Two detection methods for the endpoint of the prepared reaction of N-(oxidiethylene)-2 benzothiazolyl sulfonamide and its analysis

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Abstract
In this work, a detection method using pH and ORP for the endpoint determination of the prepared reaction of N-(oxidiethylene)-2-benzothiazolyl sulfonamide (NOBS) was reported, and the properties of NOBS samples were comprehensively investigated. According to the chemical equation of this reaction, the turning point of pH and ORP was used to determine the endpoint of this reaction. Results showed that the purity and yield of experimental NOBS samples increased to 96.4% and 81.7%, respectively. The FTIR and XRD analysis were also used to investigate the chemical structure and crystal absorption peak of NOBS samples. SEM-EDS spectra confirmed the existence of C, N, O and S elements, and there were no other elements in the products. What is more important, the properties of experimental NOBS samples were better than that of contrast samples. Thus, this paper offers an approach to determine the endpoint of the prepared reaction of NOBS.

1. Introduction
Natural rubber (NR), with many attractive properties (i.e., low cost, low hysteresis, excellent dynamic properties, and fatigue resistance), is an elastomeric material referred to as a crosslinked compound comprising an elastomer and additives [1–3]. It is also a renewable recourse material with excellent tensile strength and elongation at break [4–6]. However, NR will begin to deteriorate in a matter of days in its natural state since it is very sticky and not durable [7, 8]. Vulcanization of NR (usually performed by Sulphur and peroxide) can function as an effective method to overcome these shortcomings [9, 10]. Besides, vulcanization is an essential factor in rubber mechanical properties determination [11]. In general, the vulcanization of rubber is a chemical process during which polymer molecules are linked to each other via the presence of sulfur cross-linking agents, and this then contributes to a three-dimensional network [12, 13]. Moreover, the degree of cross-linking can have a profound impact on the properties of the natural rubber system. However, to obtain better end-use properties and to bring down the time and temperature in the process of vulcanization reaction of elastomers, vulcanization and varying types and amount of accelerators are needed [14].

Organic accelerators have been used in natural rubber vulcanization for more than 70 years [15]. Sulfonamide accelerators are one of the most widely used rubber accelerators. They can not only shorten the vulcanization time and reduce the vulcanization temperature but also improve the mechanical properties of the rubber products [14, 16, 17]. N-(Oxidiethylene)-2-benzothiazolyl sulfonamide (NOBS) is a wildly used vulcanization accelerator, which has been used in the rubber industry at home and abroad [18]. In general, the traditional method to determine the endpoint of the reaction was examined by the color change caused by the reaction of sodium hypochlorite (NaClO) and potassium iodide-starch test paper. However, the original detection method for the endpoint of this reaction is inaccurate, because it produces more by-product during the reaction. Therefore, it brings to attention the introduction of other detection methods.
In recent years, due to the rapid development of technology, hydrogen ion concentration (pH), and oxidation-reduction potential (ORP) aided technology have been widely recognized as a powerful tool in the research field of polymer materials [19]. The value of pH indicates a change of acid-base, which can determine the endpoint of this reaction. It is acknowledged that morpholine is a strong base, and the initial value of pH is above 9 [20]. With the addition of NaClO and the consumption of morpholine, the value of pH decreases gradually. At the endpoint of this reaction, morpholine gets completely consumed, and the value of pH becomes stable. On the other hand, the negative or positive value of ORP demonstrates the redox property of solution [21]. As known, a negative value of ORP implies the reducing property, and a positive value of ORP indicates an oxidizing property of the solution. In this case, at the endpoint of this reaction, morpholine gets totally consumed, and therefore the value of ORP will become positive (due to the existence of NaClO) [21, 22].

In this work, we report an accurate detection method for the endpoint of the prepared reaction of N-(oxidiethylene)-2-benzothiazolyl sulfonamide. Two methods (pH and ORP) were used to determine the endpoint of the reaction, and detection method of potassium iodide-starch test paper was used in contrast
samples. Besides, the chemical structure, morphologies, purity and other properties of all NOBS samples were comprehensively investigated. By doing this, this paper provides an accurate detection method for the endpoint of this reaction.

2. Experimental

2.1. Materials

2-Mercaptobenzothiazole (MBT) was provided by XINCE Co., Ltd, China. Morpholine was offered by Adamas Co., Ltd, China. All chemical reagents, including methanol, ethanol, hydrochloric acid, acetic acid, potassium iodide, sodium thiosulfate and other reagents were received from Sinopharm Chemical Reagent Co., Ltd, China and were directly used without further purification.

