Sago Starch-Filled Linear Low-Density Polyethylene (LLDPE) Films: Their Mechanical Properties and Water Absorption

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ABSTRACT: Composites containing various percentages of sago starch and linear low-density polyethylene (LLDPE) have been prepared. The mechanical properties and water uptake of the composites have been determined. The tensile strength and elongation at break decreased with increase in starch content. However, the modulus of the composites increased with increase in starch content. The yield strength was not significantly affected. Moisture uptake in humid air and in water increased with increase in starch content. At higher relative humidity the composites absorbed more moisture, thus indicating that the moisture barrier properties decreased with increase in relative humidity. Moisture uptake was highest when the composites were completely immersed in water. Scanning electron microscopy (SEM) shows agglomeration of the starch granules and hence, poor wetting between the starch granules and LLDPE matrix. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 29–37, 2001

Key words: sago starch; linear low-density polyethylene (LLDPE); biodegradable films; tensile properties; moisture barrier properties

INTRODUCTION

For well over 20 years, polysaccharide-filled plastics have piqued the interests of research scientists because of concern over surface litter and the dwindling availability of landfills. Starch is of particular interest among the polysaccharides because of its easy availability throughout the year, its high purity, and its low and stable price. It also satisfies the requirements of adequate thermal stability, minimum interference with flow properties, and minimum disturbance of product quality.[1] Furthermore, because of their low oxygen permeability, starch films are very attractive for food packaging.

Granular starch has been incorporated into low-density polyethylene (LDPE) as a biodegradable filler.[2] Several starches such as maize, wheat, tapioca, and potato have been successfully incorporated into LDPE. This was done by thoroughly drying the starch to a moisture content of less than 1% in order to prevent the formation of bubbles. The thoroughly dried starch was then introduced into the hot plastic melt. However, it has been demonstrated that at moisture levels below 0.5%, water vapor bubbles could virtually be eliminated by adjusting the processing conditions.[3] Sago starch is produced in great abundance in South-east Asia where it has been used in food and nonfood formulations for a long time. Unlike other starches, sago starch is derived from the pith of certain palm trees, especially *metroxylon sagu*. The extraction of the starch from the pith is a laborious and costly process involving installation of heavy machinery, because of the fibrous nature of the trunk. It is therefore not surprising that the starch has an enormous variability in quality. Despite this, it has been found to have the most advantages and the fewest disadvantages. Commercial sago starch has a mauve

tint. The starch used in this research was obtained from the Land Custody Development Authority (LCDA), Sarawak. It is sago starch of the highest purity that was specifically extracted to meet the demands and quality for applications in polymer composites as well as other industrial applications. The starch was characterized by Odusanya[4] and it was found to have a whiteness index of 8.3, among others. Information on the incorporation of sago starch into plastics, especially polyethylene, is lacking. Maize, wheat, and potato starches, which are produced in abundance in the U.S. and Europe, have attracted the attention of researchers from these regions. It is therefore worthwhile for researchers in Malaysia to focus their attention on sago starch due to its abundance in many parts of Malaysia, especially Sarawak. In this paper, we report on the mechanical properties of sago starch-filled linear LDPE (LLDPE).

EXPERIMENTAL

Materials

Sago starch was obtained from the LCDA, Sarawak. It had an average granule size of 20 μm and was used without modification. The particle size of the granules (determined by a Coulter Particle Size Counter) is in the range of 9.8 to 35 μm. Most of the granules had diameters of around 14.5 μm, which is intermediate in size between maize starch and tapioca starch, which have granule sizes between 10–25 and 12–15 μm, respectively. LLDPE, ETILINAS LL0209SA grade, was obtained from Polyethylene Malaysia Sdn. Bhd., and 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.

Compounding

A Brabender Plasti-Corder 331 internal mixer was used to prepare the composites. Mixing was done at 150°C using a rotor speed of 40 rpm. For 20 min. The materials (starch and LLDPE) were first mixed together before introducing them into the mixer. Blends containing starch contents of 5, 10, 15, 20, 25, and 30 wt % were prepared. The starch was dried prior to compounding in a vacuum oven at 60°Cfor 48 h according to the method of Kang et al.[5] With the vacuum still on, the

temperature of the oven was switched off and the starch left to cool for another 5 h before transferring it to a dessicator and kept for another 24 h.

