Study on the Factors Influencing of the Anti-aging Behaviour in Different Antioxidants/Butadiene Rubber

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Study on the Factors Influencing of the Anti-aging Behaviour in Different Antioxidants/Butadiene Rubber

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Abstract. In this work, antioxidants 6PPD, 2246, and MB were used to study anti-aging factors in butadiene rubber (BR) composites. Combined with molecular simulations, the four factors were proposed and quantified. Chemically, the free energy of the hydrogen dissociation reaction for the different structures was calculated by quantum mechanics (QM) methods. Meanwhile, the physical factors were characterized by molecular dynamics (MD) simulations. To rank the relative importance of the four factors, we employed the gray relational analysis (GRA) method. It was obtained that the free energy for the hydrogen dissociation reaction and the permeability for O_2 should be given priority.

1. Introduction

Butadiene rubber (BR) has been widely applied in multiple fields due to its excellent comprehensive properties [1]. However, under the influences of environmental factors, BR molecular chains were easy to break during service. Recent reports have presented that adding antioxidants to the rubber matrix is one of the most effective methods [2]. The aging process includes the following two processes: (1) the first process is that O_2 molecules enter the rubber matrix and (2) the second process is that O_2 molecules react with rubber molecular chains [3].

In many studies, researchers usually used complex experimental methods or practical experience to assess the anti-aging effect for antioxidant. For example, Kirschweng indicated the solubility of antioxidant in polyethylene could be characterized by color change in the polymer as a function of antioxidant content [4]. Few researchers use molecular simulation methods to explore all influencing factors synthetically.

By MD simulations based on the molecular scale, we can obtain some quantitative information about amorphous materials [5]. On the other hand, QM methods have been successfully used to reveal the protective mechanisms that are difficult to obtain from experimental studies [6]. Simultaneously, by using GRA method, the order of influence of four factors on anti-aging effect is ranked [7].

In this research, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), the antioxidants 2,2'-methylenebis(4-methyl-6-tert-butylphenol) (2246), and 2-mercaptobenzimidazole (MB) were added to BR matrix to prepare three BR composites. We presented the four factors. After determining elongation at break and tensile strength as responses, the two assessment results for four factors were consistent by GRA.

2. Materials and Methods

2.1. Experimental Methods

2.1.1. Materials. Antioxidants 6PPD, 2246, and MB, were all purchased from Sennics Co., Ltd. (China). BR 9000 was purchased in Tianjin Changli Rubber Trading Co., Ltd. (China). Rubber additives such as zinc oxide, stearic acid, accelerator N-cyclohexyl-2-benzothiazole sulfonamide, sulfur, and carbon black N330 were of commercial grades.

2.1.2. Thermo-oxidative Accelerated Aging Test. The BR samples of 2 mm thick sheet were cut into the dumbbell type splines. These splines were thermally aged in an aging oven GT-7017-E at 80 °C for 0, 1, 2, 3, and 5 d, respectively.

2.1.3. Mechanical Property Tests. The mechanical properties were measured according to Chinese standard GB/T 528-2009. Five dumbbell-shaped tensile splines under different aging times were tested and the results were the mean values of these five results.

2.2. Model and Simulation Details

The MD simulations were carried out by using the Forcite and Amorphous Cell modules in the MS 8.0 suite software. Figure 1 presents the modeling process for O_2/antioxidant/BR amorphous cell.

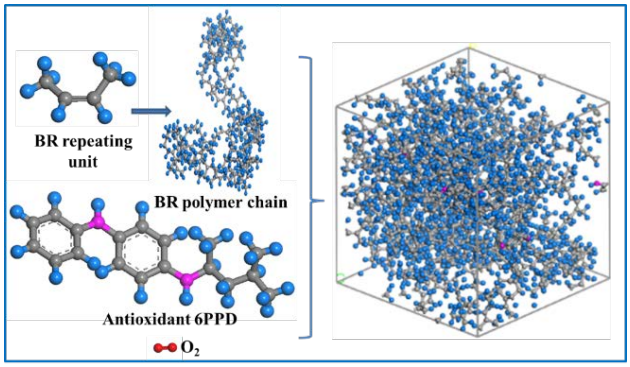

Figure 1. The modeling process of O_2/antioxidant/BR amorphous cell

In the QM methods, to calculate the free energy of dissociation reaction (ΔG), all the structures were performed under frequency analysis. Since frequency analysis produces the total electron energy (E) at 0 K, $\Delta G^{certain\ K}$ is calculated by [8]

