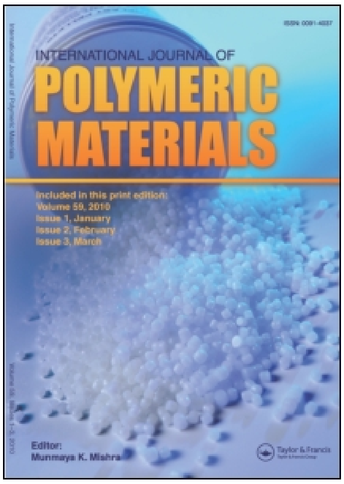

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Mechanical, Water Absorption and Enzymatic Degradation Properties of Sago Starch Filled Linear Low Density Polyethylene

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Sago starch filled linear low density polyethylene (LLDPE) composites, have been prepared by melt mixing of the granular starch and LLDPE in a HAAKE internal mixer. The tensile, water absorption and enzymatic degradation properties of the composites have been determined. Incorporation of sago starch into LLDPE led to decrease in tensile strength and elongation at break of the composites. Up to 15 wt.% of sago starch could be added to LLDPE without adverse effects on the tensile properties. The water uptake increased with immersion time and the rate of absorption is strongly controlled by the immersion temperatures. Dramatic reduction in tensile properties were observed in the composites that were immersed in water at 90°C. The recovery of the tensile strength and elongation at break upon redrying is about 37.5 and 1.6% respectively. The permanent damage to the composites was attributed to severe hydrolysis of the starch particles. The enzymatic degradation study using α-amylase revealed that both tensile strength and elongation at break reduced with time of treatment. Mode of failures of both LLDPE matrix and its sago starch filled composites, assessed by fractographic analysis in a scanning electron microscope (SEM) are discussed.

Keywords: Linear low density polyethylene; sago starch; water absorption; enzymatic degradation

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INTRODUCTION

Public concern over waste management has increased tremendously over the years. This is as a result of non-availability of landfills, environmental concern, public perception and accumulation of surface litter. Consequently, this has triggered research into the utilization of biomaterials either as fillers in plastics or as packaging material [1]. Biomaterial such as starch in particular is used because of easy availability throughout the year, its high purity and low price. It also satisfies the requirements of adequate thermal stability, minimum interference with flow properties and minimum disturbance of product quality [2]. Furthermore because of their low oxygen permeability, starch filled thermoplastics films are very attractive for food packaging.

The use of granular starch as biodegradable filler in low-density polyethylene (LDPE) was first reported by Griffin [3]. Maize, wheat and tapioca starches have been successfully incorporated in LDPE. This was done by reducing the moisture content of less than 1% through thoroughly drying the starch in order to prevent any formation of bubbles. The dried starch then will be introduced to the hot plastic melt.

Sago starch produce abundantly in South-East Asia has been used in food formulation and textile industries for a long period of time. Sago starch is derived from pith of certain palm trees especially *metroxylon sago*. The major area of cultivation is in Sarawak Malaysia; where up to 25 tons of starch can be produced per hectare annually. However, to date not much information on the incorporation of sago starch into plastics, especially polyethylene. Therefore it is worthwhile for researches in Malaysia to focus their attention on sago starch.

The purpose of this research is to incorporate sago starch into LLDPE and subsequently, to study the degradation of the composite. In this report, the effect of the starch content on water uptake, enzyme attack and mechanical properties of the composites are presented.

EXPERIMENTAL

Material

Sago starch was supplied by the Land Custody Development Authority (LCDA), Sarawak. It had an average of 20 μm and decomposition temperature of 230°C. It was used without any modification. Powdered Linear Low Density Polyethylene (LLDPE), ETILINAS LL0209SA grade, manufactured by from Polyethylene Malaysia Sdn. Bhd., was used as the base resin. It had a peak melting temperature of 128°C as determined by differential scanning calorimetry (DSC) at a heating rate of 20°C/min. α-Amylase enzyme supplied by from Sigma Chemical Company (M) Sdn. was used for the enzyme test. It activation temperature is 36.9°C.

