

Characteristics of Vulcanizate Rubber Using Composite Latex – Modified Cassava Starch as Filler

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ABSTRACT

The research on Characteristic of vulcanizate rubber using cassava starch composite (*Manihot glaziovii*) modification - latex as filler has been done. The composite variation of cassava starch concentration is 0, 40, 80, 120, 160 and 200 phr in three replications. Microstructure and elemental samples in SEM EDX and FTIR Spectroscopy method analysis, while physical properties using the standard testing equipment. The results showed that the concentration of cassava has a significant influence that is hardness, tensile strength, elongation at break, tear resistance and ozone resistance. The best rubber hardness specification was composite with modified cassava starch concentrations of 120, 160 and 200 phr with value 57, 61 and 65 Shore A. The best tensile strength of cassava starch concentration 80 and 120 phr with value 160 and 167 kg/cm², while the best result of the extension of cassava starch concentration elongation at break 80, 120, and 160 phr is 652, 741, and 748%, and tear resistance 80, 120, 160 and 200 phr with value 14.21, 15.96, 15.16 and 14.47. The ozone resistance for all concentrations meets the requirements of commercial vulcanizate rubber. The latex-modified cassava starch composite can be used as a filler for rubber products and as an alternative to commercial fillers.

Keywords: latex; modification; rubber; starch; vulcanizate

ABSTRAK

Telah dilakukan penelitian Karakteristik karet vulkanisat dengan menggunakan komposit pati ubi kayu (*Manihot glaziovii*) modifikasi- lateks sebagai bahan pengisi. Komposit dengan variasi konsentrasi pati ubi kayu 0, 40, 80, 120, 160 dan 200 phr dengan tiga kali ulangan. Struktur mikro dan sampel unsur dianalisis metoda SEM EDX dan FTIR Spectroscopy, sedangkan sifat fisik menggunakan peralatan pengujian standar. Hasil penelitian menunjukkan bahwa konsentrasi ubi kayu memiliki pengaruh yang signifikan yaitu kekerasan, tegangan putus, perpanjangan putus, ketahanan sobek dan ketahanan ozon. Spesifikasi kekerasan karet terbaik komposit dengan konsentrasi pati singkong yang dimodifikasi sebesar 120, 160 dan 200 phr dengan nilai 57, 61 dan 65 Shore A. Tegangan putus terbaik konsentrasi pati singkong 80 dan 120 phr dengan nilai 160 dan 167 kg/cm², sedangkan hasil terbaik perpanjangan putus konsentrasi pati singkong 80, 120 dan 160 phr adalah 652, 741 dan 748%, dan ketahanan sobek 80, 120, 160 dan 200 phr dengan nilai 14,21, 15,96, 15,16 dan 14,47 kg/cm. Ketahanan ozon untuk semua konsentarsi memenuhi persyaratan karet vulkanisat komersial. Komposit pati ubi kayu modifikasi-lateks dapat digunakan sebagai pengisi untuk produk karet dan sebagai alternatif bahan pengisi komersial.

Kata Kunci: lateks; modifikasi; karet; pati; vulkanisat

INTRODUCTION

Natural rubber is a renewable product of nature, has resilience, elasticity, adhesion, heat power and heat build-up is low compared to synthetic rubber. However, natural rubber is much more expensive than starch. Composite starch and natural rubber will be an alternative material to reduce the use of natural rubber in large quantities. On the one hand this plays mainly to

lower the material cost by reducing the use of natural latex and on the other hand, due to special properties of those materials to improve the chemical and mechanical properties of the rubber product. Today, carbon black is predominantly used as filler in the production of vulcanizate rubber for improving its performance and strength. But it has drawback to harm the environment due to CO₂ emission and its availability depends on non-renewable sources such as

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petroleum and natural gas. Many studies related to the use of natural materials as filler material had been carried out such as starch [1-7], silica [8-11], cellulose [12], and coconut shell [13-14]. Silica is efficient for reinforcing silicon rubber but not for other elastomers such as latex based rubber [15].

