Effect of sago starch and plasticizer content on the properties of thermoplastic films: mechanical testing and cyclic soaking-drying

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Abstract: Studies on the effect of sago starch and plasticizer concentrations on the tensile and tearing properties of the produced starch films were carried out using universal testing machine. The results showed that both sago starch and plasticizer contents significantly affected the mechanical properties of starch films. With increasing the starch concentration, an increase in tensile strength was observed. This was accompanied by radically reduced tensile strain and increased tearing strength. On the contrary, when increasing the plasticizer concentration, a reduction in tensile and tearing strength was observed, as well as an increment in tensile strain. The results of repeated soaking and drying tests made on sago starch films showed that the films with high plasticizer and low starch content exhibited lower mass loss compared to those containing lower plasticizer and higher starch concentration. Increasing the number of soaking and drying cycles reduced starch dissolution and it was probably related to retrogradation process inside the film. In a nutshell, the study provided preliminary information to assess the possible application fields of sago starch films.

Keywords: sago, starch, tensile, tearing, water absorption, crystallinity, film.

Wpływ zawartości skrobi sago i plastyfikatora na właściwości termoplastycznych folii: testy mechaniczne oraz cyklicznego przemywania i suszenia

Streszczenie: Z zastosowaniem uniwersalnej maszyny testującej zbadano zależność wytrzymałości na rozciąganie i rozdarcie wytworzonych błon skrobiowych od zawartości w nich skrobi sago i plastyfikatora. Stwierdzono, że udział zarówno skrobi, jak i plastyfikatora (mieszanina sorbitolu i glicerolu 1 : 1) wpływają wyraźnie na właściwości mechaniczne otrzymanych błon. Zwiększenie zawartości skrobi powodowało wzrost wytrzymałości na rozciąganie połączone z drastycznym zmniejszeniem wartości naprężenia. Ponadto zwiększyła się wytrzymałość na rozerwanie. Większa zawartość plastyfikatora w błonie skrobiowej, w przeciwieństwie do udziału skrobi sago, prowadziła do zmniejszenia wytrzymałości na rozciąganie przy zwiększeniu wartości naprężenia, a także do zmniejszenia wytrzymałości na rozerwanie. Wyniki testu cyklicznego moczenia i suszenia błon skrobiowych sago wykazały, że błony z dużą zawartością plastyfikatora i małym udziałem skrobi charakteryzowały się małym ubytkiem masy, w przeciwieństwie do błon z dużą zawartością skrobi i małym udziałem plastyfikatora. Zwiększanie liczby cykli moczenia i suszenia wpływało na ograniczenie procesu rozpuszczania skrobi w wodzie, co można tłumaczyć przebiegającą retrogradacją cząsteczek skrobiowych sago. Przeprowadzone badania mogą być przydatne do określenia obszarów potencjalnych zastosowań błon wytworzonych ze skrobi sago.

Słowa kluczowe: sago, skrobia, rozciąganie, rozrywanie, absorpcja wody, krystaliczność, błona.

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Sago tree is normally found between longitudes 90° to 180° E and latitudes 10° N to 10° S up to an altitude of 700 m above sea level [1]. The tree is one of the few tropical crops which can tolerate wet growing conditions such as peat swamp. In term of energy value per hectare, sago is one of the highest yielding crops in the world. Sago has a potential yield of 37 tones per hectare making it highly competitive compared to other starch crops in term of productivity. The yield of sago with a planting density of 102 palms per hectare is about 17 tones of starch per year. In Malaysia, 45.3 thousand tones of sago starch are exported each year thus generates a total Malaysian Ringgit (RM) 40.4 million revenue. Sarawak has 1.5 million hectares of sago palm plantations, where it represents 12 percent of Sarawak's total land area [2]. Besides being a basic food and industrial material, it generates many downstream activities, including food industries, livestock industries and manufacturing of industrial products such as glucose and ethanol [3]. As an export commodity, it brings a foreign exchange earning to the state.

Sago starch obtained from sago trunk has the potential to be used as raw material for bioplastic. There is much interest on this area due to the fact, that starch is abundant, has no color, taste and smell, besides it does not harm humans and environment [4–10]. Moreover, bioplastics made from starch have a short term durability and are rapidly degraded, being a renewable material fulfilling the characteristics of environmentally friendly products [9, 11, 12]. However, sago starch, as well as other types of starch, have some drawbacks such as natural brittleness due to the existence of a strong cohesive bonds among the polymer molecules. Its characteristic features such as poor melting, high water solubility, difficulty of processing, and brittleness create a need for plasticizers to make starch suitable for engineering applications [6, 13]. Acetic acid and plasticizers such as water, glycerol and sorbitol are added to the starch to increase the flexibility and extensibility of starch through the reduction of intermolecular forces between the adjacent polymer chains [14].

Although many studies on starch films were made, not much attention was given to the investigations on their tear resistance, being an important property for bioplastic performance [7, 15, 16]. Another important factor is the effect of repeated drying on the change in film mass. There were also limited studies focusing on sago starch as potential raw material for bioplastics. Therefore, this work concentrates on the determination of tearing properties as well as the effect of repeated drying on the mass of sago starch film. It may be a preliminary step to promote further research on this type of starch.

