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Mechanical and Thermal Properties of Hybrid Blends of LLDPE/Starch/PVA

Rahmah, M., Farhan, M., Akidah, N.M.Y

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***Abstract*—**Polybag and mulch film in agricultural field are used plastics which caused environmental problems after transplantation and planting processes due to the discarded wastes. Thus a degradable polybag was designed in this study to replace non degradable polybag with natural biodegradable resin that is widely available, namely sago starch (SS) and polyvinyl alcohol (PVA). Hybrid blend consists of SS, PVA and linear low density polyethylene (LLDPE) was compounded at different ratios. The thermal and mechanical properties of the blends were investigated. Hybrid films underwent landfill degradation tests for up to 2 months. The films showed gelation and melting transition existed for all three systems with significant melting peaks by LLDPE and PVA. All hybrid blends loses its LLDPE semi crystalline characteristics as PVA and SS systems had disrupted crystallinity and enhanced the amorphosity of the hybrid system. Generally, blending SS with PVA improves the mechanical properties of the SS based materials. Tensile strength of each film was also decreased with the increase of SS contents while its modulus had increased with SS content.

***Keywords*—**Appearance peak, LLDPE, PVA, sago starch.

I. Introduction

THESE days, the use of plastic in our daily life has been long question and being debate over for the past few decades due to its lack of recycling facilities and infrastructure, non-renewability, non-recyclability, as well as incorporation of toxic additives [1]. Plastic materials are tough as they are resistant to degradation in natural environment [6]. Rapid increase in the production and consumption of plastic has lead to a serious plastic waste problem so called 'white pollution' and landfill depletion due to their high volume to weight ratio and resistance to degradation [2], [3]. The possible solution for this problem is to increase the biodegradability rate of the plastic based product, and this can be achieved by incorporation of natural polymer such as sago starch (SS) into the plastic based. SS has been used as raw material for the production of biodegradable plastic due to its biodegradable properties, low price and abundantly available [1], [4]. Use of biopolymers resulted in low water resistance and high brittleness of SS films has limited their extensive application [5], [7]. Therefore many researcher had attempted to overcome this problems by blending SS with others synthetic biodegradable polymers especially PVA which is hydrophilic in nature and water soluble polymer. PVA has high water absorption, excellent film forming, emulsifying, and adhesive properties which resulted in wide industrial use such as water soluble packaging films, textile sizing agents and paper coatings [3], [8], [10]. Natural biodegradable polymers such as cellulose, SS and chitosan have been introduced. Of these materials SS is being the most attractive candidates due to its low cost, ease of availability and renewability. Although SS is totally biodegradable, but pure SS lacks of strength, water resistibility and thermal process ability. Therefore to overcome these drawbacks SS often blended with synthetic biodegradable polymers such as PVA [3]. In this work, the biodegradability of SS compounded with PVA and LLDPE have been evaluated. Hybrid blends were evaluated for their thermal and mechanical properties. The processing and suitable applications also are discussed in this paper.

Rahmah M. is an Associate Professor in Polymer Technology Department, lecturing at University Technology MARA, UiTM Shah Alam, Malaysia. She heads GREEN Polymer Research group in her Faculty of Applied Sciences, UiTM Shah Alam (Tel: 0060-3-55445548; e-mail: greenkayangan@gmail.com)

Farhan, M.A. and Nurul, A.M.Y. are with University Technology MARA, UiTM Shah Alam, Malaysia. They are PhD research students from Faculty of Applied Sciences, UiTM Shah Alam (e-mail: stelar.mohdfarhan@gmail.com, akidah87@gmail.com).

II. Methodology

A. Materials

Sago starch was supplied by Borgiap Industries Sdn Bhd. It has average particle size of 20µm and decomposition temperature of 230ºC. LLDPE supplied by ETILINAS product code LL0209SA with a melting temperature of 100ºC and melt flow index of 2.0g/10min, manufactured by TITAN (M) Sdn. Bhd., Johore was used as a resin. Carbon black masterbatch was supplied by PS POLY Sdn Bhd. Glycerol anhydrous with the molecular weight of 92.10g/mol was supplied by Chemo Industries will be used as plasticizer in this study. Polyvinyl alcohol which is reagent grade chemical will acts as biodegradable plastic was supplied by Chemo Laboratory.

