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Significant Factors Affecting the Thermo-Chemical De-vulcanization Efficiency of Tire Rubber

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Abstract

In this study, the influence of the molecular structure of the rubber, the carbon black loading and de-vulcanization time and temperature on the thermo-chemical de-vulcanization efficiency of whole tire rubber was investigated by correlating sol fraction and crosslink density (Horikx-Verbruggen method). Differences in molecular structure influence the de-vulcanization mechanisms of rubbers as well as the efficiency. Increasing carbon black loadings result in higher crosslink densities due to a deactivation of the de-vulcanization aid. Variation of de-vulcanization temperature and time results in different degrees of heat accumulation in the rubber during de-vulcanization and thus leads to different de-vulcanization efficiencies.

Keywords: Tire rubber; De-vulcanization; Recycling; Carbon black

1 Introduction

When mentioning the environmental pollution problems that almost every country is facing today, it is inevitable to discuss the issue of non-biodegradable waste like vulcanized elastomers and plastic. The molecular structure of these materials results in outstanding water resistance and in-conduciveness to growth of microbes. In addition, elastomers have a very strong network. As a result, these materials when becoming waste are difficult to decompose: some types may take more than 100 years to biodegrade completely in the environment.

Used tire rubber is one of polymer materials that is difficult to decompose. It is a durable material made of complex components consisting of various types of rubbers, reinforcing fillers and fabric. Therefore, disposal in the environment or usage of inappropriate methods of removal may cause environmental pollution in the future. Recycling and re-utilization of used rubber pose a great challenge. For end-of-life tires, incineration is currently the main outlet, impeding the re-use of this valuable raw material in new rubber products. Two recycling processes of end-of-life tires are well known: reclaiming and de-vulcanization. These two methods are often referred to as similar processes, but they are fundamentally different concerning the chemical reaction to break sulfur crosslinks, the ratio of crosslink scission to network breakdown, and the molecular structure of the polymeric material (Fig. 1). Reclaiming is usually accompanied by considerable scission of the polymeric chains resulting in a lower molecular mass fraction and poorer mechanical properties than comparable de-vulcanized and virgin rubbers due to the uncontrolled polymer scission which occurs during the reclaiming process. De-vulcanization targets at the sulfuric crosslinks in the vulcanized rubber, to selectively cleave C-S and S-S bonds. These strength of these bonds differs: -C-S-C (285 kJ/mol), -C-S-S-C- (268 kJ/mol) or –C-S_x-C- (251 kJ/mol). This can be one way to selectively break sulfur bonds in a crosslinked elastomer (1). A considerable share of material recycling can only be achieved if tire material can be used in real recycling loops: tires back into tires. This requires high-quality recycled rubber products, which can only be produced by a tailored de-vulcanization process.

Within this study, vulcanized rubber was de-vulcanized and its efficiency was investigated concerning the tendency for crosslink versus main-chain scission. Thermo-chemical de-vulcanization using the optimum conditions proposed by Saiwari and co-workers (2) was applied to rubbers used in passenger ca tires: styrene-butadiene rubber (SBR), brominated butyl rubber (BIIR), natural rubber (NR) and butadiene rubber (BR). The goal of this project was to elucidate the influence of the molecular structure of the elastomer on the de-vulcanization efficiency, and to understand the influence of carbon black in a thermo-chemical de-vulcanization process of the tire rubbers. The effect of carbon black loading (i.e., 30, 60, 90 phr) and de-vulcanization time and temperature on the de-vulcanization efficiency were also studied. The mechanisms behind the rubber network breakdown of the carbon black filled single rubbers will be investigated and discussed. The understanding of the factors affecting the de-

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vulcanization mechanism of vulcanized rubber are of major importance for the development of an efficient tire recycling.

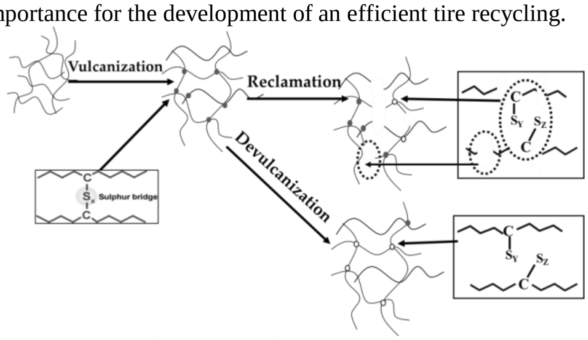

Figure 1: Simplified scheme of the two reactions occurring during rubber recycling processes: reclaming and de-vulcanization (2)

