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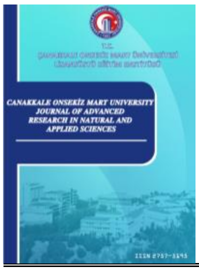

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Anti-aging effect of TMQ on EPDM for Various Cure Systems

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Research Article

Abstract − Ethylene propylene diene rubber (EPDM) is a common raw material for weather resistant rubber products used in lots of areas such as cable, automotive, marine industry and aviation applications. Superior processing behaviour, electrical properties and moderate high temperature resistance also make EPDM an attractive raw material for a wide range of further industrial performance requirements. As well as the other general purpose rubbers, EPDM needs to be protected against thermo-oxidative aging. Short and long term aging behaviour of both sulfur and peroxide cured EPDM has been studied in literature. However, to the authors' best knowledge, there is not any study in literature systematically evaluating a common rubber antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) for investigating theoretical life-time of EPDM based materials that were vulcanized with different crosslinking systems. In this study, effects of TMQ on the thermo-oxidative resistance of EPDM has been studied for conventional and efficient sulfur vulcanization systems as well as peroxide vulcanization system. Aging mechanism for different cases has been investigated by using structural, rheological and mechanical tests. Thermo-oxidative aging has been monitored by carbonyl index and activation energy. Arrhenius based life-time estimation methodology (ISO 11346) has also been employed to evaluate aging behaviour of the reference and TMQ containing (-T) compounds. TMQ was found to exhibit different levels of protection against thermo-oxidative aging for all the curing systems and at all aging conditions. As a result, higher aging activation energy for -T compounds has been attributed to extended service life of the material in the presence of TMQ.

Keywords *− Arrhenius equation, curing systems, EPDM rubber, life-time estimation, thermo-oxidative aging*

1. Introduction

Ethylene propylene diene rubber (EPDM) is a common raw material for rubber goods with superior resistance to heat, oxygen, ozone, humidity, ultraviolet radiation and electric discharge thanks to its structural properties, particularly its saturated backbone (Bouguedad et al. 2008; Tan et al. 2021). It is widely used in many applications such as cable insulation and sheathing, sealants, automotive goods, marine and aviation industries. Due to its good electrical properties, thermal aging resistance and relatively low density in their compounds, EPDM has an increasing demand particularly in cable industry and nuclear applications (Li et al. 2020). Terpolymer EPDM is synthesized by polymerization of ethylene and propylene in the presence of a diene monomer, which is commonly one of ethylidene norbornene (ENB), dicyclopentadiene (DCPD) and vinyl norbornene (VNB).

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Depending on the diene content, EPDM is able to vulcanize by sulfur as well as by peroxide and other crosslinking agents (Savran 2001; Simpson 2002). Besides, diene groups are not located on the main chain of EPDM, and this can provide exceptional resistance to weathering (Delor-Jestin et al. 2000; Sanches, Cassu, and De Cássia Lazzarini Dutra 2015). However, due to its low polarity, EPDM is not resilient to hydrocarbon based fuels and halogenated solvents. Promising heat, oxygen and ozone resistance of EPDM has been drawing attention to prepare rubber compounds for high-temperature applications by compounding EPDM with various anti-aging additives and/or various crosslinking systems. Despite the fact that it exhibits satisfactory resistance to thermo-oxidative aging, EPDM still needs to be protected against overall aging effects in order to exhibit superior performance during its long service life (Van Duin 2002). It is preferably compounded with stabilizing agents to improve its service temperature and useful service life. 2,2,4-trimethy1-1,2-dihydroquinoline (TMQ) is one of the most widely used stabilizer for EPDM. Vulcanization system has also significant impact on both service temperature and service life of EPDM based materials. Although various crosslinking agents can be used in EPDM compounds, sulfur vulcanization system is still one of the most preferred methods to produce EPDM vulcanizates. In sulfur vulcanization, accelerators and activators accompany with sulfur to shorten vulcanization time and to improve overall vulcanizate properties. The proposed reaction mechanism for sulfur vulcanization of EPDM is given in Figure 1 (Van Duin 2002). Here, diene group is ENB and vulcanization rate increases with ENB content of EPDM.

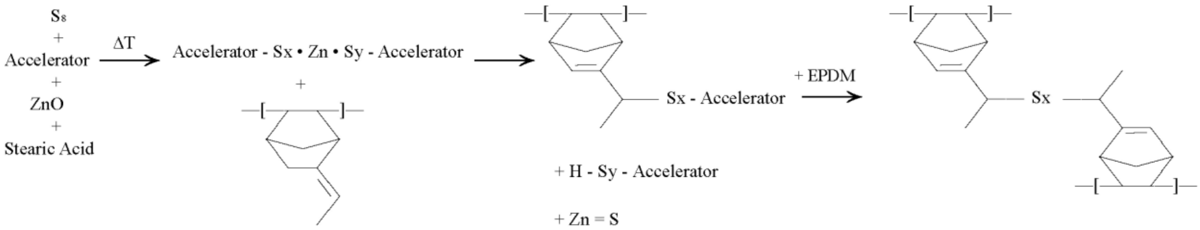

Figure 1. Proposed reaction mechanism for sulfur vulcanization of EPDM (Van Duin 2002)