EXPERIMENTAL PART

Materials and preparation of samples

A 300 cm^3 of distilled water was preheated to 100 °C before being mixed with 9, 15, 21 and 27 g of sago starch (Table 1) to produce aqueous starch solutions with concentrations of 3, 5, 7 and 9 w/v %, respectively. Sago starch was provided by OXL Resources Sdn Bhd (Kuala Lumpur, Malaysia). Thereafter, the plasticizers of 30 w/w % (based on the starch mass) were added to the mixture. Plasticizers used in this study were sorbitol (Table 2) and glycerol (Table 3) that were supplied by OXL Resources Sdn Bhd (Kuala Lumpur, Malaysia) in the mass ratio of 1 : 1.

Sago starch, distilled water and plasticizer were mixed using mechanical stirrer with the speed of 1146 rpm for 30 minutes in the water bath with temperature of 85 °C. This step was stopped when the cloudy mixture turned clear. Then the mixture was slowly poured at the central part of the polypropylene mold and gently pressed several times to remove air bubbles. Finally, the mixture was dried for 24 hours in a ventilated oven at 50 °C.

The above steps were repeated with different plasticizer contents. Firstly, 15 g of sago starch was added to 300 cm^3 hot distilled water (100 °C) to produce sago starch aqueous dispersion with the concentration of 5 w/v %.

Table 1. Sago starch specification

Properties	Unit	Specification
Density	g/cm^3	1.5
Ash	%	0.2
Amylose	%	24–27
Protein	%	0.08
Fat	%	0.24
Water content	%	10–20

Table 2. Glycerol specification

Properties	Unit	Specification
Assay	%	99.8
Relative density (20/4 °C)		1.257–1.262
Refractive index		1.471–1.473
pH		6.0–7.0
Sulfate ash	%	Max. 0.005
Chloride (Cl)	%	Max. 0.0001
Sulfate (SO_4)	%	Max. 0.0005
Ammonium (NH_4)	%	Max. 0.0005
Arsenic (As)	%	Max. 0.0004
Copper (Cu)	%	Max. 0.0005
Iron (Fe)	%	Max. 0.0005
Lead (Pb)	%	Max. 0.0005
Sugar (glucose)	%	Max. 0.0004

Table 3. Sorbitol specification

Properties	Unit	Specification
Assay (HPLC)	%	> 99.0
Heavy metals (as Pb)	%	< 0.001
Mannitol (HPLC)	%	< 0.2
Water	%	< 0.2

Then, the plasticizers (10, 20, 30, 40 and 50 w/w % based on the sago starch mass) were mixed in to produce five different mixtures, which were then stirred under the same conditions as above and dried in oven for 24 hours.

Methods of testing

Mechanical testing

There were two sets of thermoplastic sago films produced in this study: the first with different sago starch concentrations but constant plasticizers percentage and the second, with different plasticizer concentrations and constant sago starch content. Both sets of sago starch films underwent mechanical tests, namely determination of tensile and tearing strength by using Instron 3365 universal testing machine (High Wycombe, England) of 15 kN that was suitable for film testing.

– For tensile testing, specimens with length of 150 mm and 25 mm wide were prepared in six replicates for each formulation. Then, the specimens were conditioned in 24 °C and 50 % *RH* (relative humidity) for 24 hours before tensile testing was performed. During the tensile test, the specimens were clamped between two jaws with gauge length of 100 mm and crosshead speed was 50 mm/min following ASTM D 882-09 [17].

– Upon tearing test, similar procedures were repeated but using different specimen shapes. The specimens were cut according to ASTM D 1004-94a [18] as explained in Fig. 1 producing sago starch films with single notch in the middle of specimen that eventually torn apart during the tearing test. The specimens were then conditioned for 24 hours. During tearing test, gauge length used was 2.5 cm and crosshead speed was 51 mm/min.

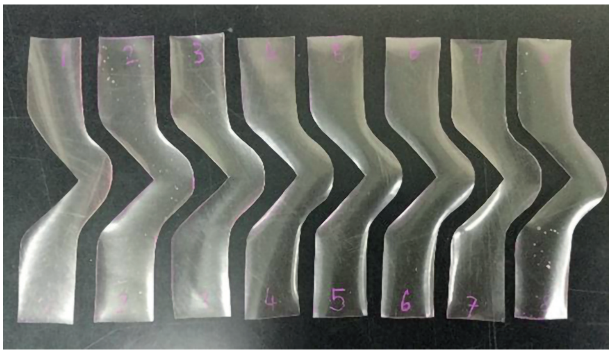

Fig. 1. Specimens prepared for tearing test

Soaking and drying test

The test was a modification of water absorption test. The two sets of sago thermoplastic films were cut into circular form to produce round films with diameter of 50.8 mm following the standard ASTM D 570-98 (1998) approach. The disk shape allows water to permeate evenly from all directions. A total of three replicates for each formulation were prepared. All of thermoplastic sago films were soaked in distilled water at the temperature of 24 °C in 2 hours before being dried for 30 minutes. Afterward the films mass were measured. The initial mass of the specimens were fixed to be 200 g. The soaking and drying cycles were repeated for 12 times. Before the test was started, the dry mass of thermoplastic sago films was weighed and recorded.