B. Sample Preparations

SS and LLDPE, along with the addition of PVA, and carbon black masterbatch were mixed until homogenized. Different compositions of materials need variably duration of mixing process until homogeneity is achieved. Prior to the mixing process, it is important to dry the starch in oven for 24 hours at 60ºC to ensure all moisture entrapped inside was evaporated completely. Any moisture content can affect the process ability of compound during extrusion. Compound then was fed into Twin Screw Extruder with setting of rotor speed at 80rpm and the temperature for heating zone were set between 125ºC and 140ºC respectively. Minimal adjustments of setting were done due to changing types of compounds fed. The percentages of LLDPE, PVA and SS for hybrid blends were

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tabulated in Table I as below:

TABLE I
COMPOSITION OF HYBRIDS

Materials (%)	Hybrid (a)	Hybrid (b)	Hybrid (c)	Hybrid (d)	Hybrid (e)
LLDPE	20	20	20	20	20
PVA	50	40	30	20	10
Sago Starch	20	30	40	50	60
Carbon Black	10	10	10	10	10

C. Films Preparation

A total of 25g of compound materials were placed on the mould of 15cm x 15cm with the thickness of 0.5mm. The mould than was pressed using Hot Press at 180ºC for 2 minutes. The pre-heating and cooling time were 5 minutes respectively. Blend films in average of 0.5-0.6mm, were trimmed and cut into strips for next testing.

1. Landfill Degradation Test

Landfill degradation was performed as describe with slight modification [11]. The garden pot with approximately 3 liter volume was filled with the soil taken from a plantation field in Ledang City, Johor. The films were cut into 2x15cm dimension and placed on the soil. The soil was kept moist by sprinkling water at regular time interval to maintain 50% humidity.

D. Degradability of Blend Films



(a) (b) (c)



(d) (e)

Fig. 1 Blend films after 30 days of landfill degradation exposure test
(a) 50% PVA/20% SS (hybrid A) (b) 40% PVA/30% SS (hybrid B)
(c) 30% PVA/40% SS (hybrid C) (d) 20% PVA/50% SS (hybrid D)
(e) 10% PVA/60% SS (hybrid E)

Fig. 1 shows the visual changes of the blend films after 30 days of landfill degradation. All film samples were cut into same dimension for homogeneity. All blends showing high rate of degradation after 30 days of landfill exposure. Defragmentation of film samples are obvious except for film blend D. Blend films A, B, C show similar defragmentation characteristics compared to blend film E where the texture of the sample is almost disintegrated. The solubility of sago starch contributed in promoting the degradation of the samples. Further degradation processes were enhanced by weathering, radical reactions and soil microorganism's activities. Soil microorganisms that help in further deprivation of samples induced the metabolism of the film's polymer structure into smaller fragments. Microbial activities are rucial in degradation the samples because it is not only metabolizing sago starch content of the film, it is also help in degrading the PVA which is also the main composition of the blend samples [9], [13]. Sago starch can be readily metabolized by wide range of microorganism to fermentation products such as ethanol, hydrogen and methane. PVA also was susceptible to degradation, however the rate was slower, and therefore increasing the amount of sago starch into the blend will increase the degradation rate of the films [3].