2 Background

The de-vulcanization of end-of-life of tire is a major challenge and was studied extensively over the past several decades. Many researchers attempted to develop a new de-vulcanization method such as mechanical (3, 4) thermo-mechanical (5) mechano-chemical (6), and supercritical CO_2 processes (7). Using microbes (8, 9, 10) and ultrasound (11, 12, 13, 14, 15, 16) in de-vulcanization is also extensively studied. Among the de-vulcanization processes, several methods were successfully developed in the laboratory; however, after re-vulcanization, the material exhibits poor mechanical properties compared to the starting vulcanizate due to aging during service life, and the fact that whole tire material is a blend of different compounds, polymers and fillers. A detailed study of some possibly complicating factors such as type of rubber: NR, SBR, BR, IIR, and presence or absence of fillers is needed. Thermo-chemical de-vulcanization by using diphenyl disulfide (DPDS) or other disulfides used as de-vulcanization aid is considered as an alternative way of recycling of used tires, which is widely studied nowadays. The main reasons to use this process and these de-vulcanization aids is that it is a rather simple process, applicable in the industrial sector, and low cost as well. The de-vulcanization mechanism of this method is shown in Fig. 2. There are two possible major reactions: The first one is thermal scission of the rubber network due to the elevated temperature of de-vulcanization. When thermal vibrations overcome bonding energies of S-S bonds or C-S bonds, the rubber network breakdown will occur mainly at the sulfur crosslinks being the weakest bonds in the network. At excessive temperatures, the rubber network is subjected to random scission: breakage of the rubber network will occur both ways, at the main chains of the polymer (C-C bonds) and at the sulfur crosslinks. For this reason, the free radicals generated during de-vulcanization include both, carbon radicals from main chain scission and sulfur radicals from sulfur bridge breakage. The second reaction is trapping of free radicals generated in the first reaction by sulfide radicals of DPDS, to prevent the recombination of broken rubber chains (Fig. 2). The trapping efficiency of free radicals in this reaction depends on the amount of sulfide radicals of DPDS.

3 Experimental

3.1 Materials

The rubber materials used in this study were butadiene rubber (BR) and emulsion-polymerized styrene butadiene rubber (SBR1502) produced by BST Elastomers (Thailand), Bromo-butyl rubber produced from KIJ PAIBOON (Thailand) and Natural Rubber (RSS#3) obtained from Yang Thai PakTai Company, Thailand. Treated distillate aromatic extract or TDAE oil (Vivatec 500) was supplied by Hansen&Rosenthal KG (Hamburg, Germany). Diphenyl disulfide, DPDS was used as the de-vulcanization aid was obtained from Sigma-Aldrich Company Ltd., England. The ingredients for preparing rubber compounds were ZnO (Global Chemical, Thailand), stearic acid (Imperial Chemical, Thailand), TBBS (Flexsys, Belgium), and sulfur (Siam Chemical, Thailand). Carbon black (N330) with a particle size of 24-32 nm and a CTAB surface area of 75 - 85 m^2/g was used. They were supplied by Polychem Chemicals, Thailand.

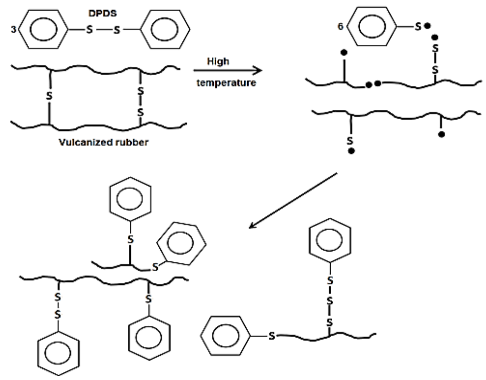

Figure 2: Simplified reaction scheme proposed for radical scavenging by DPDS in unfilled rubber (17)

3.2 Preparation of vulcanized rubber

Vulcanized tire rubbers were prepared by incorporation of vulcanization ingredients such sulfur, activators and accelerators, as well as anti-oxidants into NR, SBR, BR and BIIR in an internal mixer with a mixing chamber volume of 50 cm^3. The mixer was operated at a rotor speed of 60 rpm, a fill factor of 0.75 and an initial temperature of 50°C.