Starch is seen as a prospective alternative as filler in the making of rubber goods. Starch is the main polysaccharide used by the plant to store energy. Starch is widely found in seeds, roots, and tubers as well as in branch, leave, fruit and pollen. Starch is a renewable natural polymer that can decompose easily in the environment and can be modified to various applications [16]. So that it the advantage to be used as biodegradable filler material in rubber industry [17]. Therefore starch from rubber cassava can be used as alternative filler for developing cheap and environmentally friendly biodegradable rubber material. However, starch has some disadvantages for application as rubber filler such as having big particle size is 5 until 20 μm , strong pole surface, high cohesion energy and vulnerable to high temperature [18]. But these disadvantages can be solved by chemical modification of starch to produce polymer mixture that capable to improve the characteristics of starch and latex composite.

Modified cassava starch can be recognized as potential substitution of carbon black, silica and other conventional filler in latex. Modified cassava starch will produce starches with increased stability, resistant to high temperatures. The -OH group on the amylose or amylopectin structure can crosslink form or bridges that is connecting a starch molecule with a rubber molecule so that it can connect a crosslinked or isoprene matrix network with amylose/amylopectin [19-20], this matter, will increase the characteristics of rubber products. Additionally, rubber cassava plant is widely available in Indonesia and classified as non-edible so that its utilization has no competition with human food.

In this work, a composite of natural rubber and cassava starch as filler was produced aiming to improve physical properties such as strength and durability of natural rubber. Characterization technique using electron microscopy and diffraction technique was used to reveal the microstructure and chemical composition of the samples down to microscopic scale.

EXPERIMENTAL SECTION

Materials

Raw materials is used in this research were latex a kind of natural rubber produced in Indonesia, Cassava starch was obtained from local store in Palembang, NaOH, (p.a.), H_2O_2 (p.a.), acetic acid (p.a.), carbon

bisulfide (p.a.), were obtained from E. Merck, German, minarex oil, sulfur, ZnO, stearic acid, coumarone resin, 1,3-Dimethylbutyl-N-phenyl-p-phenylenediamine (6PPD), Mercaptodithiobenzothiazol (MBTS), Tetramethyl thiuram disulfide (TMTD). Chemicals were the commercial grades without treatment.

Instrumentation

The equipment used in this experiment were Two roll mill L 40 cm D18 cm capacity 2 kg, hot press apparatus, analytical balance (Mettler p1210, 1200 g capacity), sheet mold and glassware.

Hardness, tensile strength, tear resistant, and elongation at break was tested using Tensometer Loyd 2000R to measure the physical properties. Standard hardness tester Durometer Shore Type A (ASTM D.2240-1997) was used to observe the sample hardness. Chemical properties were measured using Toyoseki Ozon Testing device to study their ozone ageing characteristic (ASTM D.1149-1991).

The microstructure and elemental composition of the sample cross-sections were characterized using SEM equipped with Energy Dispersive X-ray Spectrometer (EDX). SEM operation used constant electron beam energy 20 keV without sample coating. The problem of electron charging was solved by using low vacuum mode at 70 torr, which allows SEM operation for non-conductive materials without coating heavy elements such as gold or platinum. The presence of gold and platinum can disturb especially the result of elemental composition measurement by EDX. The energy range of the EDX measurement was set between 0 and 20 keV to include the possible existence of high energetic X-ray from heavy elements in the samples. However, because of Barium window applied to protect EDX detector for bombardments of excess high energetic electrons or X-ray the EDX-spectrum cannot include light elements with the atom number below Barium. But there is not a problem because in this work no light elements involved.

Fourier Transform Infrared Spectroscopy (FTIR) was also used to analyze the phase occur after the process. FTIR is recognized to have higher wavelength resolution in analyzing organic materials but the lateral resolution, however, is much lower than those of EDX. FTIR measurement was performed in transmission mode at room temperature. The spectrals were aquired at wavenumbers of 4000-500 cm^{-1} .