E. Fourier Transform Infrared (FTIR) Spectroscopy

TABLE II
FTIR PEAKS OF SAMPLES

Hybrids	Peaks (cm^{-1})	Bonds
Hybrid A	1462 (w[a])	Saturated C-H bend from polyethylene
	1695 (w), 1780 (w)	C=O bond bends from carbonyl functional groups
	2816 (w)	Aldehyde C-H bend
	2955-2900 (br[d], w)	Saturated C-H stretch from polyethylene
	3303-3322 (br, s[c])	O-H bond stretch from alcoholic /carboxylic acid functional groups
Hybrid B	1462 (w)	Saturated C-H bend from polyethylene
	1695 (w), 1780 (w)	C=O bond bends from carbonyl functional groups
	2822 (m[b])	Aldehyde C-H bend
	2955-2900 (br, m)	Saturated C-H stretch from polyethylene
	3300-3322 (br, s)	O-H bond stretch from alcoholic /carboxylic acid functional groups
Hybrid C	1462 (s)	Saturated C-H bend from polyethylene
	1695 (m), 1780 (m)	C=O bond bends from carbonyl functional groups
	2820 (s)	Aldehyde C-H bend
	2955-2900 (br, s)	Saturated C-H stretch from polyethylene
	3300-3322 (br, m)	O-H bond stretch from alcoholic /carboxylic acid functional groups
Hybrid D	1465 (s)	Saturated C-H bend from polyethylene
	1690 (s), 1782 (m)	C=O bond bends from carbonyl functional groups
	2815 (s)	Aldehyde C-H bend
	2953-2900 (br, s)	Saturated C-H stretch from polyethylene
	3294-3325 (br, w)	O-H bond stretch from alcoholic /carboxylic acid functional groups
Hybrid E	1466 (s)	Saturated C-H bend from polyethylene
	1697 (s), 1775 (m)	C=O bond bends from carbonyl functional groups
	2809 (s)	Aldehyde C-H bend
	2955-2905 (br, s)	Saturated C-H stretch from polyethylene
	3295-3325 (br, w)	O-H bond stretch from alcoholic /carboxylic acid functional groups

[a]weak strength, [b]medium strength, [c]strong strength, [d]broad band

FTIR spectroscopy of blend films was carried out using Perkin Elmer spectrometer, model of Spectrum One. Spectra were recorded in transmission mode as an average of 16 scans in the range 4000-600cm^{-1}, with a resolution of 4cm^{-1}. The hydroxyl concentration was measured as the ratio of areas under the absorbance bands in the range 3303 -3306cm^{-1}. Hydroxyl is a functional group containing oxygen and hydrogen atom connected by covalent bond. Existence of

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hydroxyl acts as an indicator in this study as a result of starch degradation.

FTIR analyses are depicted in Table II, from the results the band displays medium broad bands in the region of 3303-3322cm^{-1} for all blends indicate the hydroxyl stretching vibration which possibly caused by either alcoholic OH bond or carboxylic acid OH bond. The broad band in the region of 3600-3100 cm^{-1} indicates exchangeable property of protons among the functional groups resulting from reactive reaction triggered during degradation of the polymeric chain. The band in the region of 2916cm^{-1} was due to CH_2 asymmetric and symmetric stretching vibration. The peak at 1462cm^{-1} was assigned to CH_2 bending vibration. From the spectra, it was observed that by increasing the ago starch concentration the peak at 3302-3322cm^{-1} became narrower and lower, but the peaks at 2916cm^{-1} and 1462cm^{-1} became higher and sharper.

F. Diffraction Scanning Calorimetry (DSC)

DSC measurement of the blends was carried out by means of Perkin Elmer type diffraction scanning calorimetry with the heating rate of 20^{o}C/min in nitrogen atmosphere. The heating was carried out with 10mg blend, deposited in an aluminum pan in the temperature range between 30^{o}C – 240^{o}C.

TABLE III
THERMAL ANALYSES OF SAMPLES

No.	Sample	DSC Measurements	
		Tm (°C)	Δ H (J/g)
01	LLDPE	126	122.161
02	PVA	198	23.735
03	SS	100	331.909
1	Hybrid A	125	2.041
2	Hybrid B	127	3.395
3	Hybrid C	126	1.993
4	Hybrid D	124	2.663
5	Hybrid E	126	3.489

The transitions showed peaks which are significant for LLDPE and PVA. For lesser content of PVA, the amorphorsity is enhanced with less significant PVA melt endotherm.