Sample preparation

Sago starch was dried in a vacuum over at 100°C for 24 hours. The dried sago starch was melt-blended with LLDPE in an internal mixer model Haake Rheodrive 3000 at 150°C using a rotor speed of 20 rpm for 20 minutes. The materials (starch and LLDPE) were first physically mixed together before introducing them into the mixer. Composites containing starch loading of 5, 10, 15, 20, and 30 wt.% were prepared. The compounded samples were compression molded into 1 mm thick plate on Kao Tieh Go Tech compression molding at 150°C and at pressure of 10MPa for 15 minutes. Molded samples were cut into dumb-bell specimens according to ASTM D638 and were used for all the tests.

Testing

Tensile test was carried out on a Tensometer T-10 according to ASTM D638 at a cross-head speed of 50 mm/min. All the test samples were conditioned at $27 \pm 2\,\%$ relative humidity (RH) for 24 hours before testing. For each testing 7 samples are used.

Water absorption test was carried out according to ASTM D570. Test samples were conditioned in an oven at 50°C for 24 hours and cooled in a dessicator before weighing. The test samples were completely immersed in distilled water at room temperature (27°C), 60°C and 90°C for 30 days. The moisture uptake was determined by removing the specimen periodically, wiping them dry with a towel and weigh them using a Mettler balance with a precision on 1mg. The percentage moisture uptake at any time t, M_t, is calculated according to the equation:

$$\%M_t = \frac{(W_w - W_d)}{W_d} \times 100$$

Where W_d and W_w are the weights of the specimen when dry and after water uptake respectively. The average reading of three samples was taken.

Enzymatic test was carried out according to the method of Yoon *et al.* [4] by placing the test samples in a solution containing of α-amylase-1,4-α-D-glucan glucano-hydrolase (BAN), having an activity of 480 KNU/g which is equivalent to 480 μ/ml. A buffer solution also was prepared by adding in 4.8 ml of 0.2 M acetic acid to 45.2 ml of 0.2 M sodium acetate, in 100 ml of solution. The samples were kept in an incubator (New Brunswick Scientific) at 37°C and shaken at 100 rpm for 14 days. Samples were taken out at two days intervals and washed properly with distilled water before conditioning at 50°C for 24 hours inside an over before testing.

Morphological Studies

A scanning electron microscope Leica Cambridge S-360 Model was used to study the morphology of the samples were sputter-coated with gold before scanning to avoid any electrical discharge during examination.

RESULTS AND DISCUSSION

Effect of Starch Loading

The stress-strain curves of LLDPE and its sago starch-filled LLDPE composites are shown in Figure 1. LLDPE is a soft but tough plastic with a low modulus but high elongation at break. The incorporation of up to 30 wt.% sago starch into LLDPE did not have significant effect on the shape of the curves. Yielding and cold drawing processes can still be observed in the sago starch filled LLDPE, even at a starch loading of 30 wt.%.

The effect of starch content on modulus of LLDPE is given in Table I. The Young's modulus of the material, is a measure of the

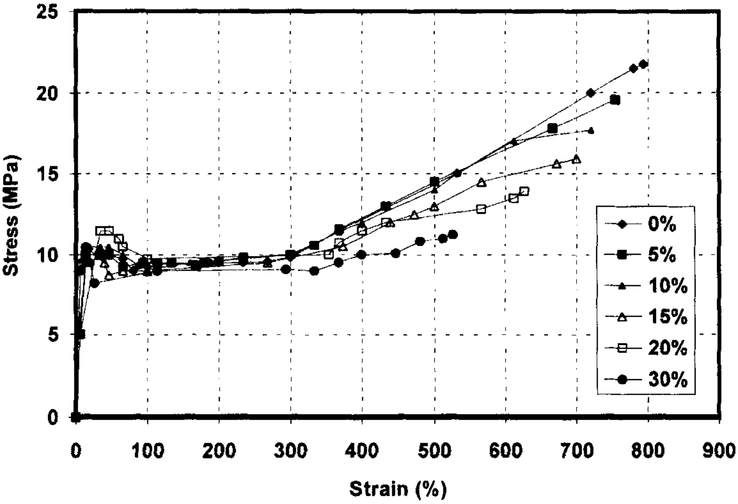

FIGURE 1 Stress-strain curves of LLDPE and sago starch-LLDPE composites.

