Optimization of The Vulcanization Formula Of Pneumatic Rubber Fender (PRF) to Increase Resistance to The Aging Process

Optimasi Formula Vulkanisasi Pneumatic Fender Karet (PRF) untuk Meningkatkan Ketahanan Terhadap Proses Penuaan

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Abstract

Pneumatic rubber fender (PRF), one of the rubber products, is fully imported, where the raw material is made primarily by synthetic rubber. PRF products have been used in the transportation sector as the impact protection of ports and ships. In this study, the mixture between natural and synthetic rubber conducted to determine the optimum formula of mixing rubber for PRF. The PRF-product was then subjected to Aging Resistance Test (ART). Physical and mechanical properties of the PRF were analyzed by tensile strength test, elongation at break test, tear resistance test, hardness test, and also some samples of the product of mixing were observed by Fourier Transform Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). The formula used in this study is the ratio of single-NR-100%; combinations of NR-70% and CR-30%; combinations of NR-30% and CR-70%; and the CR-100%. The result showed that the optimum mix formula for the PRF product is NR-70%: CR-30%.

Keywords: natural rubber, synthetic rubber, pneumatic rubber fender, FTIR, and SEM.

Abstrak

Salah satu produk karet, pneumatik karet (PRF), sepenuhnya masih diimpor, di mana bahan baku utamanya dari karet sintetis. Produk PRF telah digunakan di sektor transportasi sebagai pelindung pelabuhan dan kapal dari tumbukan. Dalam penelitian ini, campuran antara karet alam dan sintetis dilakukan untuk menentukan formula optimal campuran karet untuk produk PRF. Kemudian PRF-produk PRF diuji terhadap Ketahanan Aging (ART). Sifat fisik dan mekanik PRF dianalisis dengan uji kuat tarik, elongasi saat uji putus, uji ketahanan sobek, uji kekerasan, dan juga beberapa sampel produk pencampuran diamati menggunakan Fourier Transform Spectroscopy (FTIR), Analisis Thermogravimetry (TGA) dan Scanning Electron Microscopy (SEM). Rumus yang digunakan dalam penelitian ini adalah rasio tunggal-NR-100%; kombinasi NR-70% dan CR-30%; kombinasi NR-30% dan CR-70%; dan CR-100%. Hasil penelitian menunjukkan bahwa formula campuran optimal untuk produk PRF adalah NR-70%: CR-30%.

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INTRODUCTION

Indonesia has many natural resources, one of which is natural rubber. Indonesia is one of the largest natural rubber producer in the world after Thailand, with a production capacity of approximately 3.1 million tons per year of the total area of 3.6 million hectares. Of the total production, Indonesia exported about 2.7 million tons with a value of US \$ 6.9 billion in 2013. Meanwhile, the world's natural rubber supply is projected to grow by about 2.8% per year, but the global rubber demand is only growing at about 0.4 %. In fact, raw rubber prices are likely to decline and reach around US \$ 1.2 per kilogram in December 2015 [1].

Small growth of demand for natural rubber links with a decrease in tire production in China, a recession in Brazil and Russia, also occurred in the demand of tires and other rubber production in South America and Eastern Europe. Higher production of natural rubber in the world but a slowdown in demand is expected to have a surplus of rubber material effect on the global market of about 34,000 tons in 2015, while the supply in 2014 was a deficit of about 245,000 tons. However, Indonesian Synthetic Fiber Producers Association (Apsyfi) predicts demand for synthetic rubber will further expand next year as the national demand more and more. Prediction synthetic rubber Indonesia needs about 750,000 tons in 2015, up 7.14% of the national demand for 700,000 tons this year. The synthetic rubber imports are expected to 200,000 tons next year. The prediction was bigger than the 40,000 tons imported 160,000 tons this year. Causes of synthetic rubber imports rampant as the selling price less 10%. Currently the national sales price of synthetic rubber US \$ 1 per kilogram (kg) while the synthetic rubber imports only US \$ 0.9 per kg. Meanwhile, the current price of natural rubber per 100 kg still reached US \$ 167.15. This means that per kilogram price reached US \$ 1.6715. The government is expected to play a role together with the private sector to organize the flow of natural rubber production so as to improve the quality and efficiency of the process, which in turn can suppress the price of rubber material so that it can compete with synthetic rubber products [2].