Molding

The starch-LLDPE blends were compression-molded into 1mm thick plates for 12 min, using a Kao Tieh Go Tech Compression Molding Machine. The molding temperature and pressure were 150°C and 10 MPa respectively. After molding, the blends were dried in order to eliminate moisture that might have been absorbed during handling.

Tensile Properties

Tensile properties were determined according to ASTM standard D638 using a Monsato Tensometer T10. Dumb-bell shaped specimens were conditioned at ambient temperature (25 $\pm$ 3°C) and relative humidity (30% $\pm$ 2) before testing. A cross-head speed of 50 mm/min, gauge length of 50 mm and a chart speed of 30 mm/min were used. An average of 5 samples was used with standard deviation of $\pm$ 0.95 and $\pm$ 8.52 for tensile strength and elongation at break, respectively.

Water Absorption

Water absorption studies were carried out under two different conditions, i.e., exposure of the specimens to a humid environment and direct immersion of the samples in water. Dumb-bell samples used for tensile measurements were used in both cases. The samples were subjected to two different relative humidities, i.e., 50% and 75% in a humidity cabinet LEEC model SFC 3C. Relative humidity (RH) tests were carried out according to ASTM E104.

Water absorption test was carried out according to ASTM Standard D750-95. It involved total immersion of the samples in distilled water at room temperature, i.e., 30°C. All the specimens were previously dried in an oven at 50°C for 24 h and then stored in a dessicator.

Moisture uptake was determined by weighing the specimens at regular intervals. A Mettler balance with a precision of 1 mg was used to weigh the specimens. The moisture content was calculated according to the equation:

$$M_t = \frac{(W_w - W_d)}{W_d}$$
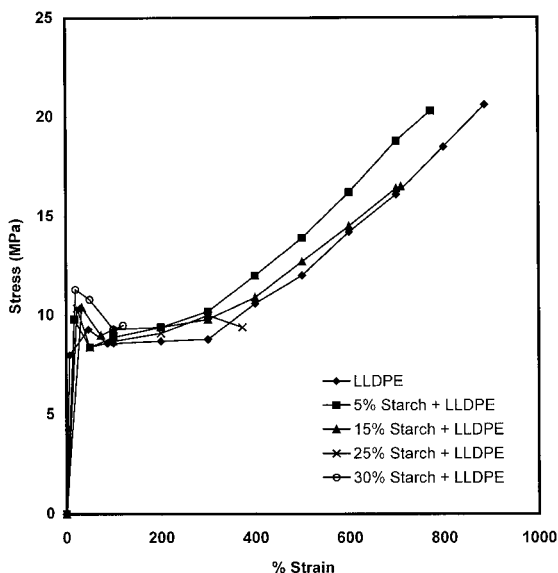
Figure 1 Stress-strain curves of LLDPE and some sago starch-LLDPE composites.

where W_d and W_w are the weight of the samples when dry and after moisture uptake, respectively. The average reading of three samples was taken in both cases.

Electron Microscopy

A scanning electron microscope (SEM) (Leica Cambridge S-360 Model) was used to study the fracture surfaces of the composites. The fracture ends of the composites were mounted on aluminium stubs and sputter-coated with a thin layer of gold to avoid electrical discharge during examination.

RESULTS AND DISCUSSION

Stress-Strain Curves

The stress-strain relationship of some sago starch-filled LLDPE composites are shown in Figure 1. The incorporation of up to 15 wt % sago starch into LLDPE did not have significant effect on the shape of the curves. LLDPE is a soft but tough plastic with low modulus but high elongation at break. With increasing starch content, the tensile properties of the composites were slightly altered.

Young's Modulus

The effect of starch content on modulus is shown in Figure 2. The Young's modulus of a material is

a measure of the stiffness of the material. It is determined by taking the slope of the tangent to the curve of the stress-strain curve at zero extension. The incorporation of sago starch into LLDPE generally led to an increase in the Young's modulus of the composites. This is in agreement with the work of Willett [6] on LDPE corn and potato starch-filled composites. At 5 wt % starch content, the modulus increased by 2.3%, whereas at 15 wt % starch content, it increased by 31%. The increase in modulus is due to the stiffness of the starch granules. Rigid fillers are generally known to increase modulus even in situations where reinforcement does not occur. The starch granules been stiffer than the LLDPE matrix in which they are dispersed increased the modulus of the composites.