$$\Delta G^{certain\ K} = \left(E_{A\cdot} + G_{corr}^{certain\ K}(A\cdot)\right) + \left(E_{H\cdot} + G_{corr}^{certain\ K}(H\cdot)\right) - \left(E_{AH} + G_{corr}^{certain\ K}(AH)\right) \quad (1)$$

Here, $G_{corr}^{certainK}$(A·), $G_{corr}^{certainK}$(H·), and $G_{corr}^{certainK}$(AH) are the thermal corrections of the free energy for the free radicals A·, H· and compound AH at the certain K.

2.3. Grey Relational Analysis (GRA)

GRA is a useful method for measuring the grade of relation among the sequences. The calculation process includes the following steps.

Step 1: Determine the reference matrix. The reference matrix is written under n conditions as follows:

$$\alpha = [\alpha_1\ \alpha_2\ \cdots\ \alpha_n] \quad (2)$$

Step 2: Determine the comparison matrix. If the types of investigated factors are m under n conditions, the comparison matrix is expressed as follows:

$$\beta = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_m \end{bmatrix} = \begin{bmatrix} \beta_1(1)\,\beta_1(2)\,\cdots\,\beta_1(n) \\ \beta_2(1)\,\beta_2(2)\,\cdots\,\beta_2(n) \\ \vdots\ \ \vdots\ \ \vdots\ \ \vdots \\ \beta_m(1)\,\beta_m(2)\cdots\,\beta_m(n) \end{bmatrix} \tag{3}$$

Step 3: A nondimensionalization treatment is employed as follows:

$$\alpha_j' = \frac{\alpha_j}{\frac{1}{n}\sum_{j=1}^{n}\alpha_j}, \quad \beta_i'(j) = \frac{\beta_i(j)}{\frac{1}{n}\sum_{j=1}^{n}\beta_i(j)} \tag{4}$$

Step 4: Compute the gray relational coefficient (GC).

$$GC_i(j) = \frac{\min_i\left(\min_j\left|\alpha_j' - \beta_i'(j)\right|\right) + \varepsilon\, max_i\left(max_j\left|\alpha_j' - \beta_i'(j)\right|\right)}{\left|\alpha_j' - \beta_i'(j)\right| + \varepsilon\, max_i\left(max_j\left|\alpha_j' - \beta_i'(j)\right|\right)} \tag{5}$$

Here, in order to ease the bias caused by maximum value, the resolution coefficient (ε) ($0 \le \varepsilon \le 1$) is introduced. In this work, ε is chosen to be 0.5.

Step 5: Determine the gray relational grade (GRG) by GC:

$$GC_i = \frac{1}{n}\sum_{j=1}^{n} GC_i(j) \tag{6}$$

3. Result and Discussion

3.1. Chemical Protective Mechanism of Antioxidants

If the active hydrogen in antioxidant can be preferentially dissociated to react with the free radicals, e.g., the peroxide compared to that in the rubber molecular chains, the antioxidant can be considered to lower the thermal-oxidative degradation rate for the rubber.

As we all known, the initiation step is the most important rate-determining step in the BR thermal-oxidative degradation process [9]. We thus calculate the free energy of hydrogen dissociation reactions for the different compounds at 298 K ($\Delta G^{298\ K}$). The calculation results are shown in Table 1. The hydrogen dissociation positions are shown from (a) to (f) (figure 2).

Table 1. The free energy of different dissociation positions for BR and the three antioxidants.