Three different sulfur vulcanization systems can be designed to control crosslink types, which most likely occur. These are conventional (CV), semi-efficient (semi-EV) and efficient (EV) vulcanization systems (R. 2002). The amounts of sulfur and accelerators and the sulfur/accelerator ratio, which depend on the type of sulfur vulcanization system, have remarkable impact on the vulcanizate properties (Ciesielski 1999). The other popular vulcanization system for EPDM is peroxide crosslinking and the proposed reaction mechanism is depicted in Figure 2 (Van Duin 2002; Matador Rubber 2007). Both saturated and unsaturated rubbers are able to vulcanize by using organic peroxides. In peroxide vulcanization, radicals, which are formed on the polymer main chain by means of peroxides, combine to give C-C crosslinks. Optimum reaction temperature strongly depends on decomposition temperature of the peroxide; yet, peroxide vulcanization mainly occurs at 140-180°C. Peroxy-vulcanized rubber materials are able to be used at relatively high temperatures, they have good thermo-oxidative aging resistance and satisfactory dielectric properties. However, these vulcanizates exhibit lower flexibility, worse tensile and abrasion properties compared to the sulfur-vulcanized ones (Matador Rubber 2007).

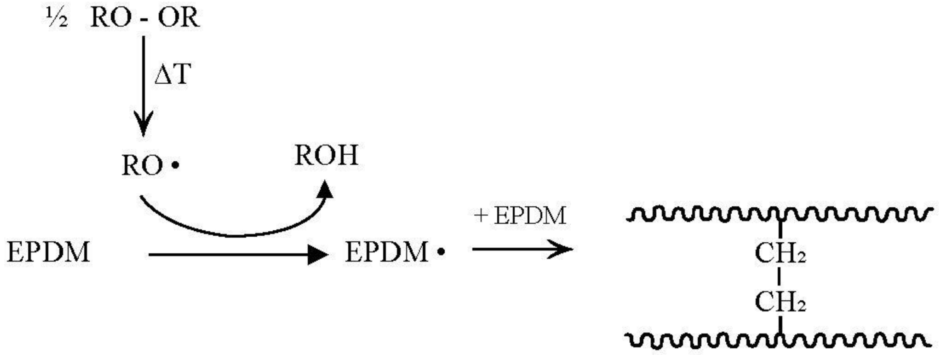

Figure 2. Proposed reaction mechanism for peroxide vulcanization of EPDM (Van Duin 2002; Matador Rubber 2007)

Along with the sulfur and peroxide vulcanization systems, resin vulcanization and high-energy ionizing radiation vulcanization are also among crosslinking methods for EPDM. Ionizing radiation and e-beam are preferred especially on cable sheathing applications (Matador Rubber 2007). Rubber materials tend to age due to radicalic reactions on the polymeric structures as for human body by time. The main approach to prevent and/or retard aging is to use various stabilizing agents such as antioxidants. These are the additives, which scavenge the free radicals so that they cannot affect the polymeric material. Chemical and/or physical changes in the polymer structure during thermo-oxidative aging depend strongly on the type polymer. Thermal aging takes place in rubber-based materials via two main mechanisms (Johlitz, Diercks, and Lion 2014; Polymer Properties Database n.d.). First mechanism is main chain scission. Common characteristics of the rubbers, which follows the first mechanism, is to have electron donor -CH_3 group connected to the C atom on the double bond. This -CH_3 group is vulnerable to oxidation. Second mechanism results with additional crosslinking. Rubbers following the second aging mechanism usually have highly electronegative groups such as halogens connected to the double bond and therefore they are highly stable (Mathew and De 1983; Nakajima 2000).

During the aging of polymers, the macromolecular structure is oxidized to form perhydrate and then these perhydrates turn into free radicals. Following that, other chain segments interact with the free radicals to form new perhydrates and then new free radicals. This consecutive process goes on over whole aging process. Antioxidants are able to inhibit/retard free radical attack onto polymer chains in order to break consecutive aging reactions. Besides, antioxidants can also decrease the concentration of hydroperoxides, which comes from thermo-oxidative degradation of the polymer (Li et al. 2020). Short and long term aging of both sulfur and peroxide cured EPDM has been studied in literature (Rojas Rodríguez, D'almeida, and Marinkovic 2021; R. Wang et al. 2020; Z.-N. Wang et al. 2020; Wang and Qu 2003; Zhang, X., Li, J., Chen, Z., Pang, C., He, S., Lin 2022). Many of the studies investigating aging mechanism of EPDM figure out crosslink density to increase during aging period. Aging behavior of EPDM due to UV exposure was studied and micro and macro surface cracks were correlated to oxidation reactions during aging by Tan et al. (Tan et al. 2021). In that study, aging of EPDM due to various external factors was explained with two main stages. In the first stage, chain scission reaction caused an increase in free volume and in gas permeability due to decreasing overall crosslink density. Accordingly, crosslink density was reported to increase in the second stage of aging process. In another study, thermo-oxidative aging of EPDM/carbon nanotube composites was investigated and increased overall crosslink density was reported (Zhang, X., Li, J., Chen, Z., Pang, C., He, S., Lin 2022).

Proposed heat and light-initiated photo-oxidation mechanism of EPDM is depicted in Figure 3. At the beginning of the reaction, peroxy radical (ROO·) is formed by means of external energy. Peroxy radical reacts with EPDM molecules to give alkyl radical (R·) and hydroperoxide (ROOH), which then immediately turn into alkoxy (RO·) and hydroxy (·OH) radicals. Alkoxy and hydroxy radicals are able to react with EPDM molecule to give H_2O molecule and R· radical. R· radical is still very active to combine with air oxygen to yield ROO· by means of a cyclic oxidation reaction. The most unstable radical among all is RO· and various oxygen containing species such as esters, ethers and ketones may occur via RO· reactions (Tan et al. 2021).

