

EFFECT OF UV AGING ON PHYSICAL PROPERTIES OF VULCANIZED RUBBER WITH THE ADDITION OF RECLAIMED RUBBER

1,2,3) Department of Rubber and Plastic Processing Technology, Politeknik ATK Yogyakarta, Jl Ring Road Selatan, Panggungharjo, Sewon, Bantul, DI Yogyakarta

Corresponding email ¹⁾ :
mw-syabani@kemenperin.go.id

Muh Wahyu Syabani ¹⁾, Yuli Suwarno ²⁾, Mertza Fitra Agustian ³⁾

Abstract. Rubber solid waste amount increased continuously and caused environmental problem since it is very difficult to be naturally degraded. Therefore, the interest of using rubber waste as raw material for new rubber product is increased. Reclaimed rubber can be used as filler aditif for rubber processing. The aim of this research was to study the effect of UV aging on the rubber product as the reclaimed filler added. The mixing of the rubber and the additives used the kneader and open mill. The vulcanization process was done by hydraulic press. In this research, the reclaimed rubber addition was varied as follows: 12,5; 37,5 and 62,5 phr. The products quality differences before and after the UV aging evaluated using physical tests. The result of FTIR showed that the polymer chain were broken by ultraviolet radiation. The physical test gives result that the hardness and tensile strength decreased, but the elongation is increased after UV aging.

Keywords : UV aging; Rubber waste; Reclaimed rubber; Physical properties; Environmental.

1. INTRODUCTION

Rubber are important elastomer [1], but since vulcanized rubbers having crosslinked structure and contain many additive its cannot degraded easily [2][3]. The solid waste potentially damaged the environment if dumped without proper treatment [4]. Many attempt has been made to solved the problems, such as landfill, electrical generator and pirolisis [2][5][6]. But, there are still many problems faced from the system, thus its needed alternative methods for rubber solid waste managements [7].

Solid waste of rubber could be used as filler to substitute some of the rubber raw materials in compound processing [8]. This substitution can reducing the amount of rubber solid waste significantly, lowering the production cost, and also improving the product characteristic such as the uniformity and dimension stability [2][8][9]. In our previous works, higher amount reclaimed rubber addition could increased hardness of the vulcanized rubber, but also gaves lower abrasion resistance and elongation at break [10].

In recent years, the characterization of vulcanized rubber has been studied in many research, however the testing are usually done for the new products. The application of the product are prone to aging under external environments, such as temperature, ultraviolet radiation and humidity. Materials aging's lead to changes in product characteristic and realibility [11][12]. The evaluation of the aging condition was important factor to analysis the materials stability [13], thus could helps to made better material preferences, predicted the wear reliability and avoided failure application of the product. Meanwhile, although the effect of aging for elastomer structure and characteristic change got many attention from researcher [14], but the effect of ultraviolet radiation to elastomer had not been established yet [15][16]. Its well known that ultraviolet radiation as part of sun rays could break the polymer chain of the materials. Eventhough, Rasool [3] reported different result which the addition of reclaimed rubber gave better aging resistance.

The aims of this research were to studying the effect of ultraviolet radiation on the vulcanized rubber. Reclaimed rubber from solid waste were used as filler for the rubber processing. The samples were conditioned on the ultraviolet chamber at certained times then analyzed using FTIR and physical testing. The results could

gave deeper understanding on vulcanized rubbers aging condition, thus could be used as guide to choose appropriate materials and predicted the wearing age.

2. METHODS

Material

The rubber compound were consisted of brown crepe and compo crepe as raw materials. The filler that be used were reclaimed rubber, silica and carbon black. Minarex oil were used as plasticizer, glycolipoprotein extract (G-90) and trimethyl dihydroquinoline polymer (TMQ) as antioxidant and antidegradation. Zinc oxide (ZnO) and stearic acid as an activator. Tetra methyl thiuram monosulfide (TMTM) and n-cyclohexyl-2-benzothiazole sulfenamide (CBS) as an accelerator, and sulfur as a vulcanizing agent.

Research Equipment

The tools that used in this experiment consisted of kneader and open mill for compounding process and the hydraulic hot press for vulcanization process. Rubber hardness were measured using Durometer (Shore A). Universal testing machine (Gester GT K-02) were used to measure the tensile strength and elongation at break. The functional groups of materials surface were confirmed using FT-IR (Perkin-Frontier). The aging process simulation was using Ultraviolet-Tester (Atlas UV Test II).

