The Effect of Recorcinol-Formaldehyde (RF) Loading as Coupling Agent on The Physical Properties and Curing Characteristics of Starch/Natural Rubber Composite

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Abstract. Starch/natural rubber (NR) composite was prepared by co-coagulating natural rubber latex and starch paste. The purpose of this research is to investigate the effect of resorcinol-formaldehyde (RF) loading as coupling agent on the properties of starch/natural rubber composite. The resorcinol-formaldehyde was loaded for each composite varied from 2 to 10% by starch mass. Technical specification of rubber, curing characteristics of rubber compound, and physical properties of vulcanizate were conducted to evaluate the properties of starch/natural rubber composite. The results revealed that an optimum raw rubber properties and tensile strength of vulcanizate at 10% by starch mass of resorcinol-formaldehyde loading and the curing characteristics of rubber was also affected by the addition of resorcinol-formaldehyde.

Keywords : composite; natural rubber; starch; coupling agent

Introduction

Carbon black is the most widely used filler in elastomeric substance, especially in the tyre industry. It can change elastomer properties in different ways and extents depending on the loading of the carbon black on the elastomeric matrix, but in recent years many researchers are attempted to replace carbon black because it pollutes environment and depends on the non-renewable source of petroleum and natural gas. Beside that, rubber composites used for the tread of “green” tyre have attracted increasing interest in recent years [1]. This is mainly due to the fact that energy consumption and carbon dioxide emission from automobiles have become a serious threat to environment [1].

The other filler have been extensively studied to replace carbon black filler were silica, clay, and starch [3]. Starch is great potential to substitute carbon black filler due to its limitless source and friendly environmental processing and has many advantages, such as low cost, abundant supply and environmental amity. Novamont (Navara, Italy), working in partnership with Goodyear Tire and Rubber, has developed tires using nanoparticles derived from corn starch, partially was replacing the conventional carbon black and silica used in making tire in order to reduce tire weight and simultaneously decrease the energy consumption in the production processes [1,4,5]. This patented innovation, called BioTRED, presents environment advantages but also allow reducing the rolling resistance of tires. In this approach, Angellier *et.al* [5] was studied nanocomposite materials that were obtained using a latex of natural rubber as the matrix and an aqueous suspension of waxy maize starch nanocrystals as the reinforcing phase.

The use of starch in rubber compounds could probably open a new application area of starch-filled rubber composite. However, starch has many hydroxyl groups on its molecular structure and extremely polar and it causes low interaction with non-polar rubber, such as styrene-butadiene rubber (SBR) and natural rubber (NR). This case due to many attemptions to study the starch modification for increasing interaction and adhesion between starch and non-polar rubber by using coupling agent. Wu *et.al* [6] have been studied starch modification by resorcinol-formaldehyde (RF) and *N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane (KH792) as coupling agent in preparing starch/styre-butadiene rubber (SBR) composite.

In this research, the effect of resorcinol-formaldehyde (RF) loading as coupling agent on the properties of starch/natural rubber composite was studied. The resorcinol-formaldehyde loading for each composite varied from 2 to 10% by starch mass. Technical specification of rubber, curing characteristics of rubber compound and physical properties of vulcanizate were conducted to evaluate the properties of starch/natural rubber composite.

Experimental

Materials

Field natural rubber latex was originated from rubber plantation of PT Riset Perkebunan Nusantara; cassava starch in technical grade was purchased from CV Tirta Kencana; recorcinol; formaldehyde; NaOH; formic acid and other compounding agent were commercially available in technical grade.