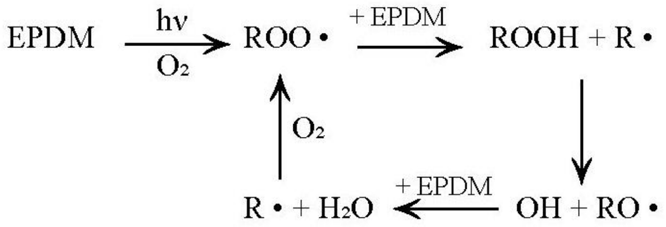

Figure 3. Proposed photo-oxidation mechanism of EPDM (Tan et al. 2021)

Anti-aging additives used in rubbers, which tend to degrade under the influence of oxygen, ozone and heat, are classified in ASTM D4676. These are basically defined as antioxidants and antiozonants and they are added into rubber compound in the amount of 1-4 phr (Ciesielski 1999; De and Jim R. White 2001). Antioxidants inhibit/retard the oxidation process by means of scavenging free radicals and hydroperoxides, which form during oxidation reaction (Li et al. 2020). The most widely used anti-aging additives in rubber industry are phenolic and amine based antioxidants (Khalaf, Helaly, and El-Sawy 2014). TMQ takes place among all with its competitive price and satisfactory anti-aging performance. It is effective for rubber materials at also relatively high service temperatures even used in 1-2 phr. Sequential configurations of TMQ during its anti-aging action is shown in Figure 4. Similar mechanisms have also been proposed in literature (Arvind Mafatlal Group and Nocil Limited 2010; Huntink and Datta 2003). TMQ follows subsequent reactions to give stable configurations in order to inhibit oxidation. Secondary amine group (=N-H) of TMQ turns into nitroxy form (-NO) and this structure is very effective on anti-oxidation process. In general, amine based antioxidants are able to form nitroxy radicals in the presence of ambient peroxy radicals, and thus they can trap alkyl radicals easily in order to terminate auto-oxidation process. This reaction cycle goes on until the nitroxy radicals to decompose by uneven side reactions.

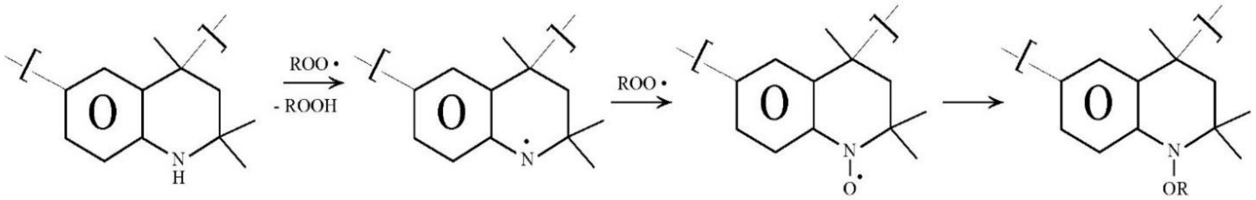

Figure 4. Sequential configurations of TMQ over its anti-aging action

Service life of the polymeric material as well as the degradation mechanisms are among the most important factors to take into account during material design. Polymers are affected by several external factors during their service life including mechanical, thermal, oxidative, chemical, biological, radiative and electrical factors. These deteriorative effects may cause further crosslinking, chain scission, chemical degradation and crystallization depending on the material type, rate and the amount of the deteriorative effect. The most common degradations result with fracture, change in color, swelling and dimensional changes in the material (Hulme and Cooper 2012).

Rubbers, due to their viscoelastic structure, exhibit time and temperature-dependent properties during deformation. For example, elastic modulus of a rubber material decreases when a constant load applied. This behavior is attributed to the molecules to change their arrangements by time in order to avoid local stress concentration. That is why the modulus value is measured as lower for short-term tests compared to long-term tests. Due to such time-dependent response, service life of the rubbers can only be measured for realistic test conditions and for a meaningful time period. However, such long tests are not practical of course; those properties reflecting the service life of the material need to be predicted by using well-defined models instead (Instruments n.d.). Service life or life-time prediction of the polymers are usually performed by employing accelerated aging tests to let aging reactions occur in a shorter time period at higher temperatures (Celina, Gillen, and Assink 2005). In this method, test samples are exposed to gradually increasing temperatures and the related properties are monitored over time for all the test temperatures to figure out the degradation reaction (aging) kinetics (Hulme and Cooper 2012). Arrhenius method (ISO 11346, Rubber, vulcanized or thermoplastic – Estimation of life-time and maximum temperature of use), which is used in this study, is the most common and practical method to evaluate the relation between temperature and thermo-oxidative degradation reaction rate of the polymers (Huy and Evrard 1998). Very well-known Arrhenius equation is given in Equation 1.1, where K_T is the reaction rate constant at temperature T, A is the frequency factor, E_a is the reaction activation energy and R is the universal gas constant (Woo and Park 2011).

$$K_T = A\, e^{\frac{-Ea}{R\,T}} \tag{1.1}$$

According to Arrhenius approach, rate of degradation reaction can be measured by following a specific property over time. In this approach, it is basically assumed that a specific level of change (due to degradation) in the related property at a relatively low temperature occurs in shorter time at higher degradation temperatures. Firstly, at least one specific property is selected to follow considering the expectations from the material on its service. Initial value of the property is recorded as the reference. Then the material test samples are subjected to thermal aging at three or more elevated temperatures, which the lowest one is at least 30°C higher than the expected service temperature of the material. Samples are tested over time with adequate intervals for each aging temperatures. For example, measurements should be performed more frequent for relatively high aging temperatures due to the fact that the service life will over earlier in this case. Threshold for service life or life-time of the material is usually defined as the time to loss half of the selected property, but the better is to consider the expectations from the material in more detail and then to define life-time threshold for individual cases. In Arrhenius model, all the test results for an aging temperature are evaluated to calculate the reaction rate constant for that temperature. Then, activation energy of the aging reaction is calculated with the rate constants obtained for different aging temperatures and used to extrapolate to time, that is called life-time of the material, to reach the same threshold at service temperature. Arrhenius method is also described in detail in ISO 11346.