Dissociation position	$\Delta G^{298.15\ K}$ (kJ·mol^{-1})
BR-(a)	348.84
2246-(b)	333.92
6PPD-(c)	308.87
6PPD-(d)	332.94
MB-(e)	364.55
MB-(f)	303.54

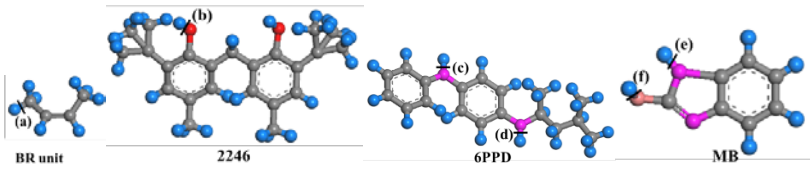

Figure 2. Hydrogen dissociation positions from (a) to (f)

Based on the data in table 1, the values of $\Delta G^{298.15K}$ for hydrogen dissociation reaction in the antioxidants 2246 and 6PPD are all lower than that at position BR-(a), i.e., the minimum $\Delta G^{298.15K}$ (348.84 kJ·mol^{-1}) required for C-H bond dissociation in BR. The result proves why the antioxidants

2246 and 6PPD can be used as primary antioxidants. However, the antioxidant MB has only one position where the $\Delta G^{298\ K}$ value is less than 348.84 kJ·mol^{-1}.

3.2. Mobility of Antioxidants

The mobility of an antioxidant as the physical factor related to the dispersion quality of antioxidant in rubber matrix is investigated. The mean square displacement (*MSD*) reflects the mobility of small molecules in polymer network, and *MSD* is described by

$$\mathrm{MSD}=<\left|r_i(0)-r_i(t)\right|^2> \tag{7}$$

Here, $r_i(0)$ stands for the initial position of particle *i*, and $r_i(t)$ represents the position of atom *i* after time *t*. $|r_i(0)-r_i(t)|$ is referred to the displacement of particle *i* over time *t*, and the brackets < > is the average square of displacement for all atoms.

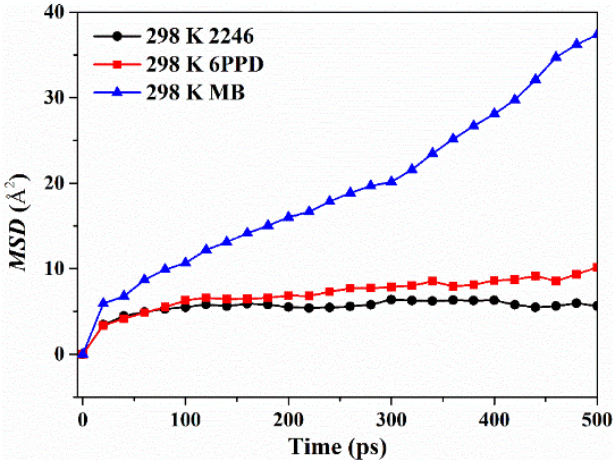

Figure 3. *MSD* for antioxidants 2246, 6PPD, and MB in BR at 298 K

Figure 3 shows that the relative migration rate of the antioxidants is in order of MB>6PPD>2246. It can be concluded that antioxidant 2246 can be stable inside the rubber matrix, which is beneficial to improve anti-aging effect of the antioxidant.

To quantitatively analyze the migration of the three antioxidants in BR network at 298 K and provide data support for subsequent GRA, we calculate the values of diffusion coefficient (*D*) for the three antioxidants [10].

$$\mathrm{D}=\lim_{t\to\infty}\frac{1}{6t}<\left|r_i(0)-r_i(t)\right|^2>=\frac{MSD}{6t}=\frac{s}{6} \tag{8}$$

