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The Effect of Accelerators on Vulcanization of Natural Rubber Compounds

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Abstract: The effect of accelerator type on vulcanization characteristics and mechanical properties of natural rubber was investigated. Also, the effect of growing quantity of MBTS on vulcanization characteristics and mechanical properties of natural rubber was investigated. The results show that the fastest cure time is obtained with thiurams and dithiocarbamates for natural rubber. Sulphenamides, especially TBBS gives the best tensile strength. Elongation at break first increases by increasing dose of MBTS and then decreases. The higher elongation at break is obtained with DPG.

Keywords: Natural Rubber, accelerator, vulcanization, dithiocarbamates, thiurams, sulphenamides

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1 INTRODUCTION

Rubber plant was first introduced by a French botanist, François Fresnau (Savran, 2001). Natural rubber is obtained from the latex of plant whose name is Havea Brasiliensis (Bateman, 1963). Christopher Colombus realized that Haitian natives was playing with the ball made of rubber during these Cond voyage to America in 1943 (kaucuk.org; Sabu et al.,2014). Vulcanization is the way to get the elastomers which is known as a different type of rubbers. Also, vulcanization is the one of the most significant technology in the modern industry. The fundamental part of vulcanization is to provide to form chemical bounds or ties combining rubber macro-molecules and converting polymeric molecules to the cross-linked form (Hoffman, 1989). Formation of crosslink is the primary condition in order to emerge the elastomeric features of the rubber (Walker & Rader, 1988). It is the most essential characteristic of an elastomer that is recovering the previous state in the following of the processes of tension or compression. In addition to this, the accelerators have the most vital role during the reaction of vulcanization by reducing the time (Susamma et. al, 2001; Akiba & Hashim, 1997). Similarly, sulfur can be beneficial for the reaction of vulcanization, but that is neither profitable as commercially nor time-saving without accelerators (Sadequil et al., 1998). Moreover, the type and quantity of accelerators and the ratio of sulfur-accelerator have a different effect on the value of hardening of rubber and its mechanical properties (Ismail et al. 2003; Fan et al. 2001; Pongdhorn et al. 2001).

NR has high rate of cross-linking along vulcanization. Natural rubber provides a good interference with other non-polar rubber because of non-polar formation. In addition, if it is intermixed by both SBR (styrene butadiene rubber) and BR (butadiene rubber), the resistance of abrasion & heat and properties of low heat is increased (Joseph et al., 1988). Similarly, in case of mixing with NBR (nitrile rubber) the endurance to oil and fuels can be enhanced and mixing with chloropyrene rubber provides high air resistance (Sirishina et al., 2001; Choi, 2002).

The products from rubber a have great importance in every part of our lives. The achievement of this product depends on the interference of correct polymers, rubber chemicals and extenders with suitable ratios (Loyd, 1976).

There are principally as what we call a prescription goes like rubber, sulfur, zinc oxide, fatty acid, accelerator, extender, softener, and anti-oxidant (Savran, 2001; Singh et al., 2015).

The effect of extender substances on textures of rubber in regard to strengthening can be monitored by measuring two main features of extenders which are ultimate strength and the value of modulus (Choi et al., 2003). The energy needed to break up rubber by stretching is getting greater when the value of modulus of rubber increases. Bonding between extender and polymer is related with their surface energy and active functional groups and the extender's surface energy should be same with polymer's one or more than that. The highest power gained by rubber is provided by carbon black as an extender. Primary extender substances used in rubber industry is calcium carbonate, clay, talcum, silica(s), zinc oxide, and so on (Gungor, 2022).

Accelerators are used to make fast cross-linking between polymer chains by means of sulfur. Accelerators and activators create active accelerator complex and this complex forms active sulfurization compound. This active compound provides cross-linking between polymer chains (Puspitasari & Cifriadi, 2019). The choice of accelerators and other chemicals is connected with the type of elastomers and intended performance characteristics (Frederick & Eirich, 1978).

