CHARACTERIZATION OF THERMOPLASTIC SAGO STARCH/ NOVOLAK AND THERMOPLASTIC SAGO STARCH/NOVOLAK/POLYVINYL ALCOHOL

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To my precious Lord Jesus,
who gives me new life, new hope and new destiny.
To my wonderful Hope family,
who makes me who I am today.
To my beloved parents and family,
who unceasingly took the risk in believing me
and giving me all they have.

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ABSTRACT

In this study, novolak type phenolic resin was blended into glycerol plasticized thermoplastic sago starch (TPS) via twin screw extrusion, in order to improve the thermal resistance and water absorption of the latter. The compression molded blends were characterized in terms of their physical, chemical, morphological, thermal and moisture absorption properties. Density and differential scanning calorimetry implied that the blends were miscible in all compositions. The interaction accountable for the miscibility was identified as hydrogen bonding between the hydroxyl groups of the TPS and novolak through Fourier transform infra-red spectroscopy. However, scanning electron microscopy and x-ray diffraction showed that the blends were immiscible when the novolak content reached 60 wt%. Results from water absorption and thermogravimetry analysis also showed that addition of novolak improved the thermal resistance and moisture sensitivity of the TPS, especially the latter. In view of the brittle nature of the blends, the study was extended by adding 60 wt% of polyvinyl alcohol to the blends. Flexural properties of the ternary blends were greatly improved.

ABSTRAK

Dalam kajian ini, novolak resin jenis fenolik telah diadun ke dalam termoplastik kanji sagu (TPS) yang diplastikkan dengan gliserol dengan menggunakan skru penyemperitan berkembar, bagi meningkatkan rintangan haba dan penyerapan air. Adunan yang diacuan mampatan telah dicirikan dari segi sifat fizikal, kimia, morfologi, penyerapan haba dan penyerapan air. Ketumpatan dan kalorimetri pengimbasan pembezaan menunjukkan adunan adalah larut dalam semua komposisi. Interaksi yang dikenal pasti untuk keserasian ialah ikatan hidrogen di antara kumpulan adunan yang terlarut campur adalah hidroksil TPS dan novolak seperti yang dikenal pasti melalui spektroskopi inframerah transformasi Fourier. Walau bagaimanapun, mikroskop imbasan elektron dan pembelauan sinar- x menunjukkan bahawa adunan ini tidak terlarut campur apabila kandungan novolak mencapai 60 wt %. Keputusan daripada penyerapan air dan analisis termogravimetri juga menunjukkan bahawa penambahan novolak telah menambahbaik rintangan haba dan kesensitifan kelembapan TPS. Disebabkan sifat rapuh adunan, kajian ini telah diperluaskan dengan menambah 60 wt % polivinil alkohol kepada adunan. Sifat-sifat lenturan adunan ternari telah bertambah baik.

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LIST OF ABBREVIATIONS

ABS	-	Acrylonitrile-butadiene-styrene
C	-	Carbon
cm^{-1}	-	Reciprocal centimeter
EVA	-	Ethylene vinyl acetate
FH	-	Flory and Huggins
FTIR	-	Fourier-transform Infrared spectroscopy
HDPE	-	High density polyethylene
HMTA	-	Hexamethyletetramine
LDPE	-	Low-density polyethylene
MMT	-	Montmorillonite
N	-	Number of segment
O	-	Oxygen
O-	-	Ortho
OH	-	Hydroxyl group
P-	-	Para
PCL	-	Polycaprolactone
PE	-	Polyethylene
PEEA	-	Poly(ethylene-co-ethyl acreylate)
PEG	-	Poly(ethylene glycol)
PEO	-	Polyethylene Oxide
PLA	-	Poly(lactic acid)
PLA-g-AA	-	Acrylic acid grafted poly(lactic acid)
PMMA	-	Poly(methylmethacrylate)
POM	-	Poly(oxymethylene)
PP	-	Polypropylene
PS	-	Polystylene

PVA	-	Polyvinyl alcohol
PVF_2	-	Poly(vinylidene fluoride)
q	-	Comparison between intermolecular hydrogen bonding and intramolecular hydrogen bonding
rpm		Rotation per minute
SAN	-	Styrene-acrylonitrile
SEM	-	Scanning Electron Microscope
SiO_2	-	Silica oxide
SMA	-	Styrene-maleic anhydride
T	-	Absolute temperature
TGA	-	Thermal gravimetric analysis
TPS	-	Thermoplastic Starch
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

α	-	Alpha
%	-	Percent
ΔG_N	-	Gibbs free energy change for nonpolar polymer blends
ΔG_m	-	Gibbs free energy of mixing
ΔH_m	-	Enthalpy of Mixing
N	-	Number of segment
O-	-	Ortho
ϕ	-	Volume fraction
T_c	-	Crystallization temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
ΔS_m	-	Entropy change
θ	-	Delta
χ	-	Flory-Huggins interaction parameter calculated by Hilderbrand's solubility parameter
η	-	Lamellar thickness factor

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In the last few decades, biodegradable polymers have been growing in their importance and are gaining more shares in the market, replacing the use of some plastic materials which are not biodegradable (Sabetzadeh *et al*., 2015). One of the reasons for this development is that biodegradable polymers can significantly reduce the volume of plastic waste. According to Kaseem *et al.* (2012), the increasing development of plastic materials from renewable resources occurs due to the increasing oil price and environmental pollution. It is well known that biodegradable polymers are perfectly well with the ecosystems and have a closed loop carbon cycle, as shown in Figure 1.1 (Philip *et al.*, 2009).

