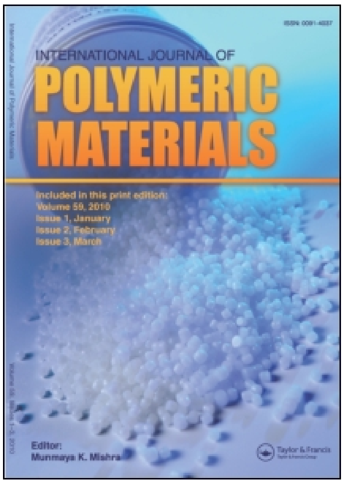

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The Effect of Dy(III) Complex with 2-Mercaptobenzimidazole on the Thermo-Oxidation Aging Behavior of Natural Rubber Vulcanizates

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A novel kind of Dy(III) complex with 2-mercaptobenzimidazole was prepared. The antioxidative properties and mechanisms of the Dy(III) complex in the NR vulcanizates were investigated by attenuated total-reflectance Fourier transform infrared (FTIR-ATR) spectroscopy, crosslinking density determination, mechanical properties testing and thermogravimetric analysis. The thermo-oxidative stability of the NR vulcanizates was found to be improved markedly by the addition of Dy(III) complex. It can be attributed to the thioether bonds, which can decompose the hydroperoxide, and the Dy(III) ions, which can capture and inactivate the oxy radicals. The apparent thermo-oxidation activation energy of the NR vulcanizates was calculated by the Kissinger and Flynn-Wall-Ozawa methods, respectively. The results show that the NR vulcanizates with the Dy(III) complex have higher thermo-oxidation activation energy than that of the samples with antioxidant MB and antioxidant 4010NA.

Keywords antioxidation mechanism, Dy(III) complex, kinetics, 2-mercaptobenzimidazole, natural rubber, thermo-oxidation aging

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INTRODUCTION

Natural rubber (NR) is widely used in industrial, technological and military fields because of its excellent mechanical and processing properties. However, natural rubber has poor aging characteristics because it contains many unsaturated double bonds in its molecular chains which can easily participate in oxidation reaction [1,2]. Oxidative aging of rubber is one of the most important problems in rubber technology because the absorption of a little amount of oxygen can cause a considerable change in the physical and mechanical properties of vulcanizates. The thermal oxidation of rubber is an autocatalytic, free radical chain reaction. There are several different approaches to prevent the oxidation reaction, and the addition of antioxidants seems to be the most convenient way to retard oxidation [3–7].

2-mercaptobenzimidazole has been widely used as a non-discoloring antioxidant in natural and synthetic rubbers [8,9]. This kind of antioxidant could efficiently prevent the hot air aging and weathering aging. But it has disadvantages of vulcanization reversion and easy scorching when it is used alone. Moreover, 2-mercaptobenzimidazole has low molecular weight. This kind of antioxidant easily gives off a bad smell and departs from the polymers by migration, evaporation or extraction. Therefore the study on its derivative and complexes as a rubber antioxidant is very interesting. Zinc salt of 2-mercaptobenzimidazole is one example. It can increase the molecular weight and reduce the migration and extraction, but it does not inherently increase the oxidation-resistant ability.

It was indicated that rare earth ions have strong oxidation-resistant ability. Rare earth complexes show great scavenging effects for free radicals [10,11]. Because rare earth ions possess many unoccupied orbits, they have the strong ability of binding and capturing the free radicals, which can terminate the chain reaction and retard the autoxidation processes effectively. Recently, a new type of rare earth complex which contains Dy(III) ions and organic ligand, 2-mercaptobenzimidazole, was prepared in our laboratory (Figure 1). It is expected that the Dy(III) complex has good oxidation-resistant properties due to the presence of thioether bonds and Dy(III) ions. In this

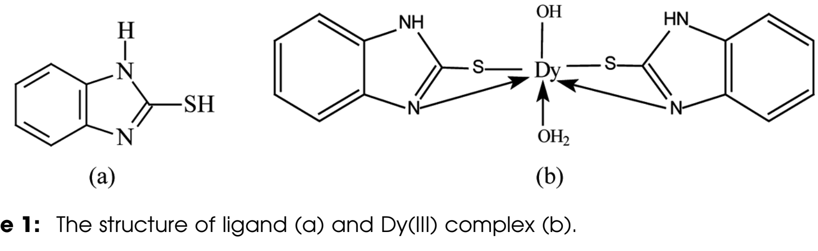


Figure 1: The structure of ligand (a) and Dy(III) complex (b).

paper, the antioxidative properties and the corresponding mechanisms of the Dy(III) complex in the NR vulcanizates are investigated.