TABLE I Effect of sago starch on yield strength and young's modulus of LLDPE

Starch content (*wt.*%)	*Yield strength* (*MPa*)	*Young's modulus* (*MPa*)
0	9.5	105.0
5	10.0	115.0
10	10.5	120.0
15	10.5	127.5
20	10.5	146.3
30	10.5	160.0

stiffness of the material. It is determined by taking the slope of the tangent to the curve at zero extension. The incorporation of sago starch into LLDPE, generally led to an increase in the modulus of the composites. This is coherent with the works of Willet [5], on corn and potato starches-filled LDPE composites. At 5% starch content, the modulus increase by 9.5%, while at 15% starch content, it increases by 21.4%. The increase in the modulus of the composites is due to the fact that the starch granules are stiffer than the LLDPE matrix in which they are dispersed. Rigid fillers are generally known to increase modulus even in situations where reinforcement does not occur.

The variation of yield strength with starch content, is shown in Table I. The yield strength did not show any significant increase with increase in starch content of the composites. This is especially true at lower filler content. The yield strength of the LLDPE was calculated to be 9.5 MPa. At 15% starch content the yield strength of the composites increase by 10.5%. However, at higher filler contents, the yield strength increased slightly. In view of the fact that the yield point of LLDPE is rather low, the slight increase in the yield point of the composites at higher filler content, would be an advantage. This is because for the same amount of material, more force would be required to bring about permanent deformation in the composites. A high yield strength is also an advantage in printing and lamination, because registration problems are reduced [7]. Figure 2 shows the variation of tensile strength with starch content. Tensile strength decreased with an increase in starch content. This is in agreement with the works of Yoon *et al.* [4], Willet [5], and Nikolov [6]. The starch granule, contain hydroxyl groups on its surface. Since LLDPE is basically a non-polar polymer, the formation of strong interfacial bonds like hydrogen bonds, is not feasible [8]. As a result, the fracture resistance of the composites is not improved. At 5% starch content, the tensile strength decreased by 3.28%, while at 15% starch content, it decreased by 21.2%. A 26% reduction in tensile strength at 5% starch

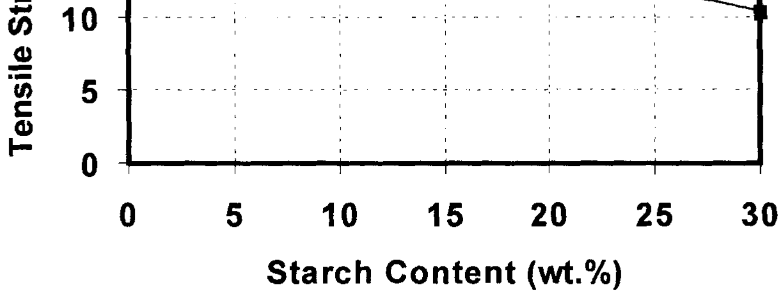

FIGURE 2 Effect of starch content on tensile strength of LLDPE.

content with subsequent 8 – 10% decrease for every 5% addition of starch into LLDPE, has been reported for maize starch [6]. This seems to indicate that sago starch-filled LLDPE systems have similar retention strength compared to maize starch filled plastics. Apart from that, this phenomenon is also commonly observed in several other thermoplastic filled with particulate fillers [9]. The drop in the tensile strength became more drastic as the starch content increased. This is because, at higher starch loading, filler – filler interaction becomes more pronounced than filler-matrix interaction. As a result of the reduction in the effective cross-sectional area of the composites caused by the filler particles, the applied force is not transferred from the polymer matrix onto the rigid filler particles. As will be shown in the SEM micrographs later, starch granules are of irregular shape and have a tendency to form aggregates especially at higher loading. These factors, plus the fact that no compatibilizer was present in the composites, resulted in poor adhesion between the starch particles and LLDPE matrix. Weak interfacial regions imply that the transfer of the stress from the polymer matrix to the filler will not be efficient.