The speed of vulcanization is affected by pattern of rubber as well as accelerator texture. Number of double bonds in polymer and the allylic hydrogen count influence the rapidity of vulcanization. Entropy starts to fall down due to too much reactive groups which is also let the ratio of reaction enhance. Furthermore, vulcanization reaction are diffusion-controlled reactions. Zinc-accelerator complex should be diffused into the elastomer (Mostoni et al, 2019). As the surface area of zinc-accelerator complex grows, the diffusion speed and in this way, the vulcanization rapidity drops (Kresja & Koenig, 1993).

In this study, the features of vulcanization of the mixtures of natural rubber by using different accelerators and the features of this after vulcanization was examined. Also, it was investigated that how the physical characteristic of the mixture of natural rubber can be changed with varied amount of accelerators during vulcanization and after vulcanization.

2. EXPERIMENTAL SECTION

2.1. Materials and Method

The structure of natural rubber is 99% cis- and 1,4% trans- poly isopyrene (Bateman, 1963).

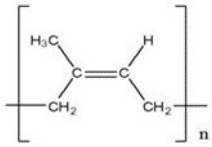

Figure 1: The structure of natural rubber (NR).

The presence of double bonds is necessary for vulcanization of sulfur. Nevertheless, this double bonds cause to aging effect by reacting with oxygen and ozone. Since the heat resistance of those is low, there is a tendency to reverse during vulcanization. Poly sulfidic crosslinks are thermally unstable and they are degraded into mono- or di-sulfidic links. The name of this process is called as reversion. In order to prevent this, the procedure of vulcanization should be carried out at low temperatures and hardening should be checked. Even though the unsaturation rate is various, there is an increment in mechanical performance (Sirqueira & Soares, 2003).

Initial: In this step, a free sulfur atom is degraded and amine is formed with MBT. Active sulfur is taken place as a result of reaction between amine and sulfur. It is also obtained that there is a reduction in the amount of sulfonamide in consequence of formation of accelerators & sulfur accelerator-poly-sulfite and di-sulfite. Until poly-sulfites reach at maximum level, this step ends.

Activation: Poly-sulfites' accelerator and di-sulfites begin to decrease and it is obtained some formations such as MBTSx. This step goes on until the accelerator is out.

Sulfurization and cross-linking: At the level of sulfonamide, di- and poly-sulfite is finished, polymeric bonds with the sulfur and cross-link is formed at the same time.

Aging and Reversion: When free sulfur runs out, accelerator complex goes on to reaction with cross-links which is poly-sulfidic. These reactions are as follows: Removing the sulfur from cross-links, breaking cross-links, development of cyclo-sulfur structure, formation of conjugate unsaturation in polymer, and collapsing zinc-sulfite.

2.2. Used Materials

SMR 10 CV and Dutralter 4038 as natural rubber and EPDM were used, respectively. Carbon blacks are labeled as FEF N 550 and HAF N 330. Along with these, accelerators used are MBT (2-mercaptobenzothiazole) MBTS (dibenzoidazole disulfur), CBS (N-cyclohexyl- 2 benzimidazole sulfonamide), MBS (2-benzimidazole-N-sulfene morpholine), TBBS (N-tertiary butyl-2 benzimidiazole sulfonamide), TMTD (tetramethylthiuram disulfide), TMTM (tetramethylthiuram monosulfide), ZDMC (zinc dimethyldithiocarbamate), ZDEC (zinc

diethyldithiocarbamate), ZEPC (zinc ethyl phenyldithiocarbamate), DPG (diphenylguanidine).

2.3. Preparation of Rubber Mixture

The mixture was prepared in the open laboratory two cylindered shaft. (ASTM D3182).

In the first trial, Natural rubber and various accelerators and a series of mixture were attained. There was a mixture prepared from the union of natural rubber. This mixture contains natural rubber 100 phr, Carbon Black 78.94 phr, Aromatic oil 6.31 phr, Zinc oxide 6.31 phr, stearic acid 1.84 phr, sulfide 1.00 phr, different accelators (MBT, MBTS, CBS, MBS, TBBS, TMTD, TMTM, ZDCM, ZDEC, ZEPC, DPG) 1 phr. Phr stands for parts per one hundred rubber.

