Article

Performance of Thermal-Oxidative Aging on the Structure and Properties of Ethylene Propylene Diene Monomer (EPDM) Vulcanizates

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Performance of Thermal-Oxidative Aging on the Structure and Properties of Ethylene Propylene Diene Monomer (EPDM) Vulcanizates

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Abstract: A thermal-oxidative aging test at 120°C was conducted on Ethylene Propylene Diene Monomer (EPDM) vulcanizates of the semi-efficient vulcanization system. The effect of thermal-oxidative aging on EPDM vulcanizates was systematically studied by curing kinetics, aging coefficient, cross-linking density, macroscopic physical properties, contact angle, Fourier Transform Infrared Spectrometer (FTIR), Thermogravimetric analysis (TGA) and thermal decomposition kinetics. The results show that the content of hydroxyl and carbonyl groups as well as the carbonyl index increased with increasing aging time, indicating that EPDM vulcanizates are gradually oxidized and degraded. As a result, the EPDM vulcanized rubber chains were cross-linked, and its conformational transformation was limited and its flexibility was weakened. The thermogravimetric analysis demonstrates the thermal degradation of EPDM vulcanizates had competitive reactions of cross-linking and degradation, and the thermal decomposition curve can be divided into three stages, meanwhile the thermal stability of EPDM vulcanizates gradually decreases with the increase of aging time. The introduction of antioxidant in the system can promote the cross-linking speed and reduce the cross-linking density of EPDM vulcanizates, while inhibiting the surface thermal and oxygen aging reaction. This is attributed to the fact that the antioxidant can reduce the thermal degradation reaction level, but it is not conducive to the formation of a perfect crosslinking network structure and reduce the activation energy of thermal degradation of the main chain.

Keywords: EPDM vulcanizates; thermal-oxidative aging; thermal decomposition kinetics; antioxidant

1. Introduction

Ethylene propylene diene copolymer rubber (EPDM) not only shows excellent flexion resistance, resilience and low temperature resistance, but also has good chemical structure stability. It is widely used in automotive industry, wire and cable, sealing materials and waterproof coiled materials and other fields. Although EPDM possesses excellent stability in chemical structure, it will still age to a certain extent under the action of external factors such as light, oxygen, heat and chemical media in the actual service and life process, which will degrade its performance and shorten the service life of products. Therefore, it is of great significance to study the aging law of EPDM.

The degradation process of rubbers is a complex and multi-stage mechanism that can be separated in several different steps [1]. It can lead to changes in material properties, which are caused by physical and irreversible chemical processes, such as polymer chain breaking, cross-linking [2,3]. These processes substantially affect the technically relevant properties of polymer materials, such as strength, stiffness, toughness and modulus [4]. Generally, the extent of aging-related changes is dependent on temperature and other aging conditions [5]. For example, the cross-linking density depends mainly on the material-dependent oxygen absorption capacity, rate of diffusion and oxygen permeability [6] as well as the vulcanization temperature, pressure and time. And aging of vulcanized rubber was shown to be related to a conversion of poly-sulfidic sulfur bridges to mono- and di-sulfidic sulfur bridges [7].

EPDM rubber has been studied in thermal-oxygen aging [8–12], photo-oxygen aging [13,14], artificial weathering aging [15], radiation aging [16,17] and medium aging [18,19]. Its research methods and test and characterization methods are diverse, such as dynamic mechanical property analysis, spectral analysis (Fourier infrared spectroscopy, Raman spectroscopy), energy spectrum analysis (X-ray electron spectroscopy, nuclear magnetic resonance), and thermal analysis (differential scanning calorimetry, thermogravimetric analysis), etc. However, most of them are limited to the research of EPM and EPDM rubber itself, and lack of research on the thermal oxygen aging of EPDM vulcanizates with antioxidant content and semi-efficient vulcanization system.

Here, in this paper, EPDM vulcanized rubber with a semi-effective vulcanization system is subjected to thermal and oxygen aging tests at 120°C(Scheme 1). The effects of thermal-oxygen aging on the structure and properties of EPDM vulcanizates were studied in detail through physical properties, aging coefficient, surface properties, cross-linking density, Fourier Transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and kinetics, and vulcanization characteristics of EPDM vulcanizates.

2. Experimental

2.1. Materials

EPDM Rubber(3760P) was purchased from Dow Chemical of the United States； carbon black(N330) was purchased from Cabot Corporation; naphthenic oil (KN4006) was purchased from China National Petroleum Corporation. Sulfur, zinc oxide (ZnO), stearic acid (SA), Tetramethylthiuram disulfide (TMTD), Poly(1,2-dihydro-2,2,4-trimethylquinoline) (RD), N-Isopropyl-N'-phenyl-p-phenylenediamine (4010NA), and they were all commercial industrial products.