2.2. Preparation of NOBS

The work was carried out in a three-necked flask. Briefly, MBT (25 g), water (64 g) and morpholine (14.8 g) were mixed in the three-necked flask. Then, the mixture was heated to 70 °C and mixed continuously for 30 min, and the rotating speed was 200 rpm min⁻¹. After that, the mixture was heated to 80 °C, and around 150 ml NaClO (1.8 g l⁻¹) was added into the flask for 2 h. After a one-hour reaction, the value of pH and ORP were recorded by pH and ORP detector. Later on, the mixture was washed with NaOH (30%) for three times, and then it was washed to neutral pH by water. Finally, the products were dried at a temperature of 70 °C for further analysis. Figure 1 shows the whole process as follows.

2.3. Titration, pH or ORP detection methods for the endpoint of reaction

The chemical equation of the preparation of NOBS is shown in figure 2(a). With the addition of NaClO, morpholine (strong base) was consumed and the value of pH and ORP changed simultaneously. As can be seen in figure 2(b), the value of pH changed, since morpholine (strong base) was consumed. Meanwhile, the existence of NaClO will influence the value of ORP at the endpoint of reaction, since NaClO presented positive value (oxidation property). At the endpoint of reaction, morpholine was totally consumed, and the existence of NaClO influenced the pH value and ORP of the mixture.

The traditional method determining the endpoint of the reaction examines the color change caused by the reaction of NaClO by using potassium iodide-starch test paper. As shown in figure 2(c), more by-products were produced by the excessive NaClO, which caused by the inaccurate traditional testing method (more NaClO was added). In this paper, however, the detection method of potassium iodide-starch test paper was used as a contrast, and the pH and ORP method were used as experimental samples (named as NOBS-1, NOBS-2 and NOBS-3). Contrast samples were prepared through the same process as discussed above.

2.4. Characterization

Fourier transform infrared (FTIR) analyses were carried out on a Thermo Nicolet FTIR spectrometer (Nicolet 6700, USA) in the wavenumber range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. X-ray analyses (XRD) of the samples. The samples were determined by an x-ray Diffractometer (D8 ADVANCE, Germany). The scanning speed was 0.5° per min in the scattering angle. The melting point of NOBS was determined by a fully automatic melting point instrument (MPA100, USA). The value of pH and ORP was determined by the detector (MIK-pH160, China) equipped with JUMO electrode.

The ash content of samples was determined by the combustion method according to the ASTM D4574-06 (2017). Firstly, NOBS samples (3 g, dried at 105 °C overnight) was placed in an aluminum oxide dish. Then, the samples were heated by using a muffle furnace (Longkou furnace SX2-12-10, China) with a heating rate of 10 °C min⁻¹. The final temperature was set to 800 °C and maintained for 30 min. The residue was the corresponding ash of samples.

The methanol of insoluble substance and free amine were measured according to ASTM D4934-02 (2017). Briefly, 2.5 g of NOBS samples and 250 ml of methanol were mixed in an Erlenmeyer flask. Then, the solutions were collected in Sand core crucible and followed by washing with methanol three times. Finally, the Sand core crucible was dried at the temperature of 70 °C for further analysis. Then, the methanol insoluble particulate contents were calculated according to the formula (1).

\[ m_2 = m_1 + m \]

Where \( m_2 \) is the weight of Sand core crucible (contained methanol of insoluble substance); \( m_1 \) is empty Sand core crucible; \( m \) is NOBS samples.

On the other hand, 2 g of NOBS samples and 50 ml of ethanol were mixed in an Erlenmeyer flask. Then, the solutions were titrated with 0.1 M hydrochloric acid by using a Bromophenol blue indicator. Finally, the free amine contents were calculated according to the formula (2).
Where $V_1$ is the volume of hydrochloric acid; $C_1$ is the concentration of hydrochloric acid; $m$ is the weight of NOBS samples; $M_1$ is the molar mass of NOBS samples.

The yield of NOBS was calculated by the initial weight of MBT, and the yield was calculated according to the formula (3).

Where $m_1$ is the weight of NOBS samples; $M_1$ is the molar mass of NOBS samples; $m_2$ is the weight of MBT; $M_2$ is the molar mass of MBT.

The purity of NOBS was tested by high-performance liquid chromatography (HPLC, Model 1260, Agilent, USA). After coated with Au, the morphologies of samples were observed using a Scanning electron microscope (SEM, Hitachi S-4800, Japan) at 3–10 kV acceleration voltage, and the elemental mapping of samples were measured by the energy-dispersive x-ray spectroscopy (SEM-EDS, Hitachi S-4800, Japan).