Procedure

Modification of cassava starch

The cassava starch powder had to be modified before using for production of the composite. Modifying

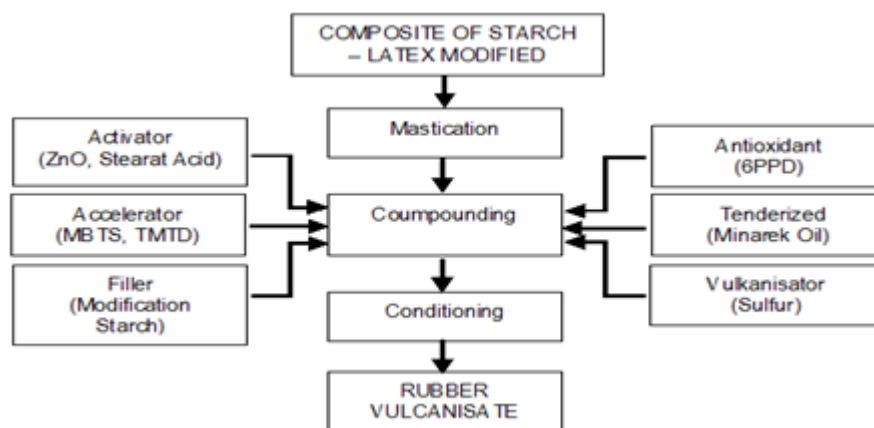


Fig 1. Processing steps of vulcanizate rubber development

of cassava starch follows the steps of the process steps 162 g cassava starch powder was dissolved in 2400 mL of distilled water and mixed thoroughly using mechanical stirring until it turned to paste. 100 mL of sodium hydroxide with a concentration of 5 mol/L was then added into the starch paste, while kept stirring for 30 min. After that, 12 mL carbon bisulfide was poured into the mixture under stronger stirring for 1 h, and subsequently, 17 mL of hydrogen peroxide 0.5 mol/L was added.

Production of starch - natural latex composite and compound

Modified cassava starch with concentration 0, 40, 80, 120, 160 and 200 phr was poured into the latex and stirred vigorously for 30 min. The acetic acid was added to form coagulation between the latex and starch. After being washed for several times by water, the coagulum was dried in an oven at 75 °C for 1 h to obtain cassava starch - latex blends or composite [12]. The next step is the mastication of cassava starch and latex composite for 1 to 3 min in an open mill. The further process was vulcanization by mixing of the composite with the rubber chemical additions such as activator ZnO and stearate acid followed by three times cutting at each side for 2 to 3 min.

Furthermore, MBTS and TMTD accelerators were added, and each side is cut two or three times for 1 to 3 min. The next step was the addition of antioxidant 6PPD, and each side was cut three times for 2 to 3 min. Then, softener of minarek oil was added, and each side is cut two or three times for 3 to 8 min. Vulkanisator of sulfur was mixed and milled for 2 to 3 min. Vulcanizate rubber was taken out from the open roll mill, and its thickness was adjusted by rolling in the sheet molder. The final product was then placed in a transparent plastics and cut according to the required size.

Raw materials used in this research were natural rubber latex, and starch powder filler important pre-work

Table 1. Material composition of cassava starch-latex compound

Materials	Formulation (phr, part hundred rubber)
Composite of starch-latex modified	100
Tapioca starch	0, 40, 80, 120, 160, 200
Stearic acid	2
ZnO	5
6PPD	1
Minarex oil	2
TMTD	0.5
MBTS	1.5
TMQ	1
Sulfur	2

was the process of cassava starch modification followed by blending with natural latex to form a composite material. Procedure for the synthesis of vulcanizate rubber or compound followed the flow chart as shown in Fig. 1. After that, rubber compound was then produced in the beginning, mastication process of the cassava-latex composite, compounding, and conditioning. During compounding process, supporting materials were added. Their specification and content are shown in Fig. 1.