In this study, thermal aging behavior of EPDM based samples, which were prepared by using various curing systems, with and without TMQ. Rheological, mechanical and structural properties were studied and life-time of these samples were calculated by using Arrhenius method.

2. Materials and Methods

2.1. Materials

EPDM rubber, Nordel 4770P with the Mooney viscosity (ML [1 + 4] @100°C) of 70±3 MU was purchased from Dow Chemicals. N550 type carbon black (CB, Omsk Carbon, Russia) was used as reinforcing filler. Kaolin (Polestar 200R, Imerys) was the other component of the filler system. Paraffinic oil (Petroyag, Turkey) was selected as process oil for dispersing the fillers in the compound matrix. The other components; zinc oxide, stearic acid, TMQ, sulfur, dicumyl peroxide, mercaptobenzotiazole disulfide (MBTS), tetramethyl thiuram disulfide (TMTD) and zinc dibutyldithiocarbamate (ZDBC) were obtained from various suppliers, which provide raw materials to tyre and rubber industries.

2.2. Methods

Rubber compounds were prepared by using various curing systems; compound formulations are given in Table 1. Compound codes were designed in order to define curing system and the presence of TMQ. Code "P" refers peroxide curing system, whereas code "SC" refers conventional sulfur curing system and code "SE" does efficient sulfur curing system. "T" in compound code means that the compound also contains 2 phr TMQ antioxidant. Compounds were prepared in a laboratory type Banbury mixer with 2 L of gross volume.

Homogenization and shaping the compounds were performed on a two-roll open mill, subsequently. Optimum curing time and rheological properties of the compounds were measured at 190℃ by RADE MR-C3 moving die rheometer according to ASTM D2084. Compounds were moulded on a hydraulic hot press at the same temperature for their respective optimum cure times. Standard blades were used to cut the standard test samples from the vulcanized plaques prior to physical and mechanical characterization. Tensile properties were measured on a universal test machine (Testometric M350-10CT) according to ASTM D412. Tensile tests were also performed after thermal aging of the samples in an air-circulating oven operating at 50℃, 70℃, 100℃ and 135℃ for respective times to loss prescribed percentage (threshold) of their tensile properties. Tensile strength and 100% tensile modulus values were followed versus aging time at all the aging temperatures. According to the Arrhenius approach, life-time threshold of EPDM based rubber materials was assumed as 50% change in 100% tensile modulus after aging.

Unaged and aged sample surfaces were analyzed with Fourier Transform Infrared Spectroscopy (FTIR) equipped with Attenuated Total Reflection (ATR) configuration. FTIR (Perkin Elmer Spectrum 100 Optica FT-IR Spectrometer) spectrums were obtained for 650-4000 cm^{-1} with the resolution of 4 cm^{-1} according to ASTM D3677 and they were used for both qualitative and quantitative analysis. Periodical carbonyl index (CI) measurement was performed for following oxidative reactions. Absorption bands of carbonyl groups are between 1850-1650 cm^{-1} and CI can be calculated by normalizing carbonyl peak to a selected reference peak in the spectrum. Here, in quantitative analysis, CI values of all the unaged and aged samples were calculated by using SAUB (Specified Area Under Band) methodology on ATR-FTIR (Almond et al. 2020).

Table 1
Rubber compound formulations (in phr)

	EP	EP-T	EPSC	EPSC-T	EPSE	EPSE-T
EPDM (NORDEL 4770P)	100	100	100	100	100	100
Carbon black (FEF N550)	70	70	70	70	70	70
Calcinated kaolin	30	30	30	30	30	30
Paraffinic oil	20	20	20	20	20	20
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TMQ		2		2		2
DCP 40	5	5				
Sulfur 80			2.5	2.5	1	1
ZDBC			1	1	2	2
MBTS			1	1		
TMTD					2	2

3. Results and Discussion

3.1. Rheological Properties

Rheological parameters such as minimum and maximum torque values (ML and MH respectively), scorch time (t_{s2}) and optimum cure time (t_{90}), which were obtained from the cure curves are given in Table 2. Cure extent (CE) that is related to amount of crosslinks occurred during vulcanization and cure rate index (CRI) values were calculated from the rheological data and they are also given in Table 2.

