The Effect of Sago Starch Filler Dispersion preparation on the Biodegradation Properties of Natural Rubber Latex Films

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Abstract. Sago starch dispersion was prepared by mechanical (ball milling) and chemical (reaction with alkali) processes in order to reduce the size of dispersed sago starch particles. The sago starch dispersion was compounded with natural rubber latex (NRL) as a filler and a NRL thin film was prepared by coagulant dipping technique. The ball milled sago starch (MSS) and alkali dispersed sago starch (CSS) filled NRL films were then subjected to soil burial test. The effect of the degradation process on weight loss percentages, surface morphologies, tensile strength behavior and Fourier Transform Infrared (FTIR) analysis of the starch filled NRL films were investigated. The utilization of sago starch dispersion prepared by alkali treatment showed the improvement in mechanical properties of NRL films compared to sago starch dispersion prepared by the ball milling method. From the results obtained, CSS/NRL films are more feasible to degrade compared to MSS/NRL films.

1. Introduction

The use of starch as bio-fillers in natural rubber latex compounding is a promising technique in producing the biodegradable NRL films. However, using starch in powdery form might result in latex destabilization. Thus, prior compounding, starch need to be dispersed in the form of the dispersion. Starch dispersion can be produced via chemical, mechanical, or temperature induced processes. During the process, starch gelatinization is expected to occur. The most common method to prepare filler dispersion before adding into NRL compound is a ball milling process. The method involves physical action without further alteration in chemical characteristic of starch [1]. The large particle size and hydrophilic in nature of starch causes the deterioration of final properties of NRL films. Therefore, starch treatment should be carried out to improve the compatibility between rubber and starch. Alkali treatment is a promising method to improve the starch dispersion. Alkali is generally used as a stabilizer in latex compounds as well as in preparing filler dispersion and it is able to gelatinize the native starch under room temperature. Alkali treatment for starch gelatinization also could prevent the retrogradation to occur in quite a long time [2]. A majority of hydroxyl groups in the anhydrous glucose units is ionised at high pH and therefore, the agglomeration of starch chains and paste retrogradation can be retarded [3]. Hence, it will improve the starch distribution in NRL matrix and enhance the final properties of NRL films. In this studies, different technique of preparing starch dispersion was conducted to observe the effect on NRL composite films.
2. Methodology

2.1 Preparation of ball milled sago starch (MSS) and Alkali dispersed sago starch (CSS)

Sago starch was mixed with anchoid (20% of filler weight), 10% potassium hydroxide (12% of filler weight) and distilled water before being stirred at 270 rpm of stirring speed for 15 minutes under room temperature. The mixture (pH 10) was then transferred into the milling jar with ceramic balls and subjected to rotary milled at 20 Hz for 24 hours under room temperature. The alkali treatment was carried out by mixing sago starch powder (NSS) with 100g of 5.35% KOH. The mixture was stirred at 200 rpm for 30 minutes before leaving it for two days under room temperature to gelatinize completely. Meanwhile, the CSS dispersion was stirred for 15 minutes at 200 rpm of stirring speed under room temperature. A faster preparation of alkali dispersed CSS mixture was due to the ability of the filler to dissolve in KOH instead of gelatinization. All pH of filler dispersion were maintained in the range of 12.60-12.80.

2.2 Preparation of MSS and CSS filled NRL composite films

The NRL mixture was prepared according to formulation as given in Table 1. The latex compound was diluted to 50% of total solid content (TSC) with distilled water.

