THE EFFECT OF CARBON BLACK COMPOSITION IN STYRENE BUTADIENE RUBBER AND NATURAL RUBBER BLENDING TOWARDS ITS AGEING AND ORGANIC SOLVENT RESISTANCE PROPERTIES

PENGARUH KOMPOSISI KARBON HITAM PADA CAMPURAN STYRENE BUTADIENE RUBBER DAN KARET ALAM TERHADAP KARAKTERISTIK PENGUSANGAN DAN KETAHANAN PELARUT ORGANIK

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Abstract

In terms of enhance thermal ageing resistance of natural rubber (NR) based products, it is common to blend NR with styrene butadiene rubber (SBR) to produce binary blends with higher thermal properties. However, reinforcement filler such as carbon black (CB) commonly added to improve physcomechanical properties of the blends. Thus, this present study investigated the effect of CB composition in SBR/NR binary blending towards its thermal ageing resistance and organic solvent resistance. CB was compounded 35 up to 75 phr into SBR/NR (50/50 phr), the standard procedure ASTM D-3182 was applied. The result show that hardness value increase significantly due to the higher addition CB. Conversely, the higher CB composition in SBR/NR binary blends cause quite significant the decreasing value of tensile strength and elongation at break. The effect of thermal aging properties was observed at dry air circulation at 70 ^{o}C for 48 hours. It is found that thermo-oxidative ageing cause a serious damage on the surface as well as decrease the hardness, tensile strength and elongation at break of the rubber vulcanizates. However, the effect of CB addition towards the decreasing value of those properties could not be seen clearly. In addition, toluene immersion for 24 hours cause the mass loss up to about 5% weight of the NR/SBR binary blends, whereas iso-octane and n-hexane immersion cause slight mass changes only approximately 0,1 % weight.
Keywords : NR/SBR Blending, Carbon Black, Organic Solvent Resistance, Thermal Ageing Resistance

Abstrak

Peningkatan kualitas tahan panas produk karet berbasis karet alam perlu ditingkatkan melalui pencampuran dengan karet sintetis seperti stirene butadiene rubber (SBR). Bahan pengisi penguat seperti carbon black biasanya ditambahkan untuk meningkatkan sifat mekanik fisiknya. Penelitian ini bertujuan untuk mempelajari efek penambahan CB terhadap ketahanan usang dan ketahanan perendaman pelarut organik. Proses pembuatan vulkanisat dilakukan sesuai dengan ASTM D-3182 dengan variasi perlakuan CB yaitu 35 sampai dengan 75 phr untuk karet SBR/NR (50/50 phr). Hasil penelitian menunjukkan bahwa kekerasan vulkanisat naik signifikan karena penambahan CB, walaupun akan berdampak negatif terhadap kuat tarik dan perpanjangan putusnya. Efek pengusangan pada suhu 70 ^{o}C selama 48 jam menyebabkan kerusakan serius pada permukaan vulkanisat karet maupun kekerasan, kuat tarik dan perpanjangan putusnya. Walaupun demikian, efek penambahan jumlah CB tidak bisa dihubungkan dengan jelas terhadap penurunan sifatnya. Perendama toluene selama 24 jam menyebabkan kehilangan massa vulkanisat sampai dengan 5% berat, sedangkan perendaman iso-octane dan n-hexane tidak berpengaruh secara signifikan, hanya 0,1% berat.
Kata kunci : Vulkanisat NR/SBR, Carbon Black, Ketahanan Pelarut Organik, Ketahanan Usang

INTRODUCTION

Natural Rubber has been used as primary rubber for some rubber products such as automotive rubber parts, tyres application, rubber construction, household, gasket and etc. Natural rubber is a renewable polymer sources and has competitive properties like high tensile properties, tear strength, high resilience properties and compatible compounding (Hasan, Rochmadi, Sulistyo, & Honggokusumo, 2013). However, NR also has negative adverse such as gradually degrade at a heat temperature, prone to be oxidized by oxygen, air, ozone that leads a serious deterioration on physical degradation during its storage (Nor & Othman, 2016). Furthermore, NR has low resistance in oil, chemical, and organic solvent, such environment could cause a serious damage on its surface's products and deterioration. Thus, to address those weakness, some works have been done to improve heating, ageing, and organic resistance such as blend it with other polymers such as EPDM, NBR, PVC, SBR, CR or chemically modified natural rubber by epoxidation, chlorination and grafting (Noriman, Ismail, & Rashid, 2010) .

