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The Effect of Different Accelerators on the Vulcanization of EPDM Rubber

Murat Teker[1,*], Esra Öztürk[1], Ayşe Usluoğlu[1]

[1]Department of Chemistry, Faculty of Art and Science, Sakarya University, 54187, Sakarya, Turkey.

Abstract: EPDM (ethylene propylene diene monomer) is a type of synthetic rubber. The products of rubber have great importance in every part of life. EPDM rubber has high tensile strength, high tension, toughness, and is weather resistant. Therefore, EPDM (ethylene-propylene-diene rubber) is widely used in many fields. The aim of this study is to examine the effect of accelerator type on mechanical properties and vulcanization characteristics of EPDM rubber. We used the accelerators; thiazole, sulfonamides, dithiocarbamate, thiuram, and guanidine groups. The results show that the fastest cure time and the best tensile strength are achieved with dithiocarbamates for EPDM rubber.

Keywords: EPDM, Accelerator, Vulcanization.

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***Corresponding author's E-mail:** teker@sakarya.edu.tr

1. INTRODUCTION

Elastomers are the most important raw materials used in the rubber industry, as they have a wide area of use in many sectors such as food, textiles, healthcare, military, automotive industry, construction, etc. (1).

Ethylene Propylene Rubber (EPDM/EPM) is a copolymer of ethylene and propylene. EPDM is extremely heat, ozone, and weather resistant (2, 3). Due to these properties, this rubber is widely used in many applications (4, 5, 6).

Vulcanization is one of the most significant technologies in modern industry. During the process of vulcanization, when we add sulphur to rubber, the C-H bonds get broken and replaced by C-S bond (7). The discovery of sulphur vulcanization of rubber by Goodyear and independently by Hancock more than 150 years ago was the genesis of one of the most important classes of engineering materials.

Accelerators are defined as the chemicals added to a rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at a lower temperature and with greater efficiency (8). Accelerator also decreases the quantity of sulphur necessary for vulcanization, thus improving the 'aged' properties of the vulcanized rubber. Accelerator choice is both important and critical (9). Selecting the best accelerator system is very difficult. Many parameters, such as raw rubber storage stability, processability, scorch, crosslinking, and cured rubber, come into consideration.

There are, principally, what we called prescriptions, such as rubber, sulphur, zinc oxide, oil acid, accelerator, extender, softener, and anti-oxidant. In this study, the features of vulcanization of the mixtures of EPDM (ethylene propylene diene) rubber by using different accelerators and the features of these after vulcanization was examined. Also, it was investigated how physical characteristic of the mixture of EPDM rubber can be changed with varied amounts of accelerators during and after vulcanization.

2. EXPERIMENTAL SECTION

2.1. Used Materials

It is used Dutralter 4038 as EPDM. Carbon blacks are also FEF N 550 and HAF N 330. Despite these, accelerators are MBT (2-mercapto benzimidazole), MBTS (dibenzimidiazole sulphur) , CBS (N-cyclohexyl- 2 benzimidazole sulfonamide), MBS (2-benzimidazole- N-sulphene morpholine), TBBS (N-tertiary butile-2 benzimidiazole sulfonamide), TMTD (Tetramethyl thiuram disulfide), TMTM (Tetramethylthiuram monosulfide) , ZDMC (Zinc dimethyl dithiocarbamate) , ZDEC (Zinc diethyl dithiocarbamate), ZEPC (Zinc ethyl phenyl dithiocarbamate), DPG (Diphenyl-guanidine).

2.2. Preparation of Rubber Mixtures

The mixture was prepared in the open laboratory on a two-cylindered shaft. (ASTM D3182). EPDM rubber, various accelerators, and a series of mixtures were attained. It contains EPDM rubber 100 phr, carbon black 109.4 phr, paraffinic oil 54.0 phr, zinc oxide 4.0 phr, stearic acid 2.70 phr, sulphur 2.50 phr, different accelators (MBT, MBTS, CBS, MBS, TBBS, TMTD, TMTM, ZDCM, ZDEC, ZEPC, and DPG) 2.50 phr. The combinations of EPDM prepared with different kinds of accerelators are shown in Table 1 (10).

Table 1: The Combination of EPDM prepared with different kind of accerelators.