Yield Strength

The variation of yield strength with starch content of the composites is shown in Figure 3. It is clear from Figure 3 that the yield strength did not show any significant increase with increase in starch content of the composites. This is especially true at lower starch contents. The yield strength of LLDPE was calculated to be 9.3 MPa. At 15 wt % starch content, the yield strength increased slightly. In view of the fact that the yield point of LLDPE is rather low, the slight increase in yield point of the composites at higher
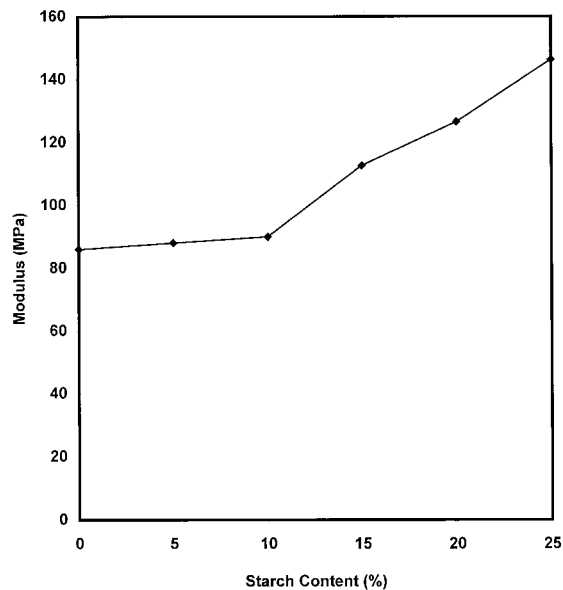
Figure 2 Effect of starch content on modulus of LLDPE.
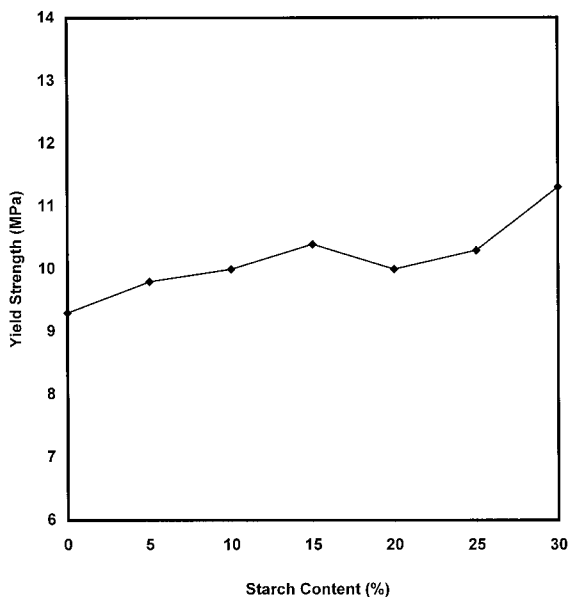
Figure 3 Effect of starch content yield strength of LLDPE.

starch contents 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 value of yield strength is also an advantage in printing because registration problems are reduced.[7]
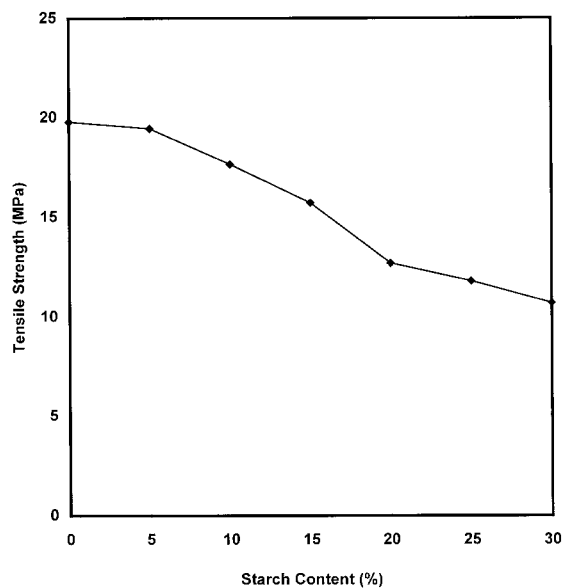
Tensile Strength