RESULTS AND DISCUSSION

Tensile and tearing test

The effect of sago starch and plasticizer concentration on the properties of sago starch films is presented in Figs. 2 and 3, respectively.

For the first set, the concentration of plasticizer was constant at 30 w/w % based on the dry mass of respective sago starch, which were 3, 5, 7 and 9 w/v % used in these mixtures. On the contrary, for the second set, sago starch percentage was kept constant at 5 w/v % and plasticizer loadings were varied at 10, 20, 30, 40 and 50 w/w %. In general, Fig. 3 shows a significant decrease in both tensile yield and tensile strengths except for 10 and 20 w/w % plasticized films. High tensile yield strength revealed that sago films have high ductility where they experienced strain hardening. Therefore, stress continued to in-

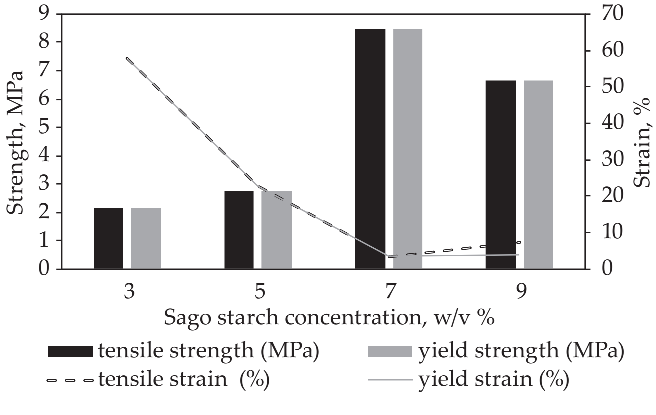

Fig. 2. Effect of sago starch concentration on tensile properties of sago films with constant plasticizers content 30 w/w %

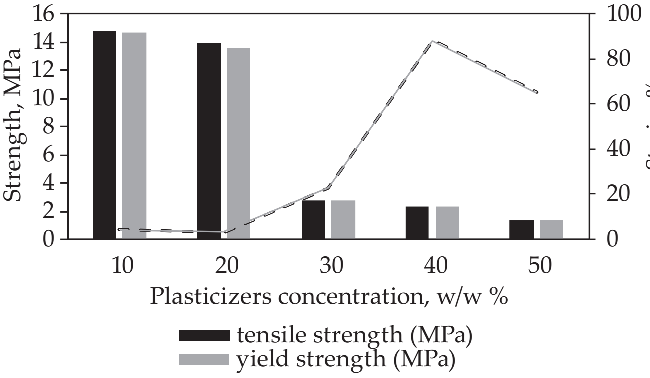

Fig. 3. Effect of plasticizers concentration on tensile properties of sago films with constant sago starch content 5 w/v %

crease until fracture occurred, to get the maximum stress that the films can withstand. For the first set, the increase in sago starch concentration led to the increase in yield strength. This may be due to the increase of starch polymer quantity in the film thus increased film density per unit area. High loading of sago starch lowered the proximity between the starch polymer chains therefore it facilitated the formation of a dense network after solution casting process was completed. Increasing from 3 to 5 w/v % of sago starch improved tensile yield by 28 %, moreover, increasing from 5 to 7 w/v % of sago starch improved it by 200 % (see Fig. 2).

Similar results were also reported for the case when the mixture of homogenized starch showed improvement in the film strength compared to starch without undergoing homogenization. Homogenizer proved to be successful in reducing the proximity between starch polymer chains, thus increasing the film crystallinity and improving the mechanical properties [6, 19].

The addition of plasticizer at more than the 7 w/v % concentration resulted in the decrement of 2.1 % in yield strength. This reduction was probably associated with the increase in equilibrium moisture content (*EMC*) of sago films. Even though all the films were conditioned prior to testing, there was a possibility that they carried different quantities of water molecules inside the films, and hence, contained different *EMC*. This was because, even though the percentage of plasticizers was constant at 30 w/w %, its actual mass followed the respective dry mass of sago starch in the formulations. As higher quantities of plasticizers and sago starch were introduced into the mixture, more active sites for hydrogen bonding were made available for interaction with surrounding water molecules increasing the moisture content in sago films. Water molecules, due to its small size, acted as additional plasticizers inside the film by lowering intermolecular bonding between sago starch polymers and extending their proximity in amorphous region. This led to a decrement in tensile strength as amorphous mobility was increased. In contrast to the first set, the second set showed a more consistent decrement trend as the rise of plasticizer loadings caused the drop in the mechanical strength. The highest tensile strength obtained was 14.76 MPa shown by the 10 w/w % plasticized film while the lowest value was 1.38 MPa recorded by 50 w/w % plasticized film. The difference between these two ends is 91 %, which is very huge. The decline can be attributed to the phase difference between the film, where lower plasticizer concentration produced a glassy state film while higher plasticizer concentration helped to reduce the film's glass transition temperature to solid rubbery state [20]. This phase difference occurred as sago films experienced anti-plasticizing to plasticizing transition determined by plasticizer contents. It has been reported that when plasticizer content was less than 21 wt %, starch lost its local mobility as shown by the increase in storage modulus [21]. It should be borne in mind that the percentage calculation for plasticizers used by Gaudin *et al.* [20] was different with the one used in this study. Even though they were referring mass percentage to the total mass of the whole system while this study calculated plasticizer content based on starch mass in formulation, both mass calculations showed a similar trend when plasticizer content was increased. According to them, loss in starch polymer mobility was due to the formation of strong hydrogen bonds between plasticizers and starch polymers. Plasticizers used in that experiment were sorbitol and glycerol in the mass ratio of 1 : 1, which at 30 w/w % was not only mechanically occupying the spaces between amorphous regions but also formed good chemical interaction with starch polymers as well *via* hydrogen bonds. Furthermore, this reduced free volume inside amorphous region and strengthened the film. This anti-plasticization effect can only be seen for starch film with low plasticizer content [20].

