

Research Article

Enhanced Ozone Aging Resistance of Natural Rubber with 2-Mercaptobenzothiazole as the Constant-Viscosity Agent

Juan Zhou,^{1,2,3} Peng Deng ,³ Hongxing Gui ,⁴ Junxiao Xu,^{1,2} Jianhe Liao ,^{1,2} and Aiwu Ding ⁵

¹College of Tropical Crops, Hainan University, Haikou, Hainan 570228, China

²School of Materials Science and Engineering, Hainan University, Haikou, Hainan 570228, China

³College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou, Hainan 571158, China

⁴Rubber Research Institute, Chinese Academy of Tropical Agricultural Sciences (CATAS),

Hainan Provincial Engineering Research Center of Natural Rubber Cultivation and Processing, Haikou, Hainan 571101, China

⁵School of Life Sciences, Hainan University, Haikou, Hainan 570228, China

Correspondence should be addressed to Peng Deng; nash_deng@163.com, Jianhe Liao; jhlhn@sina.com, and Aiwu Ding; dingaw@163.com

Received 29 November 2021; Revised 23 February 2022; Accepted 5 April 2022; Published 6 June 2023

Academic Editor: Barbara Gawdzik

Copyright © 2023 Juan Zhou et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

For the actual storage and serving, a phenomenon of hardening and cracking always occurs in the natural rubber (NR), which sharply reduces the mechanical performance and hinders the further application of NR. Recently, some type of constant-viscosity agent has played a key role to be used for the treatment of NR, especially for the effect of ozone aging resistance. In this study, 2-mercaptobenzothiazole (MBT) was introduced into NR, and the constant viscosity and ozone aging resistance of NR with different contents of MBT were investigated using an accelerated storage experiment and an ozone aging experiment, respectively. The results indicated that the addition of MBT could improve the constant viscosity of NR in a certain degree. With the MBT content of 0.15%, NR/MBT-0.15 obtained a best ozone aging resistance and maintained the original high tensile strength. Therefore, it provided a promising route to design and prepare NR with high-quality ozone aging resistance.

1. Introduction

Compared with the good characteristics of synthetic rubber in some specific fields, natural rubber (NR) has more excellent comprehensive performance and is mainly used to prepare tires for cars and airplanes. However, during the period of processing NR from raw rubber to rubber products, with the Mooney viscosity and Wallace plasticity values increased gradually [1–4], a phenomenon of hardening emerges and makes the procedure of processing and producing difficult, furthermore leading to a negative effect on the serving properties of NR. Moreover, because of the aldehyde groups existing in the molecular chain of NR, the molecular chain will cross-link and harden NR in the course of storage and application [5–7].

To solve this issue, the introduction of the constant-viscosity agent into NR is an effective method to inhibit the cross-linking caused by an aldehyde group, aiming at preparing an NR of constant stickiness [8–10]. In recent years, it has attracted much attention that MBT was a new type of thiol-based constant-viscosity agent for the constant-viscosity treatment of NR, which could effectively solve the storage hardening of rubber. Compared with traditional hydroxylamine-based constant-viscosity agents, the new thiol-based constant-viscosity agent has the advantages of low toxicity and good thermal stability [9]. Thus, the application of the thiol-based constant-viscosity agent in the production of NR is necessary and promising. On the other hand, because of the increasing environmental pollution, the concentration of ozone in the air increases quite a lot, a large part of which is derived from the emission of car exhaust in

the city. As we all know, it is very easy for ozone to react quickly with double bonds in the main chain of NR [11–13]. With the ozone in the air, a gray, hard, and brittle film is formed on the surface of NR, similar to being sprayed with frost. Under the condition of stress or strain, the film cracks until the NR is fractured with the extension of aging time. Therefore, the investigation of ozone aging resistance is of great importance to obtain high-performance NR products. There were few studies on the ozone aging properties of constant-viscosity NR, among which the samples were remained prepared by the traditional hydroxylamine-based constant-viscosity agents. What's worse, the modification effects of those conventional constant-viscosity agents on ozone aging performance are basically adverse. Wang et al. [14] from our research group had successfully developed a high-performance NR with excellent ozone aging resistance, physical and mechanical properties. However, the hardening problem still happened and degraded the quality of this NR during the storage, which immensely impedes the actual application of NR. Consequently, it is of great practical significance to investigate the comprehensive performance including ozone aging resistance, high performance, and constant stickiness of NR treated using the constant-viscosity agent.

In this paper, NR with different contents of 2-mercaptobenzothiazole (MBT) as the constant-viscosity agent was prepared via blending. The storage hardening value, chemical structure, surface morphology, and mechanical properties of the MBT-treating NR before and after ozone aging were investigated and compared with Mooney viscosity, plasticity value, Fourier transform attenuated total reflection infrared spectroscopy, low magnification magnifying glass, and tensile test, respectively. It displayed great potential of ozone aging resisting enhancement in high-performance NR.

2. Experimental Setup

2.1. Materials. The NR fresh latex was supplied by Hainan Natural Rubber Industry Group Jinlong Processing Branch. The 2-mercaptobenzothiazole (MBT) was purchased from Shanghai Aladdin Biology Co., Ltd. and dissolved in ammonia water of 2.5 wt%, preparing a constant-viscosity solution of 5 wt%. All the other chemicals were of AR grade and used as received.