Research Variable

The study of this research were focused on the addition factor of reclaimed rubber and aging time. The variation amount of reclaimed rubber were 12.5, 37.5, and 62.5 phr. Aging time variation were conducted by time span 0, 72, and 120 hours respectively.

Method

Raw materials were masticated using kneader. The masticated material was then mixed with activator, antioxidant and antidegradation, filler, and plasticizer consecutively until homogenous. The process was followed by mixing accelerators and vulcanization agents using open mill machines. Maximum temperature during compounding process was 70°C. The cooled compound sheet ($\pm 37^\circ\text{C}$) was then vulcanized using a hydraulic hot press at temperature of 160°C and a pressure of 100 kg/cm² for 15 minutes. Vulcanized rubber was then ready for testing.

Testing

Vulcanized rubber with a thickness of 2 ± 0.2 mm was cut to the size of each test sample, then placed on a holder and mounted in a UV tester. The test sample was made with three replications. The beam of ultraviolet radiation that used has a wavelength range of 280 to 315 nm. The distance between the sample and the source of the lamp was set uniformly. The temperature used was 32°C according to the average temperature of the environment in the tropics. Aging time variation were conducted by time span 0; 72; and 120 hours. Functional group transformation of the sample were analyzed using FTIR. While the physical properties were tested according to SNI 0778: 2009 and ISO 37: 2011 which included the values of hardness, tensile strength and elongation at break.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis

The effect of ultraviolet radiation were the function of penetration depth and radiation times [15]. Thus, to avoid the penetration depth variation, then the distances of the samples to ultraviolet lamp were setted using same arrangement for all samples. After aging simulation for 120 hours, visually there is no difference for all the samples. But, when the surface of the sample were rubbed, the sample with 120 hours aging had more oily texture than the 72 hours sample. The same condition also occurred for all the three reclaimed rubber addition variation.

When the ultraviolet radiation got in and adsorbed by the vulcanized rubber, the homogenous materials compound could change its behaviors [15]. The solubility of the additives in compound might be reduced and blooming to the surface. The identification of the loss of additives done by using the FTIR analysis. Fig 1, 2 and 3 below showed that the FTIR spectra of the vulcanized rubber with aging time for the addition of reclaimed rubber 12.5, 37.5 and 62.5 phr respectively. There are three functional groups wavelength that characterize the change which are 2900, 2112 and 1365 cm⁻¹. According to Liu [13], the number identified as aliphatic chain of C-H, accelerator excess of $-\text{N}=\text{C}=\text{S}$, and antioxidant C-N.