Raw Materials (phr)	Accelerator (phr)											
	MBT	MBTS	CBS	MBS	TBBS	TMTD	TMTM	ZDMC	ZDEC	ZEPC	DPG	TMTM
EPDM rubber	100	100	100	100	100	100	100	100	100	100	100	100
Carbon black	109.4	109.4	109.4	109.4	109.4	109.4	109.4	109.4	109.4	109.4	109.4	109.4
Paraffinic oil	54.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0	54.0
Zinc Oxide	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Stearic acid	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70
Sulfur	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Accelerator	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Total	275.1	275.1	275.1	275.1	275.1	275.1	275.1	275.1	275.1	275.1	275.1	275.1

phr: Parts per one hundred rubber.

2.3. Used Devices and Features

Rheometer: It is used to measure the vulcanization characteristics of mixtures and to save the vulcanization curve. It also applies oscillating stretch into mixture under high temperature and pressure, and as a consequence of an increase in the 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), Figure 1. The vulcanization state, which is made ready with each distinctive accelerator, was gauged by MDR-2000 rheorometer device (ASTMD 5289).

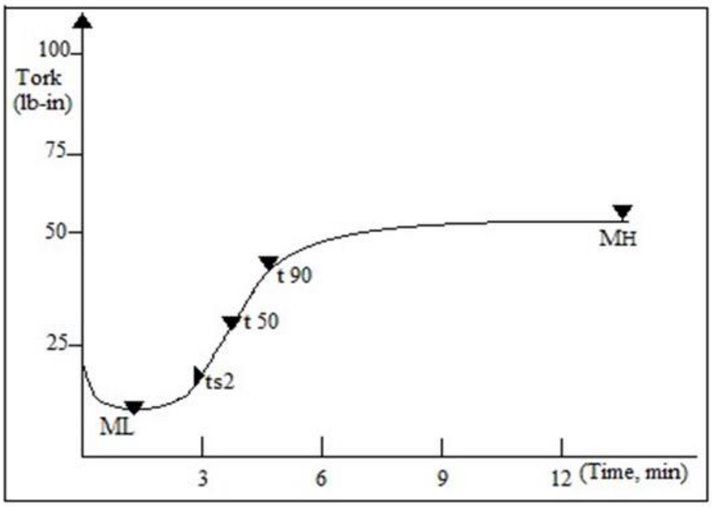

Figure 1: Graphic of curve of vulcanization.

The feature of the curve of vulcanization can be explained in such a way.

ts2; Beggining time of hardening, unit is minutes or minutes: seconds. ts2 is helpful to determine safety of procedure.

ML: Minimun torque, units N-m and ya Ib-in (pounds-inch).

MH: Maximum torque, unit is N-m or Ib-in (pounds-inch). It is related to properties such as tensile, tear, and tensile strength.

t90, Time to reach maximum cook time, unit is minutes or minutes: seconds. The t90 is helpful in determining the press time during production (11-12).

Shoremeter: The toughness of rubber materials, in general speaking, is the measurement of resistance against immersion of metal rod, marble, or needle into them. In this effort, shore type is the durometer measuring toughness, kind A. In durometers, the tip of immersion is not only marble but also frustocone. Toughness should be measured after the device's surface of measurement contacts the sample for a maximum of 3 minutes. The prepared mixtures were hardened in the hydrolytic press at 150'C. Following of vulcanization, the toughness measurement was carried out with a Shore A Durometer, whose brand is Braiss. (ASTM D2240).

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

Fracture Point: The ratio of forces between the time of failure and the beginning. (MPa or N/mm^2).

Breaking Elongation: The ratio of length between changing at the failure and changing at the beginning. (%)

Modulus: The amount of unit surface for the force applying to a specific extension. (MPa or N/mm^2).

3. RESULTS AND DISCUSSION

Vulcanization characteristics of EPDM 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.

In reference to outcomes from rheometer test, it is concluded that for the maximum ML value for EPDM rubber DPG and MBS is the best choice (Figure 2). However, the minimum value is by TMTM.

In Figure 3, the upper limit of MH values is reached with thiuram and dithiocarbamates, but the lower limit is related to DPG and mercapto groups. 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 (13).