The variation of elongation at break with starch content of the composites is shown in Figure 3. The expected trend is observed

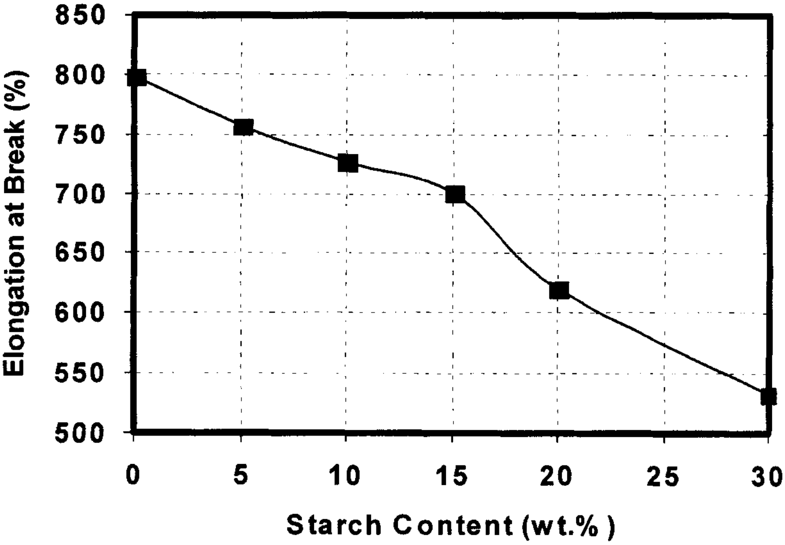

FIGURE 3 Effect of starch content on elongation at break of LLDPE.

where the elongation at break dropped with increase in starch content in agreement with the works of Yoon *et al.* [4], Willet [5], and Nikolov [6]. At 5% starch loading, the elongation at break dropped by 5.3%, while at 15% starch loading it dropped by 12.3%. It shows the same trend as in the case of tensile strength, where the decrease of elongation at break became more drastic at higher loading. Similar observations were also reported by Willet [5] on potato starch-LDPE and maize starch-LDPE composites and Nikolov [6], on maize starch-LDPE composites. The decrease in the elongation at break with increasing starch content may be attributed to the fact that the starch particles do not elongate coherently with LLDPE. Therefore less strain is required to cause the sample to fail [9]. In addition, the poor interaction between starch and LLDPE resulted in weak interfacial bonding that permits easier crack propagaion. Thus, the composites fail at a lower value of elongation at break with increase of starch loading.

Scanning electron micrographs of fracture surfaces of the composites, shown in Figures 4 and 5 reveal that the starch granules serve as particulate fillers. It can be seen that the starch granules were not properly wetted by the LLDPE matrix as manifested in the smoothness of the fracture surfaces of the composites. The weak adhesion between the matrix and the starch particles is due to poor interaction

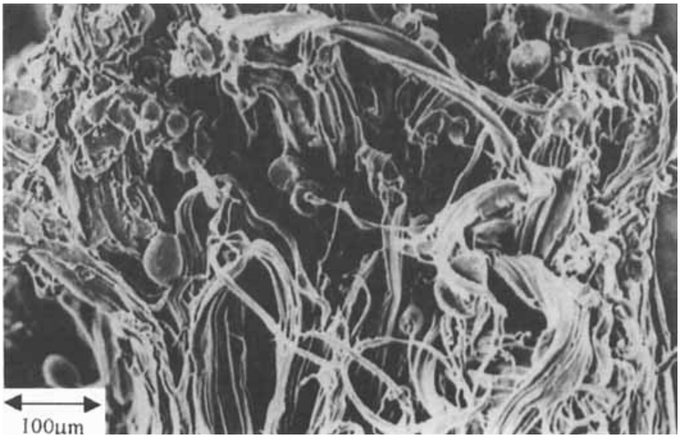

FIGURE 4 Scanning electron micrograph of fracture surface of sago starch-LLDPE composite.

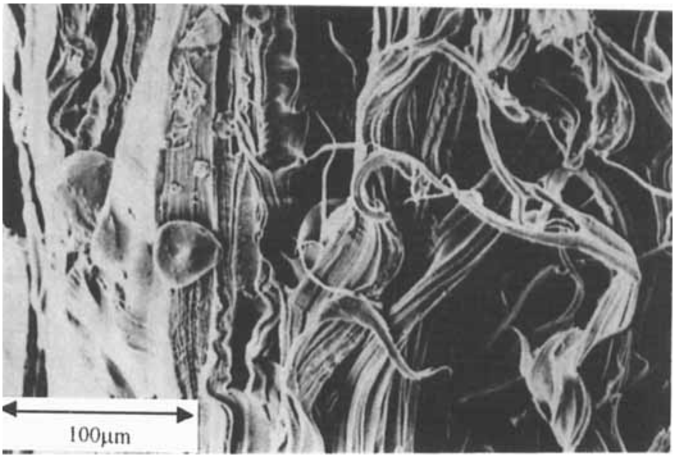

FIGURE 5 Scanning electron micrograph of fracture surface of sago starch-LLDPE composite.

