Evaluation of hot air degradation activation energy of carbon black filled hydrogenated nitrile butadiene rubber using Flynn-Wall-Ozawa approach

Jujie Sun, Xiaolei Wang, Chengzhong Zong*
School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao, Shandong, China

*Corresponding author e-mail: qdzcz@qust.edu.cn

Abstract. Diimide catalytic system was adopted to prepare hydrogenated nitrile butadiene rubber (HNBR) through hydrogenate nitrile butadiene rubber (NBR) latex. The investigation of hot air degradation kinetics of HNBR laid foundation for aging prediction in order to further study the aging resistance properties of HNBR. The TGA analysis of carbon black filled HNBR (HNBR/CB) prepared by diimide can be obtained by different heating rates under air atmosphere. Combined with Flynn-Wall-Ozawa approach, Flynn-Wall-Ozawa exponent n as a function of the temperature, activation energy (Ea), and pre-exponent (A) of HNBR/CB nanocomposite can be calculated during the air degradation process, which is compared with carbon black filled NBR (NBR/CB) before hydrogenated. The results showed that the saturated extent increased after hydrogenated by diimide. The energy barrier that the molecular chains need to overcome during the air degradation process enhanced due to the higher energy of carbon-carbon single bonds. The activation energy is higher, and the thermal stability of HNBR/CB nanocomposite demonstrated the higher level in the air degradation process.

1. Introduction

NBR [1-3] has poor aging resistance due to the existence of double bonds in its molecular chain, degradation in the presence of oxygen and ozone. Therefore, it is optimized for hydrogenation. However, current industrialized HNBR was obtained through solution method by high-cost metal catalyst under high temperature and pressure, this polymerization method characterized such following defects as long process flow, complicate process, high cost, high energy consume and environment pollution. More attention is paid to the method of latex hydrogenation of NBR. latex in-situ hydrogenation is a high efficiency and environmentally friendly method, rubber industry showed great willing to industrialize this technology and becomes important research topic in academic area [4-9], which can meet the extremely high temperature conditions and some special application areas in military [10-13].

Some polymer material service life under long-term working condition was studied, constitutive equation and model simulation were used to predict the polymer change under mixture effect of heat, oxygen, stress [14-15], however, model establish need long time to verify, so we need to catch up with a short term method to predict the lifetime [16-19]. TGA combined with Flynn-Wall-Ozawa can analyze polymer material kinetics parameters during oxygen aging process [20-22], and thus to evaluate the
service lifetime. Liu Li [23] studied the thermal air degradation behavior of NBR filled with carbon black, but there is no research on the thermal degradation activation energy of HNBR and its carbon black filled composite. This work mainly investigated the thermal air degradation activation energy of HNBR nanocomposite filled with carbon black.

2. Experimental

2.1. Raw Material
Nitrile latex (39% acrylonitrile, 17% solid latex), carbon black (N330), hydrazine hydrate (N₂H₄, 80%), hydrogen peroxide (H₂O₂, 30%), copper sulfate (CuSO₄), Sodium lauryl sulfate (SDS), zinc oxide (ZnO), stearic acid (SA), accelerator, etc.

2.2. Preparation of HNBR by diimide
237g of NBR latex and a certain amount of CuSO₄ and SDS aqueous solution were placed in a three-necked flask and mixed by mechanical stirring. The three-necked flask was placed in a water bath with a temperature of 5°C, and a certain amount of N₂H₄ (N₂H₄) was passed through it. The molar ratio with carbon-carbon double bonds is 9) and the antifoaming agent, start stirring at a constant speed, weigh a certain amount of H₂O₂ (the molar ratio of H₂O₂ and carbon-carbon double bonds is 6) and place it in a constant pressure funnel to the NBR latex at a uniform speed. Add in the system, adjust the drop rate of H₂O₂, and control the hydrogenation time of the sample to be as consistent as possible. After the drop of H₂O₂, continue to mature for 1 hour to obtain the HNBR latex. A 20% calcium chloride aqueous solution was configured to flocculate the HNBR latex, and the flocculated gel block was washed with deionized water multiple times, then dried in a 60°C vacuum drying box for 12 hours.

NBR was added as a comparison. A 20% calcium chloride aqueous solution was configured to flocculate the NBR latex. The de-ionized water was used to clean the flocculated rubber mass multiple times and placed in a 60°C vacuum drying box for 12 hours. The prepared NBR and HNBR are added to an internal mixer, and carbon black, zinc oxide, stearic acid, accelerator, sulfur and other additives are added and mixed uniformly to obtain a mixed rubber, and then vulcanized at 160°C to obtain NBR/CB nanocomposites, HNBR/CB nanocomposites.