Moreover, the increase in plasticizer concentration to 20 w/w % led to a decrease in tensile strength by 5 % (see Fig. 3). Despite the slight decline, the result shows that the addition of 10 w/w % more plasticizers had successfully reduced brittleness of sago films by lowering mechanical integrity between sago starch chains [22]. It was reported that increment of 20 % or more of plasticizer can extend the plasticity zone and change the mechanical behavior of starch films [23]. Plasticizer molecules, which were small, more mobile and easily penetrated between sago starch polymer chains, deformed the structures during the mixing process. At this concentration, they started to function as lubricants that facilitated mobility of amorphous region and increased free volume so that as external stress was applied, there was space for elongation [22]. Therefore, as the plasticizer loading was increased to 30 w/w %, the tensile strength showed a drastic decrement by 80 % compared to the 20 w/w % plasticized sago film.

Table 4 shows that, from 30 w/w % plasticizers onwards, tensile strength exhibited decreased value as

Table 4. Effects of sago starch and plasticizers concentration on tensile properties of sago films

Tensile properties	Sago starch concentration, w/v %				Plasticizers concentration, w/w %				
	3	5	7	9	10	20	30	40	50
Yield strength, MPa	2.170	2.770	8.450	6.670	14.660	13.570	2.770	2.370	1.380
Tensile strength, MPa	2.170	2.770	8.440	6.670	14.760	13.960	2.770	2.370	1.380
Yield strain, %	57.840	22.750	3.570	4.100	4.370	3.140	22.750	88.300	65.260
Tensile strain, %	57.840	22.750	3.570	7.450	4.530	3.180	22.750	88.360	65.260
Tensile modulus, MPa	13.794	47.079	535.531	354.250	799.461	858.316	47.097	6.788	4.983

yield strength, which indicated that the films have ductile behavior.

The reduction of tensile or yield strength at this stage was due to the presence of clusters of plasticizers. The formed free volume allowed starch segments to mobilize thus reduced stress at break [22, 24]. The excess plasticizers had low probability to bind with sago starch polymers due to unavailability of their free active sites as they were already occupied. Therefore, they formed clusters of their own inside the system. As these clusters grew, they produced domains rich in plasticizer and influenced the mechanical strength of the films. The rich plasticizer domain not only provided mechanical plasticizing effect to the sago film but also delocalized stress imposed on the film. Delocalization of stress was due to inefficiency of stress transfer and distribution mechanism, which led to lower tensile and yield strengths.

As can be seen in Fig. 2, the tensile strain showed the opposite trend to tensile and yield strengths as the increase in sago starch loadings produced lower tensile strain value. The 3 w/v % sago starch film produced 57.84 % strain while 9 w/v % sago starch film exhibited 7.45 %. Among the first set of sago films, that containing 7 w/v % starch showed the highest decrease in percentage as compared with 84 % for the 5 w/v % starch film. The decrease was due to a reduction of sago starch polymer mobility inside the film, which resulted from increment in polymer density per unit area as sago starch loading increased. The higher sago starch intermolecular bonding was produced due to closer proximity between starch polymer chains. This secondary bonding restrained elongation reducing greatly tensile strain value.

Tensile strain of the second set, on the other hand, showed contradicted trend to the first one. For the films with 10 and 20 w/w % plasticizer the strain was less than 5 %, which indicated brittleness [25]. Inside these films, there was limited mobility allowed in amorphous region besides less active slippage system in crystalline region, therefore permissible elongation was very small. As crack propagation occurred to be very brief and barely seen from outside, breaking of 10 and 20 w/w % plasticizers films happened almost without any warning. When plasticizer concentrations were increased to 30, 40 and 50 w/w %, amorphous region deformed easily and stress was steadily absorbed without fracture [26]. When stress reached certain point, crystalline blocks started to separate through slippage activities. Crystalline region in sago film was produced by two sources, which was one formed through re-orientation of amylose chains during drying and the second, residual native crystals originally from amylopectin chains that somehow managed to maintain their structures during mixing process [27]. Many of them were not in perfect crystal shape. Therefore, when stress was imposed on sago film, dislocation may occur inside the crystalline region, eventually producing slippage inside crystalline region [25]. Allowing starch polymer chains in amorphous and crystalline regions to move at this stage increased film elongation and tensile strain.