Table 1: Compounding ingredients for MSS- and CSS/NRL

| Ingredients | Control NRL, (phr) | NRL with filler, (phr) |
|-------------|-------------------|----------------------|
| NRL         | 100               | 100                  |
| KOH         | 0.3               | 0.3                  |
| ZnO         | 0.25              | 0.25                 |
| AnO         | 0.5               | 0.5                  |
| ZDEC        | 0.75              | 0.75                 |
| Sulfur      | 0.5               | 0.5                  |
| MSS/CSS     | -                 | 10                   |

All the ingredients were mixed and stirred for two hours using Wise Stir HS-300 mechanical stirrer at stirring speed of 270 rpm and pre-vulcanized at temperature of 70°C. The chloroform number test was carried out until chloroform number 2 was obtained. The NRL compound was maturated overnight under room temperature before films preparation. The clean aluminum plates were dipped in coagulant (10% calcium nitrate) for 5 seconds and dried in the air oven for 10 minutes at 100°C before being cooled under room temperature for 5 minutes. The aluminum plates were then dipped into the NRL compound for 5 seconds and cured in the air oven for 20 minutes at 100°C before being cooled under room temperature for 24 hours. The films were stripped by the aids of calcium carbonate powder to prevent the films from sticking together and damaging the films surfaces.

2.3 Scanning Electron Microscopy

The morphologies of fillers and NRL films were observed using SEM model ZEISS Supra-35VP. The latex films test pieces were frosted with liquid nitrogen for 30 seconds before being fractured immediately. The freeze fractured surface of the film was attached on 45° holder. The samples were sputter coated with a thin layer of gold before analysis to avoid electrostatic charging during analysis. These coated samples were inserted into the microscope and the images were captured at 300x magnifications.
2.4 Fourier Transform Infrared Analysis of Fillers and NRL Films

The FTIR spectrometer used in this study was Perkin Elmer, Model Spectrum One. Analysis was carried out under room temperature within a typical wave number range of 4000 cm\(^{-1}\) to 550 cm\(^{-1}\) under transmission mode.

2.5 Soil burial test and determination of changes in the NRL properties

Soil burial test was carried out in accordance to Chuay Juljit [4]. The films were buried in controlled soil for 1 to 10 weeks at room temperature. The weekly withdrawn films were washed off and dried at room temperature overnight before the weight loss percentages calculation were done according to Equation 1.

\[
Weight\ loss\ (%) = \frac{W_i - W_b}{W_i} \times 100
\]

(Equation 1)

where, \(W_i\) is an initial weight and \(W_b\) is the weight after soil burial of NRL films in gram. The appearance of biodegradation signs on the surface of films was observed using Dino Lite Optical Microscope at 100x magnification. The morphologies of film surface after soil burial test also was observed under SEM with magnification of 300x. Tensile strength retention and FTIR analysis were carried out to observe the changes in properties of NRL films. Tensile strength retention was conducted according to ASTM D 412-92 using tensometer Universal Testing Machine (Model Instron 3366) with a crosshead speed of 500 mm/min and for biodegraded specimens which is determined using Equation 2:

\[
Tensile\ strength\ retention\ (%) = \frac{\tau_t}{\tau_o} \times 100
\]

(Equation 2)

where \(\tau_t\) and \(\tau_o\) are the tensile strength after biodegradation and the initial tensile strength, respectively.

3. Results and discussion

3.1 Weight Loss Measurement

Table 2 shows the comparison of weight loss percentages of NRL films with the addition of sago starch dispersions prepared through the ball milling method and alkali treatment, respectively. It was observed that the control NRL films showed the slow biodegradation process where only 20.9% of weight loss obtained after week 10 of the soil burial test.

| NR Latex films | Properties / weeks | 1 | 2 | 3 | 4 | 6 | 8 | 10 |
|---------------|--------------------|---|---|---|---|---|---|----|
| MSS           | Tensile Retention, %| >80| >80| >80| >80| 35| 20| 10 |
|               | Weight loss, %      | <5 | <5 | <5 | <5 | 7 | 18| 25.1|
| CSS           | Tensile Retention, %| >80| >80| >80| >80| 7 | 2 | 0  |
|               | Weight loss, %      | <5 | <5 | <5 | <5 | 20| 23| 38.6|

