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Preparation of natural rubber elastomeric bridge bearing pad compound formula on various curing systems

S Puspitasari, W Andriani, and A Cifriadi

Indonesian Rubber Research Institute, Jalan Salak Nomor 1 Bogor 16151 West Java Indonesia

*Corresponding Email : puspitasari.santi@puslitkaret.co.id

Abstract. Commercial elastomeric bridge bearing (EBB) pad is dominated by the laminated type. Laminated EBB pad comprises of rubber composite layers which are arranged intermittently among the thin steel plates. The rubber composite uses natural rubber or chloroprene synthetic rubber as the base elastomer. Local EBB pad industries mostly produce natural rubber bridge bearing pad type due to the enormous availability of natural rubber in Indonesia. However, the quality of natural rubber bridge bearing pad product often cannot fulfil the standard requirement in compression set and accelerated aging parameters. The research studied the design of EBB pad compound formula based on natural rubber type. The EBB compound formulas were prepared by varring the curing system such as sulphur (efficient and semi-efficient) and peroxide curing system. Designing the compound formula was in accordance to the methods required in improving the compression set and accelerating aging quality of natural rubber bridge bearing pad. The result of curing characteristic of the natural rubber bridge bearing pad compound showed that peroxide curing system gave the longest optimum curing time. Further, sulphur curing system produced high crosslink density followed with good mechanical properties of natural rubber bridge bearing pad vulcanizate. The compression set value of natural rubber bridge bearing pad vulcanizates which were obtained by efficient and semi-efficient curing systems as 14.09% and 24.81%, respectively were regarded to be below the maximum requirement (25%). The peroxide curing system was not recommended due to the high compression set value of 40.68%. Meanwhile, maximum percent changes of tensile properties and retention values which indicated accelerated aging parameter of natural rubber bridge bearing pads were formed either by sulphur and peroxide curing system could fulfilled the standard requirement of EBB Duro 70 refered to SNI 3967:2013.

1. Introduction

Rubber industry can be classified as tyre and non-tyre manufacturing rubber based industry. 70% of world rubber production is consumed by the tyre industry. Meanwhile, the non tyre rubber industry produces plenty of rubber goods types which can be applied in many sectors such as engineering and construction, automotive spare part, glove and other medical, also general rubber goods especially for household equipment. Elastomeric bridge bearing (EBB) pad is one of many rubber goods which plays an important role in the construction sector. EBB pad is installed between superstructure and substructure of an bridge or flyover to absorb external wave due to earthquake or high traffic load [1-4]. Technically, EBB pad is functioned as an isolation system to protect structure [5]. Commercial EBB pad is dominated with laminated type which consists of alternating rubber composite layers among the thin steel plate. The rubber composite layer capable to absorb external wave and resist the structure deformation, while the thin steel plates are used to facilitate the lateral flexiblity of an structure [6,7]. The rubber composite can be made from natural rubber or chloroprene synthetic rubber as base elastomer.

Local EBB pad industries mostly prefer to produce natural rubber based EBB pad type due to the enormous domestic natural rubber availability in Indonesia. Indonesia is known as the second largest natural rubber producing country. However, the quality of local natural rubber bridge bearing pad product often cannot fulfill the standard requirements applied in Indonesia as stated in Indonesian National Standard (SNI) 3967:2013 especially on compression set and accelerated aging parameters. Consequently, Head of bridge and flyover development project tend to use imported chloroprene based bridge bearing pads.

The quality of local natural rubber bridge bearing pad could be improved by two techniques which are considered to produce superior quality products. The first technique is by designing the rubber compound formula followed with arrangement the fabrication procedure. Rubber compound formula is designed by adjusting the composition of rubber chemicals. Commonly, the main rubber chemicals ingredients consists of activator, antioxidant or antiozonant, rubber processing oil, filler, accelerator and vulcanizing agent [8]. The type and ratio of accelerator and vulcanizing agent determine the curing system of a rubber compound. Curing mechanism is one of the most important rubber processing since it could increase the mechanical and thermal properties of rubber product [9]. The curing system available for natural rubber type is by using sulphur and peroxide. Sulphur curing system could be group into conventional, semi efficient, and efficient [10]. The article was aimed to investigate the selection of appropriate design of a natural rubber based EBB pad compound formula by varying the curing system.