RESULT AND DISCUSSION

SEM EDX Analysis

In Fig. 2(a) SEM image of modified cassava starch in low vacuum mode is shown. The image was taken using the backscattered detector to highlights the Z-contrast feature of the particles in the carbon double tip background. From the image, it is obvious that the cassava starch particles has typical granular shape about 5 μm in size. As indicated from the EDX spectrum the elemental composition of cassava starch grains after modification is completely preserve. It can be

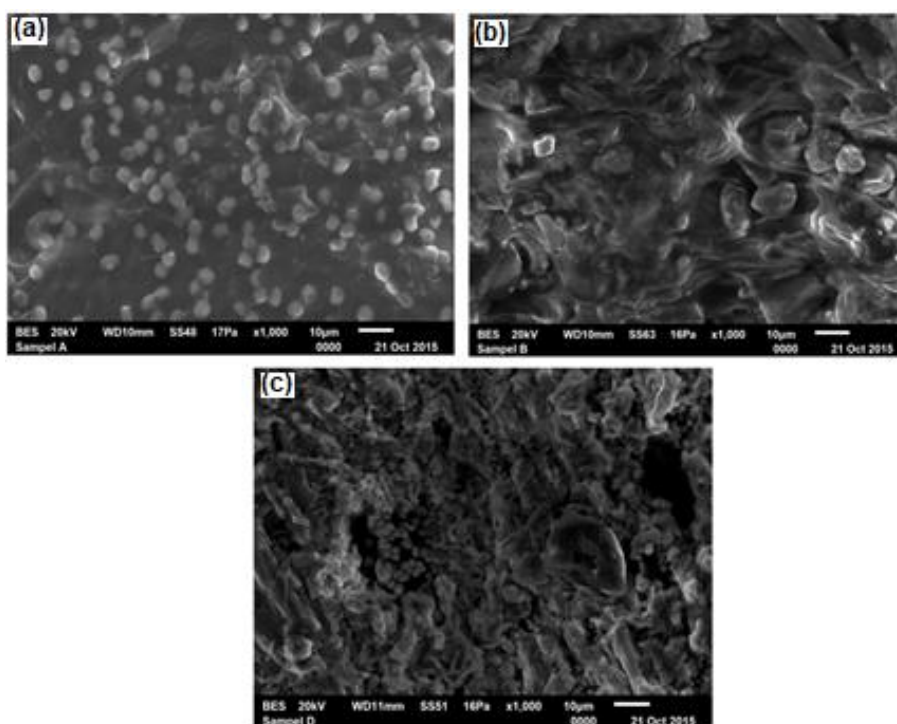


Fig 2. SEM image of (a) modified cassava starch, (b) composite starch modified - latex and (c) commercial vulcanizate rubber

Table 2. Elements content SEM-EDX results

Element (%)	Modified cassava starch	Composite starch modified latex.	commercial vulcanizate rubber compound
C	90.11	70.97	49.69
O	9.45	9.82	22.01
S	0.44	-	-
Si	-	2.66	-
Ca	-	1.67	-
Cr	-	1.87	-
Fe	-	12.60	-
Ti	-	4.69	-
Zn	-	-	17.91
Mo	-	-	10.28

assumed that the modification only change the properties, not the original composition of the starch.

After mixing and blending the cross-sectional appearance of all of the rubber compound samples are quite homogen as shown in Fig. 3 in case of the compound with cassava starch concentration 80 phr. Generally the compound exhibits typical irregular morphology while the phase distribution quite homogen. The low Z-contrast generated by the acquisition with backscattered electron indicates the homogeneity of phases occur which means that the compound mixing was very effective. The cassava starch particles were mixed with the latex homogenously so that no individual starch particles can be clearly identified.

The final overall composition of the compound, except typical organic element C and O, consists of Si, Ca, Cr, Fe and Ti, some very small particles which contain Ca and Fe was found, as obviously in EDX on the position as indicated by the arrow in Table 2. EDX in the position as shown in the Fig. 2(b) SEM-EDX results obtained elements content in Table 2.