In the second trial, different amounts of MBTS were used as accelerators and tests were performed. The recipe contains natural rubber 100 phr, Carbon Black 78.94 phr, Aromatic oil 6.31 phr, Zinc oxide 6.31 phr, stearic acid 1.84 phr, sulfide 1.00 phr, different amounts (0.40-0.60-0.80-1.00-1.20-1.40-1.60) of MBTS.

2.4. Used Devices and Features

2.4.1. Rheometer

It is used to measure the vulcanization characteristics of mixtures and to save vulcanization curve. It also applies oscillating stretch into mixture under high temperature and pressure and as a consequence of increase in a cross-link's intensity, an increment in torque is shown as a function of time. The unit of torque is N-m or lb-in (pounds inch) (Rader, 1985).

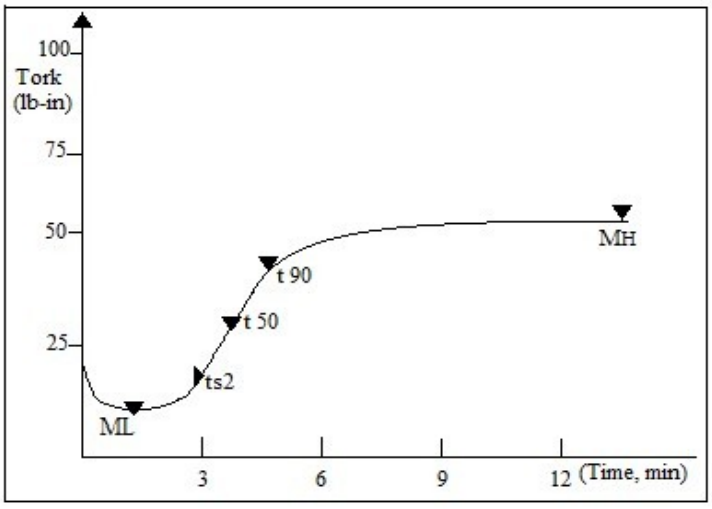

Figure 2: Graphic of curve of vulcanization.

Ts2 : Pre-vulcanization, Beginning time of hardening (scorch time) (min.)
MH : Maximum torque
T90 : Time when 90% of the maximum torque is reached (min)
ML : Minimum torque

Vulcanization state which is made ready with each distinctive accelerators was gauged by MDR-2000 Rheometer device. (ASTMD 5289). NR mix was tested throughout 5 minutes at 180 °C (Table 1). Later, hardening characteristics of NR mixture blended with a changing amount of MBTS was measured by Rheometer in the condition of 5 minutes and at 180 °C. (Table 2). (Teker et al, 2008).

Table 1 : The feature of vulcanization of NR mixture prepared with different types of accelerators.

	MBT	MBTS	CBS	MBS	TBBS	TMTD	TMTM	ZDMC	ZDEC	ZEPC	DPG
ML (lb-in)	2.00	1.73	1.45	1.83	1.74	1.33	1.28	1.54	1.46	1.29	1.48
MH (lb-in)	8.04	8.20	11.35	11.67	11.52	12.60	11.34	9.64	8.44	8.04	6.93
t90 (min)	1.38	1.28	1.47	1.75	1.59	0.69	0.94	0.61	0.73	0.76	1.46
ts2 (min)	0.57	0.57	0.70	0.75	0.69	0.41	0.62	0.36	0.43	0.41	0.53

Table 2: The feature of vulcanization of NR mixture prepared with changing amount of MBTS.

	MBTS of amounts (phr)					
	0.40	0.60	0.80	1.00	1.20	1.60
ML (lb-in)	1.51	1.30	1.83	1.51	1.86	1.84
MH (lb-in)	7.57	7.84	9.35	9.42	10.16	10.99
t90 (min)	1.57	1.35	1.24	1.12	1.10	1.02
ts2 (min)	0.60	0.56	0.57	0.60	0.59	0.60

2.4.2. Shoremeter

Followed by vulcanization, the toughness measurement was carried out with a Braiss Shore A Durometer (ASTM D2240). The results are given in Tables 3 and 4.