Table 2
Rheological properties of the rubber compounds

	ML (dNm)	MH (dNm)	t_{s2} (min)	t_{90} (min)	CE (dNm)	CRI (min^{-1})
EP	5.49	18.63	0.16	1.00	13.14	119
EP-T	6.19	17.04	0.24	1.15	10.85	110
EPSC	5.88	18.78	0.26	1.25	12.90	101
EPSC-T	5.49	18.65	0.25	1.29	13.16	96
EPSE	5.90	19.70	0.23	1.19	13.80	104
EPSE-T	5.71	18.41	0.26	1.18	12.70	109

ML value is directly related to the viscosity of the rubber compound and therefore represents processability. From Table 2, it is seen that all the compounds have similar viscosity. It is expected to have lower cure extent in the case of an effective protection against thermo-oxidative aging since a powerful antioxidant can act as a radical scavenger. Indeed, a powerful radical scavenger also inhibits vulcanization reaction by blocking active crosslinking sites on the polymer chain. This phenomena is a well-known problem in rubber compounding and requires attention on selecting the appropriate type and amount of antioxidant for getting balanced cure extent and anti-aging effect (Li et al. 2020).

EP compound, which was prepared with peroxide and no TMQ, shows the highest cure rate and it starts to vulcanize earlier than the other compounds. Once TMQ is added into the compound (EP-T), both cure initiation time and optimum cure time increases. One other effect of TMQ on peroxide curing is that it significantly decreased cure extent. Cure extent, which is also defined as delta torque value, is proportional to crosslinking degree for a rubber compound (Li et al. 2020). In other words, in the presence of TMQ, less amount of crosslinks could occur over the same curing time. This could easily be attributed to TMQ to block the peroxy radicals that occur during peroxide vulcanization and therefore it adversely affects the crosslinking efficiency (Abdel-Aziz and Basfar 2000; Li et al. 2020). Due to that, EP-T compound showed 10% lower cure rate than EP compound. The same amount of decrease was also observed for EPSE-T compound, which was prepared with efficient sulfur curing system and with TMQ. However, there was no remarkable change in cure extent due to the addition of TMQ when curing system was selected as conventional sulfur (EPSC-T vs EPSC). This can be attributed to that excessive amount of curative species (sulfur based radicals) were already available in the reaction media.

3.2. Mechanical Properties

Tensile data of the vulcanizates were collected considering their expected retention for the respective aging temperatures. All tensile data was used in life-time estimation study. Aging periods were selected as 3 days, 1 week, 3 weeks, 10 weeks and 16 weeks for 50°C whereas the samples were subjected thermal aging for 2 days, 5 days, 1 week, 1.5 week and 2 weeks for 135°C. However, tensile strength values were compared in order to evaluate their tensile retentions for the same aging period (1 week), which was available for all of the vulcanizates. Tensile strength of the vulcanizates before (original) and after thermal aging for 1 week at various temperatures are given in Figure 5, Figure 6, and Figure 7. Aging conditions were selected as practical maximum service temperature of the material. When the original tensile strength values are evaluated, a slight decrease was observed and it was attributed to lower crosslinking level due to the presence of antioxidant. This finding shows a good correlation to the literature that some of the free radicals on peroxide vulcanization are terminated by antioxidant species resulting with deteriorated mechanical properties (Li et al. 2020). However, when the amount of decrease in tensile strength is compared within each vulcanization system, there could not be seen a linear trend. This finding can readily be attributed to different overall crosslink structures occurred during the selected vulcanization systems in this study. The highest original tensile strength values belong to the EP samples and it was followed by EPSE samples. The lowest tensile strength values were measured for conventional sulfur vulcanization system unlikely that was given in literature for natural rubber and chloroprene rubber, which had basic isoprene structure (Yahya, Azura, and Ahmad 2011). For peroxide vulcanization, TMQ could significantly reduce retention in tensile strength of the vulcanizates, which were subjected to thermo-oxidative aging. This was more pronounced for relatively high aging temperatures. In contrast to the expectations, an equivalent protection could not be obtained for sulfur vulcanization.

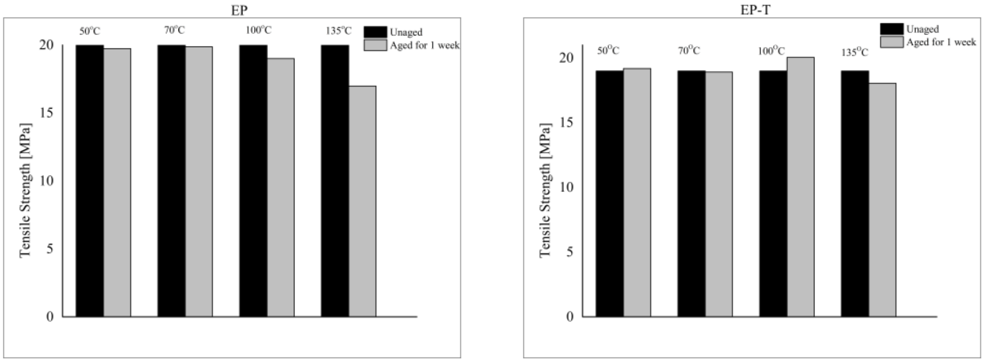

Figure 5. Tensile strength values of EP and EP-T vulcanizates before and after thermo-oxidative aging

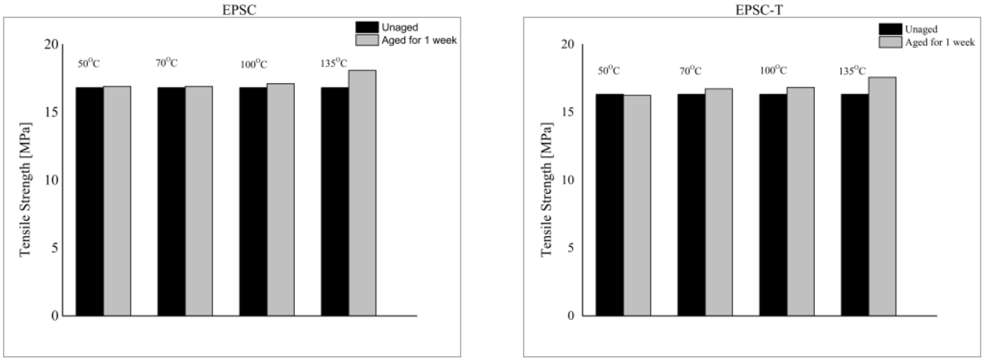

Figure 6. Tensile strength values of EPSC and EPSC-T vulcanizates before and after thermo-oxidative aging