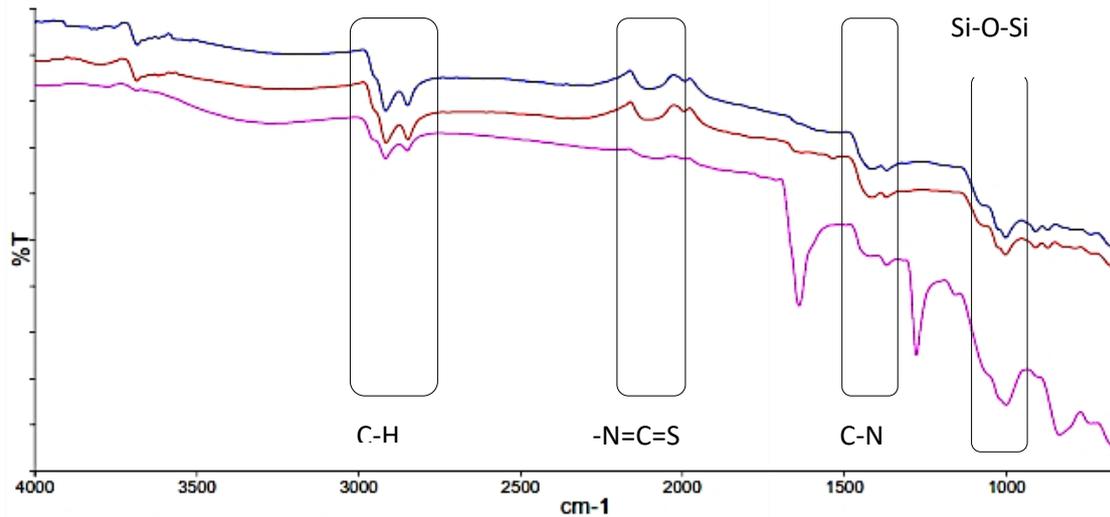


Figure 1. FTIR analysis for 12.5 phr reclaimed rubber

Absorbance measurements using FTIR for 12.5 phr were showed in Fig. 1. Its showed that all of three characterizing functional groups were relatively similar with the aging time variation. Thus, the amount of the additives in the each samples didnt change. There is only difference in the 1365 cm-1 spectra that gave slightly lower peak that indicates the decreased of the antioxidant amount. Antioxidant had function to reduce the materials defect from the aging. From the figure, we also showed that there isi decreased peak in 1000 cm-1 spectra that indicated the break of the Si-O-Si chain of the elastomer.

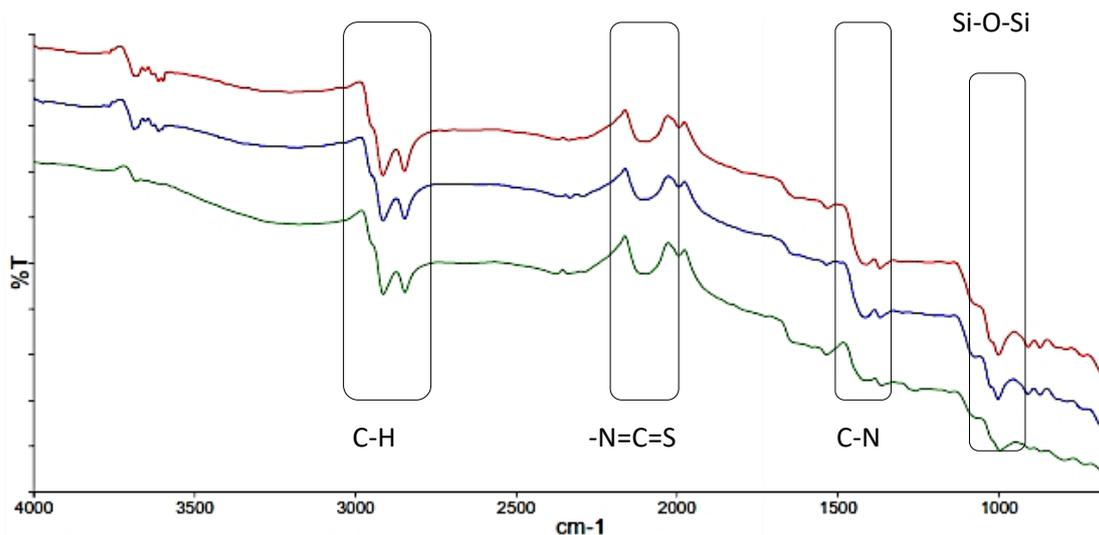


Figure 2. FTIR analysis for 37.5 phr reclaimed rubber

Fig. 2 showed that the adsorbance measurement for the addition of 37.5 phr reclaimed rubber in to vulcanized rubber. Similar trends were also occurred, three characterizing functional groups only gave slight differences. Thus, we could made conclusion that the loss of the additives were very slow for the aging time.