2.3. Characterization
The molecular structure of HNBR was tested by Bruker Fourier transform infrared spectrometer. The spectral resolution is 4cm⁻¹, and the spectral range of total reflection ATR is 4000 ~ 600cm⁻¹.

The thermal weight loss curves of NBR/CB nanocomposites and HNBR/CB nanocomposites were measured on a thermal weight loss analyzer TGA-Q50 of NETZSCH, Germany. The test conditions are: the sample weight is about 10mg, and the temperature range is 30°C-750°C. In order to calculate the activation energy of the rubber, the thermal weight loss curves of the samples were measured in air atmosphere at four heating rates of 5°C/min, 10/ min, 20°C/min, and 30°C/min.

2.4. Calculation method of activation energy
In order to determine the reaction order, Avrami’s theory is extended to describe non-isothermal conditions. The change in weight loss rate with temperature and heating rate can be described as:

\[ \alpha(T) = 1 - \exp \left( -\frac{k(T)}{\beta^n} \right) \quad (1) \]

Perform double logarithms on both sides of formula 4, where \( k(T) = A \exp \left( (-E) / RT \right) \), then:

\[ \ln[\ln(1 - \alpha T)] = \ln A - \frac{E}{RT} - n \ln \beta \quad (2) \]

Therefore, the slope of \( \ln [-\ln (1-\alpha T)] \) and \( \ln \beta \) curves obtained from multiple isotherms obtained at different heating rates at the same temperature is the slope of the reaction order or Flynn-Wall-Ozawa index n [20-21].
3. Results and discussion

3.1. Microstructure analysis of HNBR / CB nanocomposites

The molecular structure of the product HNBR obtained by hydrogenation of the NBR emulsion was analyzed by ATR-FTIR spectroscopy, and the results are shown in Figure 1. Because the carbon black filling will affect the infrared reflected light and thus affect the experimental results, the NTR and HNBR before the carbon black filling are used for the ATR-FTIR test. It can be seen from the figure that the characteristic absorption peak of the nitrile group is at 2237 cm\(^{-1}\). After in-situ hydrogenation of the diimide, no absorption peak appears near 3500 cm\(^{-1}\), indicating that it has not been absorbed. Hydrogenated to amino. At 968 cm\(^{-1}\), the absorption peak intensity of the double bond of 1,4 butadiene structural unit in the molecular chain weakened. At 912 cm\(^{-1}\), the absorption peak of the double bond of 1,2 vinyl structural unit disappeared, and at 725 cm\(^{-1}\) new absorption peak appeared at one point, that is, a saturated structure-(CH\(_2\))\(_n\) (\(n>4\)) appeared. It shows that diimide as the catalytic active center, the carbon-carbon double bond in the NBR molecular chain can be selected Catalytic hydrogenation to HNBR. And calculated that its hydrogenation degree is 59%, and the remaining part of the double bonds can provide cross-linking points in the later vulcanization process of HNBR, which is conducive to increasing the strength of the rubber. Therefore, for the HNBR curing system, a low-sulfur, multi-promoting curing system was selected to prepare the HNBR/CB nanocomposite vulcanize, and the hot air degradation performance test was performed on it.

![Figure 1. ATR-FTIR spectrum of NBR/CB and HNBR/CB nanocomposites.](image)

3.2. Analysis of activation energy of HNBR / CB nanocomposites in air

Four different heating rates of 5°C/min, 10 °C/min, 20 °C/min and 30 °C/min were used to conduct thermal weight loss analysis of NBR / CB and HNBR / CB nanocomposites in a hot air atmosphere. The results are shown in Figure 2 and Figure 3. In the TGA and DTG curves, as the heating rate increases, the temperature at which the composite material begins to degrade moves to high temperature, and it shows two stages of degradation in the air atmosphere.
Figure 2. The TGA curves of NBR/CB and HNBR/CB nanocomposites at different heating rates under air atmosphere.

Figure 3. The DTG curves of NBR/CB and HNBR/CB nanocomposites at different heating rates under air atmosphere.

Figure 4 shows the relationship between ln {-ln [1-α (T)]} and lnβ of NBR/CB and HNBR/CB nanocomposites. The Flynn-Wall-Ozawa index n as a function of temperature can be obtained from ln {The slope of the ln [1-α (T)]}-lnβ curve was obtained. The results are shown in Table 1.

