



Design of Elastomeric Bridge Bearing Pad Compound Formula Based on Hydrogenated Natural Rubber

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Abstract. Laminated elastomeric bearing pads, commonly made of natural or chloroprene rubber, function as an isolation system in bridges or flyover structures. In this research, the feasibility was evaluated of using hydrogenated natural rubber (HNR) as base elastomer in steel-laminated bearing pad production by designing the rubber compound formula. The compounding procedures for the HNR used various sulphur vulcanization systems and carbon black filler types. The physical and mechanical tests results showed that only the hardness parameter could fulfill the standard quality requirement of commercial elastomeric bearing pads in the range of 50-70 Shore A, as stated in the AASHTO M251 materials specification. The tensile property and compression set value of the HNR vulcanizates were below the required values. This was due to low rubber-filler interaction and rigidity of the crosslink network. The low interaction was more evident with increased carbon filler particle size. By applying the semi-efficient vulcanization system and using N220 as carbon filler in designing the compound formula, HNR can be regarded as a promising alternative base elastomer in elastomeric bridge bearing pad manufacture. Nevertheless, it is necessary to improve the procedure to achieve better tensile properties and compression set.

Keywords: *carbon black; elastomeric bridge bearing (EBB); hydrogenated natural rubber; laminated bearing pad; rubber vulcanization.*

1 Introduction

The application of elastomeric bridge bearing (EBB) pads in bridges and flyover constructions is very important. EBB components are installed between the super structure and the substructure to prevent span collapse during earthquakes and also to absorb waves due to high traffic load [1-4]. Nowadays, most isolated bridges or flyovers use laminated EBB pads as primary isolation devices [5]. Laminated EBB pads consist of alternating rubber layers that are bonded between thin steel plates. The rubber composite layers have the ability to absorb energy and resist deformation, while the thin steel plates facilitate the lateral flexibility of the structure [6-7]. Commercial EBB pads can be classified

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based on the rubber type used, i.e. natural rubber or synthetic chloroprene rubber. Natural rubber exhibits good mechanical properties but deteriorates when exposed to sunlight, ozone, and oxygen due to the high unsaturated content in its molecular structure [8-9]. Meanwhile, chloroprene rubber has an advantage in its thermal oxidative resistance but its mechanical properties are worse than those of natural rubber.

Hydrogenated natural rubber (HNR) is produced by hydrogenation of natural rubber latex, either by catalytic or noncatalytic reaction. The ideal hydrogenation mechanism converts reactive unsaturated C=C double bonds to stable saturated C-C single bonds of natural rubber molecular chains without being followed by chain scissioning. This new type of modified natural rubber is regarded as an alternative green polymer to substitute thermal oxidative resistant synthetic rubbers such as ethylene-propylene diene monomer, isobutyl isoprene rubber, and chloroprene rubber [9-10]. These types of synthetic rubbers are widely used as base elastomer in the manufacture of outdoor rubber goods such as rubber hose and EBB pads.

In Indonesia, the demand for EBB pads is mostly met by import since chloroprene based laminated EBB pads are preferred in national infrastructure projects due to their superiority. This paper proposes an alternative procedure in the manufacture of laminated EBB pads based on HNR in view of reducing the use of imported chloroprene based laminated EBB pads. The procedure was developed by designing an HNR compound formula at various sulphur vulcanization systems and the selection of carbon black types as reinforcing filler. The sulphur vulcanization system and types of carbon black were considered to affect the thermal and mechanical properties of HNR composite as a rubber layer of laminated EBB pads, respectively.

2 Material and Method

HNR as base elastomer in the production of EBB pad vulcanizate was provided by the Indonesian Rubber Research Institute. The technical grade rubber chemicals used in the rubber compound formula were: zinc oxide, stearic acid, paraffin wax, ionol (2,6-bis(1,1-dimethylethyl)-4-methylphenol), 6PPD (N-(1,3-dimethylbutyl)-N-phenyl-1,4-phenylenediamine), TMQ (2,2,4-trimethyl-1,2-dihydroquinoline), carbon black, CBS (N-cyclohexyl-2-benzothiazole sulfenamide), TMTD (tetra methyl thiuram disulfide), and sulfur, purchased from local supplier PT Multi Citra Chemindo Nusa, Indonesia. The instruments used for testing and characterization were an MDR 2000 rheometer from Alpha Technologies, a Frank Shore A durometer, a tensile-testing machine (Lloyd

2000R universal testing machine, Lloyd Instrument), and an ozone tester from Toyoseiki.