EXPERIMENTAL

Materials

Natural rubber (NR), ZnO, Stearic acid, N-cyclohexyl-2-benzothiazole sulpenamide (accelerant CZ), dibenzothiazole disulfide (accelerant DM) and N-isopropyl-N'-phenyl-p-phenylenediamine (antioxidant 4010 NA) were supplied by Guangzhou Rubber Institute, China. Dy(III) complex with 2-mercaptobenzimidazole was prepared in our laboratory [12]. The structures of 2-mercaptobenzimidazole and Dy(III) complex with 2-mercaptobenzimidazole are shown in Fig. 1(a) and (b). All other solvents and chemical reagents were of chemically pure grade and were further purified, if necessary, by the usual techniques.

Preparation of Vulcanizate Samples

The formulation of NR compound was as follows (phr): NR 100; stearic acid 2; zinc oxide 3; accelerant CZ 1.5; accelerant DM 0.5; sulfur 1.5; antioxidant 2.

All rubber compounds were prepared in a $\varphi 160 \times 330$ laboratory rubber mill. The rolls run at a speed ratio of 1 (front roll): 1.22 (back roll). After mixing, the compounds were left overnight before vulcanization. The vulcanization of the NR compounds were operated at 143°C for optimum curing time in a press. The vulcanized rubber samples were conditioned at a temperature of 23 ± 2°C for 24 h before testing.

Testing and Characterization

Mechanical Properties

- ISO 3417:1991 was used to determine of t_{s2}, t_{c90}, ML, MH and CRI using a U-CAN UR-2030 vulcameter.
- ISO 37:2005 and ISO 34-1: 2004 were used to determine tensile properties and tear strength using a U-CAN electron tensile testing machine.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

The FTIR-ATR spectra of the samples before and after aging were measured on a Nicolet Fourier transform infrared spectrophotometer from 4500 cm^{-1} to 800 cm^{-1} in 4 cm^{-1} resolution. For each sample, three scans were taken to identify the peaks.

Hot-Air Aging Test

Hot-air aging was performed in an air-circulating oven at 100°C for 24 h, 48 h, 72 h, and 96 h, respectively. Mechanical property measurements were performed according to standard methods ISO 188: 1998 and were carried out using an Instron Universal Testing Machine at 25°C and a crosshead speed of 500 mm/min.

Crosslink Density

The equilibrium swelling method was used to determine the crosslink density of the vulcanizates. Samples were swollen in toluene at room temperature for 72 h and then removed from the solvent and the surface toluene was quickly blotted off. The samples were immediately weighed and then dried in a vacuum oven at 80°C for 36 h to remove the solvent, and then reweighed. The volume fraction of NR in the swollen gel, V_r, was calculated by equation:

$$V_r = \frac{m_0 \times \phi \times (1-\alpha)/\rho_r}{m_0 \times (1-\alpha)/\rho_r + (m_2 - m_1)/\rho_s} \tag{1}$$

where m_0 is the sample mass before swelling, m_1 and m_2 are sample masses before and after drying, respectively, Φ is the mass fraction of rubber in the vulcanizate, α is the mass loss of the gum NR vulcanizate during swelling, and ρ_r and ρ_s are the rubber and solvent density, respectively.

The elastically active network chain density, V_e, which was used to represent the whole crosslink density, was then calculated by the well-known Flory–Rehner equation[13]:

$$V_e = -\frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_s\ (V_r^{1/3} - V_r/2)} \tag{2}$$

where V_r is the volume fraction of the polymer in the vulcanizate swollen to equilibrium and V_s is the solvent molar volume (107 cm^3/mol for toluene). χ is the NR–toluene interaction parameter and is taken as 0.42 which was calculated according to the Aprem et al. [14].

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out in a NETZSCH 209 (NETZSCH Instrument, Germany) thermogravimetric analyzer over a temperature range from room temperature to 700°C at a heating rate of 5, 10, 20 and 30°C/min, respectively. Air flow 80 ml/min was employed in thermo-oxidative degradation.

For nonisothermal degradation, the apparent activation energy (E) of thermo-oxidative degradation could be calculated by using the Kissinger method [15] and Flynn-Wall-Ozawa method [16,17] through Eqs. (3) and (4), respectively.

$$\ln\left(\frac{\beta}{T_{pi}^{2}}\right)=\ln\frac{A_kR}{E_k}-\frac{E_k}{R}\frac{1}{T_{pi}}\quad [\mathrm{i}=1,2,\ldots \mathrm{M}] \tag{3}$$

$$\lg\beta=\lg\left(\frac{AE}{RG(\alpha)}\right)-2.315-0.4567\frac{E}{RT} \tag{4}$$

In Eq. (3), $\beta = \mathrm{dT/dt}$ is the heating rate, $\mathrm{T_{pi}}$ is the temperature at which there is a maximum weight loss, $\mathrm{A_k}$ is a pre-exponential factor, $\mathrm{E_k}$ is the activation energy and R is the universal gas constant for equation. A plot of $\ln(\beta/\mathrm{T_{pi}^2})$ vs. $1/\mathrm{T_{pi}}$ gives the activation energy without a specific assumption on the degradation dependent function. This enables a single value of $\mathrm{E_k}$ to be determined by a model free way.