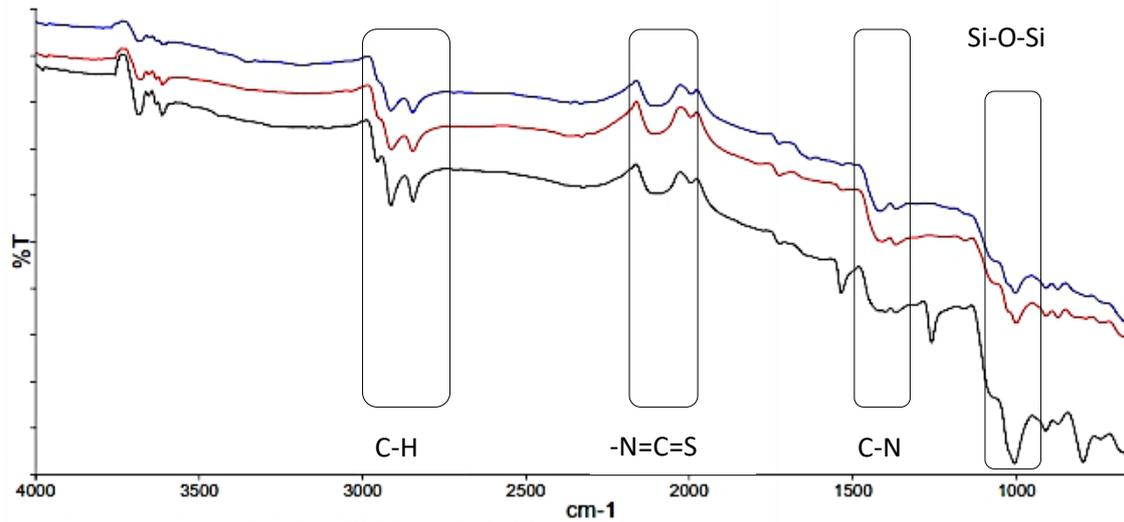


Figure 3. FTIR analysis for 62,5 phr reclaimed rubber

Similar result also presented for the addition of 62.5 phr reclaimed rubber as showed in fig. 3. Therefore, on these samples, the occurrence of the additives were also could be maintained. But, some of the additives solubility decreased then blooming to the vulcanized rubber surface. Nevertheless, at the vibration spectra of 1000 cm-1 showed lower absorbance that indicating the braking of the Si-O-Si chain.

Effects of Aging on Tensile Strength of Vulcanized Rubber

Tensile strength is a measurement of the force required to pull vulcanized rubber to the point where it breaks. Reclaimed rubber is solid rubber waste that has undergone vulcanization so that it is more difficult to form new bonds [10], while weak interactions between elastomers and fillers will have an impact on the mechanical characteristics of vulcanization [7] one of which is decreasing of tensile strength value [17]. Figure 4 below shows the effect of aging time for each sample with variations of reclaimed rubber addition.

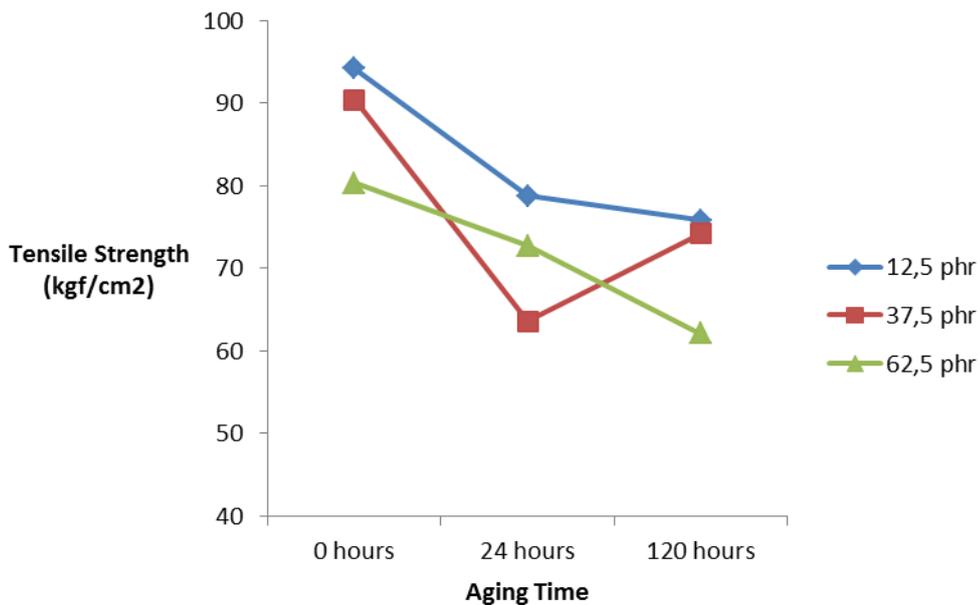


Figure 4. Tensile Strength Test Results
Source: Primary data processed, 2018

During aging, all three vulcanized rubber samples have similar tendency, that is the tensile strength value decreased with the longer aging time. The polymer chain will absorb radiation and when its value is higher than ionization energy it will cause radical formation [15]. The more radiation received will cause the polymer bonds to be damaged, so that the value of vulcanized rubber strength will also decrease. This is because the bond formation between the reclaimed rubber chain and the new rubber is more difficult than the new rubber polymer

chains. The bond between filler and elastomer is also weaker [10] making it easier to break when exposed to ultraviolet radiation. This tendency is clearly seen in Figure 4, where more addition of reclaimed rubber will result in decreasing of tensile strength faster along the aging treatment.