2.2. Method

2.2.1. Preparation of EPDM vulcanizates

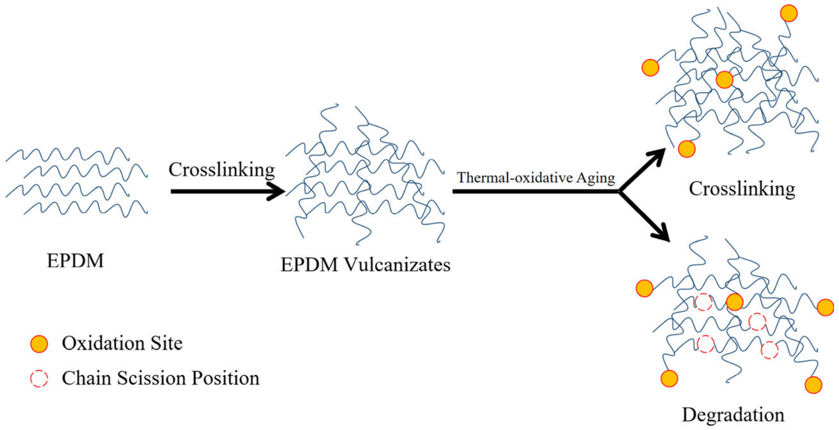
A two-stage mixing process was applied to EPDM vulcanizates by a Haake torque rheometer (Thermo Fisher Scientific, Poly Lab OS, Waltham, MA, USA) in this experiment. The speed of the internal mixer was set at 60 r/min and the initial temperature was 90°C. EPDM, ZnO, SA, carbon black (N330), and naphthenic oil were added in sequence. After dumping and pouring into the mixing mill, the two-stage mixing process was carried out. Later, sulfur and accelerator were added while the second temperature was 50°C. After storage for more than 16 hours, EPDM compound was vulcanized to the required samples with a plate vulcanizer (Huzhou Dong-fang Rubber Machinery Co., Ltd, XLB-400×400, Huzhou, Zhejiang, China) under the pressure of 15-20MPa and temperature of 170°C. The formulation of EPDM vulcanizates is listed in Table 1.

Table 1. Formulation of EPDM vulcanizates

Samples	EPDM wt %	N330 wt %	Sulfur wt %	TMTD wt %	ZnO wt %	SA wt %	KN4006 wt %	RD wt %	4010NA wt %
1#	100	100	1.5	1.5	5	1	70	-	-
2#	100	100	1.5	1.5	5	1	70	1	2

2.2.2. Thermal-oxidative aging

According to ISO 188:2011 standard, the thermal-oxidative aging test was carried out on samples in the thermal oxygen aging test chamber (GOTECH TESTING MACHINES INC., GT-7017-E, Taipei, Taiwan, China). The settings of the apparatus are as follows: temperature of 120°C, temperature deviation of ±2°C, air flow rate of 0.5-1.5m/s and air exchange rate of 3-10 times/h. The aging time was 0h, 24h, 72h, 120h, 168h, and 336h, respectively.



Scheme 1. The cross-linking and thermal-oxidative aging process of EPDM vulcanizates.

2.3. *Measurements*

2.3.1. Vulcanization characteristics

The vulcanization characteristics are tested using a Vulcanizer (GOTECH TESTING MACHINES INC., GT-M2000-A, Taipei, Taiwan, China) according to GB/T 16584-1996 with a specimen weight of approximately 5g, a vulcanization temperature of 170°C and a vulcanization time of 30min.

2.3.2. The cross-linking density

The rubber only swells and does not dissolve in the solvent, the mixing entropy increases and the swelling equilibrium is reached when the Gibbs free energy ΔGs is zero (Formula (1)).

$$\Delta G_s = \Delta G_m + \Delta G_{el} = 0 \tag{1}$$

where, ΔG_m, ΔG_{el} are mixing free energy, elastic free energy change respectively. In this experiment, the equilibrium swelling method was used to determine the crosslink density of EPDM vulcanized rubber. Assuming uniform deformation of the rubber in the solvent, the Flory-Rehner equation yields Formula (2). Cyclohexane was chosen as the solvent to determine the mass and density of EPDM before swelling, then put into the cyclohexane solvent, fully swelling, and test the mass after swelling every 24h until the difference between the two measurements was less than 0.01g, and calculate the crosslink density according to the following Equation (2).

$$\upsilon_e = -\frac{1}{V}\left[\frac{\ln(1-v_2)+v_2+\mathcal{X}{v_2}^2}{{v_2}^{\frac{1}{3}}}\right] \tag{2}$$

$$v_2 = \frac{v_1}{v_1+v_3} \tag{3}$$

$$v_3 = \frac{m_2-m_1}{\rho_3} \tag{4}$$

$$v_1 = \frac{m_3}{\rho_1} \tag{5}$$

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where v_e: crosslink density; V: molar volume of solvent; v_1: volume of rubber phase; v_2: volume fraction of rubber phase in vulcanizate; v_3: volume of solvent in rubber phase after swelling; $\mathcal{X}_{cyclohexane}$: interaction parameter between rubber and solvent: ($\mathcal{X}cyclohexane$: 0.35144524); ρ: density of rubber; ρ_1: density of reagent for swelling; m_1: mass of vulcanized rubber before swelling; m_2: mass of vulcanized rubber after swelling; m_3: mass of rubber phase.

2.3.3. Physical property

Tensile properties and hardness are measured using a AI-7000S electronic tension machine (GOTECH TESTING MACHINES INC., Taipei, Taiwan, China) and shore A hardness tester (GOTECH TESTING MACHINES INC., Taipei, Taiwan, China) according to ISO 37: 2005 and ISO 7619-2: 2004 respectively. The rate of change of performance is calculated according to the following Equation (6).

$$P(\%) = \frac{X_a - X_0}{X_0} \times 100 \tag{6}$$

where, P-rate of change of performance, %; X_a-measured value of performance of the specimen after aging; X_0 -measured value of performance of the specimen before aging.

2.3.4. Water contact angle test

The water contact angle is measured with contact angle meter (Shanghai Zhongchen Digital Technology Equipment Co., Ltd, JC2000D2, Shanghai, China). The measured liquid is distilled water, and the test temperature and humidity are 15℃ and 50%, respectively.

2.3.5. Aging coefficient

Aging coefficient (AC) [20] is the standard for evaluating the thermal aging performance of rubber and can be expressed as:

$$\mathrm{AC} = \frac{\sigma_2 \times \varepsilon_2}{\sigma_1 \times \varepsilon_1} \tag{7}$$

In Equation (7), AC refers to the aging coefficient of rubber; σ_1 and σ_2 refer to the tensile strength (MPa) before and after aging; ε_1 and ε_2 represent the elongation at break (%) before and after aging respectively.