2.4.3. Tensometer

This apparatus makes an indication of both extension of product at the time of failure and fracture resistance of product after vulcanization. The thickness of sample cut as bow-tie was measured from three different part and it was hanged on between two wangs of tensiometer and the power was applied into sample. At the time of failure of sample, tensiometer saves failure-extension curve and gives the values of them.

Breaking Point: Ratio of forces between at the time of failure and at the of beginning.

Breaking Elongation: Ratio of length between changing at the failure and changing at the beginning.

Modulus: The amount of unit surface for the force applying for a specific extension.

3. RESULTS AND DISCUSSION

3.1. The Effect of Accelerators on Features of Natural Rubber Mixture

Vulcanization charactheristics of natural rubber mixture prepared with different accelerators obtained after rheometer test were compared with the physical features of the ones obtained by tensiometer test after vulcanization.

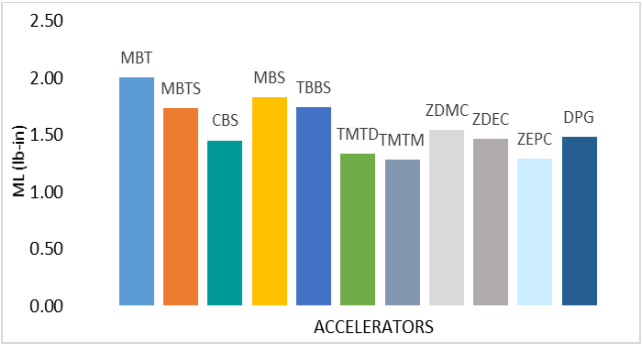

Figure 3: The effect of accelerators within natural rubber mix on ML value.

Table 3: The feature of vulcanization of NR mixture prepared with different type of accelerators.

	MBT	MBTS	CBS	MBS	TBBS	TMTD	TMTM	ZDMC	ZDEC	ZEPC	DPG
Hardness (Shore A)	58	59	62	59	65	62	62	63	61	61	53
Modulus (MPa)	10.17	10.59	15.64	13.72	16.74	15.90	15.46	13.03	11.26	10.71	7.19
Breaking strength (MPa)	16.53	17.82	21.46	20.90	23.18	18.60	19.79	20.62	19.15	17.94	12.39
Elongation at break (%)	417.9	473.4	414.9	445.5	423.8	355.7	381.7	477.8	479.6	462.2	446.1

Table 4: The feature of vulcanization of NR mixture prepared with changing amounts of MBTS.

	Amounts of MBTS (phr)					
	0.40	0.60	0.80	1.00	1.20	1.60
Hardness (Shore A)	53.00	55.00	56.00	57.00	59.00	60.00
Modulus (MPa)	8.56	9.53	11.20	18.95	20.04	20.18

According to Figure 3, The maximum ML value is provided with MBT, whereas the minimum ML value is carried out with TMTM and ZEPC.

As indicated in Figure 4, the maximum and minimum MH value is respectively reached by TMTD and DPG. With the TBBS, and sulfur donor, TMTD, a quite high MH value is achieved. Similar results were obtained with previous studies. The highest MH values were obtained with TBBS and TMTM, while the lowest MH value was obtained with DPG. (Setyadewi et al. 2020). Also, the same features of dithiocarbamide providing rapid hardening is quite weak for rubber.

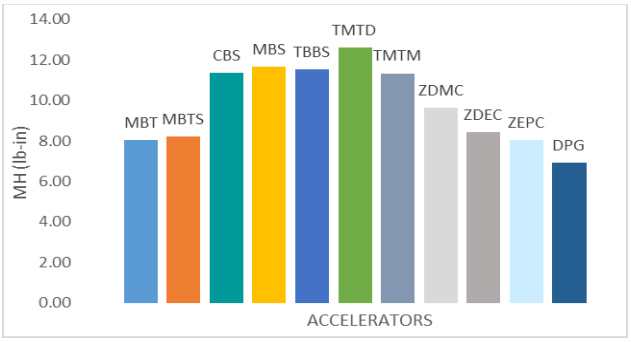

Figure 4: The effect of accelerators within natural rubber mix on MH value.