From the DSC plot in Table III of SS, PVA and LLDPE, the T_m of the blend were 100^{o}C, 126^{o}C and 198^{o}C respectively. These parameters were used as processing temperature for the blend in extrusion. Temperatures for the heating zone were set 135^{o}C, 140^{o}C, 1135^{o}C, 130^{o}C and 125^{o}C respectively. For PVA, the melting temperature was the highest, 198^{o}C. From DSC plot of Hybrid blends, the melting temperatures of LLDPE (T_m) were range from 124^{o}C–126^{o}C. Therefore these temperatures were set as processing parameter with an added increase of 30^{o}C for the production of blend films. The DSC hybrid thermograms showed three distinct peaks representing the peaks in each blend system. The SS which is of amorphous characteristics showed broader gelation peaks from 80^{o}C and ends at 125^{o}C while peaks for LLDE ranges between 124^{o}C to 126^{o}C from 132^{o}C of the LLDPE virgin materials blends, PVA peaks exhibited significant peaks around 186^{o}C -194^{o}C. Greater amount of PVA showed higher endotherm for the systems; phase incompatibility was observed as the blends have great difference in polarity especially between SS and LLDPE and PVA/LLDPE.

G. Mechanical Properties

1. Tensile Strength

Tensile test was carried out on a Tensile Testometric Micro 500 following the ASTM D-638. Specimens are placed in the grips of the Instron at a specified grip separation and pulled until failure. A cross head speed of 50mm/min and 70mm/min in the gauge length were used. The specimens were strip into 15x 200mm dimension prior testing.

Generally, tensile test is one of the most fundamental techniques to be performed on material for strength determination. In this study, each of the hybrids was tested to investigate its ultimate strength where the points of failure for the samples were identified. Besides the hybrid blends, three other compound were tested as comparison namely linear low density polyethylene (LLDPE), sago starch (SS) blended with glycerol and sago starch blended with PVA. The blending of sago starch with PVA improves the mechanical properties of the SS based compound. Fig. 2 showed the tensile strengths of the blended materials. It is showed that the tensile strength will decrease with the increases of filler (SS) contents [12]. In this study, SS acts as a filler as well as biodegradation agent as PVA cannot be accelerated in degradation without degradative filler.

It is shown that of all five hybrids, hybrid A gives highest tensile strength, followed by hybrid B, hybrid D, hybrid E and hybrid C. In hybrid A, which was consisted of 50% PVA and 20% SS, inhibited the strongest strength. This is due to addition of sago starch which helped in increased of mechanical strength.

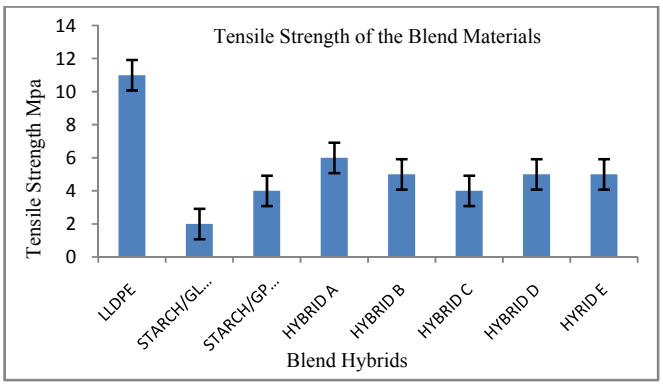


Fig. 2 Tensile Strength (MPa) of LLDPE. SS/Glycerol, SS/PVA, Hybrid A, Hybrid B, Hybrid C, Hybrid D and Hybrid E

From Fig. 2, it is also shown that LLDPE displays highest tensile strength which is of 11 MPa compared to SS/Glycerol, SS/PVA, Hybrid A, B, C, D and E which has lower than 6MPa. Hybrid of SS/Glycerol blend shows the lowest strength as the SS could not hold between each other, exhibit brittle failure due to less ductility as compared to film with LLDPE systems. Therefore the possible solution is to incorporate SS

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with stronger support based such as LLDPE and PVA and glycerol.