Preparation of in situ modified starch paste and starch/NR composite

About 10% of starch aqueous suspension was stirred at 90^{o}C on hot plate for 30 min until the solution became transparent and the starch paste was obtained. Then the base-catalyzed recorcinol and formaldehyde (RF) solution (pH 10) with a mole ratio of formaldehyde to recorcinol as 3 :1 was prepared and added into the starch paste instantly. In this research, the resorcinol-formaldehyde solution added into the starch with variation of 2 to 10% by starch mass. Then the mixture was stirred at 70^{o}C on hot plate for another 10 min and the RF-modified starch paste was obtained. This hot RF-modified starch paste was mixed with NR latex (25% on dry rubber content) and stirred for 7 h, and then about 5 wt.% formic acid was used to co-coagulate the rubber latex and starch paste. Afterwards, the coagulum was creped, then dried in oven at 70^{o}C for 3 h until about 2% moisture content was reached. The creped rubber containing starch was named starch/NR composite.

Testing of Raw Rubber

Initial Plasticity (Po), Plasticity Retention Index (PRI), Accelarated Storage Hardening Test (ASHT), ash content, and volatile matter content were determined to evaluate the properties of starch/NR composite as raw rubber material. Testing of Initial Plasticity (Po) and Plasticity Retention Index (PRI) were conducted according to ISO 2007 and 2930 respectively. Whereas the determination of ash content, volatile matter content, and ASHT were carried out according to ISO 247; ISO 248-1; and SMR Bulletin No.7, C1 respectively.

Preparation of rubber compounds

Each of the starch/NR composite samples, which contained resorcinol-formaldehyde (RF) from 2 to 10% by starch mass, and rubber chemicals were compounded according to the ACS 1 compound recipe (Rubber, 100 parts; ZnO, 6 parts; stearic acid, 0.5 parts; MBT (Mercaptobenzothiazole), 0.5 parts; sulphur, 3.5 parts). The mixing procedure was given in ASTM D3184-06. The mixing process was done on a laboratory by two-roll mill to prepare the rubber compound.

Determination of curing characteristics and physical testing

The sheeted rubber compound was conditioned at room temperature for 24 h before cure assessment. Curing characteristics were studied using a Monsato Moving Die Rheometer (MDR 2000) according to ASTM D2240-93. About 4 g samples of the respective compounds were used to test at vulcanization temperature (145^{o}C). The respective scorch time (t_{s2}) and optimum cure time (t_{90}) were obtained from MDR 2000 at 145^{o}C. The maximum and minimum torque were also determined from the rheograph.

The curing of the test pieces was done by compression moulding in electric heater, hydraulically operated press by 150 kg/cm^2 pressure at 150^{o}C. The cure times were predicted by the rheographs, which used as guide to obtain vulcanizates for the test specimens [7]. The tensile properties (tensile strength, 300% modulus, and elongation at break) of the starch/NR vulcanizates obtained were determined using LLOYD 2000R, tensile tester at cross speed of 500 mm/min. Dumb-bell test specimens of dimension (45x5x2mm) were used as described in ASTM D412. The specific gravity (S.G) and hardness of the test pieces were measured too.

Results and Discussion

Raw Rubber Properties

The effect of resorcinol-formaldehyde (RF) loading as coupling agent on the raw rubber properties of starch/natural rubber composite is shown in Table 1. It shows that the RF loading could alter the raw rubber properties, especially on the ash content, Po, PRI and ASHT.

In this research, cassava starch was used as a filler in rubber matrix. It was known that starch has many hydroxyl groups on its molecular structure, which due to low interaction between starch and natural rubber (NR). On the other hand, the purpose of this research was to study the effect of resorcinol-formaldehyde (RF) loading level as coupling agent on the starch/natural rubber composite properties, such as: raw rubber properties, curing characteristics and physical properties of vulcanizate.

The raw rubber properties observed in this research were the ash content, volatile matter content, Po, PRI, and ASHT. The addition of starch and RF were in the natural rubber latex to prepare starch/NR composite due to present non-rubber constituents in the natural rubber matrix. That was affected on the raw rubber properties, especially the ash content, Po, PRI and ASHT as presented in Table 1. The test result of ash content (see in Table 1.) shows that the increasing of RF loading hence the decreasing of ash content. Starch and RF are organic constituent in the natural rubber matrix and these due to decrease ash content because an addition of starch and RF could increase amount of organic constituent in the sample.