Table 1: Basic formulations of the rubber compounds

Ingredients	Amount (phr.)			
SBR	100	-	-	-
NR	-	100	-	-
BR	-	-	100	-
BIIR	-	-	-	100
Zinc oxide	3	5	3	3
Stearic acid	2	1	2	2
TBBS	1.5	1	1.5	1
Sulfur	1.5	2.5	1.5	0.5

The compounding formulations are simplified as shown in Table 1. Cure time ($t_{c,90}$) at a temperature of 170 °C was measured in an oscillating disc rheometer (ODR 2000). The cure time was used to vulcanize the rubber compounds in a compression molding machine at 170°C and 100 bar, into 2 mm thick sheets.

3.3 Preparation of de-vulcanized rubber

The vulcanized rubber sheets were subsequently ground in a Fritsch Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen at room temperature. Thermo-chemical de-vulcanization was performed batch wise in an internal mixer. A fill factor of 0.7, a constant rotor speed of 50 rpm and a chamber temperature of 220°C was used as de-vulcanization conditions. The de-vulcanization of ground rubbers were carried out using the optimized process conditions as elaborated for the gum tire rubbers (Saiwari *et al.,* 2013) as given in Table 2. DPDS (30 mmol/100 g rubber) was blended with 5 phr of TDAE oil relative to the polymer content of the rubber, and then mixed with the ground rubber. It was heated in an oven at 60°C for 30 minutes before feeding it into the mixing chamber. The de-vulcanization was carried out at 220°C, and the de-vulcanization time was 6 min. After de-vulcanization, the material was taken out of the internal mixer and directly quenched in liquid nitrogen and subsequently stored in a refrigerator to avoid an oxidation.

3.4 Characterization of the de-vulcanizates

3.4.1 Rubber soluble fraction

The soluble (Sol) and insoluble (Gel) fractions of the vulcanized and de-vulcanized materials will be determined by extraction in a Soxhlet apparatus by initial extraction for 48 hours in acetone in order to remove low molecular polar substances like remains of accelerators and curatives, followed by an extraction for 72 hours in tetrahydrofuran (THF) to remove the polar components: oil, non-crosslinked polymer residues, and soluble polymer released from the network by the de-vulcanization process. The extraction will be followed by drying the samples in a vacuum oven at 40°C and determining the weight loss until constant weight is achieved. The sol fraction is defined as the sum of the soluble fractions in acetone and THF.

3.4.2 Crosslink density

The extracted rubber samples are swollen in toluene for 72 hours at room temperature. The weight of the swollen vulcanizates will be measured after removal of surface liquid with absorption paper. The crosslink density will be calculated according to the Flory-Rehner (18) equation and corrected using the Kraus-correction (19).

Table 2: De-vulcanization condition

Factors	Conditions
De-vulcanization aid	DPDS 30 mmol/100 g rubber
De-vulcanization oil	TDAE 5 phr
De-vulcanization temperature	220°C
De-vulcanization atmosphere	With nitrogen gas purging
Dumping condition	In liquid nitrogen

3.5 Analysis of the de-vulcanization efficiency

The de-vulcanization efficiency was analyzed using the method developed by Horikx (20) and Verbruggen (21): the rubber sol fraction of the de-vulcanizate and the decrease in crosslink density of the rubber gel fraction were correlated. The positioning of the data points for a certain de-vulcanizate is indicative of the ratio of crosslink scission to polymer scission: the lower line as shown in Fig. 3 represents crosslink scission, while the upper line represents random scission.

4 Results and Discussion

4.1 Influence of rubber molecular structure

The influence of the rubber molecular structure on the thermo-chemical de-vulcanization efficiency of unfilled vulcanized rubber can be seen in Fig. 3. The position between the crosslink and main chain lines of the data points of each sample is different. This indicates that the de-vulcanization mechanisms of the rubbers differ. In case of NR, it is known that the molecular chains have a low thermal resistance and are destroyed easily at higher temperatures (220 °C). Therefore, almost 100% sol fraction and a crosslink density reduction to almost zero are observed in unfilled NR de-vulcanizates. This indicates that the NR network is completely broken during de-vulcanization. For SBR, the data point is located on the crosslink scission line, with a remaining crosslink density decrease of about 65% relative to the untreated SBR. This is attributed to the de-vulcanization conditions used in this investigation, as elaborated by for unfilled SBR by Saiwari (19). The de-vulcanization efficiency for BIIR is rather close to the value measured for SBR. This might be expected as both elastomers, SBR and BIIR, are co-polymeric synthetic rubbers (Fig. 4) with a lower concentration of double bond units in the carbon backbone compared to BR and NR. As the double bond is heat-sensitive, these polymers are expected have similar heat resistance properties. In the case of BIIR, the bromine atom can be thermally split off and it may interfere with the radical trapping of DPDS, causing a lower de-vulcanization efficiency.

