

Mechanical and biodegradation properties of sago starch natural rubber latex composites

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ABSTRACT

The purpose of this research is to investigate the effect of sago starch loading on the mechanical and biodegradation properties of Natural Rubber Latex (NRL) composites. The sago starch loading for each composite was varied from 5 to 25 phr. Two methods of sago starch additions have been employed in this research. Method A is addition of fillers into the latex prior to pre-vulcanization process at 80°C and Method B is addition of fillers after maturation process followed by stirring process at room temperature for 2 hours. Biodegradation test was carried out by soil burial of NRL composites and withdrawn on weekly basis to investigate the properties of the NRL composites. The results reveal that the NRL composites showed an optimum tensile strength and tear strength at 10 phr sago starch loading. The mechanical properties decreased when increased the sago starch loading up to 25 phr due to formation of sago starch agglomeration in the NRL composites. The mechanical properties of NRL composites start to decrease after 2 weeks of soil burial. The biodegradation process was initiated through decomposition of the sago starch by microorganisms through formation of fines cavities which later act as degradation site for the composites.

KEYWORDS: composite, natural rubber, sago starch, mechanical properties, biodegradation

1. INTRODUCTION

Significantly of eco-friendly materials based on easily renewable natural resources, and the finite nature of petrochemical resources, have necessities for the development of polymers from agricultural processing by products such as soy protein, sago starch, tapioca starch etc. Two main reasons for the interest in natural based industrial products are environmental friendliness and legislation. Awareness about environmental issue has

forced the industries to look for eco-friendly materials based on naturally occurring renewable resources.

Sago starch is the powdery starch made from the processed pith found inside the trunk of the sago palm *Metroxylon sagu*. It is a raw material which is abundance in Malaysia [1]. The used of Sago starch is an attractive alternative in developing cheap degradable materials which are environmental friendly, biodegradable and once degrade, it is compostable. Chemically, sago starch is a polysaccharide that consists of repeating glucose units which made up from two major molecular structures; amylose and amylopectin [2]. These structures are responsible for bonding formation between latex molecular structure particles and hence contribute to latex-sago compatibility. When an aqueous suspension of starch is heated, the hydrogen bonds weaken, water is absorbed, and the starch granules swell. This process is commonly called *gelatinization*. This is a process that breaks down the intermolecular bond of starch in the presence of water and heat, allowing the hydrogen bonding sites to engage more water [3-4]. Sago starch exhibits a 2-stage swelling process in an aqueous medium which occurs at the gelatinization temperature about 70°C, while the second stage of swelling occurs at about 80°C [5].

Cooling of gelatinized starch resulted in the re-association of the leached amylose from gelatinized granules. This is the process is called starch retrogradation, referred as a reaction that takes place in gelatinized starch when the amylose and amylopectin chains realign themselves after being cooled at lower temperature for long enough periods. Consequently, the linear molecules, amylose, and linear parts of amylopectin molecules retrograded and rearranged themselves again to become more crystalline [6]. Amylose is much more susceptible to retrogradation and amylopectin is minimally involved in starch

retrogradation [7]. This re-association and re-crystallization of amylose causes release of the water absorbed and bound during gelatinization, leading to the phenomenon known as syneresis [8]. Still another change following gelatinization and caused by gelation may occur. The gel may lose water. If cooled undisturbed, the gels remain strong, yet reassociation may be accompanied by the unacceptable water loss or recognized as syneresis. Further association of amylose occurs and the gel contracts, causing both water loss and granule shrinkage to become apparent [9].

The aim of this work is to determine the optimum sago starch loading and biodegradation properties of NRL composites. The sago starch will enhance the biodegradability of the NRL films but still retain the properties required for the NRL products. Typically in latex composites processing, starch is incorporated into latex system before pre-vulcanization process and undergoes pre-vulcanization process at 80°C. However, in this study, starch was added into the latex system after pre-vulcanization and stirred at room temperature. Compatibility of these two different methods of sago starch addition and the effect of pre-vulcanization temperature towards latex composites were investigated.

2. EXPERIMENTAL

2.1 Preparation of pre-vulcanized NRL composites

Pre-vulcanized NRL composites were prepared by a dry coagulant dipping process and the formulation of NRL compounds used are shown in Table 1. All ingredients including the sago starch filler were mixed simultaneously before pre-vulcanization. The Compounds then subjected to pre-vulcanization process at 80°C and left at room temperature for 24 hours maturation process. After maturation process, the dipped NRL composites were prepared through dipped the cleaned Aluminum steel plates into 10% calcium nitrate solution for 17 seconds and then dried in an aired-oven at 100°C for 5 minutes. After that, the plates were dipped into the pre-vulcanized NRL compounds for 13 seconds followed by drying in the oven at 100°C for 1 hour. The dried NRL composites were allowed to cool at room temperature and then stripped from the plates and stored in refrigerator for further tests.