Figure 4 shows the variation of tensile strength with starch content. The tensile strength decreased with increase in starch content. This is in agreement with the work of Nikolov et al.,[3] Willett,[6] and Kang et al.[5] The starch granule is highly hydrophilic containing hydroxyl groups on its surface, whereas LLDPE is basically nonpolar. Therefore, in such a system, 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, since the mechanical load is carried only the matrix. At 5 wt % starch content, the tensile strength decreased by 1.7%, whereas at 15 wt % starch content, it decreased by 20.5%. At an equivalent starch content of 15 wt %, the decrease in tensile strength of a corn starch-LLDPE composite determined under identical conditions was 23.71%. This is slightly more than the decrease in tensile strength obtained in the 15 wt % sago starch-LLDPE composite. This indicates that sago starch-filled LLDPE systems and corn starch-filled LLDPE

systems have comparable retention of tensile strength. Apart from starch-filled systems, this phenomenon is observed in other thermoplastics filled with particulate fillers.[9] The drop in the tensile strength of the composites became more drastic as the starch content increased. This is because at higher starch contents, 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 starch particles, the applied stress is not transferred from the polymer matrix onto the rigid starch particles. Hence the stress experienced by the matrix is higher.[5] As will be shown later in the SEM micrographs, starch granules are of irregular shape and have a tendency to from agglomerates especially at higher loadings. These factors, plus the fact that no compatibilizer was present in the composites, resulted in poor adhesion of the starch granules to the LLDPE matrix. Weak interfacial regions imply that the transfer of stress from the polymer to the starch granules will not be efficient.

Elongation at Break

The variation of elongation at break with starch content of the composites is shown in Figure 5. The expected trend is observed, i.e. elongation at break declined with increase in starch content. This is in agreement with the work of Nikolov et

Figure 4 Effect of starch content on tensile strength of LLDPE.
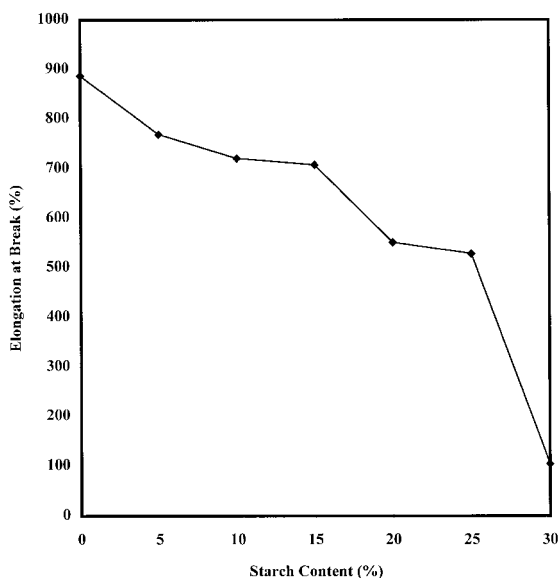
Figure 5 Effect of starch content on elongation at break of LLDPE.

al.,[3] Willett,[6] and Kang et al.[5] At 5 wt % starch content, the elongation at break dropped by 13.5%, whereas at 15 wt % starch content, it dropped by 20.4%. At 15 wt % starch content, corn starch-LLDPE composite had 23.61% reduction in elongation at break. Decrease in elongation at break of the sago starch-LLDPE composites became more drastic at higher starch contents. This observation has been made by Nikolov et al.,[3] on maize starch-LLDPE composites and Willett[6] on potato starch-LDPE and maize starch-LDPE composites. The decrease in elongation at break with increase in starch content of the composites is because the starch granules do not elongate along with the LLDPE and therefore, less strain is required to make the material fail.[10] In addition, the poor starch-LLDPE interaction that gives rise to weak interfacial regions permits easier crack propagation. Thus the composite fractures at lower values of elongation with increasing starch content.
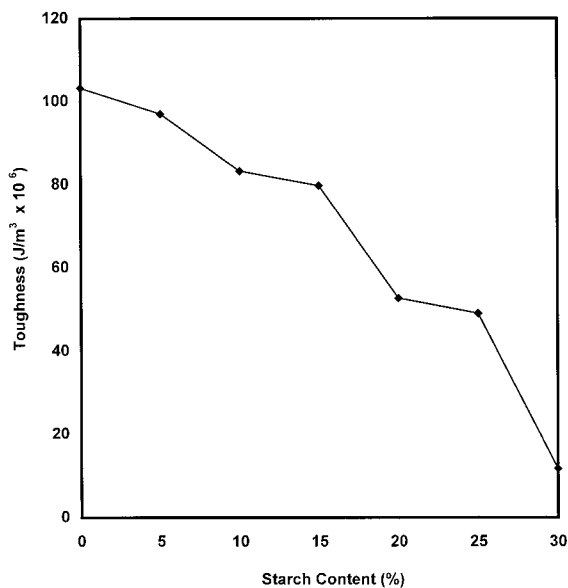
Toughness