As a comparison, in Fig. 2(c) sample of commercially available latex compound taken by SEM is presented. In contrast to the sample produced in this study, the sample of commercial vulcanizate is more irregular and grainy. The sample grains are clearly seen separated to each other, and some particles seem to bound loser to the latex matrix which is an

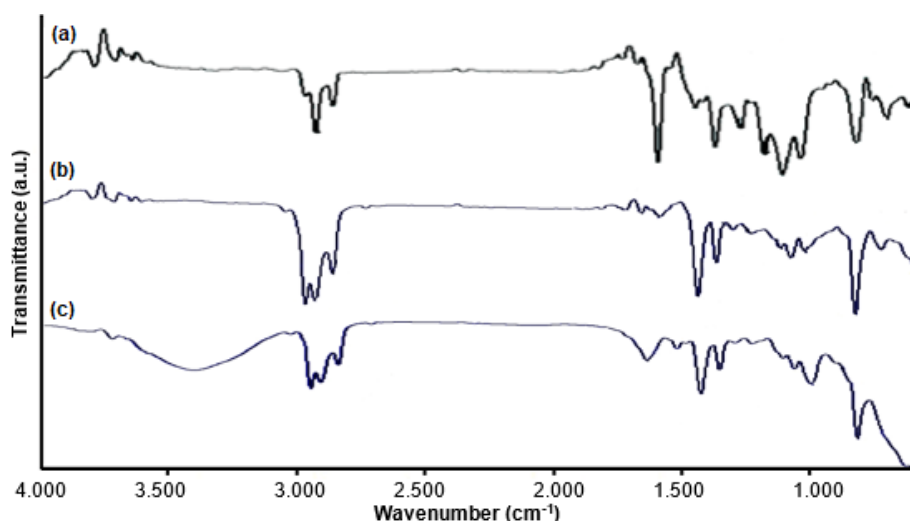


Fig 3. FTIR spectrum of (a) modified cassava starch, (b) composite starch modified - latex and (c) commercial vulcanizate rubber

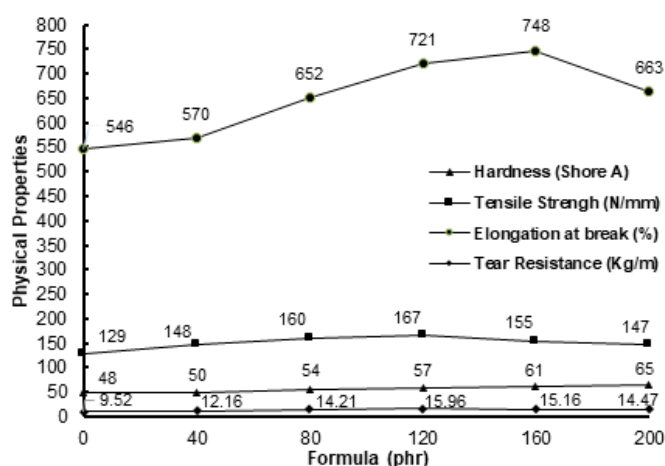


Fig 4. Physical properties vulcanizate rubber

Table 3. Ozone resistance of rubber vulcanizate

Cassava starch	Ozone resistance
0	No crack
40	No crack
80	No crack
120	No crack
160	No crack
200	No crack

indication that the blending not homogenous. EDX analysis reveals the composition of the commercial compound sample are mainly consist of C, O, Zn and Mo.

FTIR Analysis

The results of FTIR measurement on both vulcanizate and modified cassava starch samples (Fig. 3) show that the cassava starch well form quite a

homogenous composite as one can see on the correspondent peaks in the "fingerprint" region between 1500 and 500 cm^{-1} .

As also shown in Fig. 3(a), the FTIR spectra showed strong bands from the cassava starch but weaker bands from the rubber vulcanizate in the range of 3000–2700 cm^{-1} which means after compounding, this is an indication to the slight difference in asymmetric and symmetric stretching frequency of the C-H groups (C-CH₃ and -CH₂-). The presence of the strong double bonds of C=C groups observed in the 1800–1600 cm^{-1} region for vulcanizate may be due to reaction with C=S from cassava starch polymeric chain which is obviously in the spectrum in Fig. 3(b).

FTIR frequency spectrum of commercial vulcanizate rubber in Fig. 3(c) shows relevancy with those from in this work produced vulcanizate. However, the absent of strong bands in the 1129–1090 cm^{-1} region in the commercial vulcanizate may be caused by the absent of C-O bonds of cassava starch.

The Physical Properties

The results of the physical testing on vulcanizate rubber are summarized in Fig. 4 and Table 3. The concentration of cassava starch was found to have a significant impact on the physical properties of the composites.