In view of the development mentioned above, thermoplastic starch (TPS) was introduced and has gained much attention from the researchers in the field (Yu *et al*., 2013; Sabetzadeh *et al*., 2015). Since then, different blends and composites based on TPS have been developed and studied (Pereira *et al*., 2010; Yaacob *et al.*, 2012; Kaseem *et al.*, 2012; Yu *et al.*, 2013).

TPS can be considered as a new plastic material; it is formed by destructurizing starch with heat and shear forces in the presence of one or more types of plasticizers (Souza *et al.*, 2012). One of the most commonly used plasticizers is glycerol, taking advantage of its high boiling point and low cost (Sarifuddin *et al*., 2013).

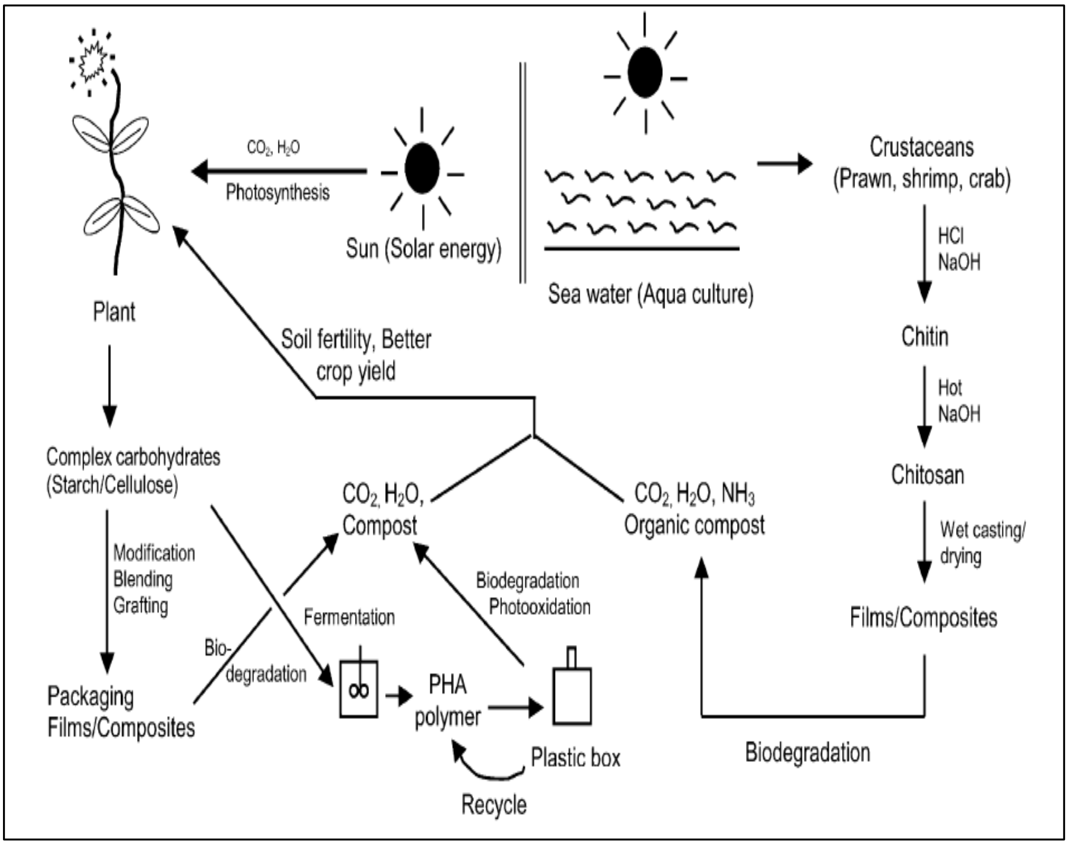

Figure 1.1: Carbon Cycle of biodegradable polymers (Philip *et al.*, 2009)

However, TPS has two major weaknesses or disadvantages, namely moisture sensitivity and poor thermal resistance (Yu *et al.*, 2013). These weaknesses have limited its applications in industries for producing marketable products. From the many attempts in improving these weaknesses, mixing TPS with other polymers has been found to be effective. For example, thermal resistance of TPS was improved by blending with ethylene-vinyl acetate (Roz *et al*., 2012).