between them. This is due to the fact that the starch is hydrophilic and LLDPE hydrophobic. Thus this explains the decrease in tensile strength and elongation at break, with increase in starch content.

From the mechanical properties of the composites determined so far, it is evident that 15% sago starch loading can be incorporated into LLDPE without significant drop in the mechanical properties. The composites seem to posses a good combination of stiffness, strength and toughness. For good retention of mechanical properties about 10–20 wt.% starch have been incorporated to LLDPE [4, 11]. In the present work 15 wt.% starch loading have been chosen as the suitable starch loading to discuss the effect of water absorption and enzyme.

Effect of Water Absorption

Figure 6 shows the water uptake increase with time for all the samples. There was a rapid water uptake within the first few days of immersion that gradually slowed down with time. It may be cause by the concentration gradient across the two materials. It has been found that initial water added to the starch are strongly bound as in a hydrate and when all available hydroxyl groups are used up in this manner will lead to composites to be less firmly held after more water being absorb [12]. Water being absorbed due to the hydrophili-

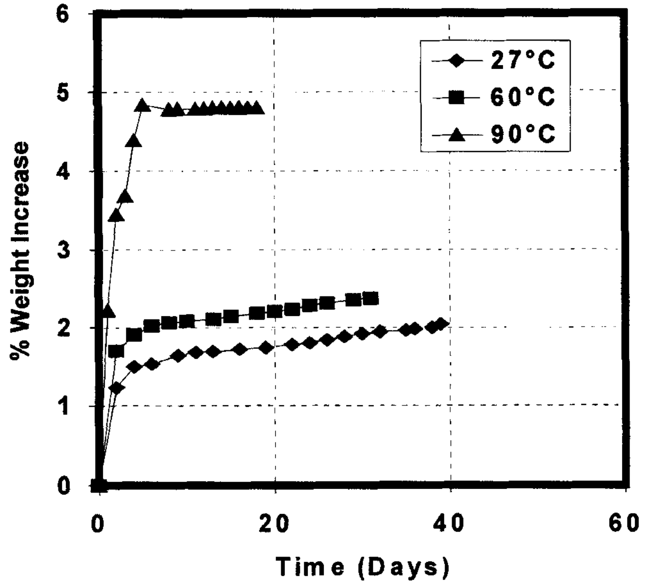

FIGURE 6 The effect of immersion temperatures on the water uptake of LLDPE and sago starch filled composites.

city nature of the sago starch. As expected the composites reached equilibrium point faster at 90°C compare to 60°C and room temperature. Based on Figure 6, composites at 90°C reached equilibrium 10 days after immersion in water. At high temperature, heat was generated which accelerated water absorption process. Apparently, the samples that were immersed at room temperature and 60°C, do not reach the saturation point. This is due to the short time span. This is coherent with the earlier findings of Willet [5]. Figures 7 and 8 show the tensile strength and elongation at break for sago starch filled samples that were conditioned at different immersion temperatures. From this figure, it is clear that tensile strength and elongation at break decreased with increasing immersion temperature. The presence of moisture at the starch-LLDPE interface is believed to weakens the interfacial adhesion and leads to a significant reduction in the tensile properties of the composites. Water is known to be a good plasticizer for starch. However according to Otey *et al.* [13], excessive of moisture could have a deteriorating effect and will lead to a reduction in the tensile properties of starch-plastics composites.