In Eq. (4), α is the mass conversion rate, T is the temperature, $\beta = \mathrm{dT/dt}$ is the heating rate, A is the preexponential factor, E is the activation energy and R is the universal gas constant. This is an isoconversional integral method. For $\alpha = $ constant, $\ln\beta$ vs. 1/T, obtained from thermograms recorded at several heating rates yields a straight line whose slope allows evaluation of the activation energy.

RESULTS AND DISCUSSION

Vulcanization Characteristics

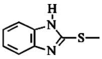
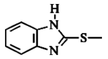
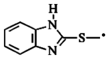
The Dy(III) complex was incorporated in the standard formula of NR. The vulcanization characteristics of the rubber compounds are given in Table 1.

Table 1 shows that the NR compounds with and without antioxidant have almost the same level of minimum torque (ML). It is clear that NR compounds with the Dy(III) complex have the highest value of the maximum torque at

Table 1: Vulcanization characteristics of the NR compounds[a].

Properties	Without antioxidant	Dy(III) complex	Antioxidant MB	Antioxidant 4010NA
ML, dN·m	1.9	2.2	2.3	2.2
MH, dN·m	12.0	14.8	14.6	12.8
t_{c90}, min	6.9	4.1	3.7	5.4
t_{s2}, min	5.5	3.0	2.5	4.3
CRI, $\mathrm{min^{-1}}$	70.9	90.0	83.3	95.2

[a] ML: Minimum torque, MH: Maximum torque, tc90: Optimum cure time, ts2: Scorch time, CRI: Cure rate index.

about 14.8 dN · m, while NR compounds without antioxidant have the lowest value of the maximum torque at about 12.0 dN · m. The Dy(III) complex can raise the cure rate index and improve the maximum torque of the rubber, which indicates that the Dy(III) complex can take part in the forming of rubber network and accelerate the curing process due to the presence of  in its structure [18]. On the other hand, the interaction between the Dy(III) ion and  is an electrovalent bond, which will weaken the vulcanizing activity of the . It will be of much significance to prevent scorch and improve production efficiency in the rubber industry.

Antioxidant Activities

FTIR-ATR Analyses

In order to study the anti-aging mechanism of the Dy(III) complex, the representative samples are analyzed using FTIR-ATR spectroscopy. Figures 2(a)–(d) presents the FTIR-ATR spectra of the NR vulcanizates with different kinds of antioxidants aged at 100°C, respectively. The assignments of various bands for the NR vulcanizates are given in Figures 2(a)–(d).

The FTIR-ATR spectra show the significant variations of the characteristic absorption bands after hot-air aging. The absorption bands at 3552 cm^{-1}, 3420 cm^{-1} and 1716 cm^{-1} are assigned to the characteristic peaks of (C=O)–O–, OH and C=O, respectively, and the absorption band at 1310 cm^{-1} corresponds to the CH wagging of methylene. It is observed that the absorbance bands for (C=O)–O–, OH and C=O increase because of the oxidation of NR [19,20]. A measurement of the oxidation can be calculated by taking the ratio of the intensity of the band at 1716 cm^{-1} to that of the band at 2848 cm^{-1}. The latter band is assigned to the CH_2 symmetric stretching mode and is relatively unaffected during the thermal oxidation. Absorbance ratio ($A_{C=O}/A_{CH_2}$) of the NR vulcanizates with different kinds of antioxidants aged at 100°C for varying time are shown in Figure 3.

As shown in Figure 3, the addition of antioxidants retards aging and increases the absorbance ratio ($A_{C=O}/A_{CH_2}$) more slowly. The addition of the Dy(III) complex exerts the best protective effect in these antioxidants. The reason is related to the structure of the Dy(III) complex, which will be explained in detail in the next section.

Crosslink Density

Thermo-oxidative aging of natural rubber is believed to occur in two ways: chain scission and chain crosslink [21,22], which results in a variation in the