Effects Of Aging On Elongation Break

The elongation at break shows the ability of vulcanized rubber to stretch when pulled until it breaks. Its value is useful for determining the selection of materials suitable for applications that require elasticity such as belts, seals, outsoles and others. In our previous study, the elasticity of vulcanization will decrease in line with the increasing number of reclaimed rubber [10]. This is because the reclaimed rubber has vulcanized so that it carries a cross bond. The existence of this cross bond will reduce the freedom of movement between polymer molecules. The test results for the breakout elongation are shown in Figure 5.

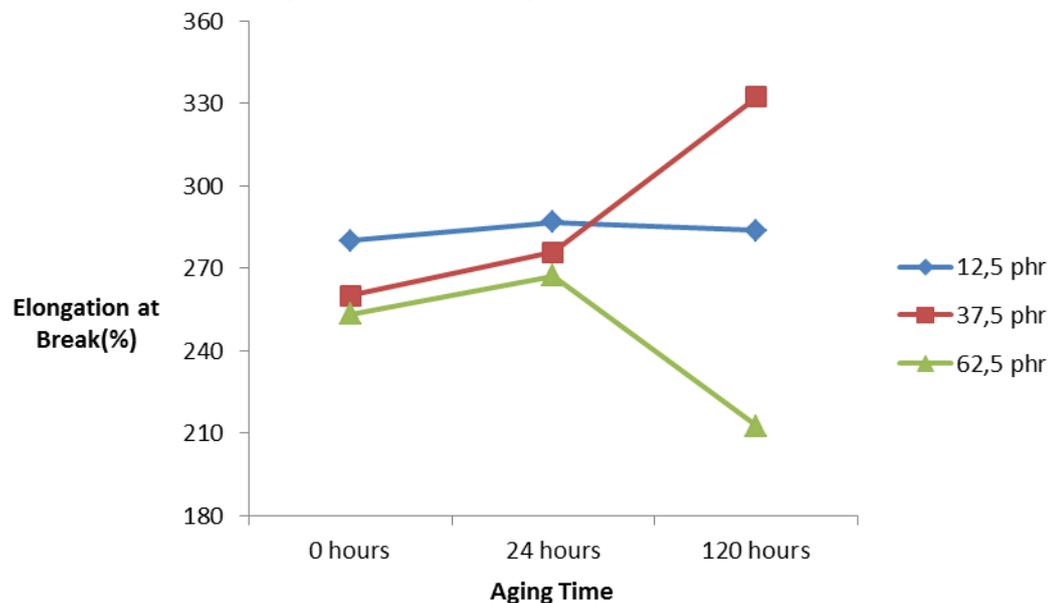


Figure 5. Elongation at Break Test Results
Source: Primary data processed, 2018

Aging causes a breakdown of some bonds between polymer chains [14], allowing slip movement between molecules. The ease of this movement can be seen from the increased vulcanized rubber elasticity. Seen in Figure 5, each sample has the same tendency, that is, elongation at break will increase at 72 hours aging time. Similar research conducted by Wu [12] also give harmonious results. Aging causes the net structure of elastomers to be damaged [11]. The elongation at break value has increased in aging 120 hours which shows that the number of broken bonds is increasing. However, it is interesting to see that the addition of reclaimed rubber 62.5 phr has the lowest increase of elongation at break. It can be explained that recycled rubber already carries a cross bond so that it has a greater crosslink density for vulcanized rubber with the addition of more reclaimed rubber.

The elasticity of vulcanized rubber is also influenced by plasticizers, where the value will decrease if the amount of plasticizer is also reduced [13]. Aging due to the influence of temperature has the potential to cause evaporation of plasticizers [13], but in this study it was seen that aging due to the influence of ultraviolet light did not have the same tendency. FTIR results indicate the presence of additives can be maintained, so that the elongation at break value is more influenced by the presence of crosslinking.

Effects of Aging on the Level Hardness

Hardness affects the appearance and durability of rubber products, and its value is related to the amount of filler added [4]. The more reclaimed rubber is added will provide a higher value of hardness [10]. This is due to the increase in the value of crosslink density from vulcanized rubber [7] as a result of cross-link formation between elastomers and reclaimed rubber. The results of the hardness test are presented in Figure 6 below.

