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Characterization of PVOH/Starch Film for use in Agriculture Application

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ABSTRACT

There is great interest in developing eco-friendly green biocomposites from crop-derived bioplastics attributable to their renewable resource-based origin and biodegradable nature. Fully nonbiodegradable and nonrenewable nature of plastic packaging has led to a renewed interest in packaging materials based on eco-friendly green biocomposites. Over the past ten years ears packaging suppliers have been introducing various forms of biodegradable plastics made from a variety of plants, in the main corn. The market of biodegradable polymers at the present is growing based on projections that consumers and recycling regulations will drive demand for environmentally-friendly packaging. Market introduction has started successfully all over Europe. Most important application sectors of biodegradable polymers today: organic food and service packaging, shopping bags, catering products, bio waste bags, mulch film such, horticulture auxiliaries. In this study the effect of starch loading on PVOH film towards soil biodegradation and water absorption behaviour were carried out. The rate of biodegradation in soil and water absorption increased significantly as the starch content was increased to 50%. Scanning electron microscopy revealed that starch promotes the biodegradation of PVOH. Gel permeation chromatography indicated a molecular weight decreased for the PVOH after soil exposure and confirmed that biodegradation was enhanced by the starch content. Results also demonstrated that the biodegradation rate also was affected by soil moisture.

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INTRODUCTION

Most of today's conventional synthetic polymers are produced from petrochemicals and are not biodegradable. These stable polymers are a significant source of environmental pollution, harming organic nature when they are dispersed in the environment. The raw materials such as fossil fuel and gas could be partially replaced by greener agricultural sources, which should also participate to the reduction of CO2emissions. Over the past five years packaging suppliers have been introducing various forms of biodegradable plastics. These materials are made from a variety of plants, in the main corn. The market of biodegradable polymers at the present is growing based on considerations that consumers and recycling regulations will drive demand for environmentally-friendly packaging. Among the biodegradable synthetic polymers, the aliphatic polymers, including the poly(ε-caprolactone) (PCL) and a blend of poly(vinyl alcohol) with starch, are considered promising materials (Darwis, 1999). The advantage of blending the polymers is that the properties of commercially available polymers can be modified by an inexpensive route(Ammas *et al* 1998, Pospisil *et al*, 1999 and Karal *et al* 1997) . Biodegradation generally allows for cheaper final disposal of plastic waste through composting and returns the polymer into the natural carbon cycle. By definition, biodegradable polymers are those that are degraded into carbon dioxide, water, and biomass as a result of the action of living organisms or enzymes. The rate of degradation and polymer crystallinity are important factors affecting the biodegradability, with degradation taking place preferentially in the polymer amorphous domains (Klun *et al* 2003). Some of these useful biodegradable polymers are poly(vinyl alcohol) (PVA) and poly(caprolactone) (PCL), which can be blended with a synthetic polymer such as poly(vinyl chloride) (PVC) to facilitate their biodegradation in the environment.

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Poly (vinyl alcohol) (PVA), a water soluble synthetic polymer prepared by the hydrolysis of polyvinyl acetate, is widely used in adhesives, paper-coating, textiles, wood and furniture, tannery, paints, agro-industries and in biodegradable polymer products. It is a semicrystalline polymer whose crystallinity index depends on the synthesis process and on physical aging. Hydrogen bonds bind the polymer chains together, even in the amorphous phase, and the glass transition and melting temperature of PVA are 85 and 240 ºC, respectively (Chandra *et al* 1998 and Dibbern *et al* 1998) . The molecular weight of PVA is its most important feature, affecting its crystallinity, adhesion, mechanical properties and diffusion8. The basic properties of these materials are strongly dependent on the degree of polymerization and hydrolysis, the distribution of hydroxyl groups, and the stereoregularity and crystallinity of PVA. Thus, the evaluation of relationships between the polymer's biodegradability and structure is also of the utmost importance (Solaro *et al* 1998).