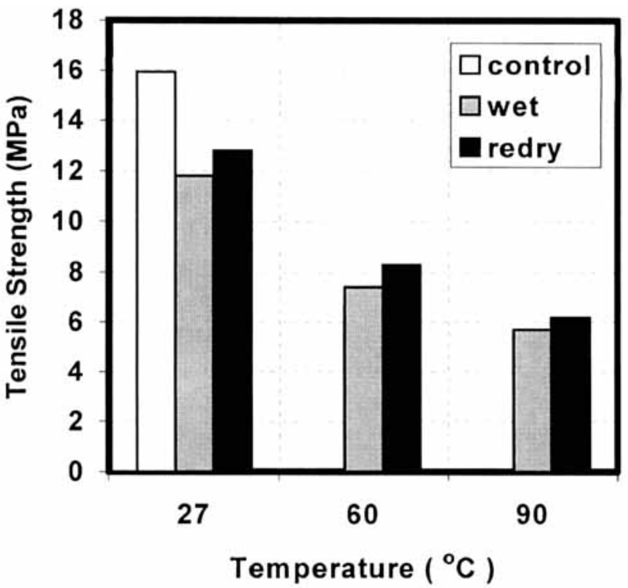

FIGURE 7 Tensile strength of sago starch filled LLDPE in control, wet and redried states.

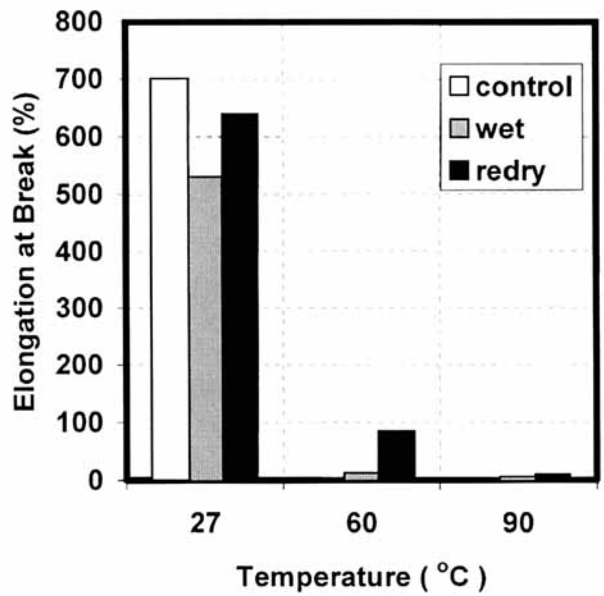

FIGURE 8 Elongation at break of sago starch filled LLDPE in control, wet and redried states.

From Figures 7 and 8 it can be seem that a moderate tensile properties were observed especially for samples that have been immersed at 27°C. However very poor recovery was observed in the samples that were immersed at 90°C. This may be attributed to fact that a high immersion temperature the starch granule already swells up and increasing in size as a result of water uptake, and been forced out of the holes because the matrix does not swell proportionately with the starch granule. After redrying, water was being eliminated from the samples and voids will appear which will act as stress concentration points. Thus, the recovery of the mechanical properties is small. In the case of samples that were immersed at room temperature and 60°C, it can be expected that the amount of starch forced out from the samples are relatively smaller and the extend of voids formation is rather limited. This perhaps explains the excellent recovery in the tensile properties of samples that were immersed at 27°C.

SEM micrographs shown in Figure 9 shows that water absorption be resulted in the morphological transformation of sago starch filled LLDPE. Unlike the as receive composite (Fig. 4), the absence of plastic deformation of LLDPE provides a good indication that the material failed in a relatively brittle manner. This explains the extremely low elongation at break of the composites. As for the samples

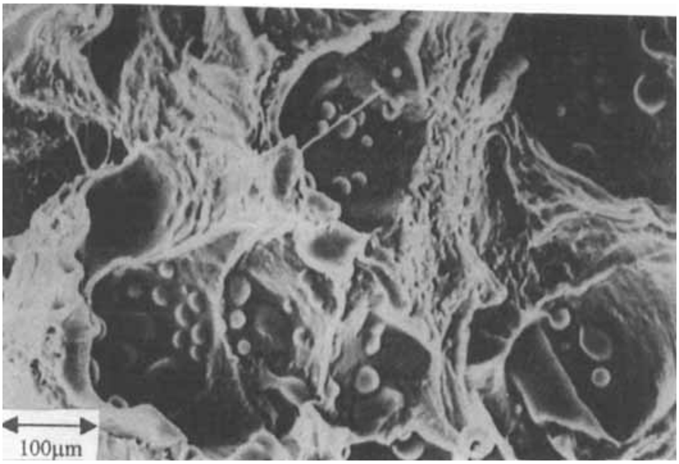

FIGURE 9 Scanning electron micrograph of fracture surface of wet sago starch-LLDPE.