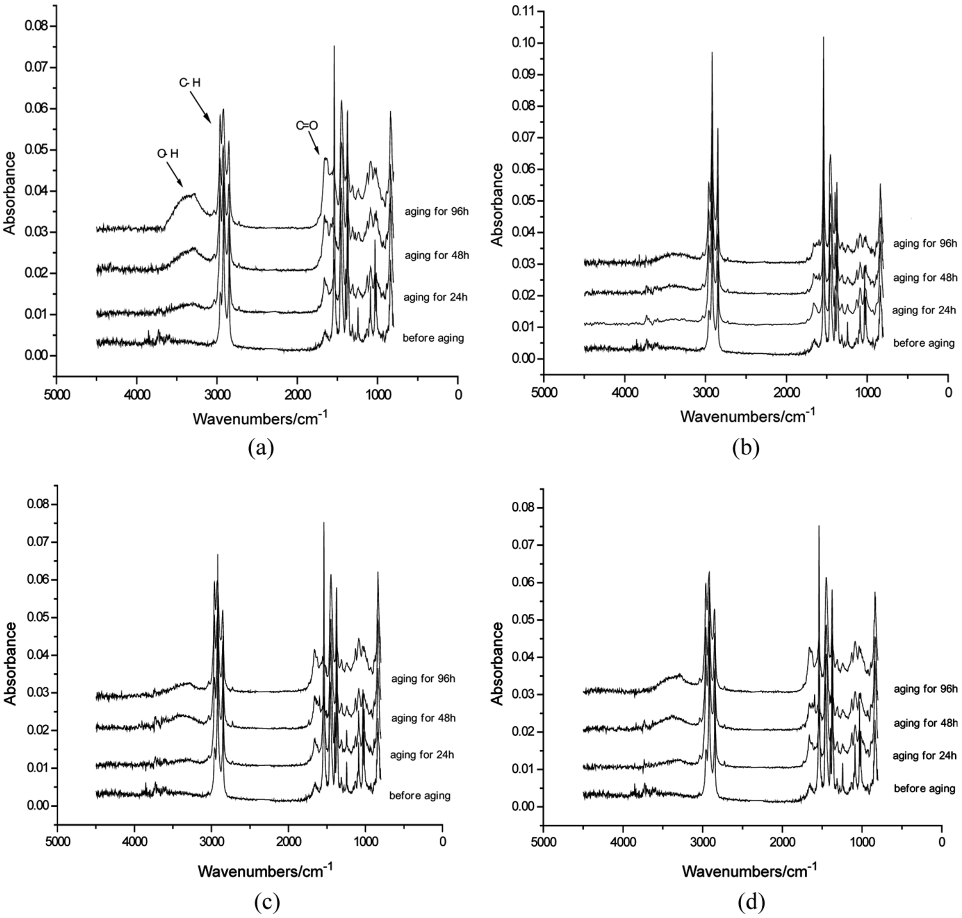


Figure 2: ATR-FTIR spectra of the NR vulcanizates with different kinds of antioxidants aged at 100°C (a) without antioxidant (b) Dy(III) complex (c) antioxidant MB and (d) antioxidant 4010NA for varying times.

crosslink density, so the crosslink density can be used to evaluate the extent of oxidation reaction. The equilibrium swelling method was used to determine the crosslink density of the vulcanizates. Crosslink densities of the NR vulcanizates with different kinds of antioxidants aged at 100°C for varying time are shown in Figure 4.

From Figure 4, it is obvious that the samples with antioxidants give higher values of the crosslink density before aging than the sample without antioxidant. During the first period of thermal aging, additional crosslinks are observed because the chain crosslink is predominant and then a period of deterioration of the network structure is followed because the chain scission plays a major role in the thermo-oxidative

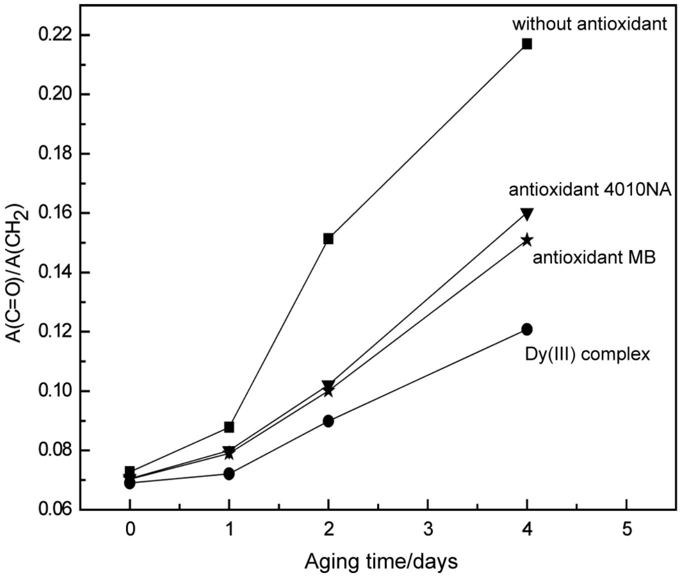


Figure 3: Absorbance ratio ($A_{C=O}/A_{CH_2}$) of the NR vulcanizates with different kinds of antioxidants aged at 100°C for varying times.

aging. After one day of thermal-oxidative aging, the crosslink density of the NR vulcanizate without antioxidant increases to a maximum value of about $2.36 \times 10^{-4}\,\mathrm{mol/cm^3}$, and then decreases rapidly. The addition