The HNR was synthesized by diimide catalytic hydrogenation of high ammoniated natural rubber latex concentrate. The diimide was generated in situ by oxydation of 42.5 phr hydrazine hydrate with 35 phr hydrogen peroxide at 40 °C for 6 hours. The natural rubber latex colloidal system was stabilized by the addition of non-ionic surfactant sodium lauryl sulfate (SLS) during hydrogenation. Boric acid and sodium thiosulfate were used as catalyst and neutralizing agent, respectively. At the end of the reaction, the HNR latex was coagulated by using formic acid to obtain an HNR sheet. The HNR sheet had degree of hydrogenation at 32%. The hydrogenation was conducted in a semipilot-scale stirred tank reactor with a capacity of 2.5 kg latex concentrate/batch.

HNR compound formulas were designed at various sulphur vulcanization systems, as described in Table 1, followed by various carbon black types as reinforcing filler, as referred to in Table 2. The sulphur vulcanization systems were determined as efficient and semi-efficient. Different carbon black types were used, i.e. N220, N330, N550, N774, and N990. The HNR compounding was done at laboratory scale in a two-rolled open mill. Rubber compounding began with mastication. During mastication, raw HNR was milled into a softened mass in order to facilitate the mixing of the solid phase of the rubber chemicals. The rubber chemicals added into the softened raw HNR were activator, antioxidant, and antiozonant, reinforcing filler and rubber processing oil, accelerator, and vulcanizing agent. The rubber mixture with its chemicals was blended and re-milled into an homogenized HNR compound. The HNR compound was matured for at least 24 hours before weighing at 50 g for curing characteristics testing using the MDR. The vulcanization characteristics condition was determined at 150 °C for 45 minutes. Further, some residual rubber compound was moulded in a hydraulic press machine (compression moulding) at 150 °C to form HNR vulcanizate. The HNR vulcanizate was used as a sample in the mechanical properties evaluation.

The mechanical properties testing parameters of the rubber composite vulcanizate referring to EBB pad quality were hardness, tensile strength, elongation at break before and after ageing, compression set, and ozone resistance. The hardness testing procedure referred to ASTM D 2240-05 and was carried out using a Frank Shore A durometer. The elasticity evaluation, based on the tensile strength and elongation at break parameters, was conducted using a Lloyd 2000R tensometer according to ASTM D 412-06ae2. The accelerated ageing test conditions were set at 70 °C for 168 hours. A compression set test was performed in accordance with ASTM D 395-03. The

rubber sample specimen was pressed at 25% of the original thickness at 70 °C for 22 hours. Further, the ozone resistance parameter was evaluated based on ASTM D.1149-07 by using an ozone chamber. The ozone concentration was arranged at 25 pphm for 48 hours, 20% strain with temperature at ± 37.7 °C.

Table 1 HNR compound formula at various vulcanization systems.

Materials	Compoition (per hundred rubber, phr)		Function
	Efficient	Semi Efficient	
HNR	100	100	Base elastomer
Zinc oxide	5	5	Activator
Stearic acid	2	2	Activator
Paraffin wax	3	3	Antiozonant
Ionol	2	2	Antioxidant
6PPD	3	3	Antioxidant
TMQ	2	2	Antioxidant
Carbon black N220	50	50	Reinforcing filler
Parraffinic oil	5	5	Processing oil
CBS	4	0.7	Accelerator
TMTD	4	0.8	Accelerator
Sulfur	0.3	1	Vulcanizing agent

Table 2 HNR compound formula at various types of carbon black.

Materials	Composition (per hundred rubber, phr)			
	CB N330	CB N550	CB N774	CB N990
HNR	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Paraffin wax	3	3	3	3
Ionol	2	2	2	2
6PPD	3	3	3	3
TMQ	2	2	2	2
Carbon Black N330	50	-	-	-
Carbon Black N550	-	50	-	-
Carbon Black N774	-	-	50	-
Carbon Black N990	-	-	-	50
Paraffinic oil	50	50	50	50
CBS	0.7	0.7	0.7	0.7
TMTD	0.8	0.8	0.8	0.8
Sulfur	1	1	1	1

Selection of carbon black as reinforcing filler in designing the rubber compound formula is highly determined by the surface area and structure of the carbon black. The specification of carbon black types that were used in this research are summarized in Table 3.

Table 3 Specification of carbon black as reinforcing filler in rubber compound [11].