Figure 4. The ln{-ln[1-α(T)]}-lnβ curves of NBR/CB and HNBR/CB nanocomposites under air atmosphere.

At the beginning of hot air degradation, the value of n increases with increasing temperature, and then at the end of the first stage of the degradation reaction, the value of n starts to decrease. It can be seen from Table 1 that the value of n is not an integer, which reflects the complexity of the hot air...
The degradation reaction. In addition, the value of $n$ depends on the degree of reaction in the degradation process of hot air, that is, it is not constant during the reaction process, which further illustrates that NBR/CB and HNBR/CB nanocomposites exhibit a multi-step degradation process in a hot air atmosphere. Generally, thermal degradation is divided into primary and secondary chemical bond breaking processes. Due to the chemical reactions that occur during thermal degradation, it is difficult to analyze them separately. In the early stage of degradation, the main chain of the molecular chain begins to degrade and break, and an oxidation reaction occurs at the same time. During the diffusion of oxygen, the polymer radical formed by the chain scission combines with oxygen to generate peroxide radicals, and then attacks more polymer radicals. To form hydroperoxides and regenerate polymer radicals. The oxidation process can be accelerated by further decomposing hydroperoxides to generate free radicals. In this case, the oxidation of the main chain of the molecular chain may become self-catalyzed, with an increase in the rate of cleavage, so the degree of reaction increases. At higher degrees of degradation, the degradation mechanism may change, so the degree of reaction decreases until the degradation is complete.

Table 1. Flynn-Wall-Ozawa exponent as a function of temperature for NBR/CB and HNBR/CB nanocomposites

| Temperature (°C) | NBR/CB    | HNBR/CB   |
|------------------|-----------|-----------|
| 400              | 0.42±0.02 | 0.38±0.01 |
| 405              | 0.45±0.03 | 0.40±0.01 |
| 410              | 0.49±0.02 | 0.43±0.02 |
| 415              | 0.49±0.02 | 0.44±0.02 |
| 420              | 0.50±0.01 | 0.43±0.03 |
| 425              | 0.50±0.01 | 0.46±0.03 |
| 430              | 0.51±0.02 | 0.51±0.03 |
| 435              | 0.52±0.01 | 0.58±0.01 |
| 440              | 0.54±0.01 | 0.62±0.01 |
| 445              | 0.55±0.01 | 0.67±0.02 |
| 450              | 0.56±0.01 | 0.71±0.04 |
| 455              | 0.56±0.02 | 0.74±0.05 |
| 460              | 0.54±0.04 | 0.74±0.07 |
| 465              | 0.50±0.06 | 0.72±0.1  |

By analyzing the activation energy of NBR/CB and HNBR/CB nanocomposites during hot air degradation, it is beneficial to further analyze the thermal oxygen aging behavior of the materials. The activation energy $E_a$ and pre-finger factor $A$ during hot air degradation of nanocomposites can be obtained from the relationship curve between $\ln \beta$ and $10^3T^{-1}$. The curve of $\ln \beta - 10^3T^{-1}$ is shown in Figure 5. The factor $A$ is shown in Table 2.

Figure 5. The $\ln \beta - 10^3T^{-1}$ curves of NBR/CB and HNBR/CB nanocomposites under air atmosphere
Table 2. The values of \( E_a \) and \( \ln A \) of NBR/CB and HNBR/CB nanocomposites composites

| Composites  | \( E_a, \text{kJ/mol} \) | \( \ln A, \text{min}^{-1} \) |
|-------------|----------------|-----------------|
| NBR/CB      | 212.1          | 37.3            |
| HNBR/CB     | 219.2          | 40.2            |

\( E_a \) and \( \ln A \) can reflect the thermal degradation stability of rubber materials. The \( E_a \) and \( \ln A \) of HNBR/CB nanocomposites are higher than that of NBR/CB. After hydrogenation of the double bonds of the NBR molecular chain, the bond energy of the carbon-carbon single bond is high. High, so the activation energy of HNBR nanocomposites is high, indicating that their thermal stability is higher in hot air environment.

4. Conclusion

HNBR can be prepared by selective catalytic hydrogenation of NBR latex using the imide catalytic active center. The Flynn-Wall-Ozawa formula was used to calculate the activation energy \( E_a \) and pre-finger factor \( A \) of NBR/CB and HNBR/CB nanocomposites of 212.1\( \text{kJ/mol} \), 37.3min\( ^{-1} \) and 219.2\( \text{kJ/mol} \), 40.2min\( ^{-1} \), indicating that HNBR/CB nanocomposites have higher activation energy and higher thermal stability during hot air degradation.

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