that been redried, a lot of holes due to inhabitant of water can be seem from the SEM micrograph Figure 10. It is interesting to look that some degrees of plastic deformation of LLDPE have been restored upon redrying. However, judging from the relatively low tensile strength and elongation at break of the redried composites (Figs. 7 and 8), it suggests that the poor tensile properties may be attributed to the serious hydrolysis of the starch particles.

Effect of Enzyme Treatment

Figures 11 and 12 shows the effect of enzyme treatment on the tensile strength and elongation at break of LLDPE filled 15 wt.% sago starch. Both properties decreased with time of treatment for all the samples. This may be due to the hydrolysis of the starch granule. However it is also believe that the loss in mechanical properties is not solely to hydrolysis alone as other factors such as the presence of moisture at the starch-LLDPE interface can also contribute to the loss of the properties. Strantz and Zottola [14] have reported a decrease in elongation at break of corn starch-PE composites with or without enzyme solution. Pranumuda *et al.* [15], have reported the removal of starch from the surface of starch-polycaprolactone

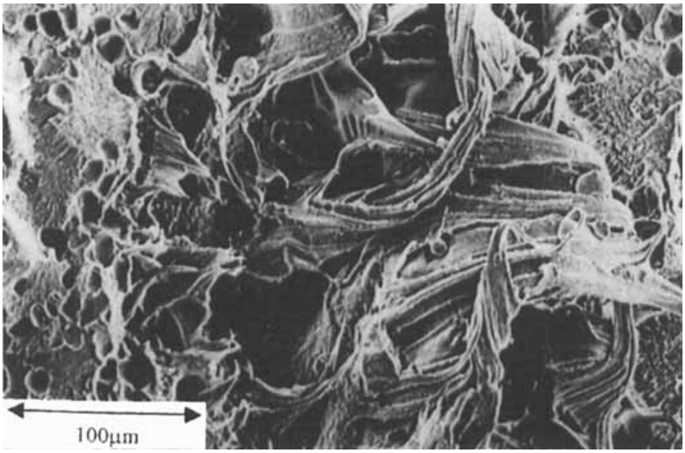

FIGURE 10 Scanning electron micrograph of fracture surface of redried sago starch-LLDPE.

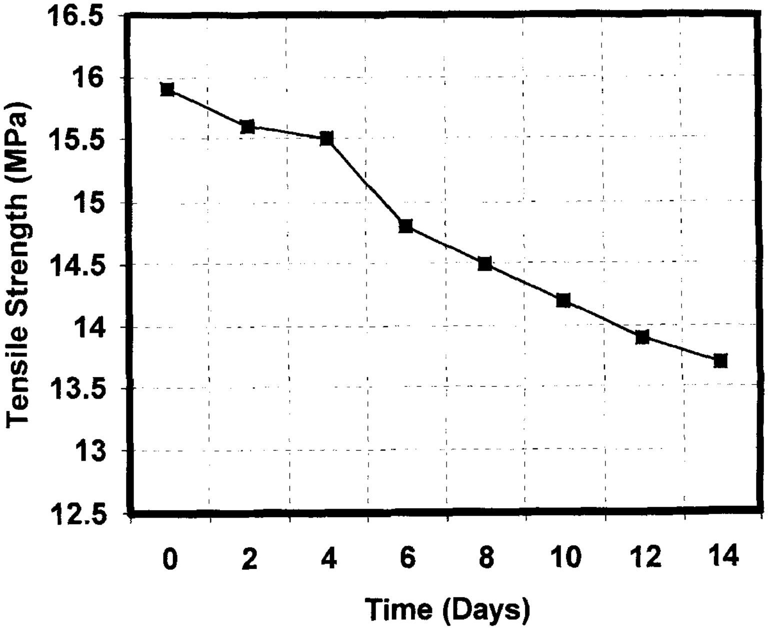

FIGURE 11 Effect of variation of tensile strength with time for sago starch-LLDPE composites to ∝-amylase.