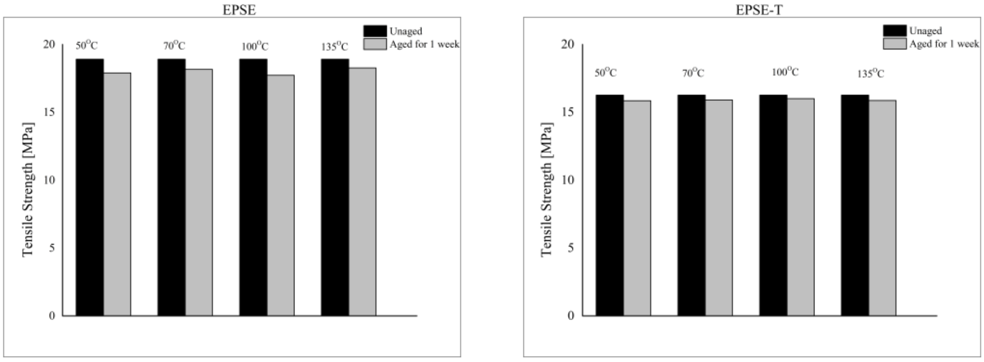

Figure 7. Tensile strength values of EPSE and EPSE-T vulcanizates before and after thermo-oxidative aging

3.3. Life-Time Estimation

To correlate long-term behaviour, theoretical life-time of the EPDM-based materials prepared with various vulcanization systems was estimated according to Arrhenius approach. For this purpose, 100% modulus values of the vulcanizates were monitored after aging for specified periods at T_1=150°C, T_2=135°C, T_3=100°C, and T_4=70°C. The time that corresponds to 50% change in the 100% tensile modulus of respective samples was considered as life-time threshold. Time data for all the aging temperatures was recorded as t_1, t_2, t_3 and t_4, where t_i represents the time corresponding to the threshold modulus value at T_i. Although they were reported by means of tensile retention in Figure 5, Figure 6 and Figure 7, aging at 50℃ was not included in life-time estimation study due to extremely long aging time to reach the life-time threshold. Aging activation energy (E_a) was calculated separately for all the aging temperatures according to the Arrhenius equation (Eq. 1.1). Then, E_a was placed into the equation 3.1 given below, which was obtained by processing Eq. (1.1) in order to yield the rate constant of the aging reaction at any temperature. Here, expected service temperature (T_s) was selected as 25°C (298.15 K) and then the reaction rate constant (K_T) was used to calculate estimated life-time (t_s) of the sample at T_s. Activation energy values corresponding to thermo-oxidative aging reaction for all the vulcanizates are shown in Figure 8 and the calculated life-times are in Figure 9.

$$\ln(K_T) = B - \frac{E_a}{R\,T_s} \tag{3.1}$$

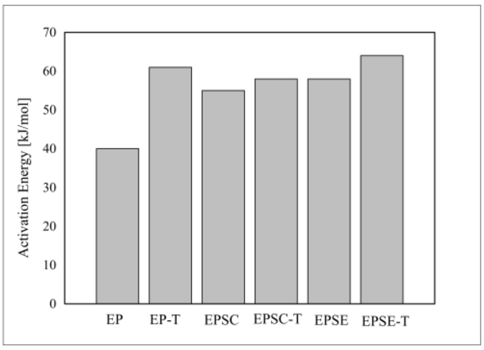

Figure 8. Activation energy for the aging reaction (kJ/mol)

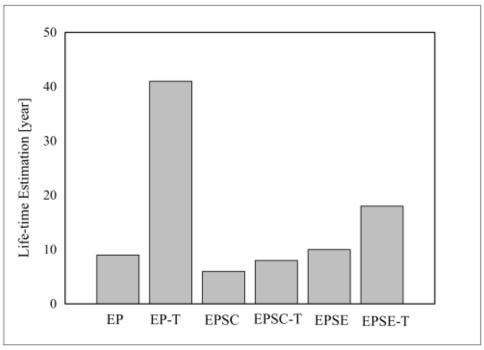

Figure 9. Estimated life time according to Arrhenius approach (in Years)

As it can be seen from the figures, the lowest activation energy was calculated for the case of peroxide vulcanization. Besides, TMQ was clearly found to improve estimated life-time of the peroxide-cured EPDM material about 4-folds by increasing aging activation energy. In spite of the fact that efficient sulfur vulcanization system could not yield good original mechanical strength compared to peroxide system, EPSE sample was found to have the longest life-time among all non-TMQ vulcanizates. Besides, addition of TMQ to that sample could almost double the life-time of the material (EPSE-T). It was concluded that, TMQ could increase aging activation energy for all of the vulcanization systems but it could improve less the conventional sulfur vulcanization system regarding life-time of the vulcanizates. As a result of the above evaluations, the main approach is to define a useful service life for the material rather than to find the time that corresponds to failure of the material. Therefore, the results can be used for comparing long-term behaviour of the materials, relatively. By using the same approach, it is available to predict life-time of rubber materials with different composition for another specified property and another threshold value.