This work focus on the blending of NR and SBR that would contribute to specified rubber products in heat resistance and high physical mechanical properties such as tyres rubber and belt conveyor . (Iqbal, Akhter, Farooqui, & Mahmood, 2008; Noriman et al., 2010) stated that SBR and NR blending of phr could improve its heat resistance and ageing resistance of the composites. Bearing in mind that designing polymer blending and rubber formulation is an important parts to comply a highly specification rubber products like tires and rubber belt conveyor for special purposes. Thus, designing rubber formulation need to be observed properly to obtain highly standard products and reasonable production costs.

The composition of SBR/NR of 50:50 phr as reported by (Iqbal et al., 2008) was the best formulation in order to achieve highly dispersed polymer matrixes and improve the reology properties. (Susanto, Affandy, Katon, & Rahmaniar, 2018) reported that blending SBR/NR in a certain number could improve heating resistance at 70 ^{o}C without decreasing tensile properties and abrasion resistance.

In order to improve the physical mechanical properties along with the dynamic properties, it is very important to add some filler particularly reinforcement filler. In terms of tyres rubber compounding, carbon black is the most suitable fillers to either reinforce the properties of vulcanized, reducing cost of production and to ease the processing. A new alternative filler such as starch extracted from cassava (Prasetya, Marlina, & Dimyati, 2019), *Dioschorea hispida denst* (Susanto et al., 2018) and other filler have been studied to fill in NR/SBR application through latex compounding mixing. Hence, due to the highly specification standard of the products, CB was chosen to be a reinforcing filler in this work. Carbon Black possibly gives significant effect on abrasion resistance (Sirisinha, Baulek-Limcharoen, & Thunyarittikorn, 2001; Sun, Wang, Zhang, & Zhao, 2012), thermo-oxidative resistance (Hamza, 1998) and oil resistance (Sirisinha et al., 2001). Meanwhile, excessive CB also could lead decreasing the elongation at break of NR/SBR blending (Zhou, Zhu, & Liang, 2007). However the study on examine the effect of carbon black addition on SBR/NR blends towards the ageing characteristics and organic solvent resistance are still limited. For instance, some weakness on blending a certain composition SBR, NR and CB leads to the lower physical properties, meanwhile, those effects need to be observed in organic solvents such as n-hexane, toluene and iso-octane. It is suspected that, NR only would have low organic solvent resistance, so it needs to be mixed with SBR and CB.

Thus, this work would contribute some information on the effect of carbon black addition on the changes of hardness, tensile strength, elongation properties due to thermal oxidative ageing. In addition, the organic solvent resistance of n-hexane, toluene, iso-octane as expressed by the percentage of decreasing mass after immersion also could be considered in handling during storage and usage. Consequently, this research would contribute a new practical information on the carbon black composition on NR/SBR blending for heat resistance rubber products such as tyres and rubber belt conveyor.

MATERIAL AND METHOD

Materials

Polymers: Styrene Butadiene Rubber Emulsion (SBR 1712) (Chandra Asri Petrochemical), Natural Rubber/ NR (Standard Indonesian Rubber/ SIR 20 (PT Felda Indo Rubber. The chemicals for rubber compounding such as peptizer, ZnO, Stearic Acid, Carbon Black N660, Silica-69, Cumaron Resin, Naphatenic Oil, MBTS, Sulphur, and TMTD (Brataco Chemicals). The organic solvents such as toluene, n-hexane and iso-octane (Merck).

Rubber Compounding

Rubber compounding was conducted based on the ASTM D3182 Standard Practice for Rubber (Materials, Equipment, and Procedures) for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets and ASTM D3184-89 Standard Test Methods for Rubber Evaluation of Natural Rubber. It was carried out using a laboratory two roll mill XK-160, Shanghai Rubber Machine Worker, China. In order to observe the effect of carbon black addition into the vulcanizates, the formulation was designed using carbon black of 35, 45, 55, 65, and 75 phr respectively as listed in Table 1.

For tensile strength, hardness, and elongation at break testing, the compounded rubber sheet was vulcanized for about 20 minutes at 120 - 130 ^{o} C using heating press hydraulic (YG-220, Shanghai Rubber Machine Worker, China). These procedures were replicated 3 for each formulas in order to obtain highly accuracy data.

Tensile and Organic Solvent Resistance Testing

Each vulcanizates were tested for parameters comprise of : hardness Shore A (ASTM D 2240-05 (ra 2010) using Hardness tester IRHD, Germany; tensile strength & elongation at break testing in accordance with ASTM D 412 at 26 ^{o}C room temperature at 500 mm/min cross head speed using INSTRON UTM Taiwan Tearing machine JT-420.