2. Materials and Method

The research used natural rubber, Standard Indonesian Rubber (SIR) 20 type as base elastomer. Meanwhold, the rubber chemicals which consisted of Zinc Oxide, Stearic Acid, Parrafine Wax, Ionol (2,6-bis(1,1-dimethylethyl)-4-methylphenol), 6PPD (N-(1,3-Dimethylbutyl)-N-Phenyl-1,4-phenylendiamine, TMQ (2,2,4-Trimethyl-1,2-Dihydroquinoline), Carbon Black N220, CBS (N-Cyclohexyl-2-Benzothiazole Sulfenamide), TMTD (Tetra Methyl Thiuram Disulfide), Sulphur, DCP (Dicumyl Peroxide) were provided by local supplier PT. Multi Citra Chemindonusa, Jakarta. Anhydride maleat was purchased at PT. Merck Indonesia.

2.1. Manufacture of elastomeric bridge bearing pad vulcanizate

The manufacture of natural rubber based EBB pad vulcanizate was conducted by using laboratory scale two rolled open mill. The procedure began with natural rubber compounding, followed by moulding of the natural rubber compound in hydraulic press machine at 150^{o}C. Natural rubber, SIR 20 type was masticated to form plastis and softened rubber mass in order to facilitate the mixing of rubber chemicals in the solid form into the rubber matrix. The type and addition order of the rubber chemicals in accordance of rubber compound formula as described at Table 1. The natural rubber compound formulas were designed based on various curing system i.e. sulphur and peroxide curing systems to achieve good compression set and accelerated aging properties of EBB pad product. The sulphur curing system which consisted of efficient and semi efficient were determined depend on the ratio of accelerators (CBS and TMTD) and sulphur content. While, peroxide curing system used anhydride maleat as the accelerator and dicumyl peroxide as the curing agent.

The natural rubber and its chemical mixture were blended and remilled six times into homogenized natural rubber compound. The natural rubber compound was matured for around 20-24 hours at room temperature. 50 g of matured natural rubber compound was weighted as sampel for curing characteristic analysis. The curing characteristic analysis was arranged at 150^{o}C by using Moving Die Rheometer (Alpha MDR 2000R). The result of the curing characteristic analysis as optimum curing time (tc90) was used as reference for moulding time at hydraulic press machine. The natural rubber vulcanizate obtained from the moulding process was analyzed its mechanical properties.

Table 1. Natural rubber based EBB pad compound formula at various curing systems

Materials	Compotition (per hundred rubber, phr)			Function
	Efficient	Semi Efficient	Peroxide	
Natural rubber, SIR 20	100	100	100	Base elastomer
Zinc oxide	5	5	5	Activator
Stearic acid	2	2	-	Activator
Parrafine wax	3	3	2	Antiozonant
Ionol	2	2	-	Antioxidant
6PPD	3	3	3	Antioxidant
TMQ	2	2	2	Antioxidant
Carbon Black N220	50	50	55	Reinforcing filler
Parrafinic oil	5	5	5	Processing oil
CBS	4	0,7	-	Accelerator
TMTD	4	0,8	-	Accelerator
Sulphur	0,3	1	-	Vulcanizing agent
Dicumyl Peroxide	-	-	5	Vulcanizing agent
Anhydride Maleat	-	-	2	Accelerator

2.2. Characterization of elastomeric bridge bearing pad vulcanizate
The evaluation of mechanical properties of rubber component of an EBB pad was referred to the standard requirement of EBB pad which was applied in Indonesia as stated in Indonesia National Standard (SNI) 3967:2013. The testing parameters included hardness (ASTM D 2240-05, Frank Durometer Shore A), tensile properties (ASTM D 412-06ae2, Tensometer Llyod 2000R), compression set (ASTM D 395-03), and ozone resistance (ASTM D 1149-07). Hardness and tensile properties were measured before and after aging condition at 70^{o}C for 168 hours. While, the rubber vulcanizate sample of compression set testing was pressed at 25% of the original thickness at 70^{o}C for 22 hours. Further, ozone resistance analysis was arranged at 25 pphm of ozone concentration for 48 hours, 20% strain, and temperature at ±37.7^{o}C.