### 3. Results and discussion

#### 3.1. Endpoint determination

As mentioned above, the original detection method for the endpoint of this reaction is inaccurate, because it produces more by-product. As can be seen in figure 2(c) (equation for by-products), if the reaction is not terminated accurately near the endpoint, continuously added NaClO will produce more by-product. Because the traditional method cannot check the reaction timely by using potassium iodide-starch test paper. However, the reported methods can measure the pH and ORP timely, and no more NaClO was dropped at the endpoint of this reaction. Moreover, the traditional method determined the endpoint of the reaction by observing the color change of testing paper, while the unreacted NaClO will influence the testing results near the endpoint. So, two detection methods (pH and ORP) were reported to determine the endpoint of the reaction, enabling researchers to check the reaction timely. The difference between the old detection method and our method is that the reported two detection can check the reaction timely and terminated accurately. Besides, the original detection method, which relies on potassium iodide-starch test paper, was used as a contrast; method of pH and ORP were used as experimental samples (named as NOBS-1, NOBS-2 and NOBS-3). Meanwhile, the properties of contrast samples, NOBS-1, NOBS-2 and NOBS-3 were comprehensively investigated.

![Figure 3. The value of temperature, pH and ORP of the experimental reaction samples ((a), temperature; (b), (c) and (d), the value of pH and ORP of NOBS-1, NOBS-2 and NOBS-3).](image)
Figure 3 (a) indicates the temperatures of this reaction and presents them in three colors. This further presents the changes of the temperatures of three NOBS samples within a period of time; also note that the temperatures stay around 80 °C from 0–70 min. The value of pH and ORP was investigated to determine the endpoint of the reaction and was recorded and shown in figures 3(b)–(d). With the increase of reaction time from 0–60 min, the value of pH decreased gradually. The addition of NaClO and consumption of morpholine led to a simultaneous increase in the value of ORP at the endpoint of reaction, morpholine (strong base) was completely consumed, and the existence of NaClO influenced the value of pH in the mixture. This phenomenon could be proved by the data shown in figures 3(b)–(d). That is to say, the value of pH in the mixture became almost stable after the endpoint. Thus, the turning point of pH is the endpoint of this reaction.

Table 1. Properties of NOBS samples.

| Sample  | Melting point/°C | Ash/% | Methanol of insoluble substance/% | Free amine/% |
|---------|------------------|-------|----------------------------------|--------------|
| Contrast| 78.5             | 0.185 | 0.006                            | 0.09         |
| NOBS-1  | 79.0             | 0.179 | 0.005                            | 0.08         |
| NOBS-2  | 80.0             | 0.176 | 0.004                            | 0.08         |
| NOBS-3  | 79.3             | 0.178 | 0.004                            | 0.09         |

Figure 3(a) indicates the temperatures of this reaction and presents them in three colors. This further presents the changes of the temperatures of three NOBS samples within a period of time; also note that the temperatures stay around 80 °C from 0–70 min. The value of pH and ORP was investigated to determine the endpoint of the reaction and was recorded and shown in figures 3(b)–(d). With the increase of reaction time from 0–60 min, the value of pH decreased gradually. The addition of NaClO and consumption of morpholine led to a simultaneous increase in the value of ORP at the endpoint of reaction, morpholine (strong base) was completely consumed, and the existence of NaClO influenced the value of pH in the mixture. This phenomenon could be proved by the data shown in figures 3(b)–(d). That is to say, the value of pH in the mixture became almost stable after the endpoint. Thus, the turning point of pH is the endpoint of this reaction.

Methanol of insoluble substance(%) = \( (m_2 - m_1/m) \times 100\% \)  
Free amine(%) = \( (V_1 C_1 M_1 / 1000 \ m) \times 100\% \)  
Yield(%) = \( (m_1 M_2 / m_2 M_1) \times 100\% \)

On the other hand, the negative potential of ORP indicated the reducibility of the whole mixture [21]. As shown in figures 3(b)–(d), the turning point of ORP (positive value) indicates that there was no morpholine left while more NaClO remained. So, the existence of NaClO will influence the value of ORP. Therefore, NOBS samples were prepared at the turning point of this reaction, and the properties of NOBS samples were comprehensively studied.

3.2. The purity and yield of NOBS samples

As mentioned above, the purity of all samples is calculated by the results of HPLC, and the yield of NOBS is calculated by the initial weight of MBT. The purity and yield of NOBS samples are shown in figure 4. It is evident that the purity of all NOBS samples is higher than that of contrast, which indicates that there are fewer remainders created by by-product and MBT in NOBS samples. Meanwhile, the yield of contrast is the lowest in all samples, and this is probably another result of fewer remainders in NOBS samples. Notably, compared with the contrast sample, the purity and yield of NOBS-2 are 96.4% and 81.7%, respectively. That is to say, pH and ORP detection methods can improve the accuracy of the endpoint detection.