3.4. FTIR Analysis

FTIR analysis is a practical method to investigate basic structural changes in rubber materials over aging in various conditions (Sanches et al. 2015). In this study, ATR-FTIR spectra of the vulcanizates over different aging times at various temperatures was monitored to investigate anti-aging performance of TMQ for various curing systems as well as the aging mechanism. Spectral characterization was performed for the range of 1000–4000 cm^{-1}. The relative FTIR spectra of all the vulcanizates were examined; one (EP) was shown in Figure 10 as an example. Changes in the oxygen containing functional groups -OH and C=O over thermo-oxidative aging were also shown in Figure 10. It is expected absorption band and the intensity of these species to increase over the aging period, which is initiated by oxygen attack to the polymer main chain (Almond et al. 2020; Ooi, Ismail, and Bakar 2013). A high intensity of the peak in the range of vibrations is explained with the eclipse for -OH and C=O groups.

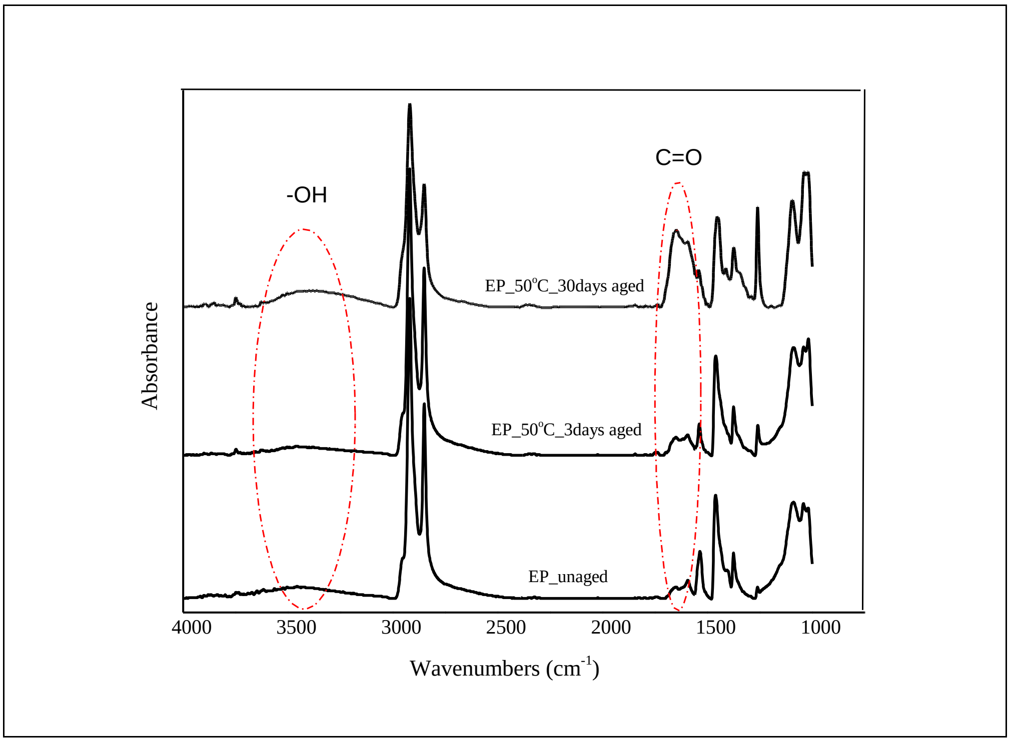

Figure 10. ATR-FTIR spectrum of EP over aging at 50°C

Figure 11 depicts structural changes in EP sample before and after aging for 3 and 30 days at 135°C. Characteristic peaks of EPDM are defined on the spectra given in the figure. 3355 cm^{-1} peak in Figure 11 corresponds to the stretching vibration of -OH. The two peaks, which exhibit decreasing intensity, one at 2925 cm^{-1} corresponds to the asymmetric stretching vibrations of methylene group whereas the other one at 2854 cm^{-1} is related to the symmetric stretching vibrations of the same group on the saturated hydrocarbon backbone (Z.-N. Wang et al. 2020). Two new peaks at 1640 cm^{-1} and 1595 cm^{-1} were observed after aging. The one at 1640 cm^{-1} corresponds to the stretching vibrations of the carbonyl group (C═O), and the other one at 1595 cm^{-1} can be assigned to C═C stretching vibrations (Z.-N. Wang et al. 2020). The peaks at 1464 cm^{-1} and 1377 cm^{-1} are due to the bending vibration of CH_2 groups and the symmetric C-H stretching vibration of methyl, respectively (Li et al. 2020). In Figure 11, it can clearly be seen the absorbance of the peaks at 3355 cm^{-1}, 1640 cm^{-1} and 1595 cm^{-1} increase indicating the higher concentration of the corresponding functional groups during thermo-oxidative aging.