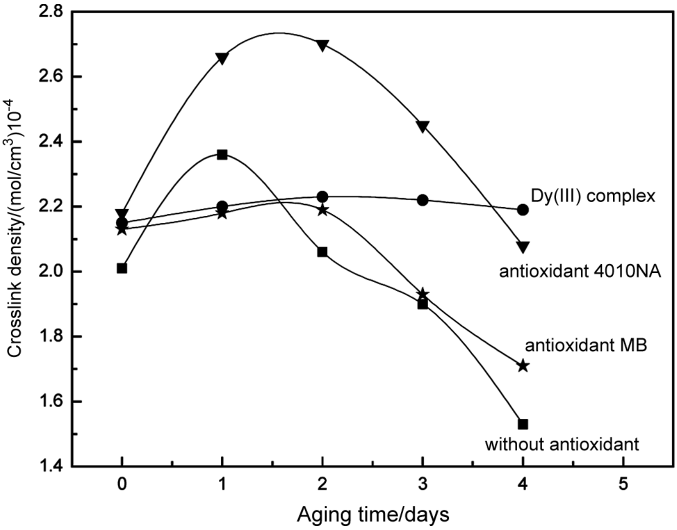


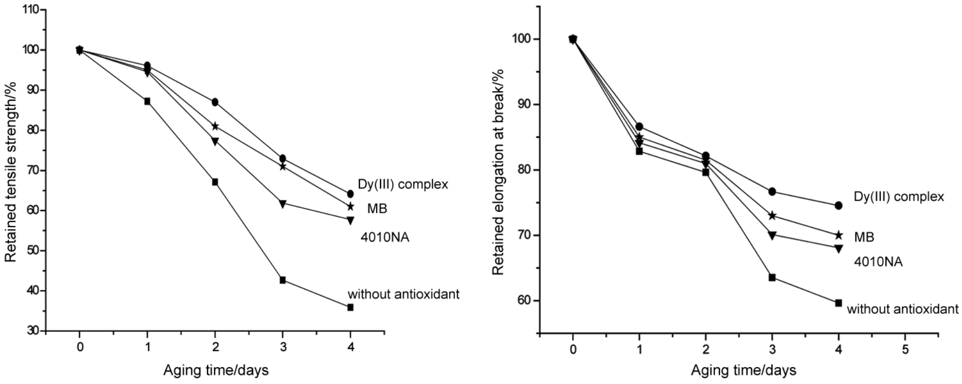
Figure 4: Crosslink densities of the NR vulcanizates with different kinds of antioxidants aged at 100°C for varying times.

of antioxidants allow the crosslink density to decrease more slowly. It is interesting that the NR vulcanizates with Dy(III) complex do not show any significant changes of crosslink density. This behavior indicates that the Dy(III) complex can more effectively protect the chemical structure of the network during the thermo-oxidative aging. The Dy(III) complex exerts the significant oxidation-resistant effect in the NR vulcanizates in two ways. On the one hand, the thioether bond in its structure can decompose the hydroperoxide [18]. On the other hand, the Dy(III) ions can capture and inactivate the free radicals in the autoxidation processes [23]. That is the reason why the antioxidant effect of the Dy(III) complex is superior to that of antioxidant MB and antioxidant 4010NA.

Hot-Air Aging Tests and Mechanical Properties

The vulcanizates were subjected to thermal oxidative aging at 100°C for different times up to four days. The retained ratios of both tensile strength and elongation at break are given in Figures 5(a) and (b).

From Figures 5(a) and (b), it is clear that the Dy(III) complex can more effectively protect NR vulcanizates against thermal-oxidative aging than the widely used antioxidant 4010 NA in rubber industry. This can be attributed to the presence of the thioether bonds which can decompose the hydroperoxide and the Dy(III) ions which can scavenge free radicals, resulting in terminating the chain reaction and retarding the autoxidation processes effectively. The results of mechanical testing are consistent with the analyses of FTIR-ATR and crosslink density.



(a) (b)

Figure 5: Mechanical properties for vulcanizates aged at 100°C: (a) the retained tensile strength and (b) the retained elongation at break.

Thermal Analysis

Thermal and Thermo-Oxidative Decomposition

The thermal and thermo-oxidative decomposition characteristics of natural rubber vulcanizates have been investigated by thermogravimetric analysis (TGA). The TGA were carried out in both air and nitrogen atmospheres at a heating rate of 10°C/min and in a temperature range from 30 to 700°C. The TG-DTG curves of the vulcanizates in air and nitrogen are given in Figures 6 and 7, respectively. The thermal decomposition characteristics of the vulcanizates are presented in Table 2.