Name	Abbreviation	ASTM Designation	Average particle diameter (nm)	Nitrogen surface area (m ² /g)
Intermediate SAF	ISAF	N 220	21	114
High Abrasion Furnace	HAF	N 330	31	78
Fast Extruding Furnace	FF	N 550	53	39
Semi-reinforcing Furnace	SRF-HM-NS	N 774	110	30
Medium Thermal	MT	N 990	320	8

3 Result and Discussion

Generally, rubber compounds with different formulations produce different vulcanization behavior since this highly depends on the crosslink density and chain entanglement. This behavior was confirmed by the cure curves, as shown in Figures 1 and 2. Sulfur vulcanization forms three-dimensional sulfur bridges of rubber macromolecular crosslinks in the form of monosulphidic, disulphidic, and polysulphidic bonds.

A higher number of covalent disulphidic and polysulphidic (S-S) bonds among the HNR macromolecular chains present in the EBB vulcanizate results in weak interaction, which causes a decrease in heat resistance. This is also indicated by a plateau pattern of the torque curve as a function of time. Therefore, semi-efficient systems exhibit lower heat resistance than efficient systems since they contain more disulphidic and polysulphidic bonds.

A high content of monosulphidic (C-S) bonds is found in efficient vulcanization systems. C-S bonds have better stability compared to S-S bonds. The difference in vulcanization characteristics is more evident in an HNR compound formula with carbon black filler variation than in a vulcanization system due to the presence of rubber matrix-filler interaction [12], as shown in Figure 2.

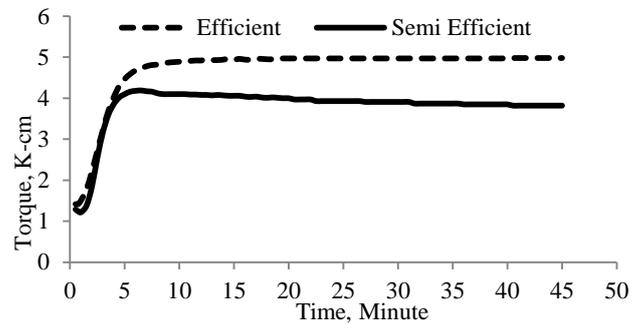


Figure 1 Cure curve of HNR based EBB compound at various vulcanization systems.

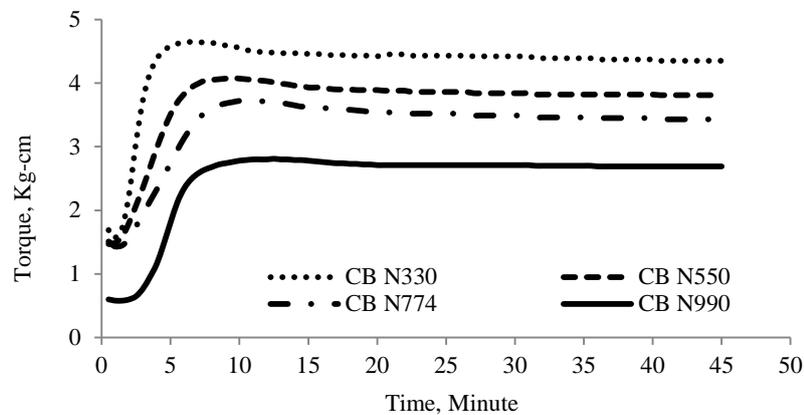


Figure 2 Cure curve of HNR based EBB compound at various carbon black types.

Surface area and surface activity of carbon black play an important role in determining the rubber-filler interaction. Small particles generate a large surface area and better dispersion of carbon black in the HNR matrix. As a consequence, sulfur vulcanization occurs more readily, followed by shortening of the scorch time and the optimum cure time.

This finding is in line with the results of previous researches [13-14]. It is obvious from Table 4 that a higher torque in the HNR compound is achieved by increased carbon filler dispersion due to the larger surface area. Excellent dispersion of filler in the rubber matrix causes a strong reinforcement effect. Further, carbon black is affected by crosslink density by reacting with the

chemical rubber ingredients of the rubber compound formulation, which also leads to a higher torque [14].

The vulcanization characteristics of the HNR compound are summarized in Table 4. The delta torque modulus ($S_{max} - S_{min}$) can be used to predict the degree of vulcanization or crosslink density [15]. The vulcanization system affects the curing characteristics through the mechanism of crosslink formation.