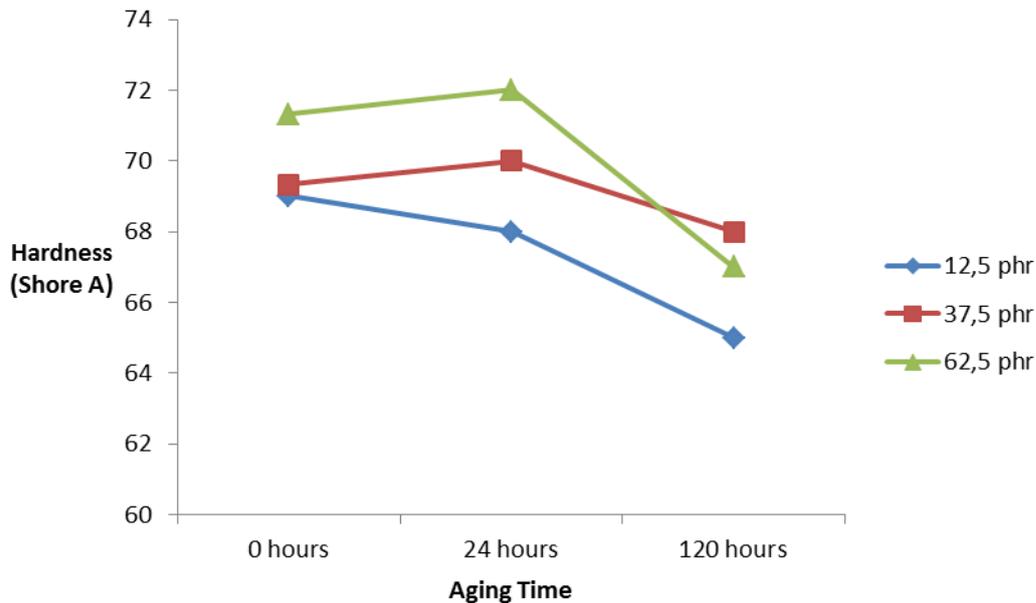


Figure 6. Hardness Test Results
Source: Primary data processed, 2018

At 72 hours aging, it can be seen in figure 7 that the hardness value will tend to increase except for vulcanized rubber with the addition of 12.5 phr. According to Goga [15] the main influence of the aging process is increasing crosslink density on the surface of the sample. Increasing cross-link density will cause the material to become hard [12]. When exposed to ultraviolet light, the surface of the sample will receive the most radiation, and the radiation value will decrease with increasing penetration depth. This causes the surface of the sample conditions are relatively different from the inside, while the hardness test is carried out on the surface of the sample. However, in aging 120 hours, more ultraviolet light radiation is received by the sample, and the more the bonds between the polymer rubber chains are broken. This is inline with the FTIR results which show the breakdown of Si-O-Si bonds in elastomers. The decrease in crosslink density causes a decrease in the hardness value of vulcanized rubber. At higher values, it will produce cracks and holes on the vulcanized rubber surface [12][16].

4. CONCLUSION

In this study, UV aging of the vulcanized rubber with the addition of the reclaimed rubber as a filler were studied using FTIR and physical testing. FTIR spectra shows that the during aging the additive were stay in the vulcanized rubber, but its solubility were decreased. UV aging effected the characteristic of the vulcanized rubber that it improve the formation of polymer network of the unsaturated vulcanized. Higher crosslink density of the vulcanized will improve the hardness, but for over 72 hours of aging will made trhe crosslink bond deteriorated, thus decreased the tensile strength and hardness. Futhermore, the breaking of the bond will make the polymer easily to moves, thus gives higher elongation at break. For better undestanding of the aging effect on the vulcanized, it need further research on the thermal and humidity aging simulation that close to real environmental aging.

5. ACKNOWLEDGEMENT

The authors gratefully acknowledge use of the services and facilities at the Politeknik ATK Yogyakarta, especially at the Workshop of Rubber Processing and Laboratory of Instrumentation.

6. REFERENCES

- [1] C. Li, J. Zhong, L. Yang, S. Li, L. Kong, and T. Hou, "Studies on the Properties and The Thermal Decomposition Kinetics of Natural Rubber Prepared with Calcium Chloride", *e-Polymers*, vol. 072, pp. 1-9, 2010.
- [2] B. Adhikari, D. De, and S. Maiti, "Reclamation and recycling of waste rubber", *Prog. Polym. Sci.*, vol. 25, pp. 909-948, 2000.

