EFFECT OF DIFFERENT TYPES OF STARCHES AS FILLERS IN NATURAL RUBBER LATEX FILMS

Y.S. Rohana, C.C. Tan, and A.R. Azura

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang, Malaysia

The main focus of this research is to investigate the tensile properties and biodegradability behavior of natural rubber latex by incorporating different types of natural fillers which are sago, tapioca and rice starches. The starch loading of 10phr is added to accelerate the biodegradation process of natural rubber latex films. Ball mills are employed to prepare the dispersion of fillers. The dispersed fillers are added into the latex compound prior to pre-vulcanization process at 70 °C. The dipped films are cured in oven at 100 °C for 20 minutes and cooled at room temperature for 24 hours before stripping. The films are buried in soil up to four weeks to study the biodegradation activities. The morphological studies on the dispersion and biodegradability of starches in natural rubber latex films are analyzed by scanning electron microscopy (SEM) and optical microscopy. The results indicated that the rice starch not compatible with natural rubber latex. The weak rubber – filler interactions of natural rubber latex with sago and tapioca starches are observed via SEM. From optical microscopy observation, the microorganisms more attracted to tapioca starch compared to sago starch, and thus increased the biodegradation activities of tapioca filled natural rubber latex film.

Keywords : Natural rubber, sago starch, sago starch, rubber-filler

INTRODUCTION

Malaysia is the world's leading supplier of natural rubber latex (NRL) products which contribution over 50% of the world demands on examination and surgical gloves [1]. Better sales indicated higher demand and more waste will be produced which contribute to the mass solid waste disposal problem. Most of the NRL products are generally disposed after single usage, hence the rate of producing NRL waste is faster than the rate for them to biodegrade. Biodegradation is the most crucial issue for polymer product since it relate to the global warming problem.

As a part of the solution, starch can be used as filler in NRL products. The protein in starch provides the site for the microbial growth which it acts as the initiator of biodegradation process. Although NRL itself contains protein, the composition is too low for microorganisms to grow, and thus require longer time to degrade. Starch exists in abundance, inexpensive, and economical to replace the mineral fillers. However, the compatibility of starch with NRL is important to obtain good dispersion. Starch is made of two main structures: amylose and amylopectin. Amylose is principally linear with α-1-4 glucosyl units while amylopectin is highly branched unit with 1-4 linked α-D-glucosyl joined by 1-6 linkages. These two molecules have their own distinct properties; amylopectin appears in aqueous form, more stable, and produces soft gels and weak films, meanwhile amylose tends to retrograde and produces tough gels and strong films [2]. Each type of starch has different composition of amylose and amylopectin; therefore, its compatibility with latex and the biodegradation activities are different.

This research was designed to study the compatibility and biodegradability of different types of starches which are sago starch, tapioca starch, and rice starch in NRL films.

MATERIALS AND METHODS

High ammonia (HA) latex with 60% of dry rubber content (DRC) was purchased from Zarm Scientific and Supplies (Malaysia) Sdn. Bhd. For different types of starches, sago starch manufactured by Sago Link Sdn. Bhd., tapioca starch (Cap Kapal ABC) from Thye Huat Chan Sdn. Bhd., and rice starch (Erawan Brand Rice Flour) from Tiga Gajah Cho Heng Sdn. Bhd. were used. Pottasium hydroxide (KOH), anchoid, antioxidant, zinc oxide, potassium oleate, zinc diethyldithiocarbamate (ZDEC), and sulfur were supplied by Bayer (Malaysia) Sdn. Bhd.

For the preparation of starch dispersions, all the ingredients in Table 1 were stirred with Wise Stir HS-300 mechanical stirrer until homogeneous mixture was obtained. The mixture was transferred into the ball mills jar and mixed at 20rpm for 24 hour.

* *Corresponding author: Tel. + 6 (04) 594 1010; Fax. + 6 (04) 594 1011*
E-mail. azura@eng.usm.my (A.R. Azura)

Table 1 Formulation for filler dispersion

Ingredients	Weight (%)
25% Starch*	25
10% KOH	3
Anchoid	5
Water	67

* Sago, tapioca, or rice starch.

The NRL film without filler (control) and filled NRL samples were prepared according to formulation in Table 2. The mixture was constantly stirred for two hours with stirring speed of 270rpm. The latex compound transferred into pre-heated water bath with the temperature of 70°C and stirred at 270rpm for another 30 minutes. The chloroform number test was carried out until chloroform number 3 was obtained. The compound was sealed and left overnight at room temperature for maturation. The steel plates were dipped in coagulant (10% calcium nitrate) for 5 seconds and dried in the air oven for 10 minutes at 100°C before cooled at room temperature for 5 minutes. The steel plates were then dipped into latex compound for 10 seconds and cured in the air oven for 20 minutes at 100°C before cooled at room temperature for 24 hours.