3. Result and Discussion

3.1. Curing characteristic analysis of natural rubber based EBB pad compound
Curing characteristic of natural rubber based EBB pad compounds at various curing systems are described in Table 2. Curing characteristic cover parameters such as modulus torque (S), optimum cure time (tc90), scorch time (ts2), and cure rate index (CRI). Maximum modulus torque (S max) correlate with rubber compound stiffness, while minimum modulus torque (S min) measures the viscosity of the vulcanizate. Further, the difference between S max and S min (S max – min) indicates the crosslink density which is formed during the rubber compound vulcanization. The optimum cure time (tc90) is the curing time needed to reach optimum physical and mechanical properties and also correspond to the optimum cure modulus torque (S 90). The scorch time (ts2) measures the premature curing time of the rubber compound [9]. Cure rate index determine the rate of curing based on the difference between optimum vulcanization and incipient scorch time [8].

Based on Table 2, it could be understood that each curing system produced certain curing characteristic pattern. Sulphur curing system resulted higher crosslink density compared to peroxide curing system. Curing process converts plastic rubber compound into elastic rubber vulcanizate by forming a three-dimensional cross-linked network structure inside the rubber matrix. The application

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of sulphur curing system leads to the presence of sulphidic bridges among the rubber macromolecular chains in the form of monosulphidic (C-S-C), disulphidic (C-S_2-C) and polysulphidic (C-S_x-C) [11]. The formation of sulphur bridge is highly effected by the composition of sulphur as vulcanizing agent and the accelerators content. At efficient sulphur curing system, the content of vulcanizing agent is lower than accelerators, meanwhile the semi-efficient sulphur curing system used vulcanizing agent dose equal to accelerator dose. Thus, efficient sulphur curing system caused the domination of monosulphidic linkage which offer good resistance to thermal oxidative aging process [12]. The peroxide curing system exhibited highest values of minimum modulus torque (S min), although it had the lowest maximum modulus torque (S max) due to the formation of rigid C-C lingkages among the rubber macromolecular chain. The carbon linkage also caused low crosslink density on peroxide curing system of rubber vulcanizate.

Table 2. Curing characteristic test result of natural rubber compund at various curing systems

Curing System	Curing characteristic at 150°C						
	S max (kg-cm)	S min (kg-cm)	S max-min (kg-cm)	S90 (kg-cm)	tc90 (minute)	ts2 (minute)	CRI
Efficient	5,71	0,41	5,30	5,18	9,17	4,12	19,80
Semi Efficient	5,66	0,33	5,33	5,13	5,02	2,42	38,46
Peroxide	2,05	0,46	1,59	1,89	39,10	NA	NA

The time required by the rubber compound to reach 90% of the state of cure by using sulphur curing system was relatively faster than peroxide curing system. Sulphur curing system used the mixture of CBS and TMTD as accelerators in order to obtain significant improvement in curing behaviour and mechanical properties of the rubber vulcanizate [13]. Efficient curing system gave longer optimum cure time and scorch time than semi efficient curing system although it consisted of more accelerator content. The length of curing time highly depends on the type and amount of accelerator mainly CBS. CBS belongs to sulphenamides type of rubber accelerator which is characterized by long induction period during the rubber vulcanization. This type of accelerator is classified as delayed-action accelerator since the sulfenamide has to split into thiazol and amine first before the thiazol act as rubber accelerator, and the amine as activator (coagent). Scorch time of peroxide curing system was a complicated mechanism because of the peroxide free radical species that were formed from the decomposition of dicumyl peroxide at the curing temperature immediately react with rubber molecular chains to form cross-links. It was regarded as the main factor of the absence of scorch time during the peroxide curing system [11].

3.2. Mechanical properties of natural rubber based elastomeric bridge bearing pad

The evaluation of mechanical properties of the natural rubber based EBB pad vulcanizate in the research was refered to SNI 3967:2013 for EBB with Duro 70 Shore A specification. Commercial EBB pad is sold based on its hardness level such as Duro 50 Shore A, Duro 60 Shore A, and Duro 70 Shore A beside based on its base elastomer (natural rubber or chloroprene rubber) and type (plain or laminated). The EBB pad Duro 70 Shore A was selected as basis specification since it was expected mechanically strong and had long durability to facilitated higher traffic load during its lifetime.