In Figure 5, the lowest hardening time, i.e., providing fastest hardening group, belongs to ZDMC and TMTD. The longest hardening time is given by sulfonamide group and DPG. Dithiocarbamate accelerators are used as ultra-fast accelerator for NR latex based compounds. Similar observations were presented in research work published by Formela et al. (2015).

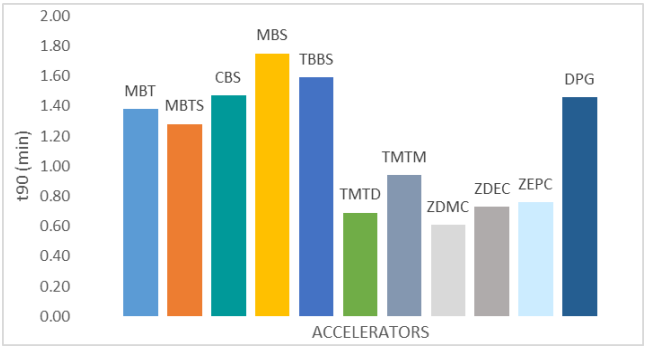

Figure 5: The effect of accelerators within natural rubber mix on t_{90} value.

As demonstrated in Figure 6, sulfonamide has the safest processing related with the highest value of ts_2. Amines also facilitate the conversion of elemental sulfur (S8) and/or polysulfide into active open chain sulfur through ring opening reaction. Amines might attack polysulfidic crosslink, either by direct reaction or by HS- generation (Heideman et al., 2004).

Also, TMTD and dithiocarbamide groups are the fastest one starting to harden. In another similar study, the lowest T90 and ts2 values were obtained using TMTD accelerator (Koc&Tuken, 2019). Generally, TMTD accelerated vulcanization offers short scorch time as TMTD is designated as an ultra-fast accelerator (Samarasinghe et al., 2020).

The comparison of toughness values after vulcanization is shown in Figure 7. According to that, the lowest is with DPG. Whereas the highest toughness value is with TBBS. ZDMC, Thiuram have also shown high hardness values. The crosslink density of rubber vulcanized also affects the hardness value. Their high stiffness was caused by the decreased mobility of polymer chains, what was also confirmed by the values of hardness and elongation-at-break (Nabil et al., 2014).

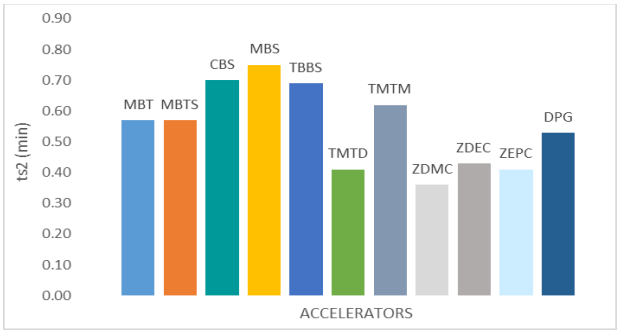

Figure 6: The effect of accelerators within natural rubber mix on ts_2 value.

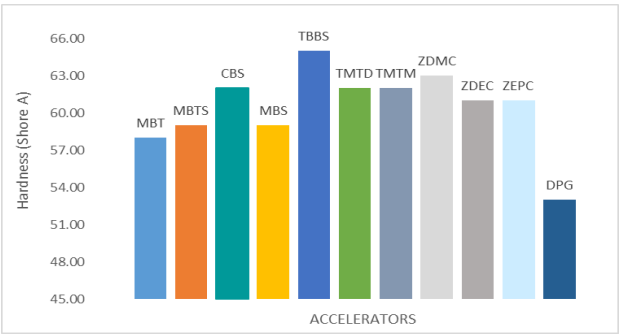

Figure 7: The effect of accelerators within natural rubber mix on hardness value.