Starch is increasingly used for various purposes due to its low cost and high availability. However the entire starch based products are lack of strength and rigidity which inhibit their application in materials engineering. In order to compensate the property weakness of entire starch products, the blend starch with the synthetic polyvinyl alcohol (PVOH) has been used to replace the entire starch plastics. The incorporation PVA into starch improves the thermal and mechanical properties of the material and thus modifies the polymer structure at both molecular and morphological level(He soon Kim *et al* 2006). Polymers have been used in agriculture and horticulture since the middle of the last century. A large proportion of the plastics used in agricultural are agricultural films. Plastic films are used in greenhouse as tunnels over crop rows, as silage covers, as bale wrap-films and mulching films to cover the soil of crop rows. In general a successful development of high performance biodegradable agricultural films mainly depends on meeting three critical design requirements: achieving good mechanical behaviour of the original films, retaining a satisfactory mechanical performance during the useful lifetime and achieving 100% biodegradation in the soil after the end of useful lifetime. The objective of the study was to investigate biodegradability of the bioplastic in soil burial with different humidity and strength and the water absorption properties.

Experimental:

Soil Burial Test:

The PVOH blend was supplied by a company with a series starch ratio of 15, 25 and 50 without any purification. For the soil burial test, the films were buried in Munchong soil that was available in RRIM Sungai Buloh. The films were cut into 30 × 50 mm pieces and buried in the soil at a depth of 10 cm. The soil was placed in the laboratory, and the moisture of the soil was maintained by sprinkling water at regular time intervals. In this experiment the moisture content was varied from 2% to 18%. The degradation of the samples was determined at regular time intervals by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried under vacuum until a constant weight was obtained. Biodegradability was assessed by visual analysis, gel permeation chromatography (GPC) and scanning electron microscopy (SEM). The surface morphology of the PVOH/starch was observed and photographed by SEM (Zeiss DSM 940A) under 10 kV of accelerated tension. The samples were coated with a thin gold layer (ca.15 nm) by vacuum deposition using a Sputter Coater BALTEC SCD 050. The molecular weight change and polydispersity was determined by GPC type TOSOH at 27°C. THF was used as an effluent with a flow rate of 1.0 mL/min using a TSKgel GMHHR-H(s) column and a RI 71 detector while polystyrene as a standard. The strength of the blend towards water absorption was also conducted according to ASTM D570. The specimens were dried in an oven for 8 hours and temperature of 30ºC and then placed in a desiccator to cool. Upon cooling the specimens were immediately weighed using Mettler balance to the nearest 0.0001g (Wo). The material is then emerged in water at agreed upon conditions, often 23°C for 24 hours for 1 day and continuous for 5, 10, 15 and 20 days. The specimens were removed, patted dry with filter paper, and weighed. The swelling degree of the samples was characterized. The experiments were carried out by measuring the weight gain as a function of immersion time. The swelling degree was calculated by using the following equation,

Water absorption (%) = x= (Wt-Wo)/Wo x 100

RESULTS AND DISCUSSION

Soil Biodegradation:

The biodegradation of PVOH/Starch blend suggests that microbe consumes starch and create pores in the materials leading to an increase in the surface area of PVOH matrix and providing susceptible groups for its biodegradation.

The effect of biodegradation on the PVOH blend in this study was analysed by SEM and visual analysis. Figure 1 shows images of the degradation surfaces of PVOH/Starch film of a ratio of 50:50 in soil with 18% with moisture content for 30 days. In the figure, the biodegradability of PVOH:Starch, 50:50 increased with days. The films became darkened as it reached 15 and 30 days of soil burial. After a 30 days of soil burial period, the films were darkened and more fragile, with significant pitting; conversely, the low loading starch film showed no visible signs of degradation. The visual analysis

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indicates that increasing the level of starch accelerates the degradation of the bioplastics, relative to the low level of starch content. This is in keeping with the SEM results which showed in Figure 7. Scanning electron micrograph (figure 4) of PVOH/starch 50:50 revealed that the film exhibited a relative smooth and clear surface before bidegradation took place. However at 30days of soil burial more numerous surface irregularities and erosions, indicating that the biodegradability surface of PVOH;Starch was attacked by the microorganism under soil environment. However a slower degradation was observed with PVOH : Starch of 75:25 and 85:15, Figure 2 and 3. In another study, the biodegradability of Polybutylene succinate also was enhanced by the incorporation of the bio-flour11-12. The degradation was rather slower as lower moisture content was used in the experiment as observed in Figure 5 and 6. The moisture content which used in the second experiment was 2%. The film was largely intact and showed no visible sign of degradation even with high starch content. Hence, in this experiment the acceleration of degradation was mainly depend on starch and water content.