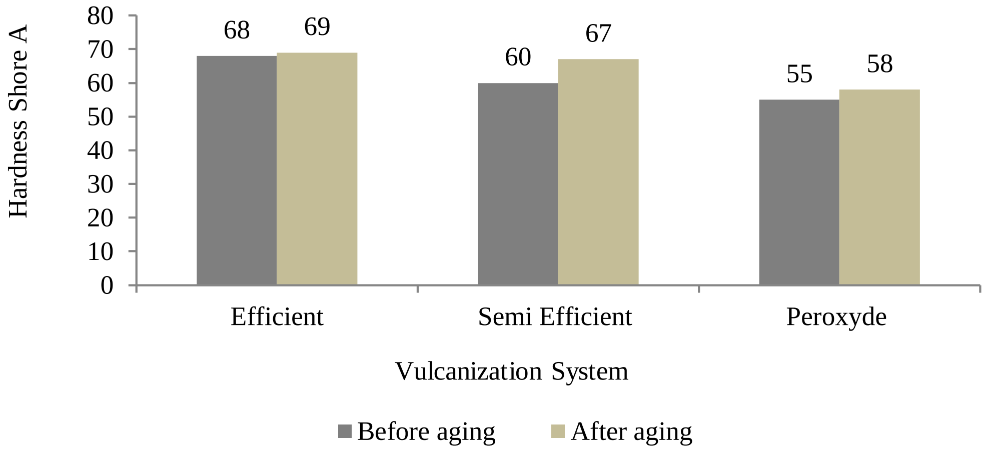

Figure 1. Hardness of natural rubber vulcanizate for EBB pad

Hardness value of natural rubber based EBB pad vulcanizate before and after aging is presented on Figure 1. Efficient sulphur curing system could fulfill the hardness standard requirement for EBB pad Duro 70 product as 70±5 Shore A. Meanwhile, the semi-efficient sulphur curing system at condition before aging and peroxide curing system exhibited lower hardness value than its minimum standard requirement (65 Shore A). High hardness value was produced from efficient sulphur curing system due to the presence of natural rubber – sulphidic molecular chain crosslink network. High crosslink density in efficient sulphur curing rubber matrix vulcanizate was followed with good mechanical properties. The increasing of hardness value after aging condition was caused by the oxidation of rubber molecules which constributes on the elimination of C=C double bonds. Oxygen in the air attacks the surface of rubber vulcanizate and it penetrates inside gradually. Thus, causing an apparent change in hardness distribution value [14].