The TGA curves in air (Figures 6(a)–(d)) show two stages in the regions of 250–400°C and 410–540°C and corresponding DTG curves indicate two peaks [24]. The major decomposition (approximately 65 to 70%) occurs between 250 and 400°C while there is 11% decomposition in the 410–540°C region. The occurrence of two peaks in the DTG curves indicates the decomposition of the NR vulcanizates in air is a two-step change. The results in Table 2 also show an increase in the decomposition temperature for the NR vulcanizates with antioxidants in air at different decomposition levels. The temperature T_5 at which 5% decomposition occurs is generally considered as an index of thermo-oxidative stability. The NR vulcanizates with a Dy(III) complex show a higher T_5 value during the decomposition in air than the samples with other antioxidants. This may possibly be attributed to the presence of thioether bonds and the Dy(III) ions in the Dy(III) complex.

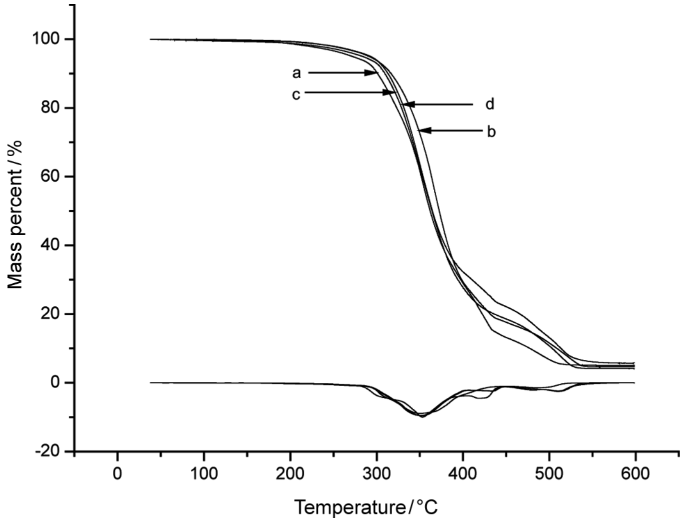


Figure 6: TG-DTG curves of the NR vulcanizates with different kinds of antioxidants in air: (a) without antioxidant; (b) Dy(III) complex; (c) antioxidant MB; and (d) antioxidant 4010NA.

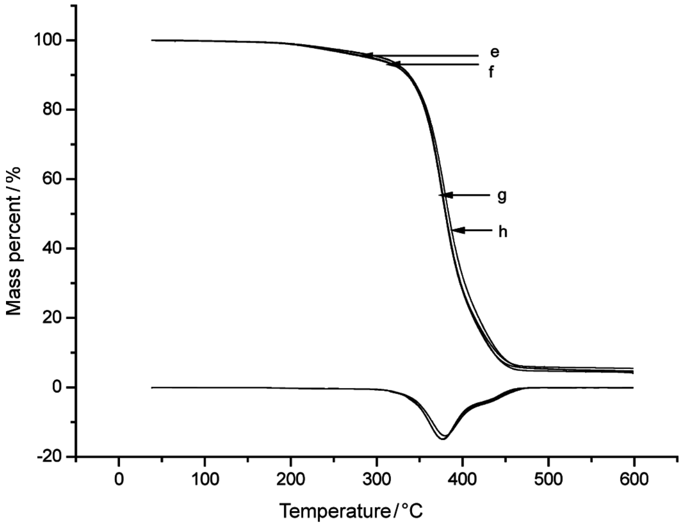


Figure 7: TG-DTG curves of the NR vulcanizates with different kinds of antioxidants in nitrogen: (e) without antioxidant; (f) Dy(III) complex; (g) antioxidant MB; and (h) antioxidant 4010NA.

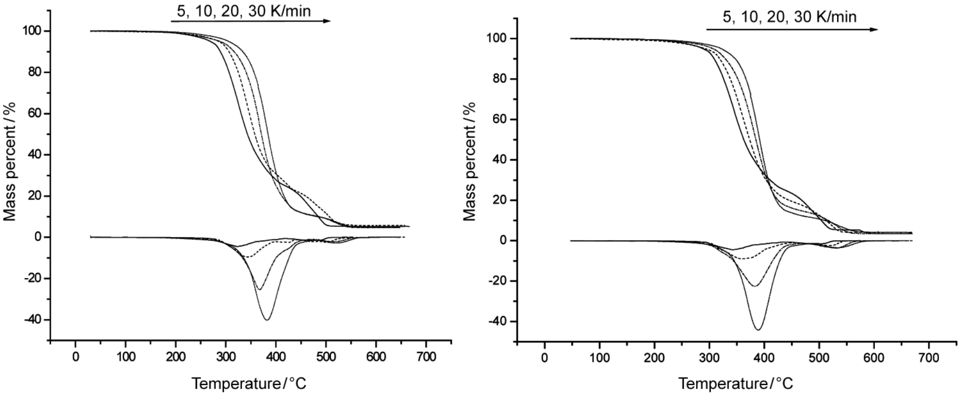
In the nitrogen atmosphere, the TG curves of the samples show only one prominent peak in the region of 300–450°C (Figures 7(e)–(h)). The NR vulcanizates with the antioxidant 4010NA show a higher value of decomposition temperature in nitrogen than that of the samples without antioxidant. However the TG-DTG curves of the vulcanizates with the Dy(III) complex, antioxidant MB and the vulcanizate without antioxidant are almost the same. It is in sharp contrast with the thermo-oxidative decomposition in air. The thermal decomposition of the NR vulcanizates in nitrogen has been known as random degradation of the chain, which produces a lot of alkyl radicals in this process, while the thermal oxidation of rubber is an autocatalytic, free radical chain reaction, which produces a lot of oxy radicals during the oxidation. The Dy(III) complex has no effect on the thermal decomposition of the NR vulcanizates, but it can improve the thermo-oxidative stability significantly, which indicates that the Dy(III) complex does not work on the alkyl radicals but on the oxy radicals to retard the oxidation reaction.