The modulus value obtained with different accelerators is displayed in Figure 8. The top number of the modulus is materialized with thanks to TBBS, ZDMC and thiuram. In the study of Markovic et al. (2009), in the mechanical comparison of MBT, TMTD and CBS in NR/CSM mixtures, it was found that mixtures made with TMTD had higher tensile strength values (Markovic et al., 2009).

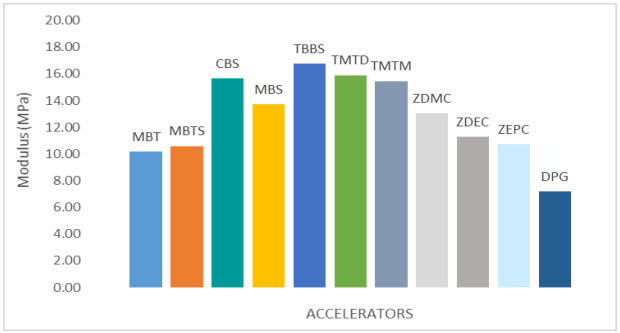

Figure 8: The effect of accelerators within natural rubber mix on modulus value.

The highest breaking strength is provided by TBBS and other sulfonamide. The comparison of these values are given in Figure 9. In contrast, the minimum value happens with DPG. However, it is realized that the strengthening properties of DPG used generally as secondary accelerator is low. This is due to the chemical structure of DPG. (Formela et al., 2015)

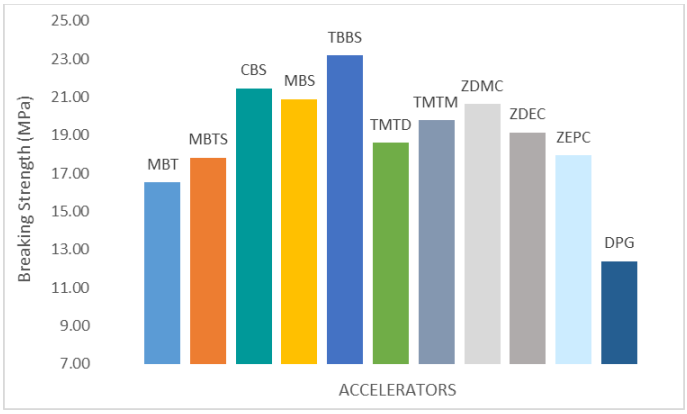

Figure 9: The effect of accelerators within natural rubber mix on breaking strength value.

When the elongation amounts are compared, the maximum and minimum level is respectively given by dithiocarbamate and thiuram groups (Figure 10). Compared to Figures 7, 8, 9, 10, as the hardness increases, the breaking strength increases, elongation decreases. High hardness can be evaluated as providing high crosslink density of these groups. The high crosslink density causes the molecular chains to move less. Similar results were obtained in the study conducted by Comez et al. with Thiuram changes, the highest hardness and breaking strength values and the lowest elongation values are observed (Comez & Ozturk, 2023).

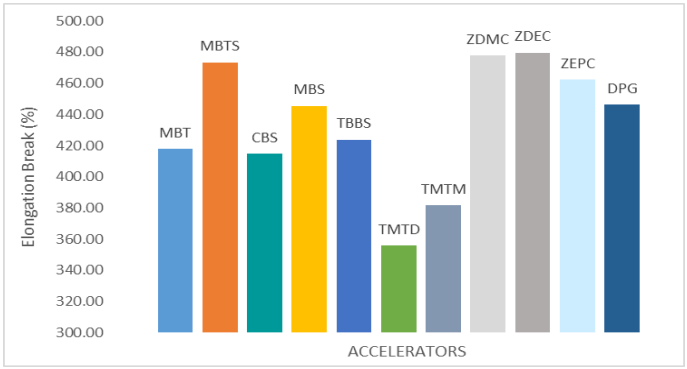

Figure 10: The effect of accelerators within natural rubber mix on elongation value.