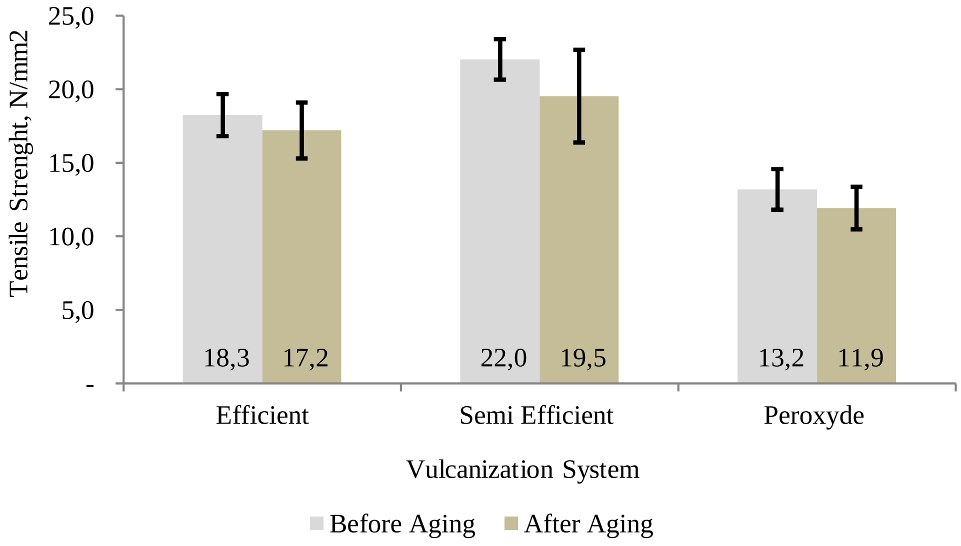

Figure 2. Tensile strenght of natural rubber vulcanizate for EBB pad

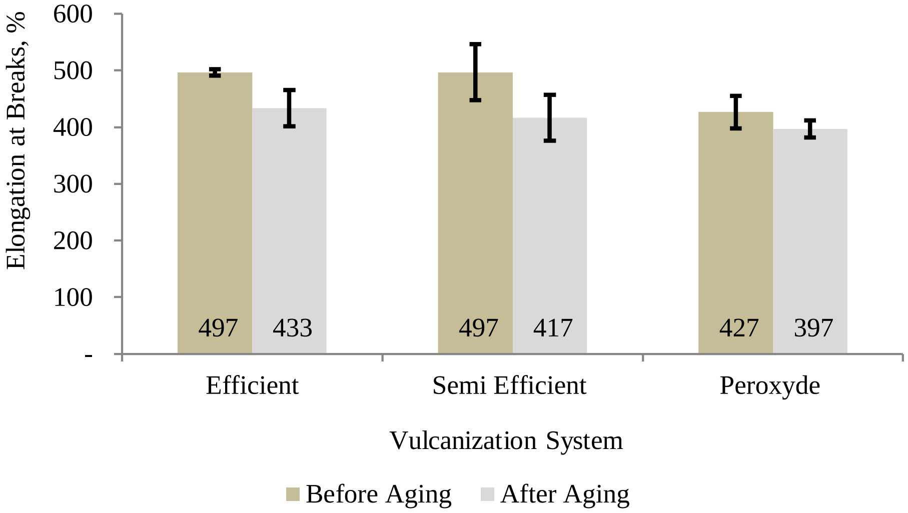

Figure 3. Elongation at breaks of natural rubber vulcanizate for EBB pad

Tensile properties also affects the determination of natural rubber based EBB pad quality. Tensile properties of a rubber product include tensile strength and elongation at breaks parameters. The results of tensile properties test are illustrated at Figure 2 and 3. Simillar to hardness measurement, only sulphur curing system could fulfill the tensile as above standard requirement (min 15,5 N/mm^2). Further, elongation at breaks parameter standard requirement could be met by the both curing systems (minimum value of elongation at breaks for EBB Duro 70 is 300%). Generally, sulphur curing system forms rubber vulcanizate with excellent tensile properties compared to peroxide curing system. Natural rubber vulcanizate which is obtained by sulphur curing system possesses high tensile properties due to natural rubber – sulphidic linkage crosslink network exhibit crystallinity upon stretching during the tensile properties test [15,16]. Strain induced crystalization usually occurs in natural rubber vulcanizate above 400% elongation [17]. Sulphidic crosslink also give higher mobility thus facilitate higher tensile properties [18]. Meanwhile, less flexible of C-C linkage which is formed inside the natural rubber vulcanizate during peroxide curing system is not long enough for crystalization upon stretching after aging condition. The reduction of tensile properties values after aging condition were regarded as the result of the changes in the original crosslink structure such as chain scission and crosslink modification. Chain scission commonly occurred at the early stages of accelerated thermal oxidative aging which indicated the presence of thermal degradation on natural rubber vulcanizate. The degradation of natural rubber vulcanizate was triggered by chain scission which leading the reduction of natural rubber vulcanizate ability to undergo strain-induced crystalization [19]. The fenomenon was also characterized by the physical appearence of rubber vulcanizate which become harder and brittle.