The effect of RF loading on plasticity and PRI was given in Table 1. The plasticity of starch/NR composite decreased until the addition of 4% starch mass of RF loading and increased at the addition of 6 up to 10% starch mass of RF loading. The phenomenon of decreasing plasticity could be attributed to the stress softening effect [10] of starch on the NR and level of RF loading attributed the increased plasticity due to toughened effect [11] of resinous material. The PRI was given to measure the oxidative resistance of NR. It was found that the decreasing of PRI value until the addition of 8% by starch mass of RF loading and at 10% of this addition could be increased of PRI value. When natural rubber matrix was contained with Recorsinol-Formaldehyde, it could be increased PRI value attributed to antioxidant effect of RF which contained subtitued phenolic on its molecular stucture. But in contrast, the PRI value on the test result was decreasing, which indicated that starch and NR were oxidized.

The hardening of natural rubber under the condition of the accelerated storage hardening test (ASHT) was expected due to the reaction of non-rubber constituents of latex with the rubber molecules to gel formation. Sekhar [8] has shown that the phenomenon of storage hardening can be satisfactorily explained if it is assumed that carbonyl groups, probably aldehydic, are present in the rubber molecule. In the test result of ASHT (Table 1.) showed that starch and RF that presented in the rubber matrix could be decreased ASHT value. This phenomenon could be attributed to the hygroscopic effect of starch and RF which contained hydroxyl groups on its molecular structure. On the ASHT, water is removed from the rubber, with a drying agent such as phosphorus pentaoxide, protein and phospholipids at the terminal of rubber chain may have a chance to form branching point by hydrogen bonding and gel fraction form. Futhermore, starch and RF that presented in the rubber matrix causing difficulties to remove water from the rubber and it is due to prevention to form the gel fraction.

In this research, volatile matter content was also determined to study the effect of starch and RF as non rubber constituent on the processing of raw rubber, especially on the drying process phenomenon. It was known that starch and resorcinol-formaldehyde have many hydroxyl groups on its molecular structure, which increase the interaction of water molecule. It is consequently due to the drying process of raw rubber needs more time. As the test result is shown on the Table 1, the volatile-matter content of starch/NR composite with the adding of 8 and 10% starch mass of RF shows this phenomenon.

Table 1. Raw rubber properties of starch/NR composite by different resorcinol-formaldehyde (RF) loading as coupling agent.

No.	Samples	Test results				
		Ash content (%)	Volatile matter content (%)	P_o	PRI	ASHT
1.	Control (NR)	0.42	1.15	62.5	78.4	32.0
2.	2 % RF	0.11	0.77	59.0	66.9	26.5
3.	4 % RF	0.11	0.85	62.0	68.5	14.5
4.	6% RF	0.09	0.14	64.5	65.1	20.0
5.	8 % RF	0.09	2.07	64.0	67.2	29.5
6.	10 % RF	0.15	1.38	70.5	81.6	10.5

Curing Characteristics

Table 2 shows the curing characteristics of starch/NR composite using different resorcinol-formaldehyde (RF) loading as coupling agent which mixed with the rubber chemical in two-roll open mill to process rubber compound. These characteristics are important because they affect the success of all basic steps in the manufacturing process, which used to convert raw rubber into final usable products [7]. The measured parameter on the curing of rubber compound are minimum torque (M_L), maximum torque (M_H), difference of max and min torque (ΔM), scorch time (t_{S2}), and optimum cure time (t_{90}). It was known that curing characteristics influenced on materials in the rubber compound recipe. Based on the test result of curing characteristics which is shown Table 2, as the RF loading increased, the time needed for optimum cure (t_{90}) and scorch (t_{S2}) decreased. When the test result was compared with control, the rubber compound contained starch and RF, the time needed for optimum cure (t_{90}) was increased. This phenomena showed that starch was indicated as acidic material, which may react with the basic ingredients, especially accelerator, which present in the rubber compound and in turn reduce the cure rate [12,13].