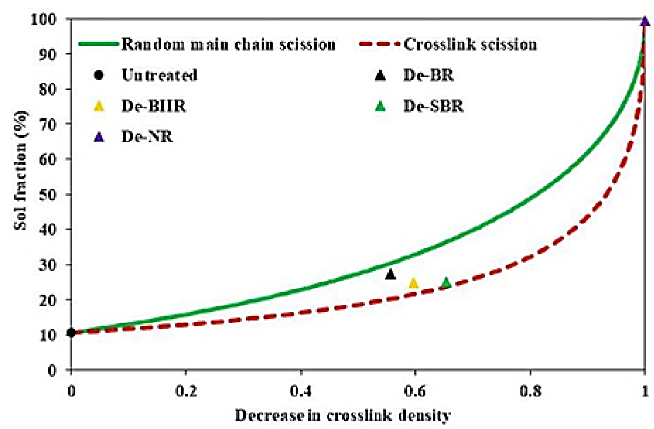

Figure 3: Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of unfilled rubber de-vulcanizates (De-xx: devulcanized polymer)

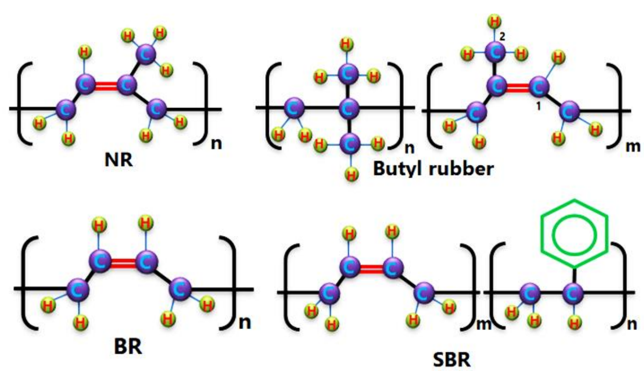

Figure 4: Basic molecular structure of each rubber

The data point of BR is located left of the points of SBR and BIIR, and close to the random scission line. It indicates a higher crosslink density compared with SBR and BIIR, thus decreased de-vulcanization efficiency. Since the molecular structure of this rubber contains a double bond in every unit of the repeating monomer, this results in lower heat resistance than SBR and BIIR. Therefore the rubber network is subjected to random scission: the breakage of the rubber network will occur at both, the main chains of the polymer and the sulfur crosslinks. Recombination of chain fragments will also occur, resulting in an increase in crosslink density.

4.2 Influence of carbon black loading

To understand the effect of carbon black loading on the thermo-chemical de-vulcanization efficiency, carbon black filled BR vulcanizates were prepared following the formulation as shown in Table 1 with varied carbon black loading from 30 phr to 90 phr. Figure 5 shows the Horikx-Verbruggen curves of this rubber. When adding carbon black, most data points get close to the random scission line. Moreover, they are shifted left as the carbon black loading is increased. This indicates a decreased de-vulcanization efficiency with addition of carbon black to BR. This is due to the two main causes: Firstly, the accumulation of heat during the de-vulcanization process increases with increasing carbon black loading, resulting in higher temperatures and hot spots compared to the unfilled rubber. As a result, the rubber network is more subject to random scission: breakage of the rubber network will occur at both, the main chains of the polymer and the sulfur crosslinks, resulting in a lower ratio of crosslink to polymer scission. Secondly, some filler aggregates and agglomerates might be broken and form radicals during de-vulcanization. The radicals will react with DPDS radicals and thus reduces the reactivity of DPDS.

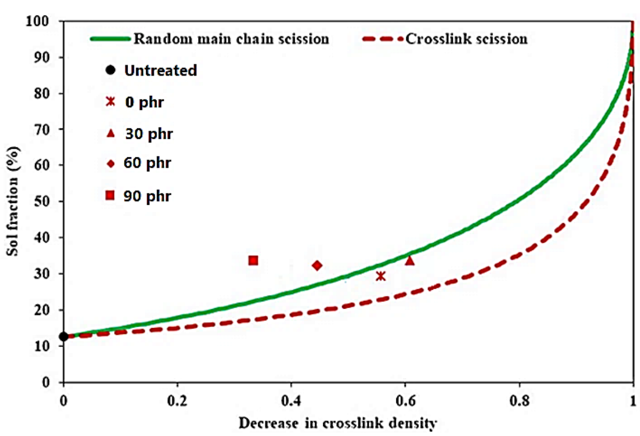

Figure 5: Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of carbon black filled BR de-vulcanizate