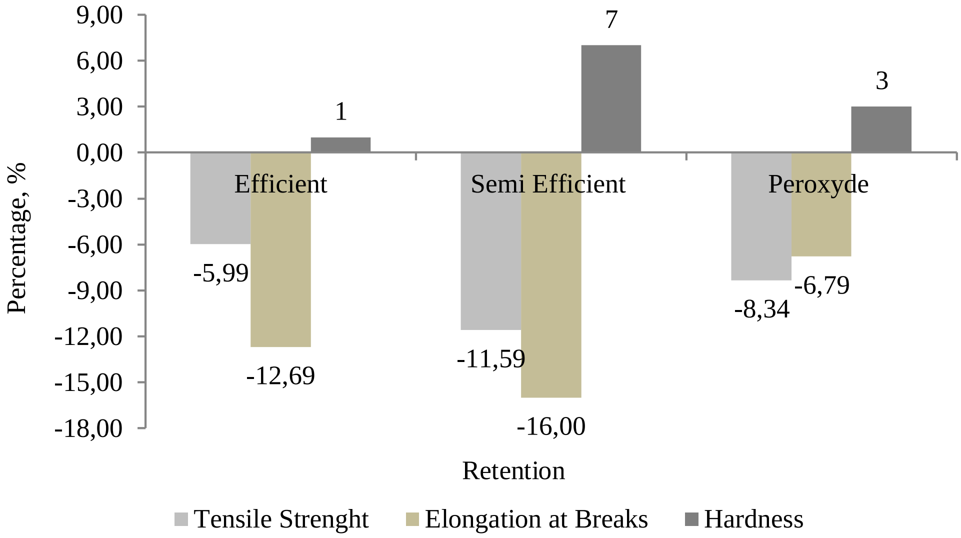

Figure 4. Retention of mechanical properties before and after aging condition

Figure 4 informs the retention value of mechanical properties of natural rubber based EBB pad vulcanizate at before and after accelerated thermal aging conditions. The three types of curing system applied in the research were able to meet the standard requirements as referred to SNI 3967:2013 i.e. maximum 10 point for hardness parameter and maximum 25% for each tensile strength and elongation at breaks, respectively. Retention value expresses aging resistance and thermal stability of a rubber vulcanizate. Thermal stability purpose as the ability to maintain the mechanical properties of materials under high temperature exposure [15].

Efficient sulphur curing system showed better thermal stability and aging resistance which was signed with lowest retention value of tensile strength followed with relatively unchanged on hardness value. This advantage was estimated due to the contribution of monosulphidic linkage on its rubber crosslink network structure. Low content of sulphur at vulcanizing agent /accelerator ratio in efficient sulphur curing system tend to form monosulphidic or disulphidic linkage. Higher content of monosulphidic or disulphidic linkage provide thermal stability and aging resistance than those of polysulphidic. The harder rubber vulcanizate after aging condition could be caused also by the enhancement the degree of crosslink density. Rubber vulcanizate produced by semi efficient curing system was dominated with polysulphidic linkage. Polysulphidic linkage has low dissociation energy which exhibit poor thermal stability properties. Similar to efficient curing system, vulcanization mechanism of rubber macromolecules by dicumyl peroxide also resulted good retention properties, so the mechanical properties after aging condition is relatively unchanged. Efficient and peroxide vulcanizing system provide slightly higher thermal stability due to the blends consisted of more stable monosulphidic and carbon-carbon linkage in the vulcanized network [20].

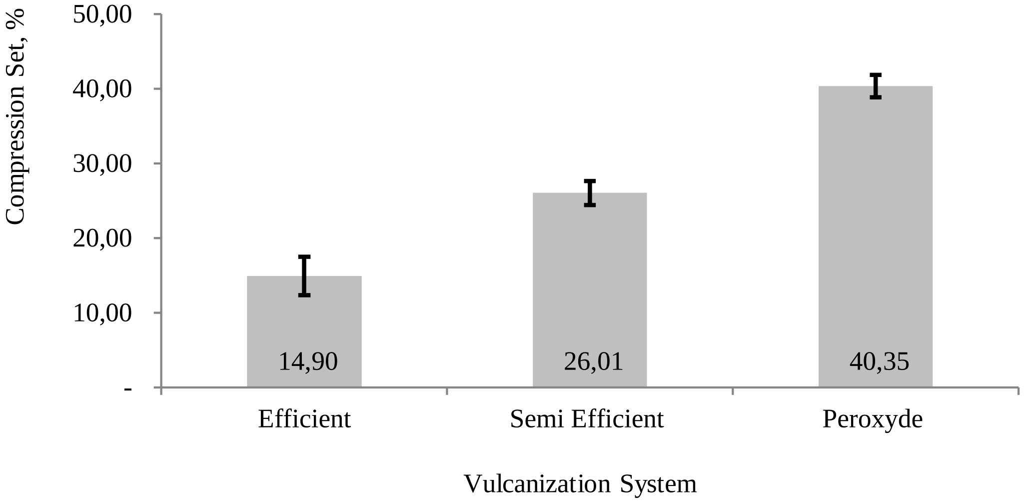

Figure 5. Compression set of natural rubber vulcanizate for EBB pad

Compression set parameter becomes one of the most important mechanical properties to determine the quality of commercial EBB pad product. This parameter which is related to stress relaxation evaluates the ability of EBB pad to facilitate the service load during use. EBB pad is primarily subjected to compression and shear since it is installed between substructure and superstructure of a bridge or flyover. From Figure 5, it could be seen that sulphur curing system relatively had lower compression set value in comparison with peroxide curing system. The presence of high degree of elastic sulphidic – rubber macromolecular crosslink network plays a significant role in maintaining of rubber vulcanizate original shape after being subjected to deformation or high pressure load. Meanwhile, the rigid character of carbon-carbon linkage in the matrix of peroxide cured rubber vulcanizate acted in the opposite direction so it produced high compression set value. The qualitative analysis by ozone resistance test showed that all natural rubber based EBB pad vulcanizate could resist the ozone attack which is indicated by the non apparent cracks on its surface (Figure 6). Degradation by ozonolysis to the elastomeric materials cause brittleness and macroscopic crack on its surface [21].