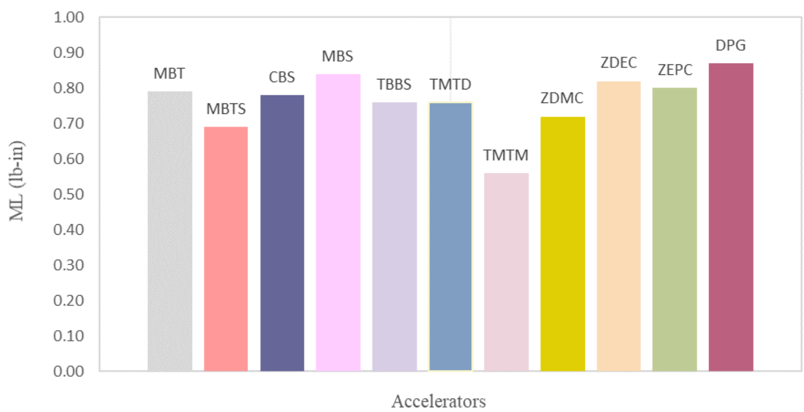

Figure 2: The effect of accelerators in EPDM mixtures on the value of ML.

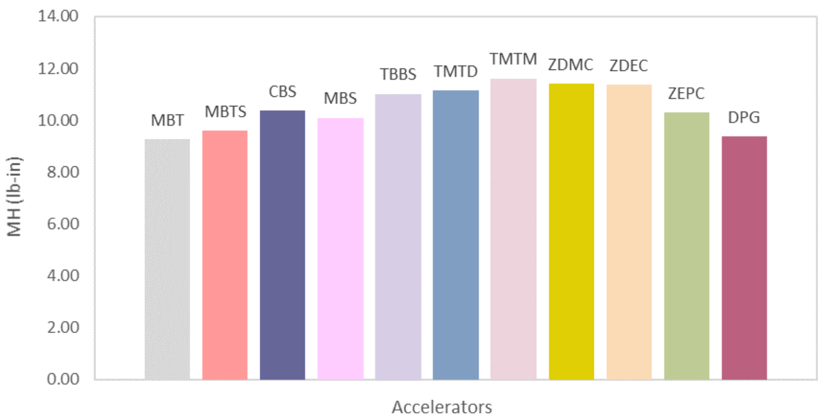

Figure 3: The effect of accelerators in EPDM mixtures on the value of MH.

In Figure 4, the lowest hardening time, i.e., providing the fastest hardening group, belongs to TMTD and ZDMC. The longest hardening times are given by MBT and MBTS. For EPDM mixture, the earliest hardening time is with thiuram and dithiocarbamates. Whereas the latest one is from the mercaptos, which are medium level accelerators. It has been observed that similar results have been achieved in previous studies (14).

The longest ts2 value is by MBTS, and the shortest one is by dithiocarbamates. MBTS has the safest processing, with the highest value of ts2. Dithiocarbamide groups are the fastest ones to start hardening. Similar results were seen in the study of

Alam et al. (15). Dithiocarbamate accelerators are used as ultra-fast accelerators for rubber compounds (16).

The comparison of toughness values after vulcanization is shown in Figure 6. According to that, the lowest is with DPG. Whereas the highest toughness value is with TMTD. Thiurams and ZDMC have also shown a high hardness value. The crosslink density of rubber vulcanizate also affects the hardness value. The higher the crosslinking density, the lower the chain mobility (17). Their high stiffness was caused by the decreased mobility of polymer chains, which was also confirmed by the values of hardness and elongation-at-break (18).

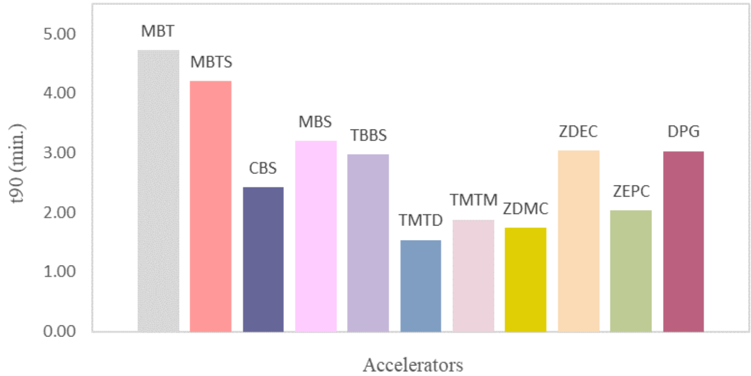

Figure 4: The effect of accelerators in EPDM mixtures on the value of t90.