The MSS/NRL films showed comparable weight loss percentages to the unfilled NRL films up to week 4 of the soil burial test. After week 6 to week 10 exposed to soil environment, the MSS/NRL films showed the increment in weight loss percentages up to 25.1%. On the other hand, the CSS/NRL films showed a slight increase in weight loss percentages from week 1 to week 4 of soil burial compared to the control...
NRL films and MSS/ NRL films. The increased in weight loss percentages of CSS/ NRL films were observed after week 6 and became more significant after week 8 and week 10 (38.6%) of soil burial. The present of KOH could change the large particle size of starch granules into the gel network formation. More amorphous regions in the gel network exist compared to starch granules could assist the biodegradation process of CSS/NRL films. The polysaccharide structures in starch generally consist of hydrolysable linkages along the polymer chain which are susceptible to biodegradation by microorganisms and hydrolytic enzymes [5-7].

3.2 Morphological Analysis

The morphological analysis of MSS and CSS/NRL films upon soil burial test was given in Figure 1, respectively. There were insignificant effect on the surface of MSS/NRL films after exposed to soil environment from week 1 to week 3 as observed in Figure 1 (a.ii- iv) due to the low filler loading and the ability of high molecular weight polyisoprene chains to withstand the biodegradation. For MSS/NRL films, it was observed that small blisters were detected after week 4 of the soil burial test (Figure 1 a.v). The NRL film surface became brownish after week 6 (Figure 1 (a.vi)) before losing their structural integrity at week 8 (Figure 1 (a.vii)) of soil burial.

![Figure 1: The morphologies of (a) MSS/NRL films at (i) control week, (ii) week 1, (iii) week 2, (iv) week 3, (v) week 4, (vi) week 6, (vii) week 8, (viii) week 10 and (ix) SEM images, and (b) The morphologies of CSS/NRL films at (i) control week, (ii) week 1, (iii) week 2, (iv) week 3, (v) week 4, (vi) week 6, (vii) week 8, (viii) week 10 and (ix) SEM images.](image)

At week 10 of the soil burial test (Figure 1 (a.viii)), the dark patch with notable cracks were observed on the MSS/ NRL films. The employment of alkali dispersed NSS showed insignificant changes on the surface of NRL films after 2 weeks of soil burial test (Figure 1 (b.i-iii)). The appearance of yellow patches was observed on the CSS/NRL films at week 3 (Figure 1 (b.iv)) before becoming more significant after week 4 and week 6 of soil burial (Figure 1 (b.v-vi)). The development of yellow colour on the films indicating that the microorganism was able to initiate the rubber degradation and decrease the average molecular weight of polymer [8]. Small void was observed on the film surface at week 8 (Figure 1 (b.vii)) and developed into a larger void at week 10 (Figure 1 (b.viii)) of CSS/NRL films. The incorporation of polysaccharides in the films could influence the ability of amylolytic microorganisms to attach to the
surface of the film for the enzymatic hydrolysis process [9]. Figure 1 (a.ix)-(b.ix) show the SEM observations on the biodegraded surface of MSS and CSS/NRL films after 8 weeks of soil burial test, respectively. As observed in Figure 1 (a.ix), MSS/NRL films showed the appearance of a number of cracks and microvoids along with surface erosion of samples owing to biodegradation activities during the soil burial test. The addition of alkali dispersed NSS could promote major surface erosion and microvoids formation on the NRL films upon disposal in soil as shown in Figure 1 (b.ix). The presence of microorganism colonies also were detected on the surface of NRL films. The well dispersed of alkali dispersed NSS, including with the gel network formation which able to consume by microorganisms could assist further biodegradation of NRL films in soil.