The effect of starch content on the toughness (as calculated from the area under the stress-strain curve) of the composites is illustrated in Figure 6. The toughness of a material is a measure of the ability of the material to have high elongation to failure, or one in which a lot of energy must be expended to produce failure.[11] Generally, toughness decreased with increase in starch content. At
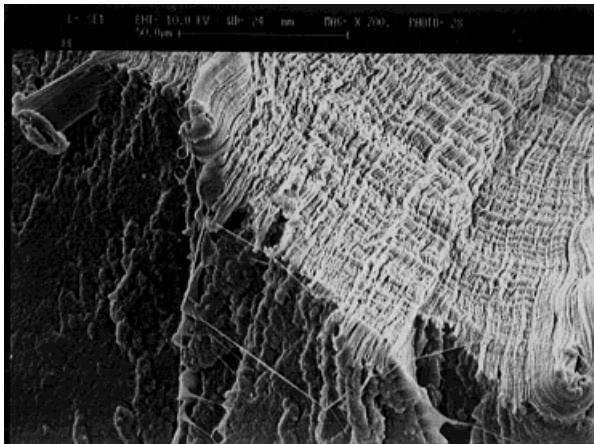
5 wt % starch content, the toughness decreased by 6%, whereas at 15 wt % starch content, the decreased was 22.7%. Save for a few exceptions, a plastic needs both the ability to elongate substantially without failing in order to have high toughness. It is clear from Figure 5, that up to 15 wt % starch content, the elongation of the composites is relatively high. It may appear that factors contributing to high stiffness (modulus) are required, but this is not true, because there is an inverse relationship between flaw sensitivity and toughness. The higher the stiffness and the yield strength of s thermoplastic, the more flaw sensitive it becomes.[11] Therefore, as expected, the toughness of the composites decreased with increase in starch content, even though the modulus was increased.

Scanning Electron Microscopy

Figures 7 and 8 are SEM micrographs of fracture surfaces of LLDPE (unfilled) and sago starch-LLDPE composites (5 wt %). Figure 7 shows a ductile material with a very hard surface, whereas Figure 8 shows a less ductile material having a comparatively weak surface. From Figure 8, it can be seen that sago starch granules are of variable shapes; some granules are oval, or egg-shaped, and others are truncated. Figure 8 also reveals that the starch granules serve as particulate fillers. The granules appear as ag-
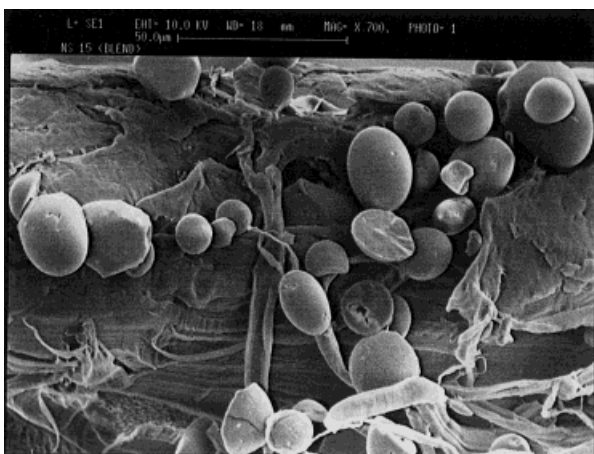

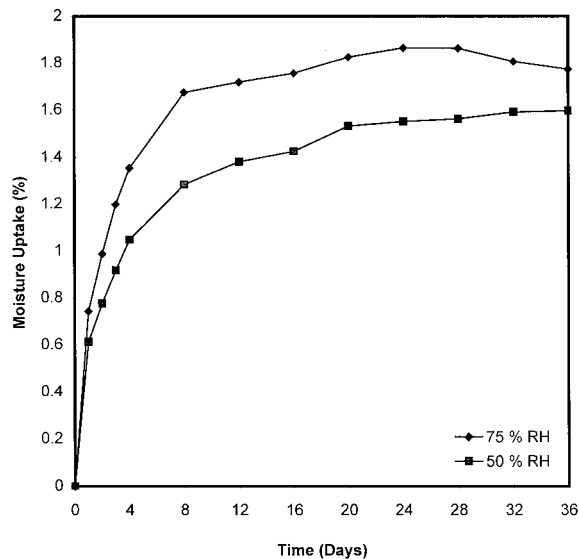**Figure 6** Effect of starch content on toughness of LLDPE.