3.3. Analysis and testing of NOBS samples

As shown in table 1, the melting point, content of ash, methanol of insoluble substance, and free amine in all NOBS samples are comprehensively investigated. The higher melting point and a lower ash content of all NOBS samples. (Mater. Res. Express 7 (2020) 115304 Y Zhang et al)
samples can be caused by the high purity (discussed above figure 4). That is to say, purity is a determining factor that affects the melting point of NOBS samples. Notably, when the melting point of NOBS-2 samples increases to 80 °C, the content of ash decreases to 0.176%. Therefore, detection methods by pH and ORP can produce higher purity NOBS samples. Besides, comparing to the other samples, the content of methanol of insoluble substance in the contrast sample is most top. The content of methanol of insoluble substance indicated the content of inorganic salt, which existed in raw materials or produced in the reaction. Moreover, it probably existed in by-product during the reaction, since the reaction of by-product can produce more inorganic salt. The percentage of free amine of all samples looks similar, which implies that different detection methods pose a small
impact on the content of free amine. Thus, pH and ORP detection methods of the endpoint are more suitable for this reported reaction.

3.4. EDS analysis

SEM-EDS spectra of contrast and NOBS-2 are investigated and presented in figure 5. The element of C, N, O and S can be found in contrast and NOBS-2 samples are shown in figures 5(c) and (d). More information about the content of elements can be seen in table 2. The content of elements in contrast samples is similar to that of NOBS-2. To be more specific, there are no other elements in the products prepared by original or pH and ORP methods. Thus, the reported pH and ORP methods are more suitable for the prepared reaction of NOBS.

3.5. Chemical structure and XRD analysis

FTIR spectra is used to analyze MBT and all NOBS samples (as shown in figure 6). In MBT sample, the band in the region of 3028–2960 cm⁻¹ is due to the aromatic hydrogen stretching vibration, and the band in 2884 cm⁻¹ corresponds to the S–H stretching vibration [23]. The band at 1587 cm⁻¹ and 1492 cm⁻¹ are related to the C=C stretching vibration in figure 6(b) [24]. In NOBS samples, the absorption bands at 1115 cm⁻¹ and 1022 cm⁻¹ are because of C–N–C and C–O–C stretching [25]. In addition, the bands which are observed at 1430 cm⁻¹ and 657 cm⁻¹ of all samples, can be attributed to C=N–S and C=S groups [24].

XRD spectra are used to analyze MBT and all NOBS samples (as shown in figure 7). The peak at 13.5°, 16°, 20° corresponds to characteristic MBT reflections, and the peak at 18.2°, 18.8°, 19.9° corresponds to NOBS samples [26–28]. Thus, NOBS is successfully prepared by the reaction between MBT and morpholine, though the FTIR and XRD spectra of contrast sample are similar to NOBS 1-3, and the purity, yield and melting point are lower than that of NOBS 1-3. Therefore, pH and ORP detection methods of the endpoint are more suitable for this reported reaction.

4. Conclusion

In summary, this paper reported a detection method for the endpoint of the prepared reaction of N-(oxidiethylene)-2-benzothiazolyl sulfonamide (NOBS) and comprehensively studied properties of NOBS samples. Two detection methods (pH and ORP) were used to determine the endpoint of the reaction, allowing researchers to timely detect the reaction. Compared with that of contrast samples, the purity and yield of experimental NOBS samples increased to 96.4% and 81.7% respectively. The chemical structure and crystal absorption peak of NOBS samples were studied by FTIR and XRD analysis. SEM-EDS spectra proved the existence of C, N, O, and S elements, and there were no other elements in the products. In particularly, the properties of experimental NOBS samples are better than that of contrast samples. In other words, the detection methods of the endpoint in this reaction by pH and ORP are more accurate. Therefore, this paper provided an approach to determine the endpoint of the prepared reaction of NOBS.
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Author contributions

Yidong Zhang: Conceptualization, Methodology, Software, Writing-original draft. Junmeng Zhao: Methodology, Resources, Software. Xilei Tong: Methodology, Resources, Software. Quan Wang: Methodology, Resources, Software. Huixiong Qin: Methodology, Resources, Software. Ruibin Qing: Resources, Software. Yanjun Liu: Resources, Software. Zhenqiu Li: Supervision, Writing-reviewing & editing, Project administration.

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Conflicts of interest

The authors declare no conflict of interest.

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