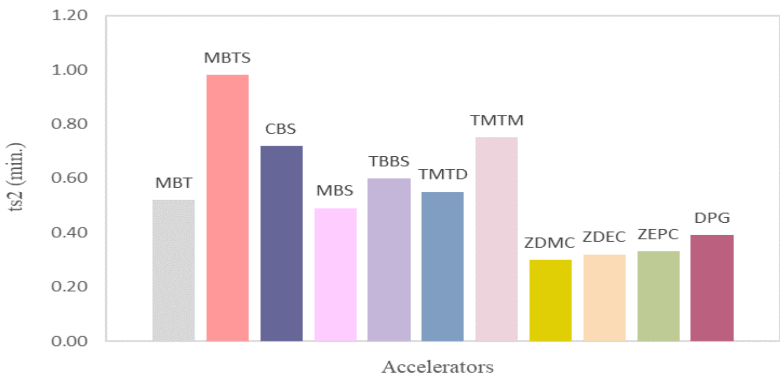

Figure 5: The effect of accelerators in EPDM mixtures on the value of ts2.

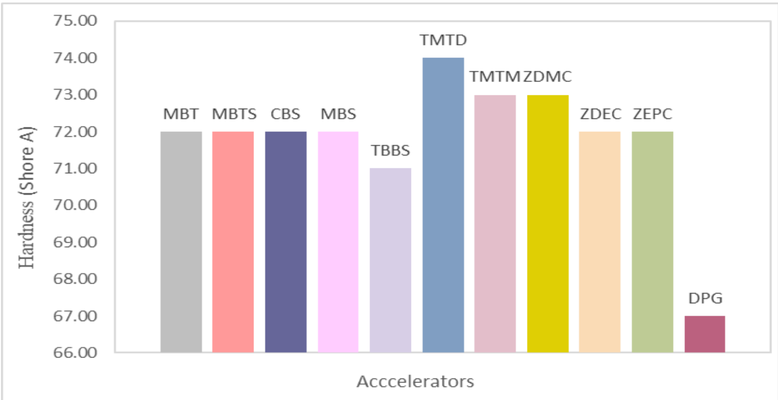

Figure 6: The effect of accelerators in EPDM mixtures on the value of toughness.

As specified in Figure 7 above, the highest modulus value is provided by dithiocarbamates and thiurams. The lowest modulus value is obtained with DPG. However, it is realised that the strengthening properties of DPG, used generally as a secondary accelerator, are low. This is due to the chemical structure of DPG (14).

In Figure 8, ultimate breaking strength is reached with thiurams and dithiocarbamates. The lowest breaking strength value is obtained with MBS and DPG. Similar results have been obtained in previous studies. It was found that mixtures made with TMTD had higher tensile strength values (19).

In case the elongation values are checked, there is a higher elongation value when DPG whose breaking strength is not good enough is used. TMTM and mercaptanes are the second-best alternatives, providing the highest elongation after DPG (Figure 9).

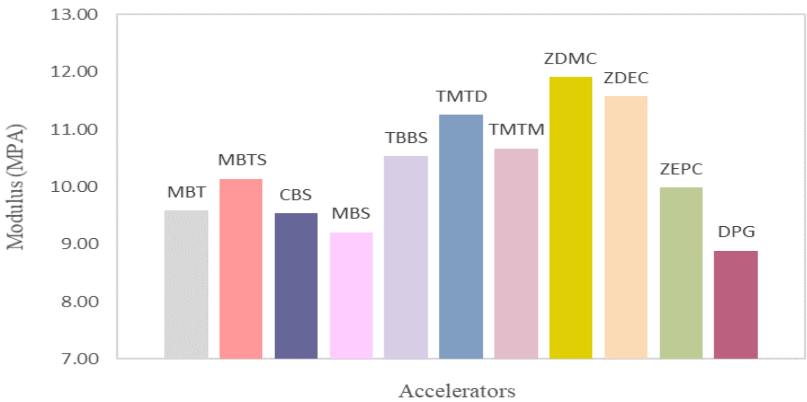

Figure 7: The effect of accelerators in EPDM mixtures on the value of Modulus.