CONCEPTUAL MATERIAL

NR/CR Mixture

Combining the two types of material specifically from natural materials and synthetic materials be interesting to be assessed, considering each has advantages certain properties. Combined these two materials is expected to reinforce each

other, in order to obtain the properties of a new material that has certain advantages. The main properties of the new material is expected to be strong, resistant to mechanical treatment, heat resistant, resistant to the use of a long and repetitive.

Under mechanical pressure, temperature, humidity, radiation, and an aggressive environment, the performance of the material decreases over time. Changes in the properties of rubber products after use so-called "aging" [3]. Evaluation of the resistance of a material is very complex, the difficulty is increased when done on rubber materials. The aging process is logically rubber chemical changes which ultimately is the embodiment of that material on the physical shifting of the mechanical properties. To reduce the cost and improve the mechanical properties, thermal aging at ambient temperature has been observed in natural rubber elastomer [4]. Dragana M. et al. have explored the properties of physico-mechanical of natural rubber (NR) and 1,4-cis polybutadiene rubber (BR), NR/BR (90/10), during the natural aging process. The aging process is being monitored by periodic examination of the properties of the physico-mechanical test sample [5].

In addition, there are some reports of a mixture of NR/BR mainly related to the physical properties of the mixture of NR/BR such as compression stiffness, tensile strength, and fatigue [6]. Through a study of the thermal behavior of aging regarded NR-based compound in terms of tensile strength, fatigue life and endurance [7]. Bristow et al. analyze the changes in the properties of the mixture of NR/BR after thermal aging [8] and Mallik et al. studying the effect of thermal aging on the physical properties of the mixture of NR/BR at different blending ratios [9]. H.T. Chiu et al. has reported mechanical properties and thermal properties after aging of a mixture of natural rubber and polybutadiene rubber at different rates [10]. Crosslink density of vulcanized rubber is modified by thermal aging [11].

Rubber mixture has been getting a lot of attention in the rubber industry because, when formulated properly, the mixture can combine the best features of the individual mixture partners. Therefore easy to obtain the desired results. Natural rubber (NR) is widely known to have excellent mechanical properties such as high tensile and tear resistance because it is able to crystallize on stretching. The properties of elastic and dynamic of NR is also very good. However, because of various reactive double bond in the molecule backbone, NR highly susceptible to degradation by thermal aging and ozone attack. In addition, resistance to oil from

NR relatively poor, compared with some polar synthetic rubber such as chloroprene rubber (CR) or acrylonitrile butadiene rubber (NBR). To overcome these deficiencies, NR is often mixed with synthetic rubber such as NBR or CR. More recently, a mix of NR/CR has been studied extensively [12,13].

Merging CR to NR help to improve oil resistance and heat resistance of NR. As CR and NR are treated in a different way, careful adjustment of the heat treatment system must be taken into account to avoid maldistribution of crosslinks in two stages. Cure system of a mixture of NR/CR generally include sulfur, thiourea derivatives by the addition of other conventional accelerators [14]. Apart from curing systems, differences in polarity of the two partners mixture can also bring high interfacial tension that are detrimental to the mechanical properties of mixtures [15]. Extra compatibilizer will be suitable because it has been recommended.