The efficient vulcanization system that was formulated by using high loading of sulfur donor accelerator composition resulted in a higher degree of crosslinking since it is involved in sulfur bridge formation between the rubber macromolecular chains. In this study, the influence of chain entanglement was ignored since the experiment used one type of HNR as base elastomer.

Table 4 Vulcanization characteristics of hydrogenated natural rubber compound.

Conditions	Vulcanization characteristic at 150 °C for 45 minutes						CRI
	S max (Kg-cm)	S min (Kg-cm)	S max-min (Kg-cm)	S 90 (Kg-cm)	tc90 (Minute)	ts2 (Minute)	
Vulcanization system variation							
Efficient	4.99	1.33	3.66	4.62	5.30	3.07	44.84
Semi- efficient	4.10	1.22	2.88	3.81	4.05	3.03	98.04
Carbon black type variation							
CB N330	4.65	1.57	3.08	4.34	3.53	2.51	98.04
CB N550	4.08	1.47	2.61	3.82	5.53	4.53	100.00
CB N774	3.73	1.37	2.36	3.49	7.15	6.43	138.89
CB N990	2.01	0.01	2.00	1.81	6.40	5.16	80.65

The quality of EBB pads is determined by the physical and mechanical properties of the rubber composite, based on parameters such as hardness and tensile properties. The result of hardness and tensile properties are shown in Figures 3, 4, and 5, respectively. Based on AASHTO M251, commercial steel plate laminated EBB pads require a hardness value in the range of 50-70 Shore A.

Figure 3 confirms that the hardness level of HNR vulcanizate can fulfill the minimum standard requirement. Referring to Figure 3, it can also be seen that rubber composite tends to harden due to aging. During the aging test, oxygen attacks the rubber vulcanizate surface and then gradually penetrates inside. Oxygen atoms then eliminate the remaining unsaturated C=C double bonds that are present in the HNR molecules. The hardness value increases linearly with the amount of saturation in the HNR molecules.

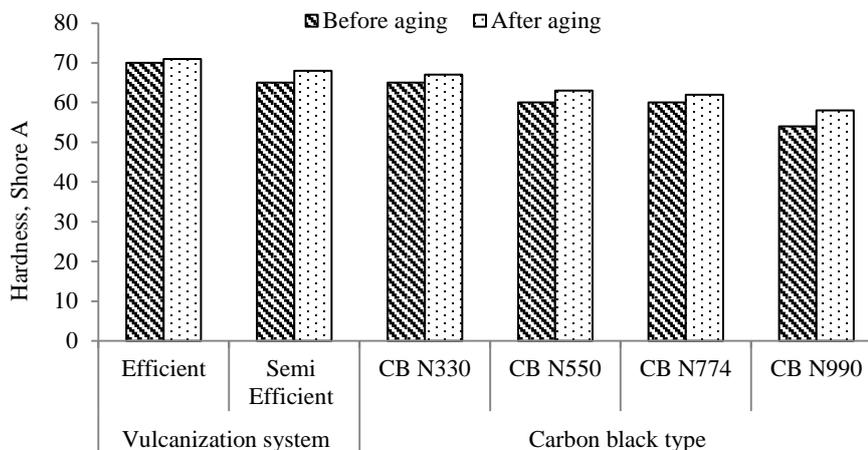


Figure 3 Hardness value of hydrogenated natural rubber vulcanizate.

The crosslink density of rubber vulcanizate also affects the hardness value. High crosslink density, indicated by less flexibility in the rubber vulcanizate molecular chain movement, is followed by an increase of the hardness value [16-17]. The formation of crosslink networks in the HNR molecular chain during vulcanization highly depends on the vulcanization system and the selected filler. A sulfur vulcanization system produces a crosslink pattern of the $-S_x-$. Higher content of sulfur should produce more three-dimensional crosslink network structures in the rubber matrix. Figure 3 shows that the efficient vulcanization system had the highest hardness value although the system contained only 0.3 phr of sulfur. Hard elastomeric vulcanizate was produced by the efficient system due to the use of a high TMTD content (4 phr). TMTD is classified as a primary rubber accelerator that can liberate sulfur at the vulcanization temperature (sulfur donor). Sulfur donors convert polysulfide bridges to monosulfide bridges in crosslink networks, which characterize efficient or semi-efficient vulcanization systems.