Change in ML amount and MBTS increase in natural rubber mixture prepared according to rise in MBTS portion is demonstrated in Figure 11. ML value is not changed more as the quantity of accelerators is varying. The cause for that can be said as being affected by mixing condition within the shaft.

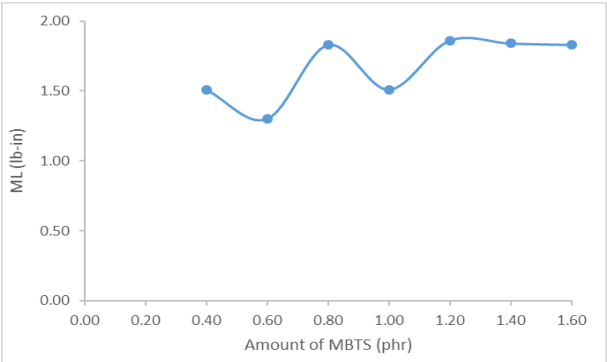

Figure 11: The change in ML value depending increase in MBTS.

As seen in Diagram 12, MH figure is generally raised with the portion of accelerators used. On the other hand, after this level, there is no such a tremendous change.

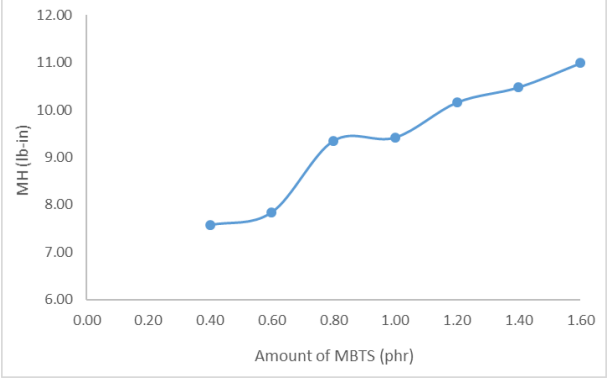

Figure 12: The change in MH value depending an increase in MBTS.

While the amount of accelerators increases, t90 value decreased as shown in Figure 13. In other words, vulcanization is accelerated.

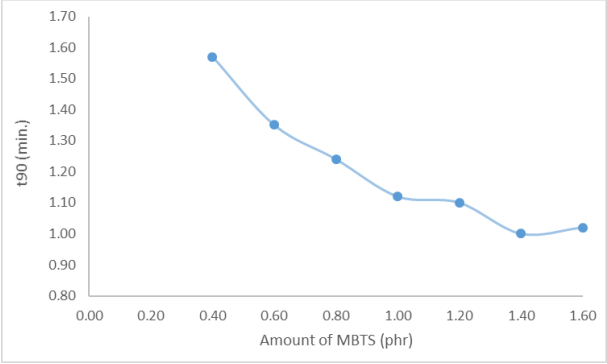

Figure 13: The change in t90 value depending an increase in MBTS.

Ts2, the time to start hardening, becomes shorter a little bit as the accelerator portion is gone up, but then, it raises and does not undergo a change so much. The values are compared in Figure 14.

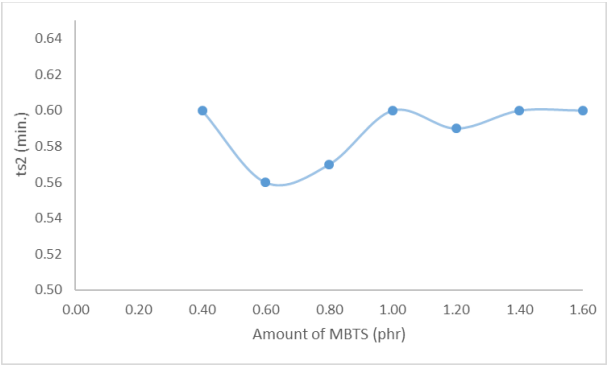

Figure 14: The change in ts2 value depending increase in MBTS.

The crosslink density of rubber increases with the rise in the amount of accelerators. So, hardness values increase.