4.3 Influence of de-vulcanization time and temperature

In this study, BR compound with 60 phr of carbon black de-vulcanized following the formulation and conditions shown in Table 1 and Table 2, respectively. Fig. 6 and 7 show the relationship between the soluble fraction generated after de-vulcanization and the relative decrease in crosslink density while varying the de-vulcanization time and temperature. It is clear that the de-vulcanization time and temperature are major factors affecting the de-vulcanization efficiency. At a constant de-vulcanization temperature of 220°C with time variation from 3 min to 15 min (see Fig. 6), the data points are shifted to the left in the graph, which indicates lower de-vulcanization efficiency. Longer times contribute to a higher degree of recombination of broken rubber chains resulting in higher crosslink density. However, this recombination is rather uncontrolled, therefore the network structure of the devulcanized rubber is different from the starting network. At an increasing de-vulcanization temperature with short de-vulcanization time (3 min.), a contradictory trend is observed as shown in Fig. 7: The data points significantly shift to the right, indicating improved de-vulcanization efficiency. It was expected that an increased temperature but short de-vulcanization time causes a higher degree of network scission and, as a consequence, a larger sol fraction. This is attributed to uncontrolled generation of broken rubber chains at this excessive temperature.

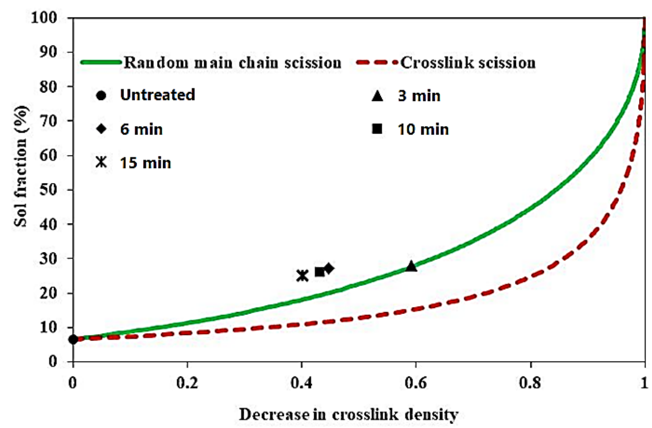

Figure 6: Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of filled BR with varying de-vulcanization time at 220 °C

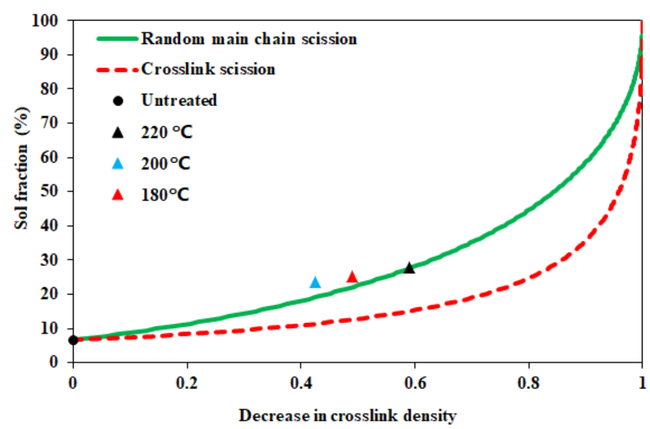

Figure 7: Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of filled BR de-vulcanizates using 3 min. of de-vulcanization time

5 Conclusion

There are 2 mechanism occurring during a thermo-chemical de-vulcanization process: firstly, generation of radicals by breakage of polymer chains caused by high temperatures, and secondly, trapping of radicals by the sulfide radical of DPDS to prevent recombination. Polymers with different molecular structures have different de-vulcanization efficiencies due to the variation in heat resistance: a lower heat resistance leads to a higher degree of random scission. When carbon black is present, uncontrolled thermal elastomer and filler network scission occurs. Depending on the type of polymer, recombination of the polymer fragments and formation of a new polymer network can happen as well. Increased carbon black loadings decrease the de-vulcanization efficiency. This is due to, firstly, breakage of main chains caused by excessive heating with increasing carbon black loading, and secondly, breaking of aggregates and agglomerates of carbon black to form a reactive surface, to which DPDS radicals are attached during de-vulcanization reducing the de-vulcanization efficiency of DPDS. For the factors of time and temperature, de-vulcanization of the ground rubber at different temperatures and times causes differences in heat accumulation in the rubber during de-vulcanization, which consequently leads to different de-vulcanization efficiencies.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing

References

1 Diao B, Isayev AI, Levin VY. Basic study of continuous ultrasonic devulcanization of unfilled silicone rubber. Rubber Chemistry and Technology.1999;72(1): 152–164.