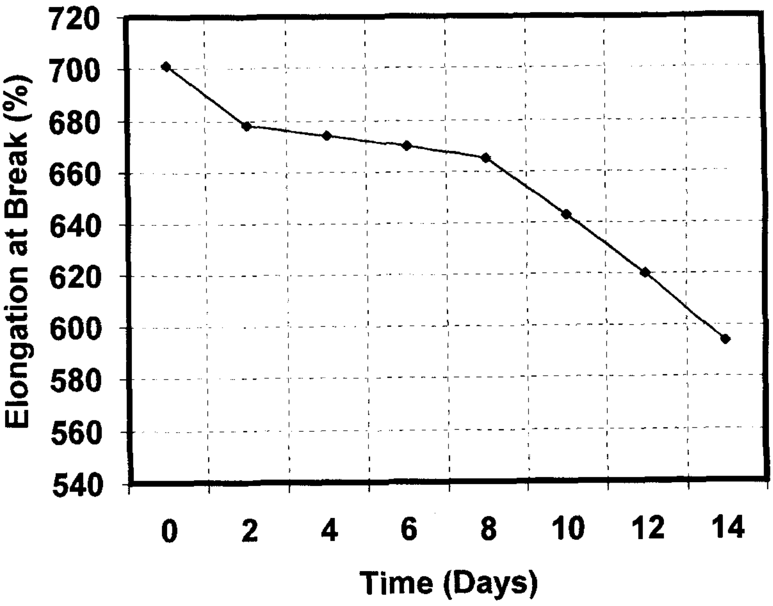

FIGURE 12 Effect of variation of elongation at break with time for sago starch-LLDPE composites to ∝-amylase.

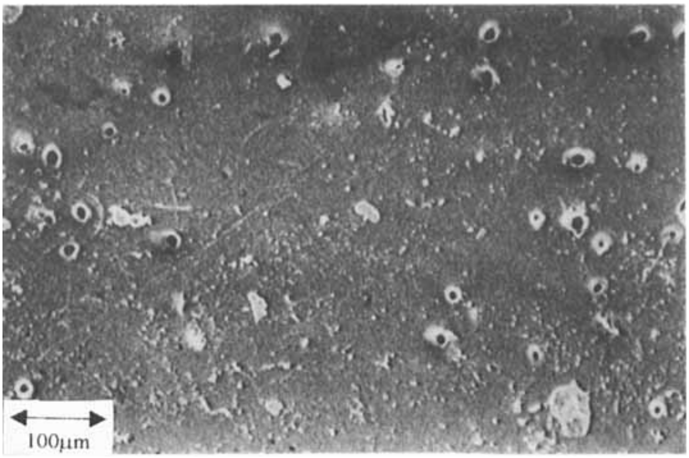

FIGURE 13 Scanning electron micrograph of surface of sago starch-LLDPE composite (15 wt.%. starch content) after enzymatic test.

films surface, after treatment with α-amylase enzyme. α-amylase enzyme attacks the starch molecule at the α-1,4-glucocidic linkages thereby breaking up the polysaccharide chain into several nits of glucose molecule. This pores leads to an increase in the surface area of the matrix, thereby facilitating other forms of degradation such as chemodegradation to take place. Once the molecular weight of the LLDPE has dropped to about 9,000 biodegradation can proceed.

SEM micrographs of the surface, (Fig. 13) show the presence of holes and agglomerates, indicating the hydrolysis of the starch granule by the enzyme. The white circular spots surrounding the starch indicate the α-amylase enzyme attack on the starch granule that leads to hydrolysis process to take place.

CONCLUSION

Sago starch can be incorporated into LLDPE by melt mixing. Mechanical properties such as yield strength, tensile strength and elongation at break, reduced with filler content while modulus increased. The suitable filler content was found to be 15 wt.%, above which a moderate drop in the mechanical properties occurred. Water uptake of the composites increased with starch content. The effect of water absorption on the tensile properties was found to be temperature dependent. The poor recovery in the mechanical properties of the composites that were immersed in water at 90°C was attributed to the severe hydrolysis of starch particles. The gradual drop in the tensile properties with respect to the treatment time provides a good indication that the enzymatic attack is a time dependent process.

Acknowledgement

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