Table 2. *D* for antioxidants 2246, 6PPD, and MB at 298 K in BR network

antioxidant	2246	6PPD	MB
D (10^{-6}cm^2·s^{-1})	0.08	0.15	0.17

3.3. Permeation Coefficient (P)

Second, permeation coefficient (*P*) for O_2 in the rubber network is calculated in this section. *P* is defined as the product of *D* and solubility coefficient (*S*). To obtain *P* for O_2, we use the method described in 3.2 to get *D* and use sorption model to compute *S* [11]. The model is expressed as

$$S=\lim_{p\to\infty}\frac{C}{p}=K_D+C_Hb \tag{9}$$

Table 3. *P* of O_2 in three antioxidant/BR systems at 298 K

Model	2246/BR	6PPD/BR	MB/BR
P ($10^{-9}cm^2 \cdot s^{-1} \cdot kPa^{-1}$)	7.57	6.97	7.97

From the data in the Table 3, we can obtain that the value of *P* for the three models is in order of 6PPD/NR<2246/NR<MB/NR. And the lower *P* is, the slower the rate is. Therefore, it is sufficiently proved that the capability of the antioxidant 6PPD for retarding the oxidation reaction of the BR molecular chain is the best.

3.4. Solubility of Antioxidants

To predict the compatibility between BR and antioxidant, we quoted the solubility parameter (δ). δ characterizes the compatibility of different components and is defined as following formula:

$$\delta = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} = \sqrt{\frac{\Delta H_{vap} - RT}{V}} \quad (10)$$

Here, *CED* stands for the cohesive energy density, E_{coh} is referred to the cohesive energy, ΔH_{vap} is the enthalpy of vaporization, *V*, R, and *T* represent the molar volume, the gas constant, and the absolute temperature, respectively.

Table 4. Solubility parameters for BR and the three antioxidants

materials	Initial density(g/cm^3)	δ^{sim} $(J/cm^3)^{0.5}$	δ^{lit} $(J/cm^3)^{0.5}$	$\Delta\delta = \lvert \delta_{antioxidant} - \delta_{NR} \rvert$ $(J/cm^3)^{0.5}$
BR	0.90	16.981	17.20	——
2246	1.06	18.542	——	1.561
6PPD	0.99	20.125	19.73	3.144
MB	1.42	27.619	26.52	10.638

Table 4 shows the δ for BR and three antioxidants by MD simulation. It can be found that the compatibility order is 2246>6PPD>MB.

3.5. Grey Relational Analysis (GRA)

The elongation at break and tensile strength are determined as the reference matrix for the GRA. The reference matrices y and y' can be determined under 15 conditions as follows:

y= [445.54 361.14 332.18 294.49 242.14 490.80 418.16 400.37 345.10 332.39 515.18 402.54 373.86 316.69 271.63]

y'= [9.68 7.84 7.37 6.58 6.06 10.49 8.82 8.59 7.61 6.99 10.47 7.61 7.38 6.09 4.34]

Based on to the calculation steps proposed in 2.3, the GRG and GRG' of four factors are listed in Table 11.

Table 5. GRG and GRG' of four factors

Internal influencing factors	solubility	$D_{antioxidants}$	P_{O_2}	$\Delta G^{298\ K}$
GRG	0.603	0.760	0.833	0.860
GRG'	0.578	0.769	0.833	0.844
Relative importance	4	3	2	1

It can be found that the dissociation reaction free energy is the most important, followed by the *P* of O_2 in GRG and GRG' from Table 5, which fully proves that the two factors are the most important in evaluating the anti-aging effect of an antioxidant.

4. Conclusions

By quantum mechanics (QM) methods, it was found that the three antioxidants could all effectively scavenge free radicals to delay aging process of BR, but MB has the worst effect.

By means of molecular dynamics (MD) simulations, the three physical factors were characterized by the mean square displacement (*MSD*), the permeation coefficient (*P*), and the solubility parameter (δ), respectively. The results showed that anti-aging effect of antioxidants 2246 and 6PPD was relatively good compared to antioxidant MB.

The relative importance of the four factors was clarified by the gray relational analysis (GRA). The result showed that, the dissociation reaction free energy and the *P* of O_2 were the most important in evaluating the anti-aging effect of an antioxidant.

5. Acknowledgments

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