Tables 5 and 6 show the times taken to propagate cracks until sago films were broken completely. The longer duration was required to split sago film apart after it experienced maximum load, which probably had higher crack propagation resistance. It was observed that different testings between tensile and tearing exhibited different results of crack propagation duration.

Figures 4 and 5 show the effect of sago starch and plasticizer concentrations on the tearing strength and modulus of sago films. Although the results demonstrate the same trend as tensile strength, they appeared in a much smaller margin. For the first set, the increment in tearing strength can be seen at 5 and 7 w/v % sago starch content, then a decrease is observed for 9 w/v % starch introduced into the mixture. The increase in tearing strength showed that more stress was required to initiate a tear. During this test, there were two important forces required; initially, the force needed to initiate tear and secondly the force required to propagate it. The initial crack was introduced when energy release rate reached a critical value. When stress concentration around notch posed constraint on starch polymers, plastic deformation tore the film [28]. Crack propagation then occurred when

Table 5. Crack propagation duration during tensile test

Crack propagation duration	Sago starch concentration, w/v %				Plasticizers concentration, w/w %				
	3	5	7	9	10	20	30	40	50
Fracture start, s	68.05	26.76	4.20	4.18	5.15	3.70	26.76	103.88	76.78
Fracture complete, s	74.83	36.18	30.76	19.11	6.02	13.93	36.18	106.68	78.94
Duration, s	6.78	9.41	26.56	14.30	0.87	10.23	9.41	2.80	2.16

Table 6. Crack propagation duration during tearing test

Crack propagation duration	Sago starch concentration, w/v %				Plasticizers concentration, w/w %				
	3	5	7	9	10	20	30	40	50
Fracture start, s	7.41	3.73	2.61	4.25	1.75	3.21	3.73	10.70	8.46
Fracture complete, s	20.56	17.04	16.81	18.71	9.38	15.63	17.04	23.98	18.61
Duration, s	13.15	13.31	14.20	14.45	7.63	12.41	13.30	13.28	9.89

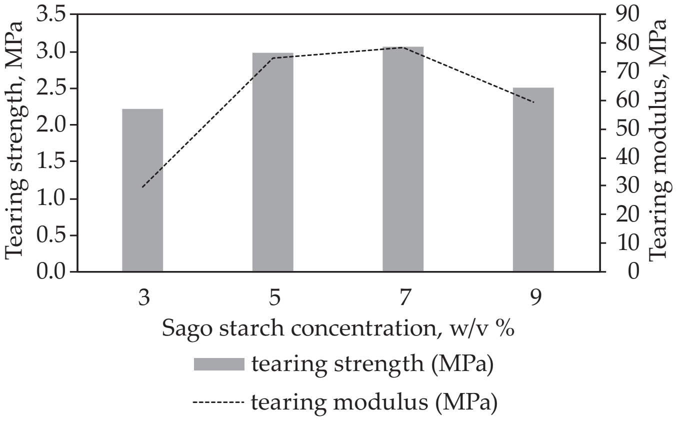

Fig. 4. Effect of sago starch concentration on tearing properties of sago films

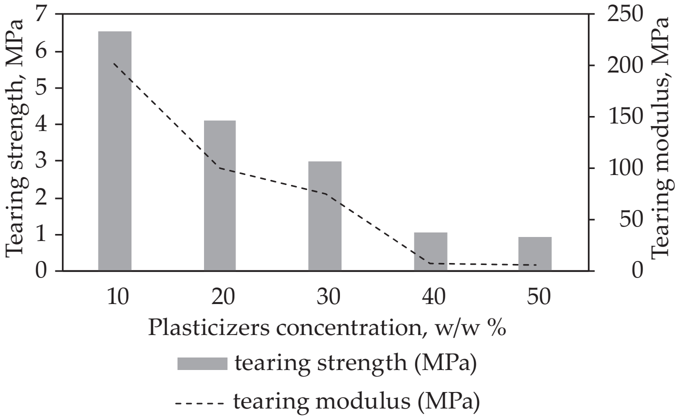

Fig. 5. Effect of plasticizers concentration on tearing properties of sago films

the energy released by breaking a starch polymer chain was transferred by plasticizer to another starch polymer chain. This propagation successfully induced the weakening mechanism of sago starch films. It was found that, although high sago starch concentration produced high resistance to initiate a tear, all films later had shown the same behavior during crack propagation. This can be observed from the duration of crack propagation, which started right after maximum load was reached until sago films were completely separated.

For the second set of the test involving 10, 20, 30, 40 and 50 w/w % plasticizer content, as plasticizer concentration was increased, lower resistance towards tear was obtained. The highest value recorded for the film with 10 w/w % plasticizer was 6.51 MPa, followed by films containing 20, 30, 40 and 50 w/w % plasticizer with 4.09, 2.98, 1.05 and 0.98 MPa, respectively. From the observation, there are two types of failure modes occurred in these films, namely brutal and progressive failure modes. The first two sago films had undergone brutal failure while the rest show progressive ones.