Table 2 Formulation for latex compounds

Ingredients	Control (phr)	Starch (phr)
60% NRL	100	100
10% KOH	0.5	0.5
20% Potassium Oleate	0.25	0.25
50% Antioxidant	0.5	0.5
50% ZnO	1	1
50% ZDEC	0.5	0.5
50% Sulfur	0.5	0.5
25% Starch**	-	10

** Sago, tapioca, or rice starch.

Protein test was carried out according to ASTM D5712-2005 to determine the extractable protein content in the films. For morphological analysis, the freeze fracture surface of gold-coated samples was observed under scanning electron microscopy (SEM) with magnification 1000x. The films were cut into dumbbell shape. Instron IX3366 machine was used to evaluate the tensile properties (ASTM D412) with the crosshead speed of 500mm/min. Soil burial test was carried out in accordance to ASTM D 6003-96 method for interval of 4 weeks and the sample weight loss was quantify to determine the biodegradation properties. The appearance of biodegradation of the films were observed using Dino Lite Optical Microscope at 500x magnification.

RESULTS AND DISCUSSION

Protein Test

Referring to Table 3, the control sample has high extractable protein content; 1565 µg/g. The proteins of NRL constitute about 2% by weight of the field latex. However, sago starch filled NRL film showed even higher extractable protein content value which is 1614 µg/g. Tapioca filled NRL film has the lowest extractable protein content; 752 µg/g and this indicated that a high volume of unextractable protein remained in the film.

Table 3 Extractable protein content of different types of NRL films

Type of NRL films	Extractable Protein Content (µg/g)
Control films	1565
Sago starch filled NRL films	1614
Tapioca starch filled NRL films	752

Morphological Analysis

Fig. 1 shows the cross-section of rice starch filled NRL film via SEM. NRL has low stability with the addition of rice starch where the films formation cannot be obtained. High amount of bubbles formed in the mixture which unable to be removed which appeared as foam-like material to the NRL film.

The freeze-fracture surface of control, sago starch and tapioca filled NRL films characterized by SEM are shown in Fig. 2(a) to Fig. 2(c). The small holes on the freeze-fracture surface of both sago starches filled- and tapioca starch filled-NRL films were found in Fig. 2(b) and Fig. 2(c) compared to the control sample (Fig. 2(a)). This observation indicated the weak rubber and filler interactions of starches and NRL matrix contribute from the incompatibility between hydrophilic starches and hydrophobic NR molecules hence prevent the starch from coalesces, re-crystallization, and formation of hydrogen bonding [3].

Fig. 1. Cross-section of rice starch filled NRL films.

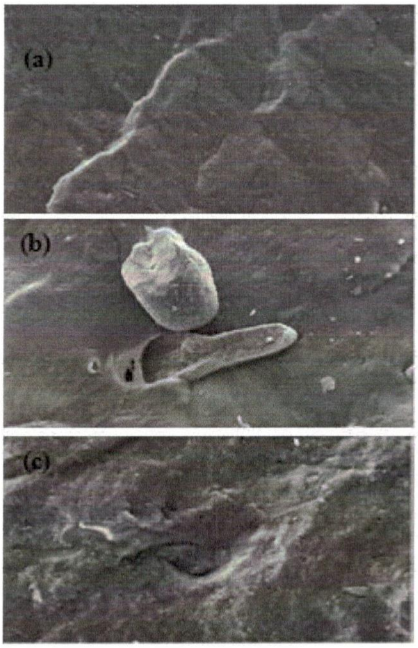

Fig. 2. Fracture surface of (a) control sample, (b) sago starch filled NRL film, and (c) tapioca filled NRL film (mag.: 1000x).

Tensile Properties

Fig. 3 shows the stress-strain curves which give the information on ultimate strength and toughness for all types of NRL films. Control sample exhibited higher tensile strength and toughness properties than sago starch and tapioca starch filled-NRL films due to the ability of NR to undergo strain induced crystallization. The addition of filler could reduce or eliminate this ability where the particles disrupted the formation of crystalline lattice by their physical presence [4].

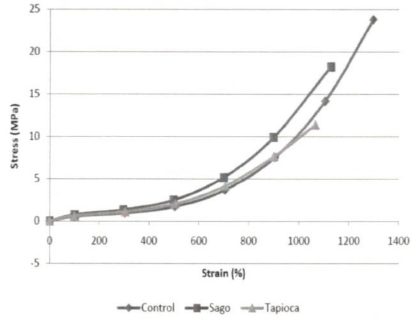

Fig. 3. Stress-strain curves of different types of NRL films.