Kinetics of Thermo-Oxidative Degradation

Kinetics of thermo-oxidative degradation are always used to study and compare the anti-aging properties of polymers [25–27]. The thermo-oxidative decomposition of the NR vulcanizates was carried out in air. Figures 8(a) and (b) depict the TG and DTG curves of thermooxidative decompositions of the NR vulcanizates without antioxidant and the NR vulcanizates with the Dy(III)

Table 2: Thermal decomposition characteristics of the NR vulcanizates in nitrogen and air.

			Mass loss (%)				
Antioxidants	**Medium**	**T_0/°C**	**5**	**10**	**15**	**20**	**T_{max}/°C**
				T/°C			
Without antioxidant	Air nitrogen	312.0 348.9	286.8 295.0	306.1 335.3	322.0 348.2	328.3 356.0	348.2 377.0
Dy(III) complex	Air nitrogen	336.0 349.5	294.7 306.4	313.1 338.1	324.3 350.2	334.9 357.4	359.8 377.0
Antioxidant MB	Air nitrogen	314.4 349.2	292.3 305.6	313.2 338.0	322.3 349.6	331.7 357.0	351.5 377.0
Antioxidant 4010NA	Air nitrogen	328.0 351.8	292.9 290.4	313.0 338.9	323.7 351.4	331.0 359.5	355.1 380.9



(a) (b)

Figure 8: TG-DTG curves of the NR vulcanizates: (a) without antioxidant and (b) Dy(III) complex.

complex, respectively. The TG and DTG curves of thermooxidative decompositions of the NR vulcanizates with antioxidant MB and antioxidant 4010NA are similar and are not listed here. The TG and DTG curves shift toward the high temperature with the increment of heating rate.

It is indicated that the decomposition of the NR vulcanizates in air are a two-step change. The first region corresponds to the autocatalytic oxidation and the second region corresponds to the decomposition of oxidation products and the deepened process of aging. So we mainly analyze the first region of the thermo-oxidative degradation. The apparent activation energy E for the NR vulcanizates in the first region is calculated through the Kissinger method and Flynn-Wall-Ozawa method, respectively.

The Kissinger Method

The Kissinger method is a differential method, and E is deduced from a plot of the temperature at a maximum rate of degradation vs. the heating rate. And the temperature at the maximum rate of degradation is determined by the differential quotient thermal analysis plots. This method can avoid the error induced by different thermal degradation mechanism hypotheses and are usually used to verify apparent activation energy obtained from other thermal kinetic methods. The values of apparent activation energy E calculated through the Kissinger method are listed in Table 3.

From Table 3, it is observed that the NR vulcanizates with antioxidants have higher value of apparent activation energy than that of the sample without antioxidants. And the NR vulcanizates with the Dy(III) complex show the highest value of apparent activation energy, about $92.013\,\mathrm{kJ \cdot mol^{-1}}$. It means that the Dy(III) complex has the strongest oxidation-resistant effect than

Table 3: Apparent activation energy E for the NR vulcanizates by the Kissinger method.

Antioxidants	**E/(kJ · mol^{-1})**	**lnA**	**r**
Without antioxidant	80.837	11.39	0.9903
Dy(III) complex	92.013	12.41	0.9966
Antioxidant MB	85.283	11.81	0.9925
Antioxidant 4010NA	87.818	11.96	0.9962

antioxidant MB and antioxidant 4010NA, which is consistent with the results in preceding discussion.

The Flynn-Wall-Ozawa Method

The values of apparent activation energy E calculated through the Flynn-Wall-Ozawa method are listed in Table 4. Plots of apparent activation energy E vs. fractional mass loss are shown in Fig. 9.