During tearing test, the film with 10 w/w % plasticizer showed little growth in crack as duration of crack propagation was the shortest compared to other sago films. Moreover, the addition of plasticizers into sago film managed to increase crack propagation with the longest period recorded for the film with 30 w/w % plasticizer (Table 7). This shows that 30 w/w % was the optimum amount of plasticizer to resist tearing in sago film. When the plasticizer loading exceeded 30 w/w %, crack propagation resistance was lowered due to excessive plasticizing effect that eventually led to increase in free volume. Therefore, as the crack tip posed stress constraint on sago film, it was easier to break due to inadequate starch polymers that serve as a backbone in absorbing plastic deformation [29].

Repeated soaking and drying test

The effect of soaking of sago starch films in water and leaving them to dry for 30 minutes was investigated throughout twelve repeated cycles of soaking and drying. The films contain different sago starch contents, namely 3, 5, 7 and 9 w/v % with constant plasticizer content (30 w/w %) according to the respective starch mass. As it is shown in Fig. 6, during the early stage of soaking and drying cycle all sago starch films exhibited increase in mass, as expected due to hydrophilic nature of the films.

The film containing 3 w/v % sago starch showed the highest mass increment (220 %), while that with 9 w/v %

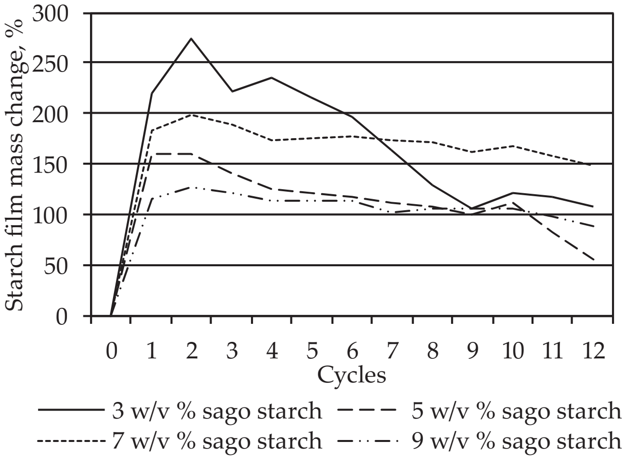

Fig. 6. Effect of repeated drying and soaking on behavior of sago starch films with different starch concentration

T a b l e 7. Effect of sago starch and plasticizers concentration on tearing properties of sago films

Tearing properties	Sago starch concentration, w/v %				Plasticizers concentration, w/w %				
	3	5	7	9	10	20	30	40	50
Tearing strength, MPa	2.22	2.98	3.05	2.50	6.51	4.09	2.98	1.05	0.93
Tearing modulus, MPa	29.865	74.576	78.446	59.422	201.766	100.471	74.576	7.954	6.357

increased its mass by 115 % after undergoing the first cycle. The difference in result was influenced probably by film strength where higher starch content caused increment in film strength, making it difficult to penetrate due to high intramolecular bonding between starch [30]. Besides, thickness factor also influenced water absorption activity as starch content was reported to have correlation with film thickness [30]. The higher content of starch caused increased thickness, that contributed to higher resistance to the flow of water through the film. Therefore, as 3 w/v % film was thinner than others, it was easily diffused by water. The water molecules then softened the starch polymer chain structures and promoted a movement in sago starch film system [31]. Consequently, more water molecules penetrated into starch films, as film barrier properties were weaken. In most edible films, including that with sago starch, interaction between the film matrix and water molecules were influenced by the structure of the film-forming polymer. The structure was affected by many factors such as increase in water diffusion, that later contributed to the increase in starch polymer chain movement [31].

The increment in film mass was continuously observed at much lower percentages. The mass of film containing 3 w/v % starch increased by 54 % of its initial value, compared with 12.5 % mass increment for the film with 9 w/v % starch. The increase in mass percentages started to slow down until the sago starch films reached certain concentration of free water, where there was no longer interaction between the starch polymer chains and water [32]. Interaction between them occurred at primary and secondary hydroxyl sites of starch chains [33]. Figure 6 shows that, after the second cycle, sago starch films begin to undergo degradation, which continued until the end of the test. The reduction of mass of sago starch films was probably related to the interaction of starch and water, where, at this point, starch molecules were moving further apart from each other, thus they can easily be dissolved. Moreover, after the ninth cycle of soaking and drying, the mass decrement by 114.72 % was recorded for the film with 3 w/v % starch, followed by the losses of 60.12 %, 22.03 %, and 8.84 % for the films containing 5, 7, and 9 w/v % starch, respectively. These results showed that as more cycles of soaking and drying were completed, the lower the percentages of mass loss were recorded. Because the mass loss might relate to the solubility of sago starch polymer into water, with an increment in the number of cycles, less starch components were solubilized. The lower solubilization probably was affected by a phenomenon known as retrogradation or recrystallization of starch polymers when left for certain period. During this time, crystalline structures were built as amylose and amylopectin, which became reoriented to linear chains parallel to each other. The changes in crystalline structures are accompanied by the changes in glass temperature (T_g), water content and plasticization efficiency. As a consequence, films become stiff and less elongable [34]. The above results suggest that repeating cycles of soaking and drying influence the crystallinity of sago starch films. The retrogradation process which occurred during the early cycles increased film crystallinity, restricting the pathway for water transport and limiting absorption capability in the subsequent cycles. Water absorption played an important role in facilitating starch movement thus increased the probability of starch alignment in amorphous region, which eventually led to the formation of crystalline structures [31]. Their existence lowered water intake shown by the reduction in film mass as more soaking and drying cycles were completed.