- [3] R.T. Rasool, S. Wang, Y. Zhang, Y. Li, and G. Zhang, "Improving the aging resistance of SBS modified asphalt with the addition of highly reclaimed rubber". *Construction and Building Materials*, vol. 145, pp. 126-134, 2017.
- [4] A. Yuniari, M. Sholeh, and I.N. Indrajati, "Pengaruh Sistem Vulkanisasi Konvensional (CV) dan Semi Efisien (SEV) terhadap Sifat Aging dan Termal Vulkanisat Campuran Karet Alam dan Karet Butil", *Majalah Kulit Karet dan Plastik*. vol. 31, no. 2, pp. 99-106, 2015.
- [5] D.C. Bomberger, and J.L. Jones, "An Evaluation of Modular Incinerators for Energy Recovery From Solid Wastes", *ACS Symposium Series* vol. 130, *Thermal Conversion of Solid Wastes and Biomass Chapter 6*, pp. 67-83, 1980.
- [6] K. Shigeo, K. Inoue, H. Tanaka, and T. Sakai, "Pyrolysis Process for Scrap Tires", *ACS Symposium Series* vol. 130, *Thermal Conversion of Solid Wastes and Biomass Chapter 40*, pp. 557-572, 1980.
- [7] K. Formela, D. Wasowicz, M. Formela, A. Hejna, and J. Haponiuk, "Curing Characteristics, Mechanical and Thermal Properties of Reclaimed Ground Tire Rubber Cured with Various Vulcanizing Systems", *Iran Polym. J.* vol. 24, no. 4, pp. 289-297, 2015.
- [8] P. Setyowati, Pramono, and Supriyanto, "Pemanfaatan Karet Reklam Dari Skrab Rubber Roll Untuk Kompon Sol Sepatu", *Majalah Kulit, Karet dan Plastik*, vol. 22, no. 1, pp. 38-44, 2006.
- [9] F.J. Navarro, P. Partal, F. Martinez-Boza, and C. Gallegos, "Influence of Crumb Rubber Concentration on the Rheological Behavior of a Crumb Rubber Modified Bitumen", *Energy Fuels.*, vol. 19, pp. 1984-1990, 2005.
- [10] M.W. Syabani, F.I. Fauziyyah, and T. Mutiara, "Pengaruh penambahan karet reklam dari limbah outsole terhadap sifat fisis dan sifat thermal produk outsole sepatu (Studi kasus di CV. Carita Niaga)". *Jurnal Sains dan Teknologi Lingkungan*, vol. 10, no. 1, pp. 26-40, 2018.
- [11] C. Neuhaus, A. Lion, M. Johlitz, P. Heuler, M. Barkhoff, and F. Duisen, "Fatigue behavior of an elastomer under consideration of ageing effects". *International Journal of Fatigue*, vol. 104, pp. 72-80, 2017.
- [12] J. Wu, K. Niu, B. Su, and Y. Wang, "Effect of combined UV thermal and hydrolytic aging on micro-contact properties of silicone elastomer". *Polymer Degradation and Stability*, vol. 151, pp. 126-135, 2018.
- [13] X. Liu, J. Zhao, R. Yang, R. Lervolino, and S. Barbera, "A novel in-situ aging evaluation method by FTIR and the application to thermal oxidized nitrile rubber". *Polymer Degradation and Stability*, vol. 128, pp. 99-106, 2016.
- [14] Q. Wang, S. Li, X. Wu, S. Wang, and C. Ouyang, "Weathering aging resistance of different rubber modified asphalts". *Construction and Building Materials*, vol. 106, pp. 443-448, 2016.
- [15] N.O. Goga, D.E. Demco, J. Kolz, R. Ferencz, A. Haber, F. Casanova, and B. Blumich, "Surface UV aging of elastomer investigated with microscopic resolution by single-sided NMR", *Journal of Magnetic Resonance*, vol. 192, pp. 1-7, 2008.
- [16] Y. Qin, J. Fu, L. Yu, Z. Yang and W. Guo, "Comparative research on aging properties of HTV silicon rubber via outdoor electric aging and ultraviolet accelerated aging". *Advanced Materials Research*, vol. 641-642, pp. 333-337, 2013.
- [17] A.M. Ajam, S.H. Al-Nesrawy, and M. Al-Maamori, "Effect of Reclaim Rubber Loading on The Mechanical Properties of SBR Compoisite". *Int. J. Chem. Sci.*, vol. 14, no. 4, pp. 2439-2449, 2016.