2 Saiwari S, Dierkes WK, Noordermeer JWM. Devulcanization of whole passenger care tire material. KGK Kautsch. Gummi Kunststoffe. 2013;66(7-8): 20–25.

3 De D, Das A, De D, Dey B, Debnath SC, Roy BC. Reclaiming of ground rubber tire (GRT) by a novel reclaiming agent. European. Polymer Journal. 2006;42(4): 917–927.

4 De D, De, D. Processing and material characteristics of a reclaimed ground rubber tire reinforced styrene butadiene rubber. Materials Sciences and Application. 2011;2: 486- 498.

5 Formela K, Cysewska M. Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder. Polimery. 2014;59(3): 83-91.

6 Hassan MH, Aly RO, Abdel Aal SE, El-Masry AM, Fathy ES. Mechanochemical devulcanization and gamma irradiation of devulcanized waste rubber/high density polyethylene thermoplastic elastomer. Journal of Industrial and Engineering Chemistry. 2013; 19(5): 1722–1729.

7 Mangili I, Collina E, Anzano M, Pitea D, Lasagni M. Characterization and supercritical CO_2 devulcanization of cryo-ground tire rubber: Influence of de-vulcanization process on reclaimed material. Polymer Degradation and Stability. 2014;102: 15–24.

8 Yao C, Zhao S, Wang Y, Wang B, Wei M, Hu M. Microbial desulfurization of waste latex rubber with Alicyclobacillus sp. Polymer Degradation and Stability. 2013;98(9): 1724–1730.

9 Li Y, Zhao S, Wang Y. Microbial desulfurization of ground tire rubber by Thiobacillus ferrooxidans. Polymer Degradation and Stability. 2011;96(9): 1662–1668.

10 Romine RA, Romine MF. Rubbercycle: a bioprocess for surface modification of waste tyre rubber. Polymer Degradation and Stability. 1998;59(1): 353–358.

11 Isayev AI, Chen J, Tukachinsky A. Novel ultrasonic technology for devulcanization of waste rubbers. Rubber Chemistry and Technology. 1995;68(2): 267–280.

12 Isayev AI, Yushanov SP, Chen J. Ultrasonic devulcanization of rubber vulcanizates. I. Process model. Journal of Applied Polymer Sciences. 1996;59(5); 803–813.

13 Yun J, Oh JS, Isayev AI. Ultrasonic devulcanization reactors for recycling of GRT: Comparative study. Rubber Chemistry and Technology. 2001;74(2): 317–330.

14 Johnston ST, Massey J, Meerwall EV, Kim SH, Levin VY, Isayev AI. Ultrasound devulcanization of SBR: Molecular mobility of gel and sol. Rubber Chemistry and Technology. 1997;70(2): 183–193.

15 Shim SE, Isayev AI, Meerwall EV. Molecular mobility of ultrasonically devulcanized silica-filled poly(dimethyl siloxane). Journal of Polymer Sciecnecs: Part B Polymer Physic. 2003;41(5): 454–465.

16 Tukachinsky A, Schworm D, Isayev AI. Devulcanization of waste tire rubber by powerful ultrasound. Rubber Chemistry and Technology. 1996;69(1): 92–103.

17 Saiwari S. Post-consumer tires back into new tires: de-vulcanization and re-utilization of passenger car tires. Thesis Ph.D. May 2013.

18 Flory PJ, Rehner J. Statistical mechanics of cross-linked polymer networks I: Rubber like elasticity. Journal of Chemical Physics. 1943;11(11): 512–520.

19 Kraus G. A carbon black structure-concentration equivalence principle: Application to stress-strain relationships of filled rubbers. Rubber Chemistry and Technology. 1971;44(1): 199–213.

20 Horikx MM. Chain scissions in a polymer network. Journal of Polymer Sciences. 1956;19(93): 445–454.

21 Verbruggen MAL, Does LVD, Noordermeer JWM, Duin MV, Manuel HJ. Mechanisms involved in the recycling of NR and EPDM. Rubber Chemistry and Technology. 1999;72(4): 731–740.

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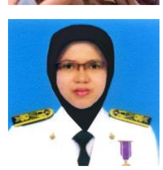

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