The film with 3 w/v % sago starch content exhibited higher percentages of mass reduction compared to those containing 5, 7 and 9 w/v % due to its thinner nature that permitted water to be absorbed easier and eventually dissolving the sago starch into immersion medium. The higher the starch content was, the lower the percentages of mass reduction were likely to occur due to thickness factor. Unlike 3 w/v % film, thicker films required longer time to evaporate the water during drying steps due to lower water penetration. Therefore, the rate of evaporation might also influence mass reduction readings beside starch solubility factor. Furthermore, all films regardless sago starch content exhibited no voids even after the twelfth cycle of soaking and drying. This showed that the film structures remain intact despite water penetration due to high intramolecular bonding between starch molecules [30].

Figure 7 shows the results of repeated soaking and drying of sago starch films with different plasticizer contents, namely 10, 20, 30, 40 and 50 w/w % while sago starch content was constant at 5 w/v %. The film with 10 w/w % plasticizer showed the most drastic mass loss compared to other films during the first cycle of soaking and drying. At low plasticizer contents such as 10 and 20 w/w %, there was no excessive plasticizer and below 25 % it may function as anti-plasticizer in starch film as reported in [35].

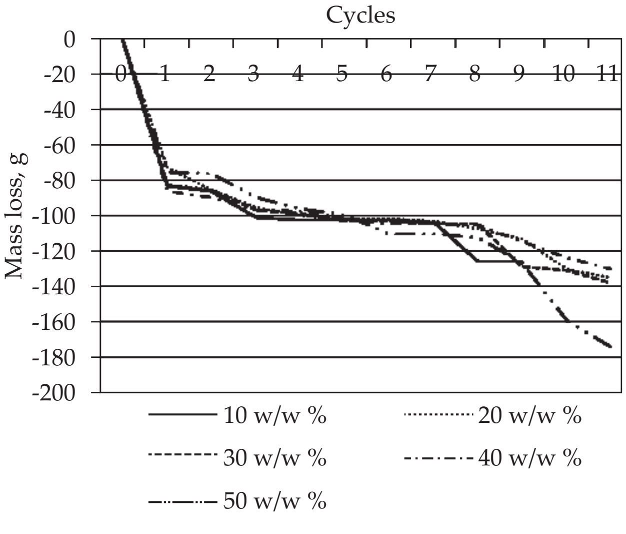

Fig. 7. Effect of repeated drying and soaking on behavior of sago starch films with different plasticizers concentrations

The absence of excessive or free plasticizer cause water molecules to reach starch polymers for bonding. When the bonding between them were increased, there was higher possibility for starch to be dissolved into immersion medium thus resulting in higher mass loss of sago starch films. The water penetration causes intramolecular interaction to become unstable and eventually disintegrate the film. The disintegration results in an increment in the film solubility [6, 11, 36]. According to Gaudin *et al.* [20], water absorption was higher at high plasticizer content in the film but it may not necessary cause higher solubility of starch film as well. In this experiment, the low plasticized film solubilized starch more despite a lower water absorption, where starch solubilization was observed through the film mass loss [20].

Furthermore, during the second cycle, a consistent trend was observed where 10 w/w % plasticized film exhibited the highest mass loss again. In this case, it was probably caused by lower retrogradation process in the film during the first cycle resulted in higher water absorption during the second cycle. The lower retrogradation process in low plasticized film may be explained by limited movement of starch polymer chains and alignment during the first cycle due to the low water absorption, resulting in lower degree of crystallinity during drying step of the first cycle. According to Thirathumthavorn and Charoenrein [34], the crystalline phase formed in the starch film successfully slowed down the vapor transmission. Similar result was obtained in this experiment when an increase in the crystallinity during the first cycle influenced water absorption of the subsequent cycles. The lower degree of crystallinity in 10 w/w % plasticized film means probably that more amorphous region causes the film to absorb more water compared to other ones. It is well known that amorphous region provides more exposed hydroxyl sites able to absorb water compared to crystalline region of starch polymers [37].