Table 4 and Figure 9 show that the apparent activation energy (E) changes with the increasing of the mass conversion rate (α). The thermo-oxidative degradations of the NR vulcanizates might be carried out in three stages. The first stages of the thermo-oxidative degradations of samples are over a range of α from initiation to 0.075. The apparent activation energy (E) increases with increasing α in this stage; the second stages are over a range of α from 0.075 to 0.15. The apparent activation energy (E) decreases with increasing α, which corresponds to the autocatalytic oxidation; the third stages are over a range of α larger than 0.15. The apparent activation energy increases gradually again, which corresponds to the decomposition of oxidation products and the deepened process of aging.

The results in Table 4 and Figure 9 also show that the apparent activation energy (E) of the NR vulcanizates with the Dy(III) complex are higher than

Table 4: Apparent activation energy for the NR vulcanizates as a function of fractional mass loss (α).

	Without antioxidant		**Dy(III) complex**		**Antioxidant MB**		**Antioxidant 4010NA**	
α	**E(kJ/mol)**	**r**	**E(kJ/mol)**	**r**	**E(kJ/mol)**	**r**	**E(kJ/mol)**	**r**
0.05	105.51	0.9940	110.71	0.9901	109.54	0.9959	110.55	0.9929
0.075	115.75	0.9990	125.10	0.9934	120.48	0.9985	120.74	0.9945
0.10	114.44	0.9961	121.06	0.9932	119.61	0.9978	119.92	0.9991
0.125	113.59	0.9925	118.64	0.9967	117.74	0.9937	118.47	0.9995
0.15	111.88	0.9986	117.08	0.9935	112.80	0.9929	114.72	0.9969
0.175	114.76	0.9924	118.12	0.9954	116.21	0.9913	116.83	0.9947
0.20	118.80	0.9941	122.64	0.9967	120.39	0.9946	122.01	0.9916
0.30	120.42	0.9959	125.36	0.9933	122.52	0.9973	124.12	0.9990

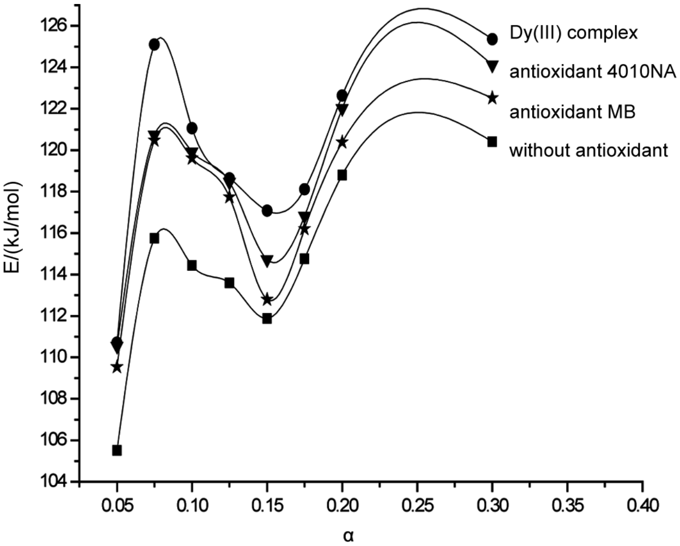


Figure 9: Plots of apparent activation energy E vs. fractional mass loss.

those of the samples with antioxidant MB and antioxidant 4010NA at different decomposition levels, which indicates that the oxidation-resistant effect of the Dy(III) complex in natural rubber is superior to that of the antioxidant MB and antioxidant 4010NA.

CONCLUSIONS

- The Dy(III) complex can raise the cure rate index and improve the maximum torque of NR compounds, which indicates that the Dy(III) complex can take part in the forming of the rubber network and accelerate the vulcanization process.
- FTIR-ATR results show that the Dy(III) complex retards aging and allows (C=O)–O–, OH and C=O to increase more slowly.
- The NR vulcanizates with the Dy(III) complex do not show significant changes of crosslink density during thermal aging. This behavior indicates that the Dy(III) complex can protect the chemical structure of the network during the thermo-oxidative aging.
- The NR vulcanizate containing the Dy(III) complex have higher retained ratios of the tensile strength and elongation at break than those of the samples with antioxidant MB and antioxidant 4010 NA.
- The Dy(III) complex has no effect on the thermal decomposition of the NR vulcanizate, but it can improve the thermo-oxidative stability significantly,

which indicates that the Dy(III) complex does not work on the alkyl radicals but on the oxy radicals to retard the oxidation reaction.

- The values of the apparent thermo-oxidation activation energy of the NR vulcanizates calculated by the Kissinger and Flynn-Wall-Ozawa methods are very close. The apparent activation energy of the NR vulcanizates with the Dy(III) complex are higher than those of the samples with antioxidant MB and antioxidant 4010NA at different decomposition levels, which indicates that the oxidation-resistant effect of the Dy(III) complex in natural rubber is superior to that of the antioxidant MB and antioxidant 4010NA.

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