Thus, based on filler variation using the semi-efficient vulcanization system, the hardness value decreased with an increasing particle size of the carbon black. As the particle size of the filler decreased, the viscosity, which is correlated to the hardness, was increased. This is affected by the bonding between the rubber with filler particles. During the compounding process, part of the rubber matrix becomes attached to the filler particles. Fine filler particles bind high percentages of rubber, while coarse filler binds practically none. Table 3 shows that the N220 carbon black had the smallest particle size, highest structure, and largest surface area compared to the other carbon black filler types used in the

experiment. The characteristics of N220 provide the largest reinforcement effect on HNR based EBB vulcanizate.

Similar to the hardness parameter, the tensile property of HNR vulcanizate exhibits a reduced value due to the larger filler particle diameter and weakening of the rubber-filler interaction, as indicated by Figures 4 and 5 respectively. The sulfur vulcanization mechanism of HNR compound resulted in low tensile strength owing to the absence of strain-induced crystallization, which usually occurs in natural rubber above 400% elongation.

The maximum value of tensile strength came from the balance between the contributions of crosslink joints and stretch-induced orientation and/or crystallization of inter crosslink chains. Furthermore, residual hydrogen peroxide contained in HNR, which forms hydroxyl free radicals along the vulcanization process at high temperature, potentially causes macromolecular chain scissioning, followed by a reduction in the tensile property of EBB vulcanizate produced by sulfur vulcanization. Significant reduction of the tensile property after ageing occurred in all HNR vulcanizates. The changes in the tensile property is due to the reduced crosslink linkage among HNR macromolecular chains.

The compression set parameter describes the ability of EBB vulcanizate to return to its original size after prolonged compressive stress at a certain temperature and deflection [18]. A low compression set value gives better deformation resistance of EBB pads since this is regarded to produce the highest level of elasticity. AASHTO M251 specifies a maximum compression set value of commercial EBB pads of 25%.

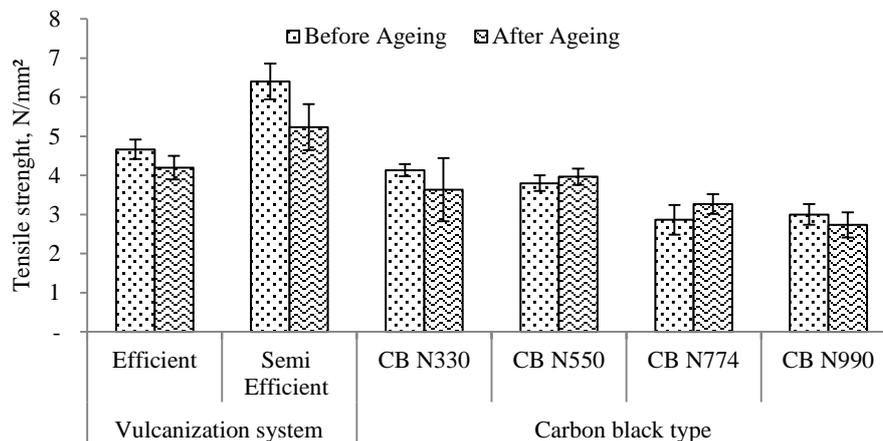


Figure 4 Tensile strength value of hydrogenated natural rubber vulcanizate.

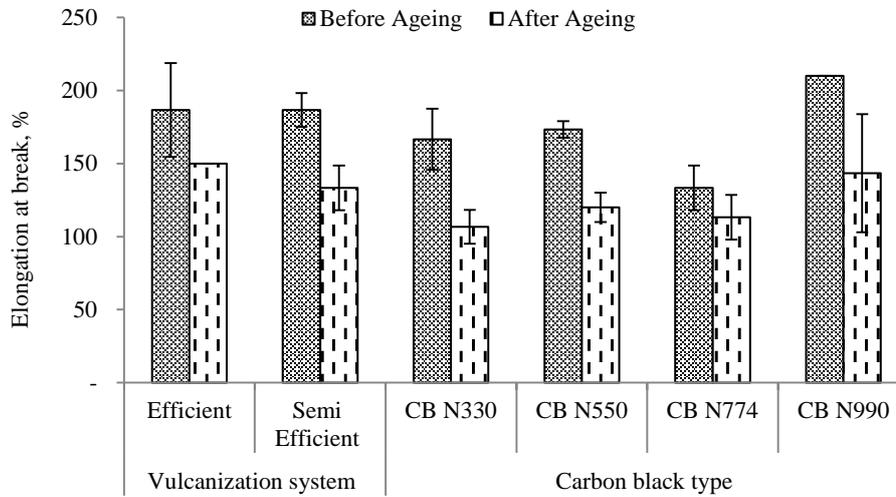


Figure 5 Elongation at break value of hydrogenated natural rubber vulcanizate.