The explanation of Fig. 4 and Table 3 is the compounding process resulted in the best physical properties of the vulcanizate rubber with starch concentration 80, 120 and 160 phr. The assessment of the results was based on the data taken from the commercial vulcanizate which the mechanical hardness ranges between 55–75 Shore A, the tensile

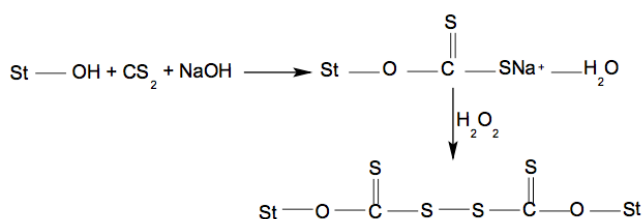


Fig 5. Bonding formation C=S [23]

strength 160–170 kg/cm², the elongation at break 650–750% and the tear resistance 14–15 kg/cm. The Addition of starch increases linearly for hardness, while tensile strength, elongation at break and tear resistance will be optimum at a certain concentration. The resistance of vulcanizate to ozone is quite good independently on the starch content. No visual observable cracks occur at a temperature of 108 °C over a period of 48 h. Starch contains high magnitude of hydroxyl cluster [21]. Hydroxyl cluster reacts with rubber molecules to form hydrogen bonding. These two elements have strong surface bonding increasing tensile strength. On the other hand, there may be main chain movement of rubber polymer after addition of starch polymer. Modification of starch with esterification tends to form C=S as a bonding within starch molecules that will act as cross nuclei and resulting in an increase of composite cross bonding density during vulcanization process. However, crosslinking increases will make saturation of the rubber molecules so that the vulcanizate will easily break [17–22], this can be seen in Table 3, the starch concentration of 200 phr, tensile strength, elongation at break and tear resistance of the decrease vulcanizate. Formation mechanisms of C=S bonding can be seen in Fig. 5. The C=S bond reacts with the carbon bond (C=C) to form a starch modified composite so that the physical properties of the rubber compound become strong, Fig. 6.

Composite of modified starch and natural latex has strong crosslinks that protect vulcanizate rubber from damage caused by oxygen, ozone, and sunlight. As stated in some study, the hardness of vulcanizate rubber can be strongly affected by the kind of filler and content properties such as quantity, particle size and molecular structure [14–24]. Small particle size will produce higher porosity in cassava starch particles increasing surface area. Higher concentration of modified starch will increase its interaction capability with rubber molecules which in turn produce stiffer and harder compound.

CONCLUSION

The composite of modified cassava starch – latex had a significant effect on vulcanizate rubber characteristics covering of microstructure and physical properties. The vulcanizate rubber showed quite homogenous morphology, and phase appearance

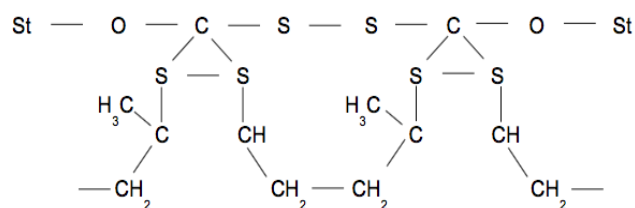


Fig 6. Composite of starch-modified latex

compared to the commercial one. The best treatments which fulfill rubber vulcanizate specification according to quality standard of commercial rubber vulcanizate were modified starch-latex composite concentrations of 120, 160 and 200 phr with hardness values of 57, 61 and 65 Shore A. The best treatments for tensile strength were modified starch-latex composite concentrations of 80 and 120 phr with tensile strength values of 160 and 167 kg/cm². The best treatments for elongation at break were modified starch-latex composite concentrations of 80, 120 and 160 phr with an elongation at break values of 652, 741 and 748%. The best treatments for tear resistance were modified starch-latex composite concentrations of 80, 120, 160 and up to 200 phr with tear resistance values of 14.21, 15.96, 15.16 and 14.47 kg/cm. Ozone resistance for all treatments had fulfilled the requirement of the commercial vulcanizate rubber quality standard.

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