Figure 7 Scanning electron micrograph of fracture surface of LLDPE.

Figure 9 Variation of moisture uptake with time for sago starch-filled LLDPE composite (15 wt % starch).

glomerates and thus, stress concentration points. It is also obvious that there was poor wetting between the starch granules and the LLDPE matrix. This is manifested in the smoothness of the fracture surface and the amount of debonding of the starch granules from the matrix. Hence tensile strength and elongation at break are expected to decrease with increase in starch content. It is a common practice to add nonreinforcing fillers to a thermoplastic in order to reduce cost and extend the resin and to improve the heat resistance of the material. By having lower coefficients of thermal expansion, they are able to reduce shrinkage and warpage of plastics after molding.[12] Except in a few instances, fillers do not improve the tensile

Figure 8 Scanning electron micrograph of fracture surface of sago starch-LLDPE composites.

properties of composites. In this case, in addition to reducing cost, the starch granules are added in order to impart biodegradable properties to the composites.

Effect of RH

Figure 9 shows the variation of moisture uptake with time at 50% RH and 75% relative humidities. Because of the presence of hydroxyl groups on the surface of the starch granule, the affinity for water is very high. This reduces the moisture barrier property of the composites. Generally, moisture uptake increased with time, with the highest uptake occuring at 75% relative humidity. Moisture uptake was highest during the first 4 days and increased gradually until it tended to reach a plateau between the 20th and 24th day. The absorption of water is related to its rate of diffusion into the composite. Exposed starch granules or those at or near the surface absorb moisture rapidly, whereas water absorption is slower for granules buried within the interior of the LLDPE matrix. Equilibration of the composites did not occur even after 36 days at both relative humidities. Willett[6] demonstrated that the equilibration time for molded starch-PE composites is in the order of months even when completely immersed in water.

The variation of moisture with starch content after exposure for 24 h at 50% and 75% relative humidities is shown in Figure 10. As expected,
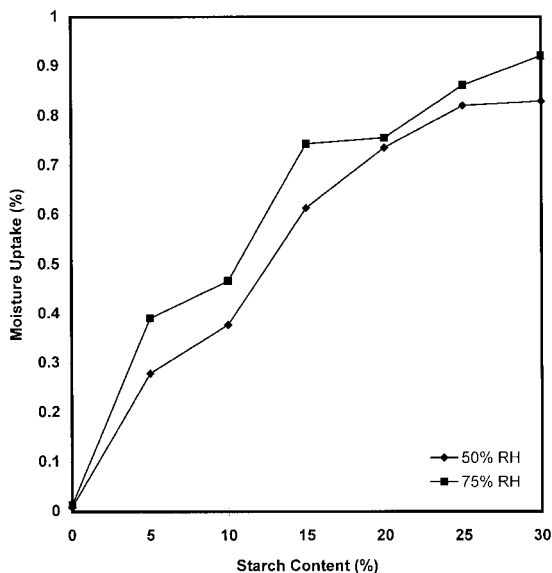
Figure 10 Variation of moisture uptake with starch content after 24 h for sago starch-filled LLDPE composite (15 wt % starch).