Some studies have reported that precipitated silica is widely used as a reinforcing filler for most rubber, silica can form a strong interaction with the CR through hydrogen bonds [16,17]. The presence of silica in the CR can also cause additional crosslinking due to chemical reactions between the silanol groups on the silica surface and allylic chlorine atom in CR [18]. These reports confirm that the silica interacts with CR in a special way that is different from the most commonly used fillers, carbon black. It is therefore interesting to use silica as a reinforcing filler to mix CR/NR. In this study, mechanical properties and resistance to aging, thermal and ozone were investigated, but the effect of silica as a CR/NR mixer was not investigated.

Pneumatic Rubber Fender

One Japanese company has developed a Pneumatic Rubber Fender since in 1958 based on the company's technology rubber for car tires and rubber aircraft fuel tanks. Progress in the development of such floating pneumatic rubber fenders is closely related to the progress and development of ship technology, and must continue to address the increasingly large oil tankers such as VLCC, ULCC, vessels large gas carriers, bulk carriers and floating structures. Floating pneumatic fenders are used worldwide for the removal process of the ship-to-ship (STS), a terminal, and for all types of vessels. Since its creation until today, more than 60,000 fenders have been provided worldwide both for the operation of ship-to-ship and ship-to-dock serving customers. Fender has played an important role in the safe operation of the berthing and mooring his boat [19].

After that many companies have developed a fender for a variety of principle interests to prevent violent collision between objects, and so we need an object that has the elasticity properties and can dampen and withstand hard knocks. The properties are owned by the rubber. At first widely used natural rubber is then switched to synthetic rubber for natural rubber supply shortage.

Manufacture of pneumatic rubber fender using ISO17357:2002 [20], the "standard high-pressure floating pneumatic rubber fenders", which was published in 2002, then in 2014 has been revised with ISO 17357-1: 2014 to strengthen standards on the design, material and certification of floating fender pneumatic.

Indonesia with the potential of the world's second largest natural rubber has the opportunity to manufacture rubber goods products with high added value for absorbing rubber in the country and create jobs. One rubber products with high added value is "Pneumatic Rubber Fender"

In the future, Indonesia needs to develop downstream industries to provide added value to raw rubber, however, the development of the local rubber industry is very important to absorb the local natural rubber production and also to create jobs for the community. One interesting rubber products to be developed are pneumatic rubber fenders (PRF). More recently, it was made mainly by synthetic rubber. In fact, Indonesia has fulfilled the needs of his industry with PRF imports from countries such as Japan, Sweden, and China.

To minimize imports of rubber products and optimize the potential of domestic natural rubber, research was conducted by mixing natural rubber (NR) and synthetic rubber (CR) to find the optimal characteristics of the product mix. The research was carried out on a variety of formulas of natural rubber and synthetic rubber, and then the results were subject to several tests to observe the physical and mechanical characteristics of the product mixture. Several other samples were observed using FTIR, TGA and SEM tests.

MATERIALS AND METHODS

Materials

In this research, natural rubber used is grade SIR 10 (The Standard Indonesian Rubber) supplied by PTPN VIII (one of state own company) in Indonesia, and synthetic rubber used is the CR-Skyprene B30 supplied by Murni Kusuma Jaya (China), Homogenizer (Struktol 60 NS), Activator (Stearic acid, ZnO- Red Seal and MgO 150), Age resister (TMQ-Flektol TMQ , Wax S-RP 3 Rubber,

Santoflex-6PPD), Filler carbon black (HAF N-330), Processing aid (Paraffinic Oil), Accelerator (ETU 80 and DPTT-Acel-TRA), and Vulcanizator (Sulfur) were technical grade.

Methods

Sample Preparation

Compound formulations used in this study are given in Table 1, where the combination formula only between natural rubber (NR) and synthetic rubber (CR), while other compounds such additives are still the same for all combinations. As shown in Table 1, the ratio of the combination of the Sample A (NR-100%), Sample B (NR-70%: CR-30%), the sample C (NR-30%: CR-70%), and Sample D (CR-100%).