For different methods of addition of Sago starch for pre-vulcanized NRL films, the typical method has been improvised by adding the sago starch after latex compound being pre-vulcanized at 80° C and left at room temperature for 24 hours maturation process. Typical filler addition method was noted as Method A while improvised filler addition method was noted as Method B before the dipping process.

Table 1: Compounding formulation

Chemical	Dry weight , phr
61.0% NR latex	100
10.0 % Potassium Hydroxide	0.3
51.3% Sulfur	0.5
53.4% ZDEC	0.75
33.1% Zinc Oxide	0.25
52.2% Antioxidant	0.5
25% Sago Starch	5,10,15,20,25

2.2. Testing

Soil degradation was employed in this research. Soil was standardized by using similar type of soil filled into designated poly-bags which corresponded weeks of degradation period. One film of each starch loading from both Method A and B was grouped according to number of week. Grouped samples were buried within soil in stacking manner in ten different poly-bags and taken out from the soil on weekly basis. These withdrew films were leached to remove soil residues on the film before being dried at room temperature. The tensile test was carried out by using Instron Machine according to ASTM D412. The NRL composites were cut into dumbbell shapes before being subjected to the tensile test. The crosshead speed for the Instron tensile machine was set at 500 mm/min. Fourier Transform Infra-Red (FTIR) Analysis was used to recognize the functional group present in latex composites. Wave range of 400 cm⁻¹ to 4000 cm⁻¹ was selected to primarily monitor the changes in terms of its functional groups in the latex films buried for different time period. Scanning Electron Microscopy (SEM) type Zeiss SUPRA™ 35VP was employed to analyze the topography of the surface of the film. Samples were coated by a layer of gold palladium. These coated samples were then inserted into the microscope and images of the samples are taken at three magnifications, 100x, 500x and 1000x.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties NRL composites

In general, Figure 1 showed the tensile strength of latex composites at optimum filler loading based on different type of filler addition methods. Tensile strength of films processed by Method B showed higher value than Method A. In Figure 1, tensile strength for both methods during Week 0 is nearly equivalent. However, after 1 week of soil burial, tensile strength by Method A decreased dramatically, more than that of Method B. This lost in tensile properties depicted severe biodegradation process has taken place in composites processed by Method A. In biodegradation perspective, Method A offered faster biodegradation with decreased in strength offered by Method B. This result depicted the different

level of starch-latex system's cohesiveness. Low tensile properties of composites with filler added by Method A reflected poor interaction between starch and latex in the system and more likely to fail under tensile force. Composites with filler addition after pre-vulcanization showed higher tensile strength and hence hypothetically suggested a very cohesive latex-starch system due to effective interaction between filler and matrix.

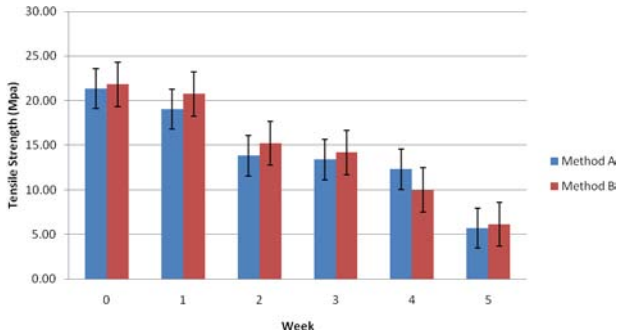


Figure 1: Tensile strength comparison between Method A and Method B

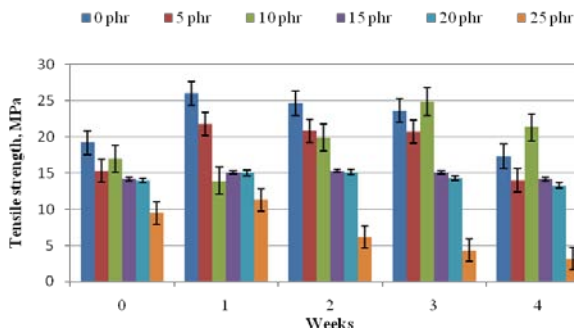


Figure 2: Tensile properties for the NRL films with different filler loading and biodegradation durations.

Figure 2 shows the tensile strength of the NRL composites for 5 different week of soil burial including control films. The test was done up to week 5 only due to a formation of pores and holes after week 5 on the surface of the composites which not applicable for further test. From the figure, highest tensile strength observed in Week 0 or by the control sample. For the control sample, there is no biodegradability has occurred. As week pass by during the soil burial, the tensile strength for all types of samples decrease gradually start from week 1 until week 5. The decreased in tensile strength is due to the biodegradation that take place during the soil burial process. The protein in the composites will react with various enzymes in the soil then lead to the pores and crack then result in decreased in tensile strength of the composites [10]. Also from the figure it is observed that the composites suffers most

from the biodegradation is the filler with the highest amount of sago starch. This phenomenon gives evident that degradation of films is accelerated with addition of sago starch as fillers in NRL composites [11].