water uptake increased with increase in starch content, irrespective of the relative humidity. At any starch content, higher moisture uptake was observed in samples exposed to higher humidity, i.e., 75% relative humidity. The increase in moisture uptake is due to the more hydrophylic starch absorbing water. The higher the starch content, the more the water uptake in the high-starch composites. If used as a packaging material, the original moisture content and the humidity conditions inside and outside the material are important factors that should be considered. The inside humidity will be determined by the permeability of the material.[13] A relative humidity below 60% does not promote significant mold growth. Controlling the moisture uptake of starch composites is therefore necessary in order to prevent mould growth. In a high humidity environment, it may be useful to add a humectant to prevent mould growth on the composites during storage.
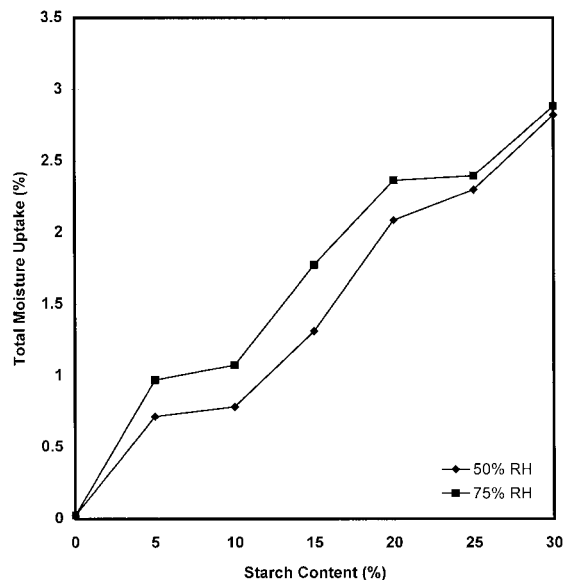
Figure 11 shows the variation of total moisture uptake with starch content at 50% and 75% relative humidity for 36 days. A similar trend is observed with the water uptake with starch after 24 h. Moisture uptake increased with starch content at both relative humidities. As expected, the highest moisture uptake occurred at 75% relative humidity.
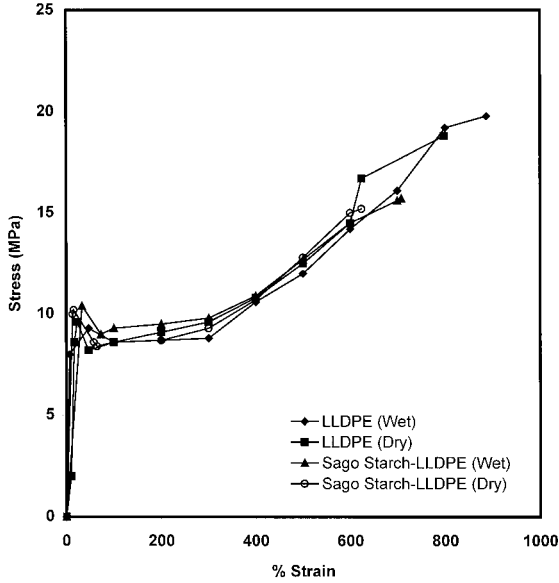
Effect of Immersion in Water

Starch-PE composites have been found to exhibit good retention in mechanical properties if the starch content lies between 10–20 wt %.[5,14] From the mechanical properties determined so far, at 15 wt % starch content, the composites seem to possess a good combination of stiffness, strength, and toughness. This was therefore selected as the optimum starch content. The stress-strain curve of the composite at 15 wt % starch content after complete immersion in water is shown in Figure 12. No change occurred in the shape of the stress-strain curves of the composites. It is clear that the tensile strength and elongation at break of the composites increased slightly. The increase in elongation at break could be due to the plasticizing effect of absorbed moisture. The elongation at break and impact resistance of a polymeric material is increased with increase in moisture content.[11]

The variation of water absorption of the composites with time of immersion is shown in Figure 13. The trend is similar to that of relative humidity. Water absorption increased with increase in starch content, in agreement with the work of Nikolov et al.[3] The composites did not equilibrate even up to 36 days immersion in water, in agreement with the findings of Willett,[6] who demonstrated that the equilibration time for starch-PE composites is in the period of months even when completely immersed in water. As expected, there were no significant changes in the water uptake of LLDPE even after 36 days immersion in water.
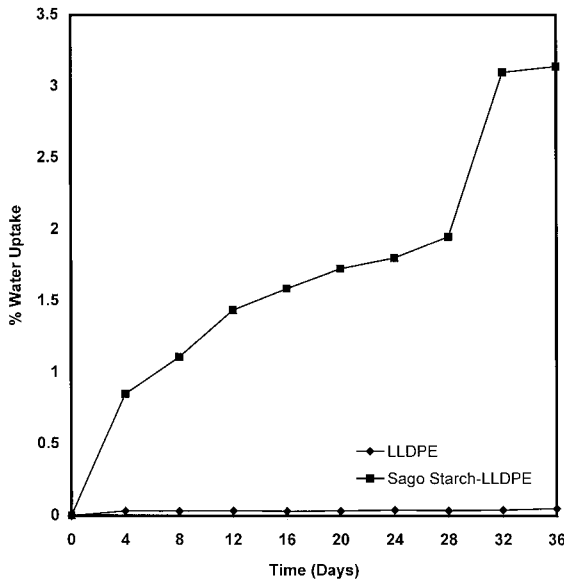