2.3.6. Fourier Transform Infrared Spectrometer (FTIR) Analysis

The FTIR spectra of the polymer samples were obtained using a Nicolet IS 10 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The measurements of all of the samples were made with a signal average of 32 co-added scans and a resolution of 4 cm^{-1}, 10 times of scanning, within a wave number range of 600~4000cm^{-1}.

2.3.7. Thermal degradation kinetics

The thermogravimetric test was carried out in a N_2 atmosphere. The initial temperature was 30℃, and the heating rate was 20℃/min. After heating to 600 ℃, a constant temperature shall be kept for 10 min. After that, it was switched to the air atmosphere with a heating rate of 20℃/min and a 10min constant temperature after heating to 800 ℃.

2.3.8. Thermal degradation kinetics

The thermogravimetric analysis plays an important role in the structure and thermal stability of polymers. The relationship between quality and temperature or time is tested under a certain flow rate atmosphere, so as to analyze the thermal stability and thermal decomposition of samples.

The degradation reaction equation is usually used to describe its kinetics.

$$\frac{d_\alpha}{d_t} = kf(\alpha) \tag{8}$$

$$G(\alpha) = kt \tag{9}$$

Where, α refers to conversion rate, k refers to the rate constant, while $f(\alpha)$ depends on the reaction mechanism. The relationship between the rate constant k and the reaction temperature T can be expressed by Arrhenius equation:

$$k = Aexp(\frac{-E}{RT}) \tag{10}$$

Where A is pre-factor (min^{-1}); β is heating rate (℃/min); T is temperature (K); E is the activation energy (kJ/mol); n is reaction order; and R is molar gas constant (8.314472 J/(mol.k)). For the simple reaction equation $f(\alpha)$.

$$f(\alpha) = (1-\alpha)^n \tag{11}$$

The Equation (12) can be obtained by substituting Equations (10) and (11) into Equation (8):

$$\frac{d_\alpha}{d_t} = \mathrm{Ae}^{(\frac{-E}{RT})}(1-\alpha)^n \tag{12}$$

Freeman-Carroll method [21] is a method to calculate the activation energy by obtaining the difference between two points according to the reciprocal of the weight loss rate and temperature at several points on a thermogravimetric curve (TG curve). Assuming the heating rate at a constant $\beta = \frac{d_T}{d_t}$, Equation (13) can be obtained from the dynamic equation and Arrhenius equation:

$$\frac{d_\alpha}{d_T} = \frac{\mathrm{A}}{\beta}\mathrm{e}^{(\frac{-E}{RT})}(1-\alpha)^n \tag{13}$$

By taking logarithms on both sides of Equation (13) and dividing them by $\Delta\, lg(1-\alpha)$ at the same time, Equation (14) can be obtained:

$$\frac{\Delta\, lg\left(\frac{d_\alpha}{d_T}\right)}{\Delta\, lg(1-\alpha)} = -\frac{E}{2.303R} \times \frac{\Delta\left(\frac{1}{T}\right)}{\Delta\, lg(1-\alpha)} + n \tag{14}$$

Adopting a temperature range of 450-480℃ and a temperature interval of 2℃, this paper performed the Freeman-Carroll operation. The activation energy E and the reaction order n were obtained respectively according to the slope and intercept of the fitting line of $\Delta\, lg(da/dT)\,/\,\Delta\, lg\,(1-\alpha)$ for $\Delta(1/T)/\Delta\, lg\,(1-\alpha)$.

3. Results and Discussion

3.1 Vulcanization characteristics

Figure 1 shows the vulcanization characteristics curve of EPDM. The formulation in this article uses a semi-effective vulcanization system (accelerator to sulfur dosage ratio of 1, which is between CV and EV). The resulting EPDM vulcanized rubber has both polysulphide bonds and a moderate amount of single and double sulfur cross-linked bonds. This combines the characteristics of both CV and EV vulcanization systems to improve the thermal and oxygen ageing and fatigue resistance of the vulcanized rubber. The change in torque during rubber vulcanization is proportional to the change in cross-linking density and the rate of change in torque can be used to characterise the rate of vulcanization. The equation for the rate of vulcanization can be expressed as

$$V = \frac{dln(M_H - M_t)}{dt} = K(M_H - M_t)^n \tag{15}$$

Where, M_H, maximum torque; M_t, torque at vulcanization time t; K, rate constant; n, number of reaction stages.

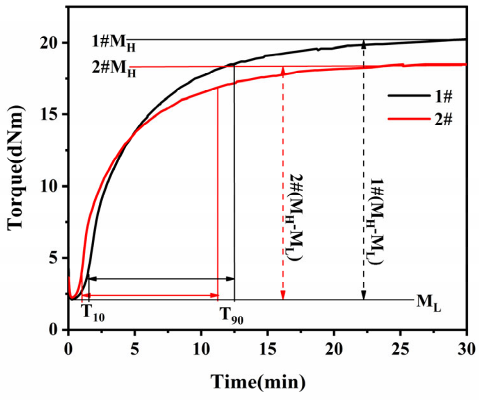

Figure 1. Vulcanization Curves of EPDM vulcanizates: (1#) without antioxidant; (2#) with antioxidant.

According to the reaction model for the coking phase derived by Coran [22], the reaction equation for the vulcanization phase can be expressed as in equation (16).

$$V_{ut} = V_{u\infty}[1 - e^{-K_2(t-t_i)}] \tag{16}$$

In addition, the reaction during the scorch period is not a primary reaction, but rather the true primary reaction begins when the rate of change of the torque reaches a maximum, and the sulphation kinetics can be expressed as

$$\ln(M_H - M_t) = lnA - K(t - t_{dis}) \tag{17}$$

In this case, t_{dis}, the moment when the rate of change of torque reaches its maximum, is plotted against (t-t_{dis}) by $ln(M_H$-$M_t)$ (Figure 2). K and lnA can be obtained from the slope and intercept, respectively.