3.3 Tensile Strength Retention

The effect of the soil burial test as a function of time on tensile strength retention of MSS and CSS/NRL is shown in Table 2. Both the control and MSS/NRL films exhibited deliberate reduction up to week 4 before it showed drastically decreased in tensile strength retention after week 6 of the soil burial test. Further exposure to soil environment caused the decreased in tensile strength retention of NRL films up to week 10. Overall, the MSS/NRL films showed more significant decreased in tensile strength retention compared to the control NRL films. The starch is metabolized first and acts as growth substrate for the microorganism so that the microorganism population rises, thus increase the rate of degradation of NR [8]. For CSS/NRL films, the tensile strength retained up to week 2 before decreasing after week 3 and week 4 of the soil burial test. At week 6 of soil burial, the tensile strength retention of CSS/NRL films was reduced remarkably, and became very weak after buried for week 8 and week 10. These results can be correlated with weight loss (Table 2) and morphological studies (Figure 1). As the microorganisms consumed the starch, the NRL lose their structural integrity which led to the deterioration of the strength of the polymer [10]. The voids formation also was expected to decline the tensile strength of the films upon soil burial.

3.4 Fourier Transform Analysis

The FTIR analysis before and after week 4 and week 8 of the soil burial test of sago starch filled NRL films are shown in Figure 2. The addition of MSS and CSS in NRL films exhibited the decreased in bands after week 4 as observed in the region of 3420-3250 cm⁻¹ which indicated the dehydration and depolymerisation of starch occurred upon composting. The MSS/NRL films showed an increase of the band in this region after week 8 of the soil burial test which attributed to the increased in biodegradation by-products. The significant increment of the band at 1641 cm⁻¹ for both MSS and CSS/NRL films were observed in the spectra, especially after exposed to soil environment for week 8 which corresponded to tightly bound water present in amorphous region of fillers. At longer period of soil burial, the decrement of transmittance peaks at 1442 cm⁻¹, 1375 cm⁻¹ and 875 cm⁻¹ were detected in the FTIR spectra of MSS and CSS/NRL films. These results were signified the reduction of C-H deformation as well as decreased in C-O-C stretch in glucosidic linkages of starch. Both types of NRL films also exhibited the appearance of a new peak at 1544 cm⁻¹ which was attributed to the present of amide groups after soil burial.
4. Conclusion
Results indicate that CSS filled NRL (CSS/NRL) films shows the highest weight loss percentage at 10 week of soil burial. Optical analysis shows that CSS/NRL film undergo rapid development of void at week 10 compared to ball milled sago starch filled NRL (MSS/NRL) films. Further observation on the morphology of both films by Scanning Electron Microscopy (SEM) shows that, the CSS/NRL film undergoes a severe degradation process at week 8. Tensile retention obtained indicate the rapid deterioration of CSS/NRL films compared to MSS/NRL at week 6. The reduction of C-H (wavenumber 1442 cm$^{-1}$) and C-O-C (wavenumber 1375 cm$^{-1}$) bond in both starch filled films were recorded via FTIR analysis. From the results obtained, CSS/NRL films are more feasible to degrade compared to MSS/NRL films.

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References
[1] Huang Z Q, Xie X L, Chen Y, Lu J P, and Tong Z F 2008 C R Chim 11 73
[2] Karim A A, Nadiha M Z, Chen F K, Phua Y P, Chui Y M, and Fazilah A 2008 Food Hydrocolloid 22 1044
[3] Han J A, and Lim S T, 2004 Carbohydr Polym 55 (2) 193
[4] Chuayjuljit S, Su-Uthai S, Tunwattanaseree C, Charuchinda S, 2009 J Reinf Plast Compos 28 1245
[5] Afiq M M, and Azura A R 2013 J Chem Chem Eng 7 137
[6] Abraham E, Pothen L A, and Thomas S 2012 European Conference on Composite Materials, Venice, Italy.
[7] Chandra R, Rustgi R, 1998 Prog Polym Sci 23 1273
[8] Watcharakul S, Umsakul K, Hodgson B, Chumeka W, and Tanrattanakul V, 2012 Electron J Biotechnol 15 (1) 1
[9] Imam S H, and Gould J M, 1990 Appl Environ Microb 56 872
[10] Shamala R, Hanafi I, and Yamuna M, 2014 J Vinyl Addit Technol 21(2) 128–133