscopic structures offer a convenient basis for the production of biosorbent particles suitable for sorption process applications. This is due to the fact that this saccharide contains sulphonic compound to their molecular chain. This compound acts as a good adsorption platform for various metal ions. It is also stated that the presence of phenol group in the chain aid the biosorption process as it aids localised attachment of outer substances conjuring metal ions. As for the result of the study, green algae exhibited very high copper, cobalt and nickel biosorption capacities in packed column compared to most of the biosorbents. This alga showed unique ability to remove all three heavy metal ions and retain its uptake capacity in three regeneration cycles. In context of this research, we can conclude that this quality can ease the structural modification as the bonding platform is already present in the algae regarding reagent which involves metallic catalysts and so on

Algae are also widely considered an alternative source for bio-fuel generation. On a study done by Gholamhassan Najafia, Barat Ghobadiana, Talal F. Yusafb titled Algae as a sustainable energy source for biofuel production in Iran, they stated that Algae can be converted directly into energy, such as biodiesel, bioethanol and biomethanol and therefore can be a source of renewable energy. This is due to fact that like other commercialized crop, it is a plat with natural fibre or contains vast amount of polysaccharide which can be easily converted to the above stated products. Because of its higher yield non-edible oil production and its fast growth that does not compete for land with food production. Thus it is nothing but a naturally occurring biomass in the since that the cultivation time is bare minimum compared to commercialized crops. This is significant to our study as primary algae oil extracted can be used to create plastic blending. With this abundant amount of algae with no specific use, it can be commercialized via the waste to wealth concept where the algae itself does not cost much investment.

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The red algae are chosen as the research raw material due to the fact that it contains high amount of amino proteins primarily. This chains acts as the building block for the protein formation which is a natural polymer. Besides that algae also have good bond strength due to the presence of sulphite bonds in its microstructure which aids the plant to grow in turbulent deep waters. Rhodophyta (red algae) have this natural proteins and cellulose structure compared to other species according to Nirmal et et (2010). This makes it a suitable bio-filler which is to be used in plastic blending. There are many types of protein present in red algae. Researches are conducted utilizing these chains in order to achive dimensional stability of the plastic produced from red algae. The table below represents the types of amino acid concentration and nitrogen content in Eucheuma cottonii as reported by Patricia Matanjun (2007).

Table 2.1: Proteins in algae

Amino Acid	(mg g-1 dry Weight)
Aspartic Acid (Asp)	2.65 ± 0.15
Glutamic Acid (Glu)	5.15 ± 0.13
Serine (Ser)	2.27 ± 0.04
Glycine (Gly)	2.27 ± 0.32
Histidine (His)	0.25 ± 0.10
Arginine (Arg)	2.60 ± 0.14
Threonine (Thr)	2.09 ± 0.01
Alanine (Ala)	3.14 ± 0.11
Proline (Pro)	2.02 ± 0.09
Tyrosine (Tyr)	1.01 ± 0.12
Valine (Val)	2.61 ± 0.07
Methionine (Met)	0.83 ± 0.17
Isoluesine (Ile)	