As the sulphidation process after coking is usually divided into two stages, a linear fit to the data was performed separately and the fit was also found to be a smooth straight line, consistent with a first order kinetic reaction. This sulphidation process can therefore be divided into two first order kinetic reactions.

Due to the addition of antioxidant, T_{10}, T_{dis} are shortened, indicating that the start reaction time is earlier, the reaction is easier to carry out; vulcanization rate K, CRI value increases, the vulcanization speed becomes faster, but the crosslink density is lower than sample 1, EPDM vulcanization rubber characteristics data as shown in Table 2.

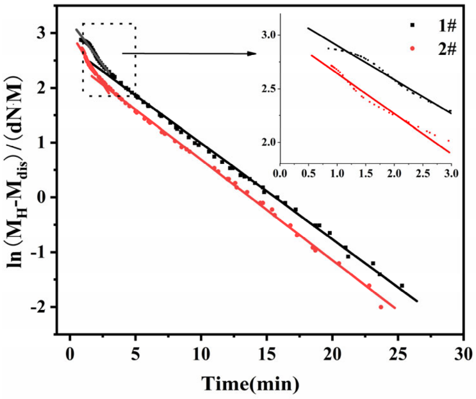

Figure 2. Relationship between $ln(M_H — M_t)$ and t of EPDM vulcanizates: (1#)without antioxidant; (2#) with antioxidant.

Table 2. The Data of vulcanization characteristics.

sample	M_H/(N·M)	M_L/(N·M)	M_H-M_L/(N·M)	T_{10}/(min)	T_{90}/(min)	CRI/(min^{-1})	T_{dis}/(min)	K	R
1#	20.29	2.09	18.2	1.46	12.23	9.07	1.89	0.23*/0.17	0.990*/0.998
2#	18.55	2.25	16.3	0.98	11.32	9.57	1.19	0.27*/0.18	0.987*/0.997

Note: T_{10} is the time corresponding to a torque of 10%. T_{90} is the time corresponding to a torque of 90%. CRI is the sulfur addition index, $CRI=100/(T_{90}-T_1)$, reflecting the speed of vulcanization, the larger the CRI value, the faster the speed of vulcanization. *: First stage fitted data.

3.2. Physical properties and cross-linking density

Figure 3 shows that physical properties and cross-linking density changes of EPDM vulcanizates after aging. The specific data of changes in the performance of EPDM vulcanizates after aging was shown in Table 3. It can be seen that the tensile strength, hardness, and cross-linking density of two EPDM vulcanizates gradually increase but the elongation at break decreases with increasing aging time. Basically, EPDM vulcanizates would continue to be cross-linked at 120 °C, the conformation transition of the polymer chain was constrained and the flexibility was weakened, which lead to the increasing tensile strength and surface hardness [23].

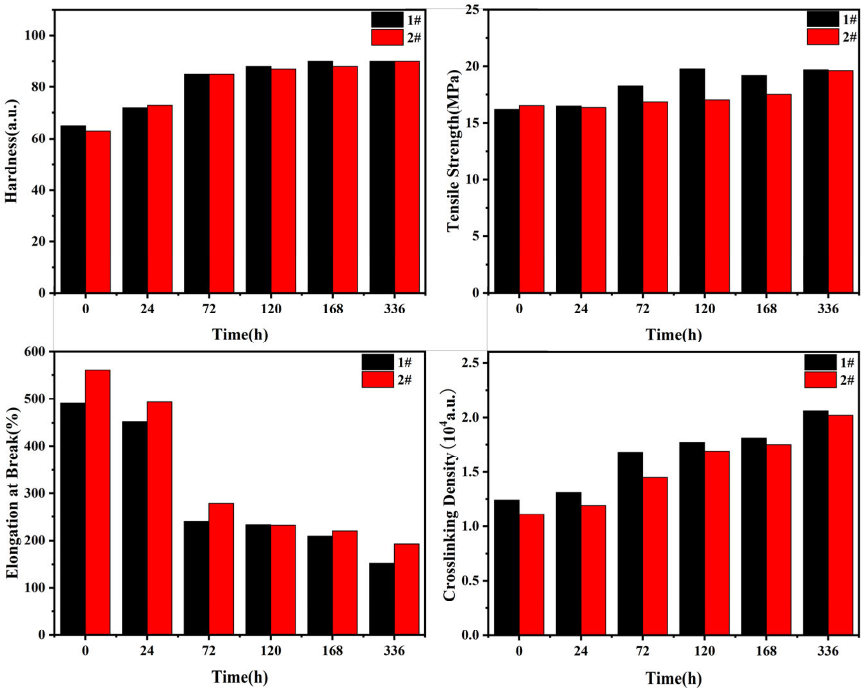

Figure 3. Changes in performance of EPDM vulcanizates after aging: (1#) without antioxidant; (2#) with antioxidant.

Table 3. Changes in performance of EPDM vulcanizates after aging.

Aging time/h	Hardness		Tensile Strength /MPa		Elongation at Break /%		Cross-linking Density	
	1#	2#	1#	2#	1#	2#	1#	2#
0	65	63	16.22	16.55	490.84	561.17	1.24×10^{-4}	1.11×10^{-4}
24	72	73	16.51	16.83	452.52	493.58	1.31×10^{-4}	1.19×10^{-4}
72	85	85	18.24	16.86	239.86	358.80	1.68×10^{-4}	1.45×10^{-4}
120	88	87	19.77	17.03	232.94	329.11	1.77×10^{-4}	1.69×10^{-4}
168	90	88	19.20	17.52	209.55	295.17	1.81×10^{-4}	1.75×10^{-4}
336	90	90	19.69	19.62	152.53	258.21	2.06×10^{-4}	2.02×10^{-4}

The oxidative degradation of the carbon-carbon backbone during the thermal-oxidative aging of EPDM vulcanizates increases the polarity and decreases the flexibility, while aging produces more silver lines and increases the number of weak points leading to lower elongation at break.