Thermal ageing properties were tested according to the ASTM D573-99 Standard Test Method for Rubber - Deterioration in an Air Oven. The rubber products were aged using hot air circulation in oven at temperature 70°C for about 48 hours at speed of test frame 5 rpm (Aging Oven Chamber, Model VAT 60, ASLI (China) Test Equipment Co., Ltd. The tensile and physical properties before as well as after ageing were tested.

Dumbbell-shaped (punched out using die C, ASTM D412-92) test specimens were immersed in organic solvent namely toluene (p.a), iso-octane (p.a) and n-hexane (p.a) at room temperature for 70 h. Thereafter, the specimens were removed from the organic solvents, quickly dipped in acetone, and blotted lightly with filter paper to eliminate the excess solvents on the specimen surfaces. The decreasing percentage of mass changes observe by comparing the changes mass after and before the immersion.

Table 1. Formulation of Carbon Black in NR/SBR Blending.

No.	Rubber dan Chemicals	Formula (phr)				
1.	NR/SIR 20			50		
2.	SBR			50		
3.	*Peptizer*			0,1		
4.	ZnO			10		
5.	*Stearic Acid*			1,5		
6.	*Carbon Black* N 660	35	45	55	65	75
7.	*Silica*-69			10		
8.	*Cumaron Resin*			4		
9.	*Naphatenic Oil*			4		
10.	MBTS			0,2		
11	*Sulphur*			3		
12.	TMTD			1		

RESULTS AND DISCUSSION

During the storage and usage, rubber products will also encounter the occurrence of ageing due to lighting (UV), heating, ozone and air oxidation (X. Liu, Zhao, Yang, Iervolino, & Barbera, 2018). It is commonly known that carbon black is reinforcing filler to improve physical mechanical properties by protecting the oxidation effect in the vulcanizates. Natural rubber are susceptible to thermal- oxidative ageing due to their unsaturated carbon-carbon double bonds in the backbone (n-isoprene) (Bouthegourd, Rajisha, Kalarical, Saiter, & Thomas, 2011).

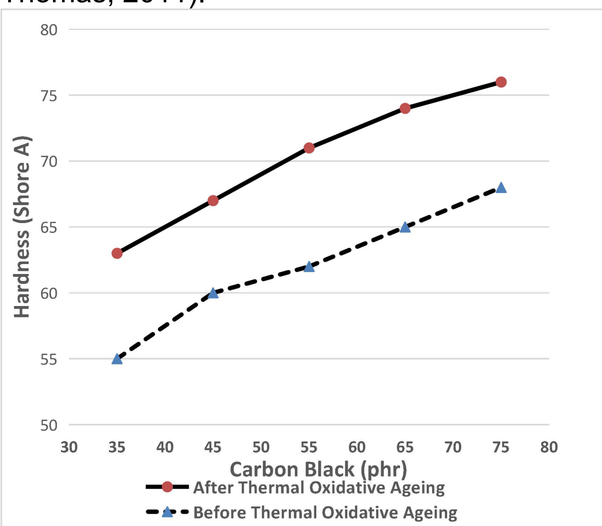

Figure 1 Changes Hardness of SBR/NR Blends with Various Carbon Black Composition After Thermal Oxidative Ageing

Figure 1 shows the differences value of hardness before and after ageing. It could be seen that the hardness of CBR/NR filled with carbon black and silica experience increasing value due to the high carbon black added into the blends significantly. It could be seen in the figure 1 that the hardness value of NR/SBR filled with carbon black decrease due to the thermal ageing. The number of carbon black loading might contribute slight effect on its changing hardness value due to the thermal oxidative ageing. In addition, the physical appearance of vulcanizate experience a slight damage such as small crack on its surface after aging at 70 ^{o}C for about 48 hours.

During aging process, NR-SBR-CB composites becomes hard and brittle because predominant oxidation in temperature at 70 ^{o}C during 48 hours and cross linking reactions (Pourmand, Hedenqvist, Furo, & Gedde, 2017). The carbon double bonds (propilene and isoprene) are susceptible to be attacked and form radicals that initiate oxidation and cross linking reaction (Hong, Seo, Jang, & Lee, 2015). Normally, the first stage of thermal oxidation is the loss of additive; and then gradual increase in crosslinking density and oxidation occur (Li, Gao, Guo, & Bolf, 2018). Fortunately, in this work the mineral oil was used as as lubricant and plasticizer to protect the rubber from serious crosslinking density. Thus, the value of hardness of each NR/SBR filled with carbon black and silica tend to increase.