Fig. 1: Visual Analysis of PVOH:Starch 50:50 in 18% of soil moisture content.

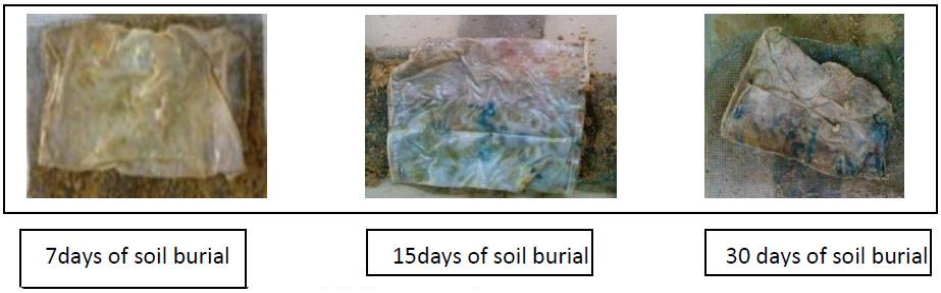

Fig. 2: Visual Analysis of PVOH:Starch 75:25 in 18% of soil moisture content.

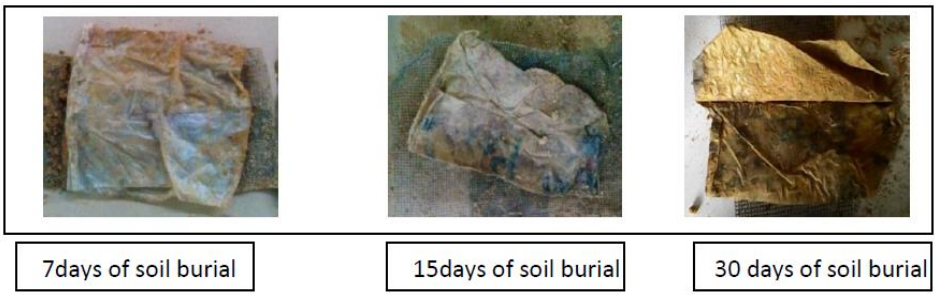

Fig. 3: Visual Analysis of PVOH:Starch 85:15 in 18% of soil moisture content.

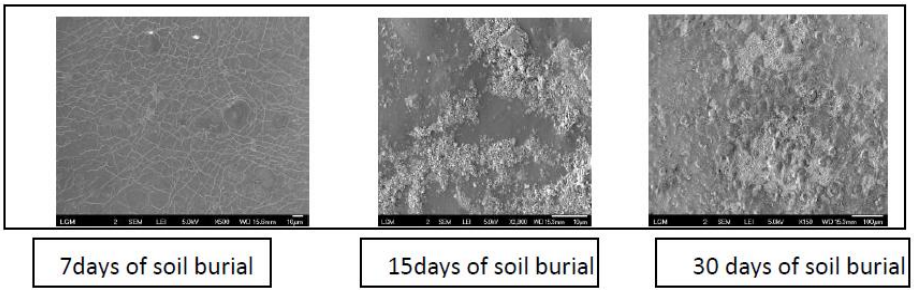

Fig. 4: SEM micrograph of PVOH /Starch 50:50 in 18% of soil moisture content.