Figure 11 Variation of total moisture uptake with starch content after 36 days for sago starch-filled LLDPE composites.
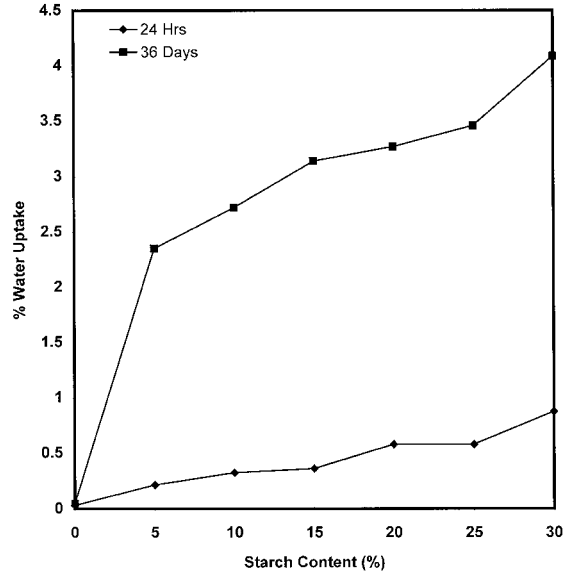
Figure 12 Stress-strain curves of LLDPE and sago starch composites (15 wt % starch) before and after immersion in water for 24 h.

It can also be seen that LLDPE possesses a very high moisture barrier property. It is obvious therefore that the starch granules are responsible for the high moisture uptake of the composites.

Figure 14 shows the variation of water absorption with starch content after 24 h and 36 days immersion in water. In both cases, water absorp-


Figure 14 Variation of water uptake with starch content for sago starch-filled LLDPE composite.

tion increased with increase in starch content. The increase in water after 36 days agrees with the findings of Nikolov et al.[3] At all starch contents water uptake was higher after 36 days immersion in water.

Figure 15 shows the difference in total water

Figure 13 Variation of water uptake with time for LLDPE and sago starch-filled LLDPE composite (15 wt % starch).
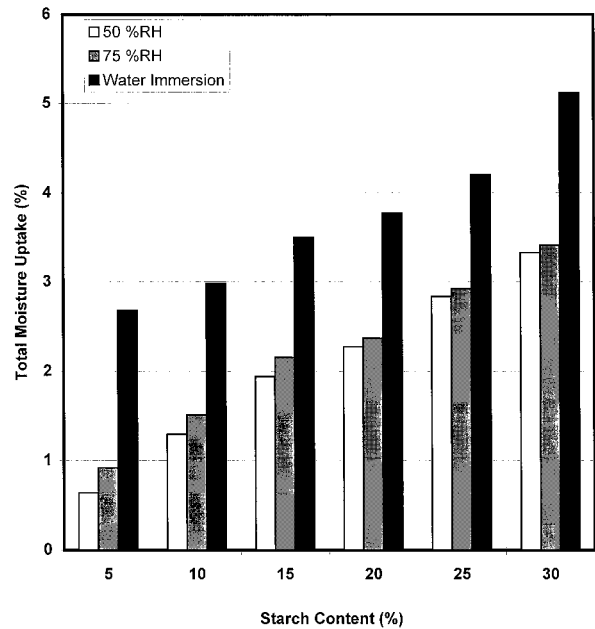
Figure 15 Comparison of total moisture uptake at 50% and 75% relative humidity with complete water immersion after 36 days for sago starch-LLDPE composites.

uptake of the composites in humid air and when completely immersed in water after 36 days. As expected, the composites absorbed more moisture when completely immersed in water. In humid air, moisture uptake was higher at 75% relative humidity than at 50% relative humidity, indicating that starch has a lot of affinity for water.

CONCLUSION

Blending of sago starch with LLDPE is feasible. Addition of sago starch to LLDPE alters the mechanical properties of LLDPE. Mechanical properties of the composites such as tensile strength, elongation at break, and toughness decreased with increase in starch content, whereas the Young's modulus increased. However, there was no significant effect on yield strength. Water uptake increased with increase in starch content and was highest when the composites were completely immersed in water. SEM reveal poor adhesion between the starch granules and the LLDPE, and that the starch granules are dispersed in the form of particulate fillers.

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