After that, all samples were subjected to Aging Resistance Test using ozone aging tester for about 72 hours. All samples were then subjected to mechanical and physical test. Samples that have been

formed according to ASTM standard, and then put into an oven/chamber with a temperature of 70°C for a certain time 24 hours, 72 hours and 96 hours. Subsequently the samples were retested mechanical properties such as abrasion, tensile strength, tear strength, and modulus EAB. Aging test refers to ASTM D-572.

Sample Analysis

Mechanical characteristic of blending sample was analyzed using tensile strength test, elongation at break test, tear resistance test, and hardness test, with standard methods shown in Table 2. Beside that chemical characteristic of compound was analyzed using Fourier Transform Infrared Spectroscopy (FTIR), and the morphological of surface was analyzed using Scanning Electron Microscope (SEM).

Table 1. Formulation of Pneumatic Rubber Fender base on ratio of NR and CR (phr*)

No.	Materials	Sample Blending			
		A	B	C	D
1	Natural rubber (NR)	100.0	70.0	30.0	0.0
2	Synthetic rubber (CR)	0.0	30.0	70.0	100.0
3	Activator	13.5	13.5	13.5	13.5
4	Accelerator	6.5	6.5	6.5	6.5
5	Filler	35.0	35.0	35.0	35.0
6	Processing Aid	5.0	5.0	5.0	5.0
7	Anti-oxidant	3.0	3.0	3.0	3.0
8	Vulcanization agent	1.0	1.0	1.0	1.0

*phr = for per hundreds rubber

Table 2. Standard of Mechanical Analysis

Test Item	Standard Methods	
	ISO	ASTM
Before Aging		
☐ Tensile strength	ISO 37	ASTM D 412
☐ Elongation	ISO 37	ASTM D 412
☐ Tear Resistance	ISO 37	ASTM D 412
☐ Hardness	ISO 7619	ASTM D-2240
After Aging		
☐ Proses Aging	ISO 188	ASTM D-572
☐ Tensile strength	ISO 37	ASTM D 412
☐ Elongation	ISO 37	ASTM D 412
☐ Tear Resistance	ISO 37	ASTM D 412
☐ Hardness	ISO 7619	ASTM D-2240

RESULT AND DISCUSSION

Mechanical and Physical Properties of Compound

All samples in this study were subjected to Aging Resistance Test using ozone aging tester. After that all samples before and after aging were subjected to mechanical and physical test.

Tensile strength (TS)

The tensile strength (TS) values at the initial time of aging process, 0 – 24 hours, show increasing value as effect of heating, but the further heating process will decrease the tensile strength's value of compound. The decreasing of tensile strength value influenced by aging process was caused by degradation of main structure of rubber. Figure 1 shows profile of tensile strength value influenced by aging process.

NR vulcanized with different crosslink densities are ready to investigate the effect of early crosslink density in aging thermal behavior [21]. Thermal aging effect on the mechanical properties of different rubber formulations have also been reported by various authors [22]. A. A. Basfar et al. studying the effect of thermal aging on the mechanical properties of NR formulations cured with sulfur peroxides or radiation [23].

Figure 1 shows natural rubber has higher tensile strength value than synthetic rubber. The natural rubber contains non-rubber component such as protein and phospholipids that will increase elasticity of NR. Although the NR has higher value of tensile strength, but NR relatively has lower aging resistance rather than CR. Furthermore, in order to increase aging resistance of rubber compound, the blending of NR and CR were done. Figure 1 shows optimum formulation that has highest tensile strength value was vulcanized rubber B (70 % NR and 30 % CR).

Figure 1. Tensile strength of Vulcanized Rubber Samples A, B, C, D after aging at 24, 72, and 96 hours.

Elongation at Break

Figure 2 indicates value of EAB of vulcanized rubber A, B, C, D after 24, 72, and 96 hours aging. Initially, NR has higher value of EAB than that of CR, however, after 72 hours aging, EAB of vulcanized rubber A and D decrease gradually. In contrast to vulcanized rubber blend B and C, it is EAB increase clearly. This shows that formulation play important role for increasing of EAB value. The optimum formula with the best value of EAB is Formula B (70% NR, 30% CR).