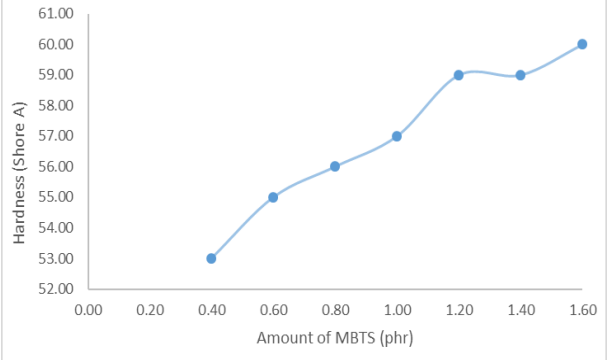

Figure 15: The change in toughness value depending increase in MBTS.

Modulus values increase with the rise in the amount of accelerators, but then, they do not undergo a change so much. The change in modulus value depending increase in MBTS is shown in Figure 16.

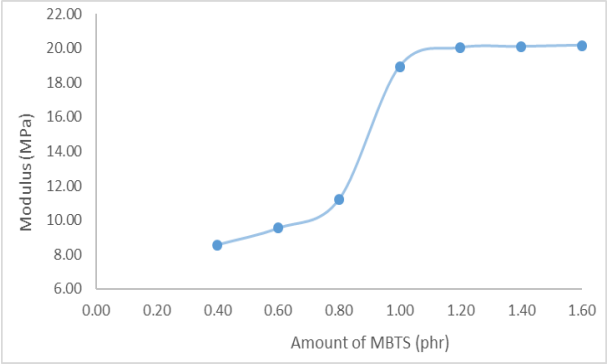

Figure 16: The change in modulus values depending increase in MBTS.

4. CONCLUSION

ML value named as number of minimum torque depends on mixing condition and time. ML values give an idea about the viscosity of mixture. For the natural rubber, the medium level accelerator provides high ML values, whereas rapid level accelerator gives low ML values. The lowest ML values were obtained for Thiuram and dithiocarbamate groups. The number of ML is interrelated with physical features such as stretching, breaking, and tearing resistance. The highest MH values were obtained with TBBS and TMTM, while the lowest MH value was obtained with DPG. TBBS among all sulfonamide provides the highest cross-linking intensity as an accelerators. Therefore, it shows good enough strength characteristics. Also, thiuram gives good cross-linking intensity in conventional systems and thus, they provide great breaking strength values. As a result of this, thiuram and sulfonamide having the highest MH values indicates sufficient breaking strength and modulus properties. Moreover, zinc dithiocarbamides give good breaking strength. Toughness features proportional with cross-linking intensity are also high in the mixture prepared with thiurams, dithiocarbamides, and TBBS. The minimum t90 value is obtained with thiurams and dithiocarbamides whose rapidity of vulcanization is great. On the contrary, medium level accelerators such as mercapto compounds and sulfonamides give longer t90 value. Sulfonamide giving quite late activation of vulcanization provides the greatest ts2 values. Dithiocarbamides whose processing safety is pretty low and which reacts rapidly indicates very low ts2 values. In other words, they react as quickly as possible.

In the studies regarding to variance in the amount of MBTS, if the portion of acceleration increases, t90 value goes down, i.e., vulcanization steps up. As the intensity of cross-linking bond is gathered, MH quantity also rises and thus, breaking strength, modulus and toughness level increase, too. Additionally, ML and ts2 values are not affected so much from such kind of changes. Hence, the stability can not happen. At the beginning the elongation content is advanced because of similarities in the value of sulfur and accelerators & excess poly-sulfidic bonds. Later on, it can be diminished due to acting as an active system. Until the MBTS proportion reaches to the level as 1.6 phr, either MH or fall in toughness may be clarified with reversion.

Finally, while the cross-linking intensity increases, breaking strength, modulus, toughness values rises, too. Increment in this textures is generally directly proportional to augmentation in MH value. When t90 is short enough, MH becomes dominant, so intensity of cross-linking bond of rapid accelerators is greater. Elongation portions for natural rubbers except dithiocarbamate groups generally decreases as the time of vulcanization becomes shorter.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

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