This project was carried out in order to study the effectiveness of novolak type phenol formaldehyde resin (novolak) in overcoming the aforementioned limitations of TPS. There are many advantages of phenolic resins over other plastic materials, namely, low cost, high rigidity, good dimensional stability, better flame retardancy to name a few. Ma *et al.* (1997) reported that novolak has decomposition temperature of 370 ^{o}C. This temperature is relatively high compared to that of TPS. On the other hand, Chai *et al.* (2009) showed that novolak is relatively less moisture sensitive. Therefore, it is believed that the addition of novolak would be able to improve the weaknesses of TPS, specifically in these two areas. Moreover, it is not uncommon to produce polymer blend using novolak since different blend formulations have been developed by blending novolak with ethylene vinyl acetate (Mekhilef and Hadjiandreout, 1994), poly(ethylene oxide) (Zhong and Guo, 1999), styrene-butadiene rubber (Shojaei and Faghihi, 2010), poly(vinyl acetate) (Huang *et al.*, 2002), polyamideimide (Kundu *et al.*, 1985) and other polymers.

Miscibility is an important aspect to be considered in developing polymer blends since it determines the properties of the blends. Some of the most important techniques for polymer–polymer miscibility are thermal analysis, electron microscopy, dynamic mechanical studies and viscometric techniques. In this study, miscibility of TPS/Novolak blends was evaluated based on the data obtained via thermal analysis, density test, X-ray diffraction and infra-red spectroscopy.

1.2 Problem Statement

TPS has been blended with different polymers in order to improve its moisture sensitivity and thermal resistance. Blends with poly-ε-caprolactone (PCL) depicted significantly reduced water sensitivity but the blends soften and melted at very low temperatures, namely at 40 ^{o}C and 60 ^{o}C, respectively. Thus the blends have very limited applications (Nafchi *et al*., 2013).

Addition of poly(lactic acid) or PLA increased the water resistance of TPS besides improving their mechanical properties (Wang *et al.*, 2007; Ferrarezi *et al.*, 2013). However, the relatively high cost of PLA makes it an unfavorable choice to manufacturers. Some researchers blended TPS with low cost commodity plastics, for example low density polyethylene (LDPE) for the same target (Gonzalez *et al.*, 2003). The moisture sensitivity was improved, but at the expense of reduced mechanical properties due to incompatibility.

PVA is strong, durable and possesses high crystallinity structure. Many researchers studied about PVA blends especially in terms of their mechanical properties. Tang *et al.* (2008) found that addition of PVA to starch improved its tensile strength and elongation at break. In another study, Yang and Nie (2011) reported that addition of PVA to novolak resulted in a blend with impact strength 2 times higher than that of the novolak.

In view of their very good moisture and thermal resistance, novolak is of great potential to be utilized to overcome the limitations of TPS in terms of their low thermal resistance and high moisture sensitivity. To the best of the author's knowledge, no works on the addition of novolak to TPS has been reported except the formulations patented by Gibbons and Chiang (1978). However, their works were different from what is reported here (refer to Section 2.6 - Thermoplastic Starch Blends).

Since research pertaining to the addition of novolak to TPS is still currently lacking, thus the need for related R&D works has certainly been recognized in order to validate the hypothesis proposed based on the available information. The outcomes of the study could provide insights on miscibility, mechanical, thermal, crystallinity and moisture absorption properties of TPS/Novolak blends. This study gives the fundamental ideas on TPS/Novolak blends which will help researchers for future studies.

1.3 Objectives of the Study

This study was conducted in order to fulfil the following objectives:

(i) To study the miscibility of TPS/Novolak blends.

(ii) To characterize the TPS/Novolak blends in terms of their physical, morphological, thermal and moisture absorption properties.

(iii) To study the effects of novolak contents on thermal and moisture absorption properties of the TPS/Novolak blends.

(iv) To study the effect of PVA addition on flexural properties of the TPS/Novolak blends.

1.4 Scope of the Study

In this study, altogether nine formulations of TPS/Novolak blends were prepared by adding 0-70wt% of novolak type phenol formaldehyde resin to 100-30wt% of TPS produced from sago starch. The blends contained 20 phr of water and 25 phr of glycerol as destructurizing agent and plasticizer, respectively.

In terms of processing method, the blends were compounded via high speed mixing and twin screw extrusion while samples for different tests were formed using compression molding.

The blends were studied in terms of their miscibility via density, Fourier transform infra-red spectroscopy (FTIR) and differential scanning calorimetry (DSC). Supplemental data from X-ray diffraction (XRD) and scanning electron microscopy (SEM) complement the miscibility study by providing morphological information. Thermal resistance and moisture sensitivity of the blends were evaluated based on the data collected from thermogravimetric analysis (TGA) and moisture absorption test, respectively.

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