Figure 2. Elongation at Break of Vulcanized Rubber Samples A, B, C, D After aging 24, 72, and 96 hours

Tear Resistance (TR)

Figure 3 showed that TR of NR occur the sharp decrease after 24 hours aging, but it come gradual increase for 72 hours. After that, it decreases because of structure damage of main NR backbone as shown on graph A.

Figure 3. Tear Resistance of Vulcanized Rubber Samples A, B, C, D after aging 24, 72, and 96 hours

Aoshuang Y. et al. studied the effect of thermal aging on the operator NR /CR mixture at 70 ° C to 168 h [24]. More recently we have reported a correlation between psycho mechanical properties of NR/CR blend formulations of the tire tread with their thermal behavior [25].

The same thing is also indicated by synthetic rubber as shown on graph C. Therefore, optimum composition is achieved by NR/CR Blend with formula B (70% NR, 30% CR).

Hardness

SR has hardness value higher than that of NR. This value will increase gradually after aging. This is caused by crosslink formation of main rubber chain as shown on Figure 4.

Figure 4. Hardness of Vulcanized Rubber Samples A, B, C, D

Hardness material obtained from samples A, B, C and D (figure 4), shows that the hardness of samples A, B and C tends to decrease at 24 hours the aging process and increased again after 72 hours of the aging process, and it only applies to samples contains natural rubber (NR), whereas for synthetic rubber (CR) that the process of aging will increase the hardness of the sample (D) gradually. This indicates that the natural rubber following the pattern of decline in hardness in the initial 24 hours and then gradually increases in hardness in accordance with the length of time. While the mixed rubber NR/CR follows the pattern of change in hardness NR (see figure 4)

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of vulcanized rubber with variation formula are shown at Figure 5, meanwhile finger print of vulcanized NR and SR can be seen on Table 3. Figure 5 shows the infrared spectra of samples A, B, C and D. Here, we can see distinct peaks at wavelengths of 800, 1400, 2850 and 2925 cm^{-1} , which may be caused by asymmetric

stretching of C-H bonds of NR. Peak seen at 2925 cm^{-1} is due to symmetric stretching C-H bond. Peaks in the frequency range of 1022 cm^{-1} is probably due to styrene.

Further details of the polymer functions groups were studied using ATR-FTIR analysis. Fig. 5 shows the main characteristic peaks of NR. It is at 3025 cm^{-1} ($=\text{CH}$ stretch), 2956 cm^{-1} (CH stretch of methyl group), 2915 cm^{-1} (C-H stretching of methylene group), 1375 cm^{-1} (CH stretch of methyl group), 1453 cm^{-1} (CH stretch of methylene group), and at 835 cm^{-1} (CH wagging).

Figure 5. Profile FTIR of Vulcanized Rubber Samples A, B, C, D before aging

Table 3. Finger Print FTIR spectrum of NR and SR

Wave Number (cm^{-1})	Functional groups	Note
3000 - 3700	C-H	NR, CR
2956	CH_3	NR, CR
2915 and 2849	CH ($\text{C}-\text{CH}_3$ and $-\text{CH}_2-$)	NR, CR
1597	$\text{C}=\text{C}$	NR, CR
824	$\text{C}=\text{C}$	NR, CR
800	C-Cl	CR

Characterization of vulcanized rubber after aging 96 hours, A, B, C, and D, using FTIR can be seen on Figure 6. There is a degradation on vulcanized rubber which is indicated by increasing of peak at 3000-3700 cm^{-1} wave number which indicate that there is a formation of functional group of hydroxyl (O-H) because of degradation of $\text{C}=\text{C}$ bond.