The heating effect is able to destroy the molecular chain of natural rubber (n-1,4 cis isoprene)/ styrene butadiene rubber and initiates the movement of the filler within the matrix, hence degradation occurs inside of the polymer matrix which lead to the breaking of the filler, filler-rubber and rubber-rubber bonding (Wang et al., 2010; Wang et al., 2009). Moreover, (J. Liu, Li, Xu, & Zhang, 2016) reported that a main-chain scission polymer backbone or sulfidic cross linking scission occurs during the aging periods, which lead to the cleavage of vulcanizates network structure and changes of physical properties.

Figure 2 shows the tensile strength as carbon black increased due to incorporation of carbon black-silica in SBR/NR composites and the ability of molecular chain of SBR/NR matrix to slip and orient around the carbon black. High carbon black loading increase its contact surface with NR/SBR matrices, assisting for a better stress transfer so that tensile strength with higher loading. Similar finding was reported by (Hu, Li, & Liu, 2013). However, at about 60 phr carbon black overloading, the tensile strength experience decreasing and will remain stable due to agglomeration effect that restricts the mobility of rubber chain. Thus, the interaction of SBR/NR with carbon black in the crosslinking effect between rubber polymer and sulphur would improve the tensile strength properties.

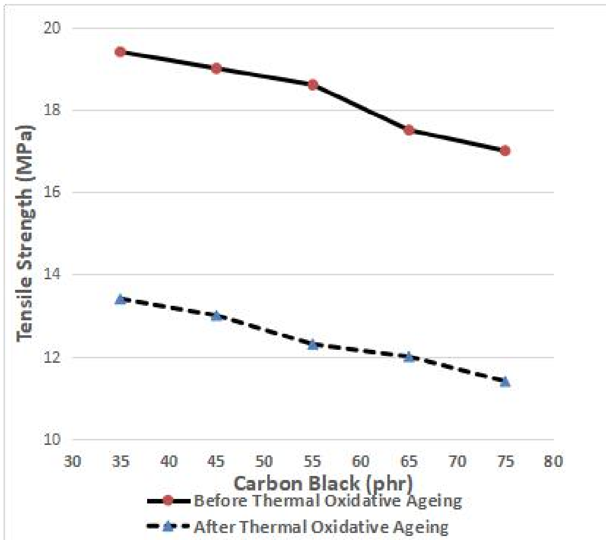

Figure 2 Figure 1 Changes Tensile Strength of SBR/NR Blends with Various Carbon Black Addition After Thermal Oxidative Ageing

Carbon black loading plays a significant effect on the tensile strength as confirmed by the research (Samaržija-Jovanović, Jovanović, Marković, Zeković, & Marinović-Cincović, 2014; Tan & Isayev, 2008). This due to the presence of reinforcing filler within the NR/SBR rubber matrix that contribute to crosslinking effect along with the bonding reaction of filler-rubber (CB-SiO_2-NR-SBR) and rubber-rubber NR-SBR (Mat, Ismail, & Othman, 2016). Normally, tensile strength increase as the filler loading, where as when it reached optimum, tensile strength would drop. This could be explained that the high carbon black addition lead to aggregations, interruption, and agglomeration the filler-matrix bonding of the carbon in the SBR-NR matrix formation, so it reduces tensile properties.

Thus, stiffening effect modify the interface between NR-SBR-Carbon Black - Silica that restrict the mobility of the rubber - rubber and rubber filler network so results in decreasing elongation at break. This phenomena also reported by (J. Liu et al., 2016). In addition, the overloading carbon black enhance the rigidity of NR-SBR that caused by the higher brittleness of carbon black into the rubber matrixes.

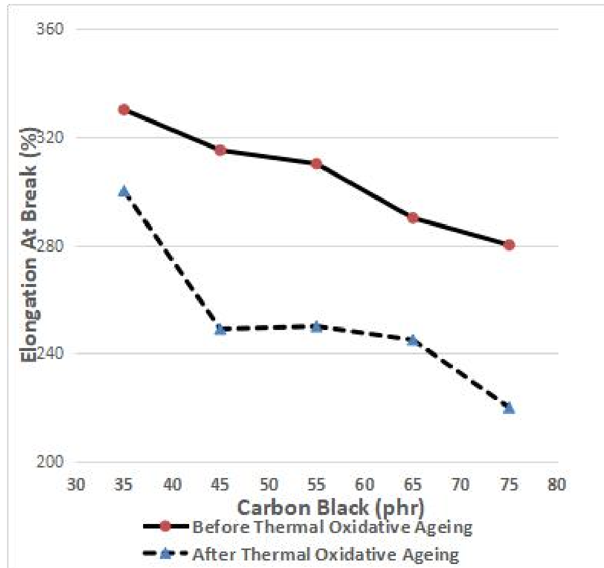

Figure 3 Changes Elongation at Break of SBR/NR Blends with Various Carbon Black Addition After Thermal Oxidative Ageing