By adding PVA into the blends, the tensile strength increase up to 4Mpa. PVA has high tensile strength and flexibility as well as high oxygen and aroma barrier properties. However these properties are dependent on humidity. The higher the humidity, more water was absorbed. The water which acts as plasticizer will reduce the tensile strength of the blends. This result is related to previous study [9]. The result shows that SS/Glycerol without PVA had a tensile strength of 1.8Mpa meanwhile those containing PVA had a tensile strength of 4 Mpa. Previous study [9] concluded that the addition of PVA to SS/Glycerol blend helps to prevent development of surface cracks, indicating relatively good compatibility of SS and PVA. This is due to both SS and PVA are polar substances having hydroxyl groups (-OH) in their chemical structure, these highly polar hydroxyl groups tend to form inter molecular and intra molecular hydrogen bonds which improve the integrity of SS/PVOH blends [1].

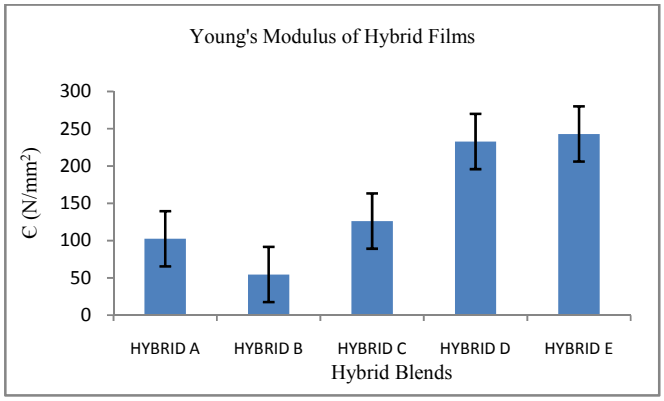


Fig. 3 Young's Modulus of blend films Hybrid A, Hybrid B, Hybrid C, Hybrid D and Hybrid E

Fig. 3 shows the Young's modulus of all five hybrids. Young's modulus or also termed as modulus of elasticity measures the stiffness of materials. This indicator is important to provide information on the property of each hybrid. The hybrid with higher modulus represents better resistance upon deformation. The effect of SS content on the Young's modulus of the blend films is showed in the above graph. The incorporation of the SS into the blend has led to an increase in the modulus of the films as shown in hybrid B, C, D and E. This was because the SS granules were stiffer than the LLDPE matrix in which they were dispersed. This result also in agreement with previous work [12] where the study was explaining the composites of corn starch, sago starch and potato starch filled LDPE.

Both Figs. 2 and 3 show reduction in tensile strength and modulus observed in hybrid blend B which contained 20% of SS compared to other blend films or hybrid. This formulation was found to be the most suitable for the application of biodegradable films because moderately strength and low brittleness are required during the degradation process. Film that has low strength and modulus was easier to be broken down by bacteria and microbial activities when buried in the soil.

III. Conclusion

Hybrid films were prepared by extruding LLDPE, PVA, SS along with plasticizer by varying the amount of PVA and SS in each formulation. FTIR spectra displayed broad peaks at 3301–3336cm^{-1} indicating the hydroxyl stretching vibration were present in the films. Melting temperature of hybrid films were range from 124°C – 126°C and these has been used as the processing temperature for the films preparations. Tensile strength of each film was decrease with the increase of SS contents meanwhile the modulus was increase with the increase in SS concentration. The optimum filler content was found to be 20% where the drop in mechanical properties occurred. These parameters are useful ranges for commercial application of polymeric products such as trash bags and agricultural mulch systems, where mechanical properties such as tensile strength and modulus are critical up to certain lifetime due to single time usage.

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