The elongation at break of EPDM vulcanizate with antioxidant is higher than that of sample without antioxidant, while the tensile strength, cross-linking density and hardness are slightly lower than that of sample 1#. It is indicating that antioxidant has an effect on the vulcanization characteristics, which can inhibit the generation of cross-linking network structure, and make the macromolecular chain have a larger free volume. The degradation reaction and cross-linking reaction of EPDM vulcanizates are competitive reactions during thermal-oxidative aging. Antioxidants increase the imperfection degree of cross-linking structure, at the same time, chain breaking and oxidation reaction play a leading role with increasing thermal-oxygen aging time.

3.3 Aging coefficient and retention

The aging coefficient (*AC*) is obtained from the relationship between physical and mechanical properties (e.g. tensile strength, elongation) before and after thermal and oxygen aging. It is usually a key indicator used to evaluate the overall performance of rubber aging. Figure 4 shows the changes of aging coefficient and tearing elongation retention at break of EPDM vulcanizates with aging time. The specific data are shown in Table 4. The aging coefficient and elongation retention rate of EPDM vulcanized rubber with the addition of antioxidant are larger than those of the sample 1# without the addition of antioxidant. It means that the addition of antioxidant obviously improves the retention rate of the macro physical properties of EPDM vulcanized rubber with thermal and oxygen aging.

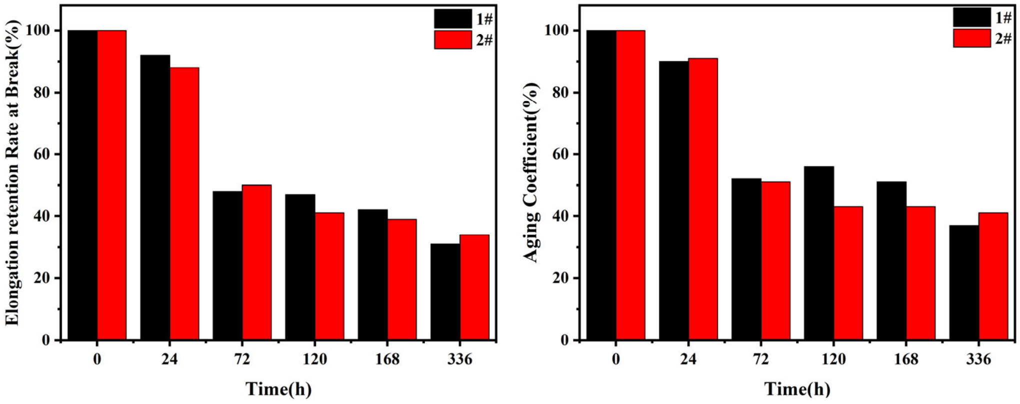

Figure 4. Elongation retention at break and AC of EPDM vulcanizates after aging: (1#) without antioxidant; (2#) with antioxidant.

Table 4. Performance of EPDM vulcanizates after aging

Aging time/h		0	24	72	120	168	336
Elongation retention at break/%	1#	100	92	48	47	42	31
	2#	100	88	64	59	53	46
AC/%	1#	100	90	52	56	51	37
	2#	100	90	65	60	56	54

3.4 Fourier Transform Infrared Spectrometer (FTIR) Analysis

In this paper, the structure of EPDM vulcanizates was analyzed by ATR total reflection method after aging, which is a simple and efficient method for analysing the structure of EPDM vulcanized rubber after aging. The change of the infrared spectrum of EPDM vulcanizates are showed by Figure 5 with aging time. The infrared absorption peaks of the two EPDM vulcanizates at different wavelengths show the same change rule.

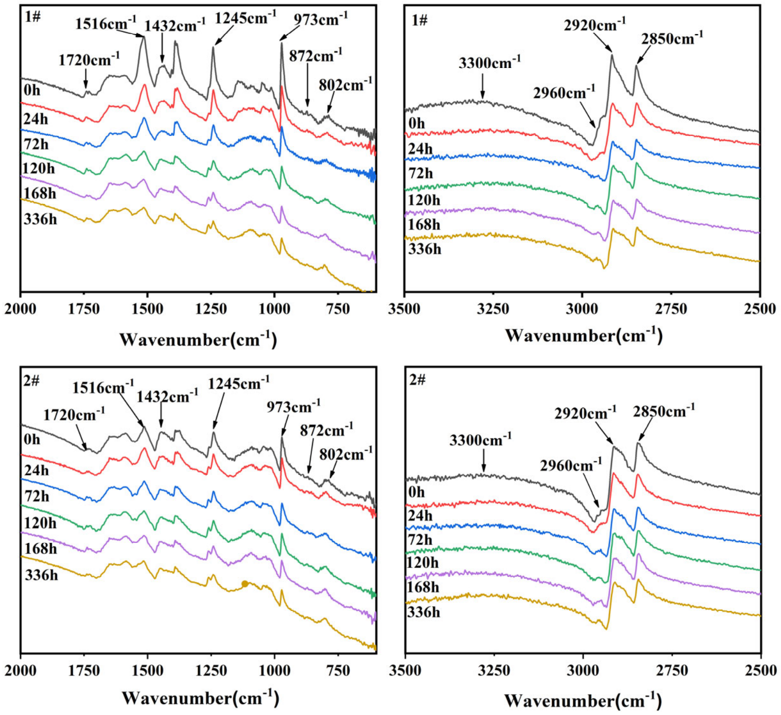

Figure 5. Infrared spectra of sample EPDM vulcanizates: (1#) without antioxidant; (2#) with antioxidant