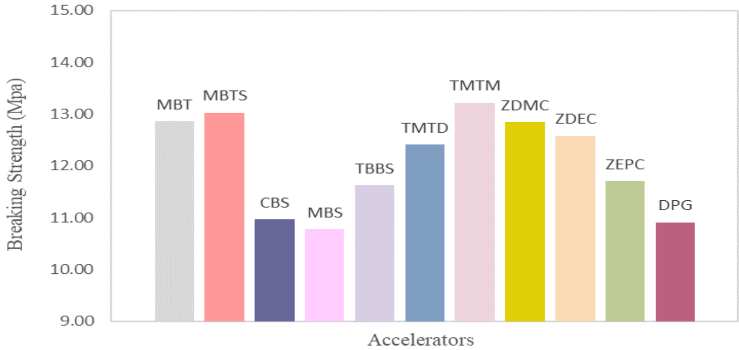

Figure 8: The effect of accelerators in EPDM mixtures on the value of Breaking Strength.

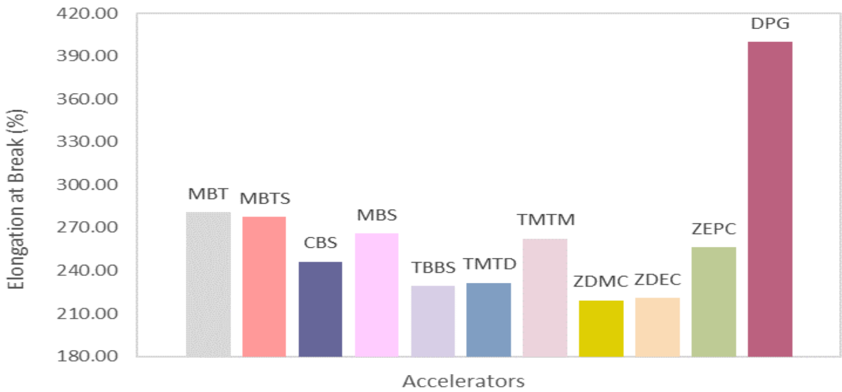

Figure 9: The effect of accelerators in EPDM mixtures on the value of Elongation.

Table 2: The feature of vulcanization of EPDM mixture prepared with different type of accelerators.

	MBT	MBTS	CBS	MBS	TBBS	TMTD	TMTM	ZDMC	ZDEC	ZEPC	DPG
ML (Ib-in)	0.79	0.69	0.78	0.84	0.76	0.76	0.56	0.72	0.82	0.80	0.87
MH (Ib-in)	9.25	9.60	10.37	10.09	11.02	11.15	11.61	11.41	11.37	10.30	9.37
t90 (min.)	4.72	4.20	2.42	3.20	2.98	1.54	1.88	1.74	3.04	2.03	3.03
ts2 (min.)	0.52	0.98	0.72	0.49	0.60	0.55	0.75	0.30	0.32	0.33	0.39
Hardness (Shore A)	72	72	72	72	71	74	73	73	72	72	67
Modulus (MPa)	9.59	10.14	9.54	9.21	10.53	11.26	10.67	11.91	11.58	9.99	8.89
Breaking Strength (MPa)	12.86	13.03	10.97	10.78	11.63	12.41	13.22	12.85	12.58	11.71	10.91
Elongation at Break (%)	281.00	277.60	246.30	266.05	229.25	231.50	262.40	219.30	220.97	256.15	400.15

According to Table 2, as the hardness increases, the breaking strength increases, while the elongation decreases. High hardness can be evaluated as providing a high crosslink density for these groups. The high crosslink density causes the molecular chains to move less. Similar results have been presented in previous published studies. The highest modulus values and the lowest elongation values are observed with dithiocarbamates (20). When DPG was used, the lowest modulus value and the highest elongation value were obtained.

4. CONCLUSION

Thiurams and dithiocarbamates forming high intensity of cross-linking bonds in EPDM rubbers provide great MH, breaking strength, modulus value, and toughness value. Thiurams and dithiocarbamates are known to have the lowest t90 values which is the time of hardening. Since dithiocarbamates react as rapidly as possible, they have the lowest ts2 values. Furthermore, MBTS from the mercapto groups recognized as providers of late activation expresses high ts2 values. Although the strengthening behaviour of DPG is quite marginal, the best elongation levels are provided by DPG. The reason for that is that DPG has a polysulphite capacity as high as possible. Finally, while the cross-linking intensity increases, breaking strength, modulus, and toughness values also rise. Increment in this texture is generally directly proportional to the augmentation in MH value. When t90 is short enough, MH becomes dominant, so the intensity of the cross-linking bond of rapid accelerators is greater. Elongation portions for EPDM rubbers except dithiocarbamate groups generally decrease as the time of vulcanization become shorter.

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