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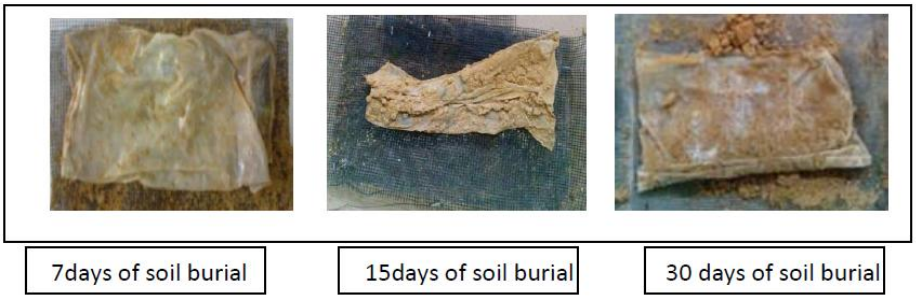

Fig. 5: SEM micrograph of PVOH /Starch 50:50 in 2% of soil moisture content.

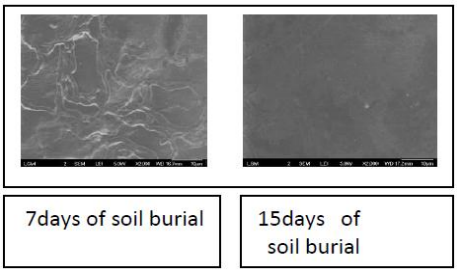

Fig. 6: SEM micrograph of PVOH /Starch 50:50 in 2% of soil moisture content.

Although weight loss measurements are widely applied in degradation tests, it can be difficult to adequately clean the samples following soil burial, especially if the test material disintegrates excessively. Due to this, the soil biodegradation was not evaluated by weight loss measurements.

Gel Permeation Chromatograph(GPC):

Gel Permeation chromatograph (GPC) for degraded PVOH/starch films has been carried out. The GPC chromatograms for all starch filled PVOH exhibited a bimodal distribution after soil test exposure at least 15 days which illustration is not shown here. These data indicate that the incorporation of starch in the blend resulted in a different mode of attack on the PVOH components on the films. Incorporation of starch resulted in a disruption of some linkages. The weight average of degrade film with effect starch loading are presented in Table 1. As anticipated, the incorporation of starch into the blend resulted in more rapid decrease in the molecular weight of PVOH/Starch film during soil exposure. For example, whereas there was only a 303 (Daltons) in the molecular weight of the PVOH/Starch of 50/50 after 15days test exposure , table 1. The molecular weight of PVOH component of 85/15 and 75/25 PVOH/Starch system decreased by less than 50% during the same exposure period.

Table 1: Weight average of molecular weight of PVOH/Starch samples.

Starch /PVOH	Before soil exposure Mw (Daltons)	3d of soil exposure Mw (Daltons)	15 days of soil exposure Mw (Daltons)
50/50	905	890	303
75/25	839	800	508
85/15	949	801	625

Water Absorption:

PVOH is a water soluble polymer whose water solubility depends on whose water solubility depends on the degree of hydrolysis, molecular weight and tendency to form hydrogen bond in aquous solution. The water uptake for the blends is illustrated in Figure 1. The figures show progressive increase in the amount of water absorbed by PVOH/starch blends with increase in the amount of starch incorporated into the blend and period of water absorption. For most of the blends, the amount of water absorbed tended to level off (i.e. equilibrium absorption) after the fifth day of immersion in water.

The water uptake in the blends is due to the presence of hydrophilic starch particles in the blends. Starch particles possess an abundant of hydroxyl groups in their molecules and which are available for interactions with water molecules. Thus, water molecules can saturate the surface of the polyolefin/corn starch blends easily and penetrate into the composites through voids which result in higher water uptake in a short immersion period (Sanadi *et al* 2001 and Danjija *et al* 2001).

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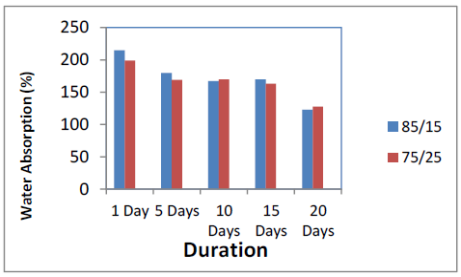

Fig. 7: Effect of Water absorption on PVOH/Starch blend.

Conclusion:

1. The degradation process and water absorption of PVOH/Starch increases with starch content .
2. The biodegradation of the PVOH/Starch depends on soil moisture content.

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There is no conflict of interest.

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