Aforementioned, the tensile strength increased and reached a maximum value with the increase of cross linking density. During thermal aging process, the cross link density along with the cross link points increased. Further serious increasing cross link density that exceed a critical value cause decreasing average molar mass of SBR-NR chain between two adjacent each cross link points so that mobility chain segment becomes less effective (Choe, 2000). More over, thermal aging cause a surface damage of SBR-NR and lead matrix polymer become severe and in homogeneous, the oxidation reactions initiated from its surface and extend to the inner structures (Delor-Jestin, Lacoste, Barrois-Oudin, Cardinet, & Lemaire, 2000).

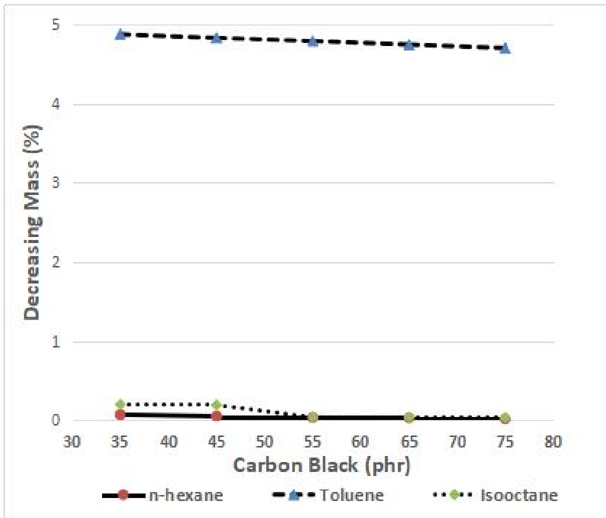

Figure 4 Changes Mass of SBR/NR Blends with Various Carbon Black Addition After Organic Solvent Immersion

Figure 4 shows that immersion using iso-octane and n-hexane only affect very slightly decreasing mass. It could be seen that the higher carbon black added into the binary blends of SBR/NR the less decreasing mass due to the immersion. Conversely, figure 4 indicates that toluene significantly influence the vulcanizates during the immersion. It could be seen clearly that the immersion cause about 5% weight loss due to the dilution effect between the polar organic solvent such as toluene within the polar rubber SBR/NR binary blends. The decreasing mass in percent of samples were calculated before and after organic solvent immersion. The low percentage decreasing mass represent high organic solvent resistance of the vulcanizates. It can be seen in Figure 4, at the same carbon black composition, the change mass of SBR/NR immersed in toluene is significantly higher rather than either in iso-octane or n-hexane. It could be said that SBR/NR filled with carbon black and silica could resist in non-polar organic solvent rather than in a polar solvent such as toluene. It is known that NR-SBR are high polar rubber, and toluene is a polar solvent, thus it is like dissolves like dissolves so that the rubber-rubber and rubber-filler networking dissolved in the polar solvent, and it experience the decreasing mass significantly (Mousa, Ishiaku, & Ishak, 1998; Sae-Oui, Sirisinha, & Hatthapanit, 2007). In addition, due to the polarity carbon black filled within natural rubber and styrene butadiene rubber, the diffusion solvent molecules and absorption might not be hindered (Susanto, 2019). The dilution effect probably cause the deterioration on the surface and lead to decrease the tensile and physical mechanical properties after organic solvent immersion.

CONCLUSION

The effect of thermal oxidative ageing at temperature 70°C for about 48 hours of SBR/NR blends on various carbon black composition has been studied. Generally, carbon black addition into the SBR/NR blending cause a positive effect on hardness value. Meanwhile, the carbon black loading cause a slightly decreasing on elongation at break and tensile strength. It is clearly shown that thermal ageing leads to decrease the hardness, elongation at break and tensile strength. Those percentage changes were quite significantly number at approximately 10%. It is inferred that thermal oxidative ageing 70°C for about 48 hours cause a serious physical damage of the rubber vulcanized due to surface attack and oxidation. Furthermore, iso-octane an n-hexane as non polar organic solvent were not deteriorate the NR/SBR blending significantly, mass losses after immersion with both solvents were less than 1%. Conversely, the toluene solvents cause a serious mass loss of the NR/SBR vulcanizates that affect the physical damage of the rubber products. However, the correlation between the number of carbon black addition in NR/SBR blending with either the ageing properties or organic solvent resistance could not be explained clearly.

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