The peak at 3300cm^{-1} was the stretching vibration peak of the hydroxyl group which is attributed to the extended oxidation group of -OH (alcohol, hydroperoxide and carboxylic acid) [24]. As a result of thermal oxidative degradation, which content increased with with increasing aging time. For pure EPDM, the peaks between 2800cm^{-1} and 3000 cm^{-1} are related to CH3, CH2 and CH [25]. The peak at 2850cm^{-1} and 2920cm^{-1} belonged to symmetric stretching vibration and asymmetric stretching vibration of (-CH2-) group respectively [26], which decreases with aging time. The peak at 2960cm^{-1} reflects the asymmetric stretching vibration of methyl [27–30]. Its content increases with the extension of the aging time, indicating a chain rupturing reaction of the EPDM structure.

The peak at 1720 cm^{-1} was the characteristic peak of carbonyl, in which the peak area is a measure of the oxidative degradation degree of the polymer [31–33]. As carbonyl was the main product of oxidative degradation of EPDM vulcanizates, the carbonyl index can be determined, namely, the value of carbonyl sulfide line strength at 1720 cm^{-1} divided by methylene line strength at 1432 cm^{-}

^{1}[34]. Carbonyl content and carbonyl index were shown in Table 5. The upward trend of carbonyl content and carbonyl index with increasing aging time implied that EPDM vulcanizates were gradually oxidized and degraded.

The carbonyl content and carbonyl index of the sample 2# with the addition of antioxidant are smaller than those of the 1# EPDM vulcanized rubber, so it can be inferred that the addition of RD and 4010NA antioxidants can reduce the oxidation reaction on the surface of EPDM vulcanized rubber to a certain extent and improve the heat and oxygen aging resistance.

In the IR absorption region of 1500-800 cm^{-1}, the peak at 1432 cm^{-1} was the -CH2- shear vibration mode of propylene unit of EPDM and CH band lossed due to oxidative degradation [35]. The peak at 1245cm^{-1} was caused by macro-molecular skeleton vibration, the content decreased with increasing aging time also implied that thermal oxygen aging would lead to the fracture of the macro-molecular skeleton.

Table 5. Changes in the peak area of different groups of EPDM vulcanizates after aging.

Aging time/h	3300cm^{-1}	2960cm^{-1}	1720cm^{-1}	1516cm^{-1}	1432cm^{-1}	1245cm^{-1}	1# ^{1}	2# ^{1}
0	200.17	1.46	2.42	40.59	1.16	24.75	2.086	0.638
24	204.51	2.11	2.71	33.6	1.13	25.14	2.398	0.638
72	209.6	3.12	3.07	34.39	1.28	23.04	2.398	0.728
120	213.87	3.17	3.19	21.46	1.32	19.97	2.417	0.815
168	220.48	3.39	3.77	21.06	1.48	18.62	2.547	0.867
336	231.69	5.12	4.67	18.66	1.67	17.04	2.796	0.969

^{1} carbonyl index.

The peaks at 872 cm^{-1} and 802 cm^{-1} were the deformation vibration of the typical unsaturated zone C=C-H of the diene part, and 973cm^{-1} was the shear deformation vibration of C-H in the third monomer with double bond C=C-H. Its content increased firstly and then decreased with the increasing aging time, which was due to cross-linking firstly, and then breakage loss of double bonds caused by the thermal oxidative aging degradation [36,37]. The carbonyl and ester groups were formed and the unsaturation of the third monomer decreased rapidly, which indicated that chain branching [38] and cross-linking reactions [39] occur simultaneously during the aging process of EPDM vulcanizates. Therefore, thermal-oxidation aging of EPDM vulcanizates can be seen as a process of breaking of the main chain and oxidation.

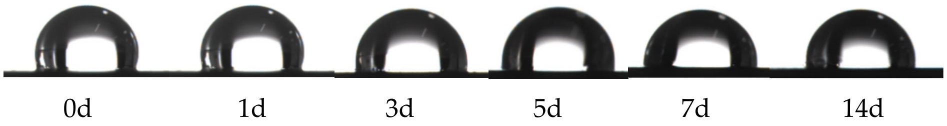

Figure 6. Contact angle of 1# EPDM vulcanizates.

3.5. Surface property

Contact angle is the angle between the tangent line of the gas-liquid interface and the solid-liquid junction line made by the liquid at the intersection of gas, liquid and solid phases after the formation of the Young-Laplace arc on the solid surface. The contact angle is an important parameter to measure the wetting performance of the liquid on the surface of the material, and can express the change of polarity, hydrophilicity and surface energy of the material surface.

Figure 7 shows the variation of contact angle of EPDM vulcanized rubber with aging time, the specific data is shown in Table 6, it can be seen that the contact angle of 2 types of EPDM vulcanized rubber shows a gradual decrease with the increase of aging time. The reason is that the main chain of EPDM vulcanized rubber is broken and oxidised, and the oxygen-containing groups such as carbonyl and carboxyl groups on the surface gradually increase. The number of carbon atoms in the main chain decreases and the water solubility gradually increases, which shows that the hydrophilic energy gradually increases and the contact angle decreases. As the aging time increases, the oxidative degradation of the main chain of EPDM further intensifies, leading to an increase in the carbonyl index, and thus the contact angle decreases.