Similarly, we can see the peaks of different frequencies on 2900 cm^{-1} to C-H bond. Peak at 1600 cm^{-1} may be due to C-H bond of NR. Another similar peak as above appears due to the presence of CR. The remaining curve shows the frequency of the same bond as compared to the above chart for the same composition continues with varying ratios. Therefore,

we only observe a slight shift in the frequency band. The peak seen at 2345 cm^{-1} is due to C-H bond of SBR and also peak at 1600 cm^{-1} is due to the bond C5C of NR.

Another important observation is that unlike Padella et al. [26], there is no peak at 1730 cm^{-1} (C=O stretch peak), indicating that oxidation of the main polymer chains does not occur during aging process.

TGA analysis

The results obtained in this study are discussed in relation to the thermal behavior, curing properties and tensile strength of the rubber mixture. Thermogravimetric analysis of uncured NR/CR mixture shows the degradation temperature of initial NR is lower than CR. The main degradation product of NR containing isoprene and dipentene [27] and that the BR showing two stages of weight loss [28, 29]. The first phase, said almost exclusively due to volatile products depolymerization, (butadiene and 4-vinyl cyclohexene), plus a small amount of another unidentified hydrocarbon and the second phase is due to degradation of a residue resulted from cyclized and crosslinked CR.

Figure 6. FTIR Spectrum of Vulcanized Rubber Samples A, B, C, D after 96 hours aging

Figure 7 shows that the sample A, namely 100% natural rubber began to change in the ambient temperature of 250°C - 330°C , then weight loss is quite substantial at temperatures 340°C - 410°C , further degradation occurs slowly. In the sample B (NR 70% and 30% CR) weight loss at a temperature of 340°C is large enough, then the sample degraded slowly as the temperature increases. In the sample C (NR 30% and CR 70%) is almost the same as the B sample but the onset of obvious degradation occurs quite a bit faster at a temperature of 320°C . While the sample D (CR 100%), degradation starts to happen at temperatures of 300°C . This can be explained that mixing with the composition of NR 70% and 30%

CR may slow degradation.

Figure 7. TGA result of Sample A, B, C and D

Scanning Electron Microscope (SEM)

SEM was used to identify differences in the surface of the sample before and after the aging process. In figure 7 shows that the surface of the sample A, B, C, D before aging. Figure 7 shows the sample A surface looks more smooth and flat, the B sample is starting to look rough, sample C is more rugged and sample D was very rude. This indicates that the mixing and the addition of CR on NR affect the surface structure of the sample mixture of rubber.

SEM is also used to identify the effects of the aging process of the sample A, B, C and D after aging process for 96 hours. Figure 8 shows that the sample A look still smooth despite the visible changes in color, the sample B is starting to look a crack, sample C visible cracks grow in size and the sample D is clearly visible cracks that resemble tear lines irregular. This was different with rupture occur when the mixture NR/BR was caused by filler, found by K. Pal et al. 1988[30]. This shows that NR has good resistance against aging process compared to CR.

From these data, we can conclude NR and CR blend composition that can be used with consideration of the result of the aging process is the B sample or a mixture of NR/CR (70/30).

CONCLUSION

Vulcanized rubber blending has superior mechanical, chemical properties and morphological surface than of each rubber origin (100% NR, and 100% CR). The best formula using this research was indicated by the sample composition of blending NR 70%: CR 30%. Therefore, it can be concluded that the best formula for obtaining good material as the material for pneumatic rubber fender is a formula mixture of 70% natural rubber and 30% synthetic rubber that has better resistance to the aging test.

Figure 7. Surface image of Vulcanized Rubber Samples A, B, C, D before aging (origin); **A.** 100% NR, **B.** 70%NR:30%CR, **C.** 30%NR:70%CR, **D.**100%CR

Figure 8. Surface image of Vulcanized Rubber Samples A, B, C, Dafter 96 hours aging; **A.** 100% NR, **B.** 70%NR:30%CR, **C.** 30%NR:70%CR, **D.**100%CR

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