Table 4 shows the tensile strength and elongation at break (EB) values for all types of samples. The incorporation of starches decreased the tensile strength and EB values of NRL films. Starch is highly polar and tends to not compatible with NR molecule which is non-polar. The weak interfacial interaction between filler and rubber particles caused inefficient stress transfer from polymer to starch granule [5]. Sago starch filled NRL film showed better tensile strength and EB values compared to tapioca starch filled NRL film. Referring to Table 3, tapioca starch filled NRL film has lower extractable protein content than sago starch; therefore, the film has more amorphous region with low degree of crystallinity. This region resulted in less of molecular orientation, and thus lower energy required to break the secondary bonding of the align molecules which contributed to the low tensile strength and EB values [6]. Although sago starch filled NRL film exhibited lower tensile strength and EB than control sample, the values still complied with product specification which according to ASTM D3578, the minimum tensile strength is 18MPa and EB value is 650%.

Table 4.Tensile strength and elongation at break of different types of NRL films

Types of NRL films	Tensile Strength (MPa)	Elongation at Break (%)
Control film	23.32	1269
Sago starch filled NRL films	18.05	1121
Tapioca starch filled NRL films	10.86	1028

Biodegradation

Biodegradation was measured by weight loss and observation on the surface condition of NRL films. Fig. 4 shows the weight loss percentages of NRL films after 0, 1, 2, 3, and 4 weeks of soil burial. The results indicated that at week 4, tapioca starch filled NRL film showed the highest weight loss, followed by sago starch filled NRL film and control sample. Weight loss is related to the porosity formation in latex films resulted from the consumption of starch by microorganisms [7].

The changes in physical condition from week 0 to week 4 of biodegradation for all samples were analyzed using optical microscopy as shown in Fig. 5, Fig. 6, and Fig. 7. It is clearly seen from Fig. 5(a) to Fig. 5(c), the biological activity on the control sample was not visible but the weight loss occurred for the first two weeks of soil burial. Fig. 5(d) and Figure 5(e) show the significant changes on the surface of control sample, where a large patch of yellow-orange in color was observed. These showed that microbial activities began significantly at the third week and became more vigorous at the forth week which also detected by the increased in weight loss percentages but not too significant as starch filled NRL films. In general, biodegradation of NRL film without a starch is a slow process which longer time to degraded [8].

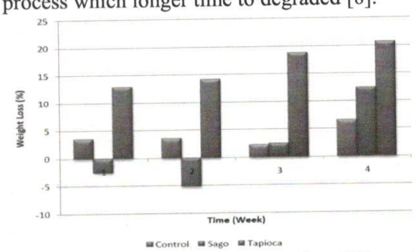

Fig.4. Weight loss percentages for different types of NRL films.

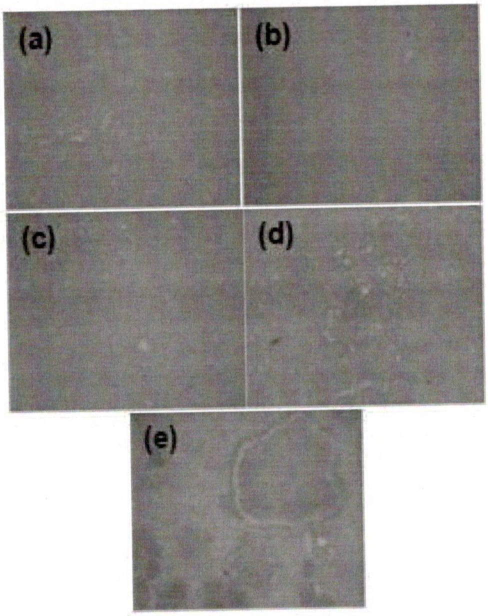

Fig. 5. The physical changes of control films from week 0 to week 4 (mag.: 500x).

Fig. 6(a) shows that no visible microbial activities occurred on the sago starch filled NRL film at week 0. Fig. 6(b) clearly showed that the blisters appeared on the film which indicated the activities of microorganisms occurred after one week of soil burial. Microbial degradation of starch normally leads to the production of oligosaccharides and eventually glucose [9] resulted in increased in weight of the samples. Small dark brownish spots were observed on the surface of sago starch filled NRL film at week 2 (Fig. 6(c)) and became more obvious at week 3 (Fig. 6(d)). These spots were believed as the evidence of accelerated microorganisms' growth in the film within week 2 and week 3. At week 4 (Fig. 6(e)), biodegradation occurred significantly where more microorganisms 'growth with larger pores were observed, and thus increased the weight loss.