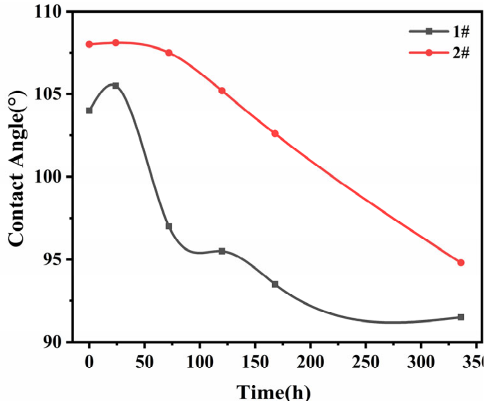

Figure 7. Contact angle of EPDM vulcanizates after aging: (1#) without antioxidant; (2#) with antioxidant.

The contact angle of sample 2# with the addition of antioxidant was larger than that of sample 1. This is probably due to the fact that the addition of the antioxidant affects the crosslinking reaction and network of the EPDM vulcanized rubber while reducing the oxidation reaction during the vulcanization process. Further, the oxidative degradation of the EPDM vulcanized rubber surface is more intense as the aging time increases. It is suggested that the addition of antioxidants RD and 4010NA can significantly reduce the generation of oxidation groups on the surface and thus the carbonyl index.

Table 6. Contact angle of EPDM vulcanizates after aging.

Samples	0h	24h	72h	120h	168h	336h
1#	104.0	105.5	97.0	95.5	93.5	91.5
2#	108.0	108.1	107.5	105.1	102.6	94.8

3.6 Thermal degradation behavior and kinetic

The thermal stability of materials can be analyzed by TGA, which can reveal the relationship between the mass of the sample and temperature or time under a certain flow rate atmosphere. The TGA test is the change of sample quality at the same heating rate and isothermal time. The TG curve can not only show the different stages of thermal decomposition of the sample, but also allows qualitatively and quantitatively analyze the composition change after aging. The DTG curve represents the weight loss rate, which can be derived from the TG curve, and the two curves correspond. The decomposition stage, decomposition temperature, decomposition rate, thermal stability, thermal decomposition activation energy of polymer materials can be obtained by the thermogravimetric analysis. Figure 8 shows the TG/DTG curve of EPDM vulcanizate after aging.

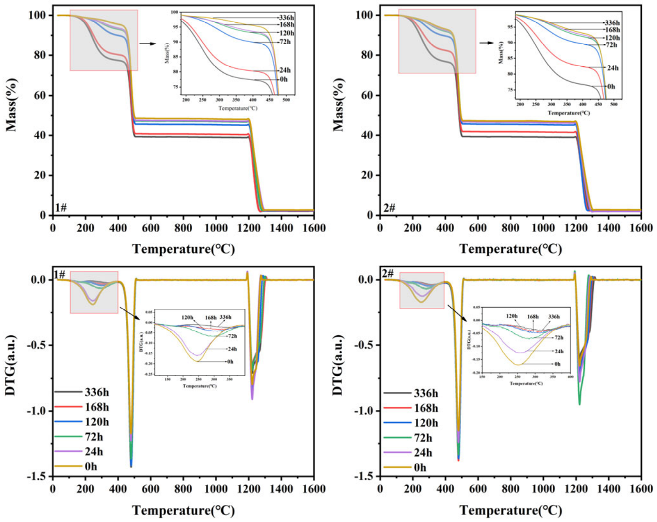

Figure 8. TG/DTG curve of EPDM vulcanizates after aging: (1#) without antioxidant; (2#)with antioxidant

According to the TG/DTG curve in Figure 8, the thermal weightlessness of EPDM vulcanizates can be divided into three stages. The specific data was listed in Table 7. It can be seen that the change trend of the initial weight-loss temperature in the first stage gradually reduced with increasing aging time; and were not change with time in the second and third stages. The initial weight-loss temperature in the first stage also represents that its thermal stability gradually decreases. The weight-loss rate of EPDM vulcanizates in the first stage was gradually reduced with increasing aging time. The major losses were highly volatile substances (plasticizers, accelerators, water vapor, etc.), whose aging were accompanied by the quality degradation in the first stage at 120°C. In the second stage, medium volatile substances (EPDM rubber) losed away largely. Some scholars [40] had tracked the degradation and pyrolysis process of EPDM by gas chromatography to confirmed that the main products were CO_2, H_2O, CO, CH_4, and C_2H_6. combustible substances (carbon black, etc.) burn slowly in the third stage. The remaining materials were some mineral additives, such as ZnO.

The peak of the first weight-loss temperature increased with increasing aging time, while the peak of weight-loss temperature in the second and third stage did not change significantly. This was due to the loss of plasticizers, cross-linking and degradation (the competitive reaction), which were caused by the decomposition of the carbon main chain that affected the free volume of the material during the thermal oxidative aging process of EPDM vulcanizates. The degradation is attributed to the oxidative degradation of the main chain of crosslinked EPDM in the second stage [41].

In this paper, the temperature interval 450-480°C was chosen to calculate the heat drop activation energy. This interval is mainly attributed to the EPDM main chain structure, where the weight loss reaction is relatively intense. The activation energy E and the number of reaction steps n can be obtained from the slope and intercept of the straight line, respectively, by the Freeman-Carroll method for graphing (Figure 9). Table 8 shows the data of the thermal analysis of the TG/DTG curve of EPDM vulcanization rubber ageing.

Table 7. TG/DTG curve data of EPDM vulcanizates after aging.