The minimum torque (M_L), maximum torque (M_H), and difference of max and min torque (ΔM) are affected by RF loading and the value of these rheological behavior increased relatively small with an increase in RF loading up to 10% by starch mass as shown in Table 2. The minimum torque in a rheograph measures the viscosity of the rubber compound. It can be considered as the measure of the stiffness of the unvulcanized compoud [7]. The maximum torque is generally indicated with the modulus of the vulcanizate, and crosslink density of the vulcanizate correlated with the difference of max and min torque (ΔM) [7].

Table 2. Curing characteristics of starch/NR composite by different resorcinol-formaldehyde (RF) loading as coupling agent.

No.	Samples	Test results				
		M_L (kg-cm)	M_H (kg-cm)	ΔM (kg-cm)	t_{90} (min.s)	t_{S2} (min.s)
1.	Control (NR)	0.28	4.10	3.82	17.11	6.07
2.	2 % RF	0.42	4.98	4.56	21.42	7.26
3.	4 % RF	0.52	5.32	4.80	21.17	6.40
4.	6 % RF	0.52	5.32	4.80	20.04	6.22
5.	8 % RF	0.39	5.31	4.92	16.24	4.42
6.	10 % RF	0.40	5.15	4.75	17.11	5.31

Physical Properties of Vulcanizate

The physical properties of vulcanized rubber are given in Table 3. Physical properties of vulcanizate (hardness, tensile strength, 300% modulus, elongation at break and density) was affected by starch as filler in rubber composite and RF loading as coupling agent. The test result of hardness, tensile strength, and 300% modulus of starch/NR compound showed that the improvement was due to the contribution of starch as filler and effectiveness of RF as coupling agent for the increasing of rubber-filler interaction, even for the RF loading as 10% by starch mass has the highest tensile stregth than the others. It shows that resorcinol-formaldehyde as coupling agent was effective to increase the natural rubber-starch interaction. On the other hand, elongation at breaks of starch/NR composite decrease gradually with the increasing of RF loading up to 8% by starch mass. This indicated that the incorporation of starch in rubber matrix by adding RF as coupling agent reduce the mobility of the macromelecular chains of the rubber and consequently increases the rubber stiffness [14]. It hence resistance to stretch when the stain is applied, resulting in the decreasing of elongation at breaks of vulcanizate.

The relationship between specific gravity and the loading level of RF is shown in Table 3. Specific gravity is a measure of the density of a material compared to water. From this table, it can be seen that the specific gravity show decreasing with the loading level of RF. This is because of the void filling [15] by starch and RF. Starch and RF have specific gravity lower than natural rubber, this makes low dense per unit volume of rubber composite.

Table 3. Physical properties of starch/NR composite by different resorcinol-formaldehyde (RF) loading as coupling agent.

Physical Properties	Test results					
	Control	2% RF	4% RF	6% RF	8% RF	10% RF
Hardness, Shore A	32	37	38	37	38	37
Tensile Stength, N/mm^2	14.2	20.1	17.1	17.3	17.9	27.4
300% Modulus, N/mm^2	1.5	2.4	2.5	2.8	2.5	2.6
Elongation at break, %	760	720	670	670	680	760
Specific gravity, g/cm^3	1.007	1.002	1.004	0.996	0.997	0.986

Conclusion

Starch/natural rubber (NR) composite was prepared by co-coagulating natural rubber latex and starch paste with different resorcinol-formaldehyde (RF) loading level as coupling agent. The results revealed that the starch/natural rubber composite showed an optimum raw rubber properties and tensile strength of vulcanizate at 10% by starch mass of resorcinol-formaldehyde loading and the curing characteristics of rubber was also affected by the addition of resorcinol-formaldehyde. The addition of resorcinol-formaldehyde (RF) as coupling agent in preparation starch/natural rubber composite could increase natural rubber-starch interaction.

Acknowledgements

The author wishes to express his appreciation for the encouragement and helpful support to carry out extensive experiment to Indonesian Rubber Research Institute and to Dr. Suharto Honggokusumo.

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