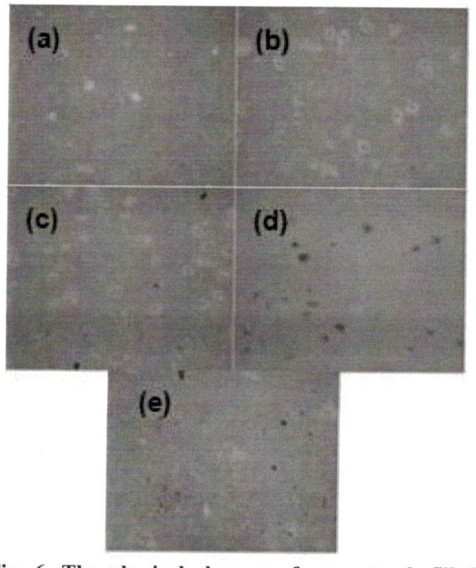

Fig. 6. The physical changes of sago starch filled NRL films from week 0 to week 4 (mag: 500x).

Fig. 7(a) also show no visible microbial activities on the tapioca starch filled NRL film at week 0. However, in week 1, some small dark spots were observed on the film as shown in Fig. 7(b) which indicated the microorganisms' growth occurred. More pores were found in tapioca starch filled NRL film at week 2 (Fig. 7(c)) compared to sago filled NRL film and this proved that microorganisms more attracted to tapioca starch. As discussed earlier in Table 3, tapioca starch has high unextractable protein content which assists in initiation for more microbial activities, and thus increased the weight loss of the film. At week 3, the dark spots with small yellow patches were discovered (Fig. 7(d)) and at week 4, they became larger with many pores were observed on tapioca starch film (Fig. 7(e)).

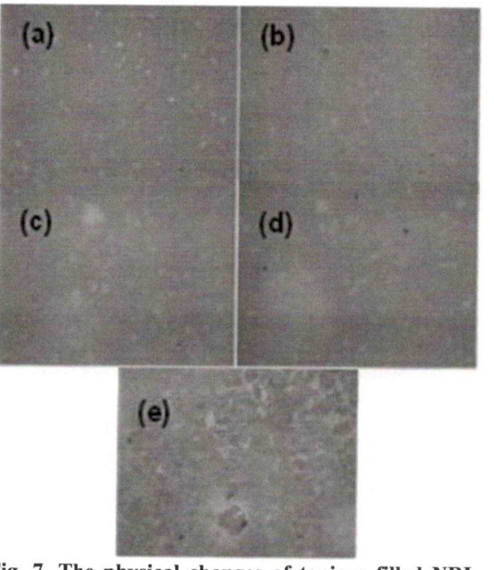

Fig. 7. The physical changes of tapioca filled NRL films from week 0 to week 4 (mag.: 500x).

CONCLUSIONS

- The rice starch was incompatible with NR matrix.
- From morphological analysis via SEM, both sago and tapioca starches showed weak interaction with NR matrix.
- The observation from optical microscopy indicated the microorganisms more attracted to tapioca starch filled- compared to sago starch-filled NRL films.
- However, sago starch showed high potential as filler in NRL film since it provides good tensile properties and able to initiate and accelerate the biodegradation activities.

ACKNOWLEDGEMENT

This work is supported under the RU grant No. 1001/PBAHAN/814093. The authors gratefully acknowledge the support provided by USM.

REFERENCES

[1] Malaysian Rubber Export Promotional Council *(MREPC)*, (2011). Malaysian Rubber and Rubber Products Statistics (www.mrepc.com).

[2] BeMiller, J.N., Whistler, R.L. (2009). *Starch Chemistry and Technology*. BeMiller, J.N., Whistler, R.L. eds, 3rd ed. Amsterdam: Academic Press, 771.

[3] Liu, C., Shao, Y., Jia, D. (2008). Chemically Modified Starch Reinforced Natural Rubber Composites, *Polymer*, 49, 2176 – 2181.

[4] Bauman, J.T. (2008). *Fatigure, Stress, and Strain of Rubber Components: Guide for Design Engineers.* Munich: Hanser Verlag, 16.

[5] Fakirov, S., Bhattacharyya, D. (2007). *Handbook of Engineering Biopolymers: Homopolymers, Blends and Composites.* Munich: Hanser Verlag, 117.

[6] Nagdi, K. (1993). *Rubber as an Engineering Material: Guideline for Users*. Munich: Hanser Verlag, 34.

[7] Bertolini, A.C. (2010). *Starches: Characterisation, Properties, and Applications.* Florida: CRC Press, 255-265.

[8] Warneke, S., Arenskőtter, M., Tenberge K.B., Steinbűchel, A. (2007). Bacterial degradation of poly(trans-1,4-isoprene) (gutta percha) *Microbiology*, 153, 347–356.

[9] Schlemmer, D.; Sales, M.J.A. and Resck, I.S. (2009). Degradation of different polystyrene/thermoplastic starch blends buried in soil. *Carbohydrate Polymers*, 75, 1, 58-62.