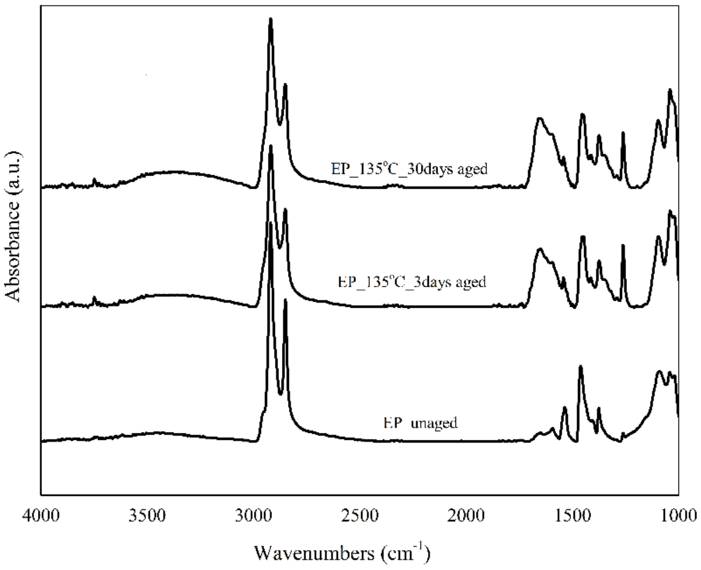

Figure 11. ATR-FTIR spectrum of EP over aging at 135°C

Since the carbonyl groups are known as the most indicative oxidation product, “carbonyl index (CI)” is a useful tool to determine extent of thermo-oxidative aging of EPDM based vulcanizates (Bouguedad et al. 2015). In this study, SAUB-CI (Specified Area Under Band-Carbonyl index) method has been used for quantitative analysis of the ATR-FTIR spectrum. CI was calculated by comparing the integration of 1850 to 1650 cm^{-1} band absorbance (C=O) to that of -CH_2- scissoring peak from 1500 to 1420 cm^{-1}. The related expression for calculating CI is given in Equation (3.2) (Almond et al. 2020). Integration of the band absorbance, which is the area under the band, was calculated by using peak analysis tool of PerkinElmer Spectrum 10 Spectroscopy Software.

$$\text{Carbonyl index (CI)} = \frac{\text{Area under band}_{\ 1850\ \mathrm{cm}^{-1} - 1640\ \mathrm{cm}^{-1}}}{\text{Area under band}_{\ 1500\ \mathrm{cm}^{-1} - 1420\ \mathrm{cm}^{-1}}} \tag{3.2}$$

Carbonyl index values of all the vulcanizates were calculated over aging at 135°C and the results are given in Figure 12. A systematic increase in the concentration of C=O groups is clearly seen for all the samples as expected. However, TMQ showed a positive effect on protecting the vulcanizates against thermo-oxidative aging. This is more prominent for peroxide cured EPDM compound (EP-T), especially for long aging periods.

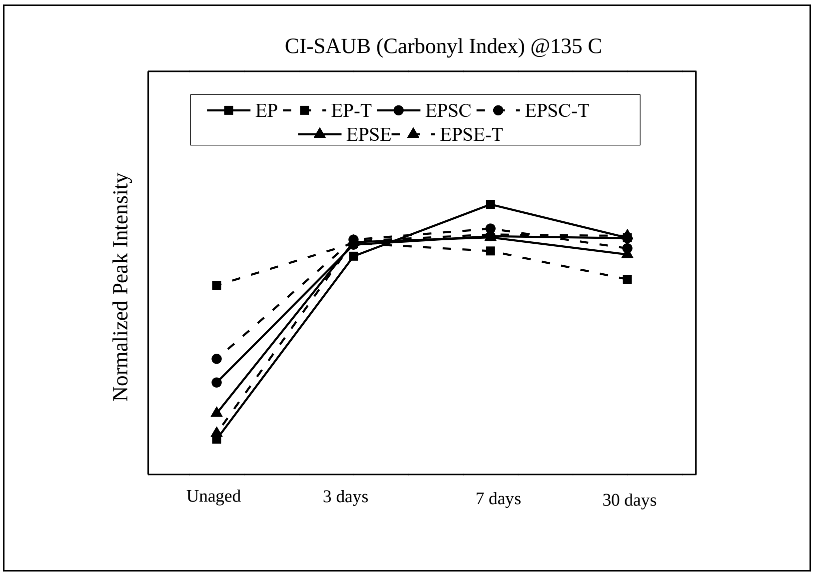

Figure 12. Calculated carbonyl index (CI) of the vulcanizates during aging at 135°C

4. Conclusion

In this study, TMQ, which is a very common and commercially available antioxidant for industrial rubber applications, has been evaluated regarding its anti-aging effect on various curing systems. Arrhenius method (ISO 11346, Rubber, vulcanized or thermoplastic – Estimation of life-time and maximum temperature of use), which is widely used for characterizing industrial rubber goods, has also been used for predicting life-time of the compounds prepared with and without antioxidant. TMQ has found to be an effective agent for stabilizing EPDM based rubber compounds against thermo-oxidative aging, especially for long aging periods. Degree of stabilization depends strictly on the curing system. Due to the fact that different crosslink types occur in different amounts with peroxide and sulfur curing systems makes it harder to evaluate individual effect of TMQ on rheological and mechanical properties. However, it was concluded that TMQ could increase aging activation energy for all the vulcanization system studied and therefore longer useful life-time for the vulcanizates could be obtained. Significantly lower cure extent along with longer cure time for peroxide system in the presence of TMQ was attributed to radical scavenging activity that also indicated a powerful antioxidant.

Author Contributions

Şehriban Öncel: Organized the study plan, performed analysis, analyzed the data and wrote the article.

Gürcan Gül: Contributed to the experimental study and analyzed the data.

Mahir Burak Efe: Contributed to the experimental study.

Hakan Erdoğan: Performed analysis.

Bağdagül Karaağaç: Co-organized the study plan, analyzed the data and wrote the article.

Conflicts of Interest

The authors declare no conflict of interest.

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