Aging time/h	Initial weight loss temperature/°C				Maximum weight loss temperature/°C			
	First stage		Second Stage	Third Stage	First stage		Second Stage	Third Stage
	1#	2#	1#、2#	1#、2#	1#	2#	1#、2#	1#、2#

0	93	101	393	800	245.67	253.33	479.33	1222.33
24	89	100	393	800	244.30	257.00	479.33	1222.33
72	89	107	393	800	298.00	283.00	479.33	1222.33
120	89	97	393	800	300.00	313.67	480.33	1222.33
168	86	89	393	800	318.67	306.67	480.33	1222.33
336	84	87	393	800	325.00	327.67	479.67	1222.33

The results show that the degradation process of EPDM is complex and its degradation reaction is not a simple stepwise reaction but a random degradation process [42]. The degradation of EPDM follows the Avrami-Erofeev two-dimensional nucleation model or random chain breaking mechanism [43]. The activation energy E of thermal degradation of the EPDM vulcanized rubber backbone structure tends to decrease with increasing thermal and oxygen aging time. This is due to the dual effect of chain breakage and cross-linking occurring simultaneously during thermal oxygen aging, with EPDM vulcanized rubber continuing to cross-link at 120℃ under thermal oxygen [35]. The crosslink density gradually increases leading to a relatively smooth decrease in the magnitude of its thermal degradation activation energy. However, as the aging time increases, the oxidative degradation reaction of the EPDM backbone dominates and the activation energy continuously decreases [44,45].

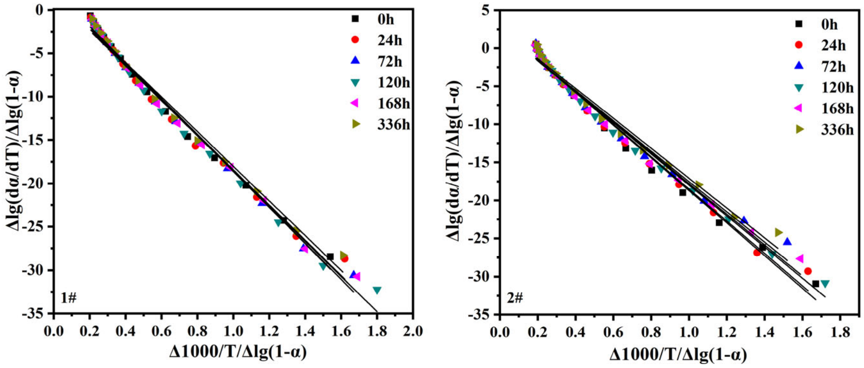

Figure 9. Relationship between *Δlg(dα/dT)/Δlg(1-α)* and *Δ1000/T/Δlg(1-α)* of EPDM vulcanizates after aging: (1#) without antioxidant; (2#) with antioxidant

A comparison of the results from the 2# (with antioxidant) and 1# (without antioxidant) samples shows that the addition of antioxidant increases the EPDM vulcanization starting weight loss temperature and the first stage weight loss peak temperature. At the same time, the number of reaction stages is reduced, indicating that the addition of antioxidant can reduce the thermal degradation reaction and thus inhibit the oxidation effect. This is generally consistent with the macroscopic physical and mechanical properties. The activation energy of thermal degradation of sample 2 is smaller than that of sample 1. This is due to the competition between degradation and cross-linking of the EPDM backbone. The antioxidant enhances the crosslinking rate but does not help to form a complete crosslinking network of the EPDM curing rubber, thus reducing the stability of the carbon-carbon backbone. Herein, the degradation reaction plays a major role in reducing the thermal degradation activation energy.

Table 8. Thermal analysis data of TG/DTG curve of EPDM vulcanizates after aging.

Aging time/h	activation energy E/kJ.mol^{-1}		the number of reaction stages		R	
	1#	2#	1#	2#	1#	2#
0	440.111	434.951	4.4084	4.0562	0.96104	0.96488
24	434.981	431.557	4.1105	3.9756	0.95935	0.9649
72	426.952	411.185	4.0395	3.9283	0.97098	0.94975
120	420.865	413.527	3.9563	3.7456	0.9716	0.97406
168	424.908	412.543	3.9393	3.8535	0.97151	0.96355
336	418.352	405.043	3.9443	3.7375	0.96546	0.95589

4. Conclusions

The structure and properties of EPDM vulcanizates with two kinds of semi-efficient vulcanization system before and after thermal-oxidative aging were investigated in detail, including vulcanization characteristics, macroscopic physical properties, surface properties, thermogravimetric behavior and kinetics, and so on.

The vulcanization characteristics showed that the vulcanization process of EPDM vulcanizates consisted of two first-order kinetic reaction stages. Antioxidants can promote the cross-linking reaction and improve the cross-linking speed, but cannot form perfect cross-linking network structures. With increasing aging time, EPDM vulcanizates can continue to cross-link so as that the conformational transformation of polymer chain is constrained, and the flexibility is weakened. And finally, the macroscopic physical properties (such as strength, elongation, hardness, etc.) are affected. The antioxidant can significantly improve the aging coefficient and macroscopic physical retention of EPDM vulcanizates, which can inhibit cross-linking density and have a larger free volume, and thus promote the retention of elongation and hardness.

The FTIR shows that the infrared absorption peaks of two EPDM vulcanizates at different wavelengths have the same changes. It is implied that the oxidation and degradation of the surface intensifies as the aging time increases, and the carbonyl content and carbonyl index gradually increase. This phenomenon is demonstrated macroscopically as an increase in contact angle. Antioxidants can reduce the degree of oxidation and degradation of the surface of EPDM vulcanizates, and improve the thermal oxygen aging properties of the surface.

The thermal degradation behavior and kinetics displayed that the thermal decomposition of two EPDM vulcanizates can be divided into three stages. The 2# sample with the addition of the high boiling-point antioxidant greatly increased the initial weight-loss temperature and the peak of the first weight-loss temperature in the first degradation stage. The kinetic study of the backbone of EPDM vulcanizates under the temperature range of 450-480°C showed that the antioxidant can reduce the reaction order and promoting the formation of incomplete cross-linked network structure, which intensifies the degradation reaction and reduces the thermal degradation activation energy of the backbone.

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