As a consequence, during the eighth cycle of soaking and drying, 10 w/w % plasticized film exhibited a drastic mass loss and end up with having cavities and cracks after the tenth cycle as it became too ductile. Furthermore, the water absorbed by 10 w/w % plasticized film during these cycles had successfully dissolved some of starch polymer chains into immersion medium assisted by increasing the proximity between them. The dissolution process was indicated by higher mass loss of the film compared to others. On the other hand, the films with higher plasticizer content absorbed more water during the first cycle, which resulted in the higher degree of film crystallinity throughout the test. These films were not torn or having cracks at the end of soaking-drying test, which is probably related to high coherency between starch polymer chains contributed by high crystallization degree of the starch films [6].

Besides film mass, other properties were also undergoing noticeable changes. For instance, prior to the testing, 10 w/w % plasticized film exhibited brittle behavior but changed to rubbery state when contacted with water during soaking. It is reported in [38], that water molecules were responsible for lowering T_g of the starch film and hence increased its flexibility. Furthermore, the thickness and diameter of sago starch films were also undergoing changes as absorbed water molecules induced movement of starch molecules and allowed them to slide over the adjacent polymer chains quite easily [6]. The swelling reaction can be observed through the increase in the thickness and diameter of sago starch films. According to Godbillot *et al.* [33] continuous increment of water content should be observed until the film reached saturated concentration, which was achieved when three hydroxyl groups of anhydroglucose were completely bound with water molecules. Nonetheless, in this experiment, saturation of water was not measured, because from the beginning the films showed dissolution of sago starch, which indicated that saturation point had already been exceeded.

On the contrary, starch films with high plasticizer content showed lower mass reduction as they underwent repeated cycles of soaking and drying. The lower mass reduction was probably affected by drying steps of the test where retrogradation process took place. During the first cycle, 50 w/w % plasticized film absorbed a lot of water thanks to excessive plasticizer inside. This later induced increment in water activity in rich plasticizer region as film hygroscopic property was enhanced by hydroxyl groups of plasticizer used thus increasing the film permeability [20, 38, 39]. Similarly, in this experiment, highly plasticized films seemed to have more crystalline structure formed, which can be observed through more pronounced brittle behavior of the films. The higher crystallinity can be explained by the increment of probability of starch polymer chain alignment to occur due to high water absorption during the first cycle. The higher crystallinity ensured sago starch polymers to stay together thus mitigated drifting of them into immersion medium by water molecules. As a consequence, this had conserved starch polymers inside the films thus lowering the mass loss in subsequent cycles.

Not merely starch polymers were thought to dissolve during the first soaking and drying cycle but plasticizer as well. The plasticizer dissolution might lead to an increment in the film crystallinity. This is in accordance with other studies where plasticizer was reported to be released into the liquid medium when the film was placed inside high moisture environment [33]. The removal of plasticizer contributed to the growth of crystalline structure. This was in agreement with the findings of Van Soest and Essers [40], who concluded that high water content environment indeed contributed to the increment in crystallinity properties of starch film, which was directly related to the existence of free plasticizer inside the film. The study also reported that crystallinity of starch film was increased by 35 % after being placed inside 90 % relative humidity [40]. As soaking provided higher humidity, the possibility for crystalline structure to be formed during the first cycle was higher. The crystalline structure might limit starch polymers from being dissolved into immersion medium therefore notable mass loss was seen during early cycles and it became lesser towards the final cycle. It is good to note that the films were alternated between soaking and drying steps in a given time interval, therefore it might not be completely dried during drying step before undergoing the next soaking of the new cycle. It was because evaporation process of drying step only involved water molecules that were near to film surface. The water molecules escaped slowly from the film surface when energy absorbed from environment was enough to overcome the water intermolecular bonding [41]. Therefore, low plasticized films were rapidly dried during the time given in drying step as they absorbed less water. On contrary, the films with high plasticizer content probably contained residual water that had been inclusively calculated as film mass.

CONCLUSIONS

With the goal to examine the potential of sago starch to be developed as bioplastic, this study focuses on its tensile and tearing properties under the conditions of repeated soaking and drying of sago starch films, which are important properties for the bioplastic performance. It was observed that sago starch and plasticizer concentrations contributed great impact on these properties. The increment in sago starch concentration increased the tensile and tearing strengths while increasing the content of plasticizer showed the contradicting effect. However, these two parameters provided a similar trend to crack propagation resistance when increases in both concentrations resulted in an increased propagation duration of sago starch films. This result suggested that sago starch films have the potential to be developed as bioplastics but their low tearing properties need to be improved. The changes in film mass were investigated through repeated soaking and drying tests. During the early cycles, all sago starch films regardless of starch content showed increment in film mass, followed by gradual decrement from the third cycle onwards. The differences in mass decrement indicated that at low starch content the films exhibited higher solubility, and consequently, higher mass loss percentages. On the contrary, the high plasticized film also showed high mass loss. The films with low starch content showed higher mass loss compared to those with higher starch concentration, which was probably caused by easier starch solubilization due to lower thickness. As the number of cycles was increased, a lower mass reduction was observed. Besides, the film thickness and mechanical strength may also be responsible for water absorption behavior of the sago starch films as in the first cycle they showed higher mass increment at low starch content. The increment was observed in the first two cycles before all the films underwent degradation, which was caused by dissolution of starch into the immersion medium.

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