3.2 Latex morphological analysis.

Figure 3 (a) clearly shows the gap between the starch and matrix and this suggest poor starch-matrix interaction while Figure 3 (b) shows no significant gap between starch and latex and hence give a cohesive starch-matrix interaction. To understand this, it is worth to understand the main difference of filler addition before and after pre-vulcanization process. The only difference that would have underpinned this appearance of gap was the temperature effect towards sago starch in latex compound.

For films with filler added by Method A during compounding, they have undergone pre-vulcanization process at 80°C which was higher than the gelatinization temperature for sago starches that ranged from 69.5 to 70.2°C. At high temperature, starch gelatinization has taken place. It is understood that sago starch exhibits a 2-stage swelling process. The first stage of swelling and solubility has occurred at the gelatinization temperature about 70°C, while the second stage of swelling occurs at 80°C [12]. This is merely a process that breaks down the intermolecular bond of starch in the presence of water and heat, allowing the hydrogen bonding sites to engage more water [3]. Penetration of water has increased randomness in the general structure and decreased the number and size of crystalline region. In other words, it is more amorphous at this gelatinized state.

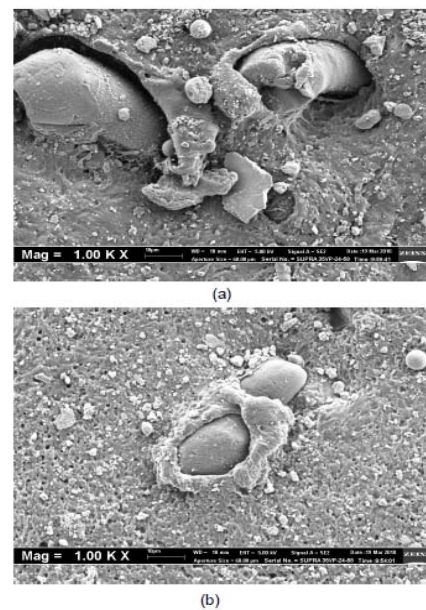


Figure 2: SEM images of starch particle in latex composites (a) Method A)while (b) Method B

3.3 Fourier Transform Infra-Red (FTIR) Spectroscopy Analysis

However, in terms of molecular structure, both methods show nearly no difference in that respect. This can be evident in Figure 4 and Table 2 lists the FTIR assignment of major peaks from the spectrum. This similar FTIR spectrum patten of the two filler addition methods advocates that there is no discrepancy in terms of molecular structure to cause the poor interaction between the starch and latex.

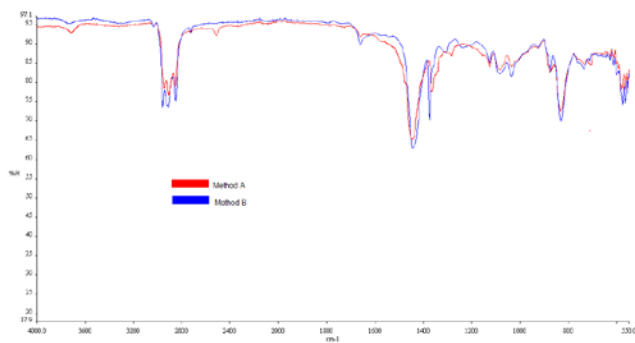


Figure 4: FTIR spectrum of NRL composites with different type of filler addition methods

Table 2: FTIR assignment of different type of filler addition methods

Wavenumber (cm ⁻¹)	Assignment
3700 – 3600	Alcohol –CH ₂ OH
3000 – 2815	Methyl Group – CH ₃
1645 – 1605	Vinyl Group –C=C-
1190 – 950	Carbon-Oxygen C-O

4. CONCLUSIONS

As the conclusions, incorporating natural fillers into NRL composites decreased the strength of the composites with a reversal effect upon the biodegradation feasibility. The studies confirm the significant effect of different filler loading towards the NRL composites on tensile strength and biodegradation properties. Overall, the optimum filler loading obtained was at 10 phr for sago starch fillers and further increased in their loading will lower the films physical/mechanical properties. This effect is merely due to the intensification of protein substances as the filler loading increased. The studies on the different filler addition methods concludes that, the effect of gelatinization, retrogradation and synerisis process plays an important role towards the composites strength and biodegradation properties. The studies also imply the significant effect of temperature, pressure, and molecular activities that may affect the NRL composites.

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