Figure 6. Surface of natural rubber based EBB pad after exposed to ozone

4. Conclusion

Referring to the result of curing characteristic and mechanical properties analysis, efficient sulphur curing system was regarded as the most appropriate curing system which could be applied in the manufacture of natural rubber based laminated EBB pad. All of the mechanical properties parameters of natural rubber based EBB pad as listed in the standard requirement SNI 3967:2013 Duro 70 could be fulfilled by efficient curing system especially on accelerated aging (represented by retention) and compression set values. Otherwise, peroxide curing system was not recommended due to the high compression set value on the rubber vulcanizate.

References

[1] Weisman J and Warn G P 2012 *J. Struct.Eng*. 138(2) 215
[2] Filipov E T, Fahnestock L A, Steelman J S, Hajjar J F, LaFave J M and Foutch D A 2013 *Eng.Struct.* 49 168
[3] Asl M J, Rahman M M and Karbakhsh A 2014 *Open Journal of Earthquake Reserach* 3 1
[4] Shresta B, Hao H and Bi K 2013 *Proc. of the Australian Earthquake Engineering Society 2013 Conference (Tasmania)* (Australian Earthquake Engineering Society) 12p
[5] Lewangamage C S, Abe M, Fujino Y and Yoshida J 2004 *Proc. of the 13th World Conference on Earthquake Engineering (Vancouver)* (Canadian Association for Earthquake Engineering & International Association for earthquake Engineering) 14p
[6] Gu H S and Itoh Y 2012 *Journal of Beijing University of Technology* 38(2) 186
[7] Choun Y S, Park J and Choi I K 2014 *Nucl.Eng.Technol.* 46(5) 605
[8] Ngamsurat S, Boonkerd K, Leela-adisorn U and Potiyaraj P 2011 *Energy Procedia* 9 452
[9] Yahya Y S R, Azura A R and Ahmad Z 2011 *J.Phys.Sci.* 22(2) 1
[10] Shuhaimi N H H, Ishak N S, Othman N, Ismail H and Sasidharan S 2013 *J.Elastom.Plast.* 46(8) 747
[11] Kruzelak J, Dosoudil R, Sykora R and Hudec I 2017 *Bull.Mater.Sci.* 40(1) 223
[12] Pimolsiriphol V, Saeouni P and Sirisinha C 2007 *Polym.Plast.Technol.Eng.* 46(2) 113
[13] Oliveira M G and Soares B G 2001 *Polym.Polym.Compos.* 9(7) 459
[14] Hamaguchi H, Samejima Y and Kani N 2009 *Proc. of 11th World Conference on Seismic Isolation, Energy Dissipation, and Active Vibration Control of Structures (Guangzhou)* (Anti-Seismic Systems International Society) 16p
[15] Arayapranee W and Rempel G L 2009 *J.Appl.Polym.Sci.* 114 4066
[16] Ikeda Y, Phinyocheep P, Kittipoom S, Ruancharoen J, Kokubo Y, Morita Y, Hijikata K and Kohija S 2008 *Polym.Adv.Technol.* 19 1608
[17] Rajan R, Varghese S and George K E 2012 *Prog.Rubber.Plast.Re.* 28(4) 201
[18] Kruzelak J, Sykora R and Hudec I 2015 *J.Polym.Res.* 22 636
[19] Surya I, Sukeksi L and Hayeemasae N 2018 *IOP Conference Series: Material Science and Engineering (Medan)* (Universitas Sumatera Utara) 7p
[20] Hayeemasae N, Ismail H and Azura A R 2014 *Mater.Des.* 53 651
[21] Hinchiranan N, Lertweerasirikun W, Poonsawad W, Rempel G L and Prasassarakich P 2008 *J.Appl.Polym.Sci.* 111, 2813

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