The HNR vulcanizates obtained in this research had a slightly higher compression set value than the maximum required value, as shown in Figure 6. The semi-efficient vulcanization system showed a relatively high compression set value (26.42%) compared to the efficient vulcanization systems (26.05%). A high accelerator/sulfur weight ratio and longer cure time (t_{c90}) in the efficient vulcanization system mainly provided more monosulfide crosslink formation at the expense of polysulfide crosslinking.

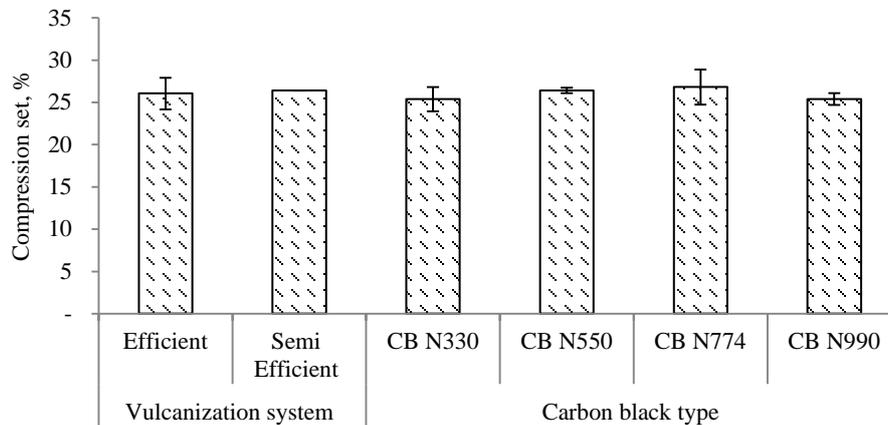


Figure 6 Compression set value of hydrogenated natural rubber vulcanizate.

Such EBB vulcanizate produced by the efficient vulcanization system exhibited a lower compression set value due to better stability of the C-S bonds compared to the S-S bonds. More S-S bonds were contained in the EBB vulcanizate resulted from the semi-efficient system. The compression set value of the HNR vulcanizates remained relatively unchanged with the addition of various types of carbon black filler. The result of the ozone resistance analysis referring to ASTM D.1149-07 is summarized in Table 5 below. This result shows that HNR based EBB vulcanizate had good ozone resistance, as indicated by the absence of surface cracking during ozone exposure in standard test conditions.

Table 5 Ozone resistance analysis result of HNR based EBB vulcanizate.

Condition	Vulcanizate surface observation
Vulcanization system variation	
Efficient	No crack
Semi-efficient	No crack
Carbon black type variation	
CB N330	No crack
CB N550	No crack
CB N774	No crack
CB N990	No crack

Apart from the physical and mechanical properties, the quality of commercial EBB pads as isolation system can also be evaluated based on their dynamic properties. The dynamic properties, i.e. stiffness in compression and stiffness in shear parameters, play a significant role in the support of bridge performance since EBB pads are designed based on the assumption that they are subjected to compressive and shear loads as a result of wind, seismic, and traffic load. Dynamic property modeling was used to study their behavior by using a numerical simulation approach in the next research stage. The result of the numerical simulation can be considered relatively close to the real conditions.

4 Conclusion

HNR obtained from catalytic diimide transfer hydrogenation of natural rubber latex was investigated as an alternative base elastomer for steel plate laminated EBB pads. The manufacture procedure of EBB pads based on HNR was investigated by applying various sulphur vulcanization systems and carbon black reinforcing filler types. The effect of carbon black type on the mechanical properties of the HNR vulcanizate highly depended on the rubber-filler interaction, which has a correlation with the surface area and the structure of the carbon black particles. The vulcanization system influences the degree of macromolecular crosslinking formation. The recommended manufacture process of HNR based bearing pad products is the semi-efficient vulcanization system with the usage of carbon black N220 for the rubber compound formula

design. The procedure yielded an appropriate hardness value as required by AASHTO M251 (50-70 Shore A). A high hardness value is required to create the ability to resist elastic deformation or sliding as a result of vertical load. Nevertheless, the procedure should still be improved because the tensile properties and the compression set value of the HNR based EBB vulcanizate did not meet the AASHTO M251 standard.

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