2.2. Preparation of High-Viscosity NR with Constant-Viscosity Treatment. First, 6 samples of NR fresh latex were taken and diluted with water until the dry rubber content is about 25 wt%. Then, relative to the content of dry rubber, the MBT with given amounts of 0, 0.05, 0.1, 0.15, 0.2, and 0.25 wt% was added into the samples, which are named by raw NR: NR/MBT-0.05, NR/MBT-0.10, NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25, respectively. Second, the activator [15], prepared from a ratio of 1:1 between silica and sodium bisulfite, was added, stirred, and placed for a while with the content of 0.1 wt%. To form the clot, a certain amount of

biological coagulant was added and stirred evenly. After that, the clot was dehydrated, rinsed, pressed, and dried in an electric blast drying oven at a temperature of 70°C for 7~15 days. The normal NR sample for comparison is the NR with a standard of No. 5 produced from the same batch of fresh latex in the factory and solidified by formic acid with a standard producing process of rubber.

2.3. Accelerated Storage of Raw Rubber. The raw rubber was evenly made to be thin slices with the thickness of 3.2 to 3.6 mm and placed in a dryer with P₂O₅ preheated at 60°C in advance. Subsequently, the samples were stored in a drying oven with the constant temperature of 60°C for 6, 12, 24, and 48 h, respectively. Then, the samples were taken out and cooled to room temperature. Finally, the raw rubber with an accelerated storage was obtained.

2.4. Preparation of Vulcanizate. According to the formula of pure rubber, 100 g of NR, 0.5 g of stearic acid, 6 g of zinc oxide, 0.5 g of accelerator, and 3.5 g of sulfur were mixed in the two-roll mill of JTC-T52, the sample was prepared and placed for a period to be homogenized. Then, the vulcanization curve was determined. Eventually, the vulcanized rubber was obtained through the processing of vulcanizing in a QLB-D vulcanizing machine.

2.5. Characterizations. The storage hardening value can be determined by the difference between Mooney viscosity and plasticity values before and after accelerated storage, expressed as follows. $\Delta M_v = M_v - M_{v_0}$, where M_v is the Mooney viscosity after 48 hours of accelerated storage at a temperature of 60°C and M_{v_0} is the Mooney viscosity before storage. $\Delta P = P - P_0$, where P is the plasticity after accelerated storage for 48 hours at a temperature of 60°C, P_0 is the initial value of plasticity [9]. According to GB/T1232.1-2000, a domestic MV2-90E Mooney viscometer was used to measure the Mooney viscosity of the raw-rubber samples without and with accelerated storage for different times. According to GB/T3510-2006, the plasticity values of the samples were measured on the Wallace rapid shape meter.

The Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR) test of raw rubber named A~F with different MBT dosages were carried out on a German Bruker TENSOR27 type Fourier transform infrared spectroscopy analyzer with 16 scans and the scanning range of 650~4000 cm⁻¹. In addition, the surface of the samples taken was smooth and flat.

The ozone aging resistance test of vulcanized rubber was conducted referring to GB/T7762-2014. The vulcanized rubber of raw NR, NR/MBT-0.05, NR/MBT-0.10, NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25 was sampled into a dumbbell type and fixed in the dark for 48 hours. Subsequently, the samples suffered the ozone aging process with the temperature of 40°C, a humidity of 65%, and an ozone concentration of 100 ppm for 24 hours. The surface morphology of each sample was observed by a low-magnification magnifying glass, and the time when the crack began to

appear on the surface of the sample was recorded. The Nikon Digital Sight DS-U3 was used to catch the microscopic digital photograph of each group enduring the ozone aging for 6 h with the magnification of 20 times. Then the number of cracks on the photograph was compared to determine the ozone aging resistance of each sample.

The mechanical properties test of vulcanizate before and after ozone aging was carried out on the AI-3000 tensile tester with a tensile speed of 500 mm/min, according to GB/T528-1998.

3. Results and Discussion

3.1. The Constant-Viscosity Effect of MBT on High-Performance NR. As shown in Figures 1 and 2, the Mooney viscosity (Mv_0) and initial plastic value (P_0) of raw rubber with different amounts of MBT were tested at different accelerated storage times. It can be seen from the curve that with the delay of the accelerated storage time, the Mooney viscosity and plasticity values of the raw NR without MBT added, while the samples with MBT added were obviously gentle. It can be concluded that the addition of MBT as the constant-viscosity agent exactly has a constant-viscosity effect on the storage of raw rubber. When the content of MBT is 0.05 wt% in the rubber, the change of the values of NR/MBT-0.05 is still large, representing a poor constant-viscosity effect due to the insufficiency of MBT. When the dosage of MBT reaches 0.15% or more, the curve is basically gentle, and the change of Mooney viscosity and plasticity before and after accelerated storage is small, indicating that the rubber has achieved a good constant-viscosity effect.

To confirm the constant-viscosity effect, it is convenient to introduce the concept of storage hardening value and visually see the numerical changes of each group of samples before and after accelerated storage. As shown in Table 1, along with the increasing amount of MBT, the values of ΔMv and ΔP decreased, indicating that the constant-viscosity agent of MBT has a certain constant-viscosity effect during the accelerated storage of rubber. This is consistent with the previous results [16], where Yu reported that the storage hardening value can be effectively reduced to below 4 with the MBT content of 0.14 phr, achieving a constant-viscosity effect. For NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25, the $\Delta Mv \leq 4$ and $\Delta P \leq 4$ indicated that the constant viscosity of the rubber was favorable under these three groups. That is, when the amount of MBT as the constant-viscosity agent is 0.15% or more, NR/MBT achieves a positive constant-viscosity effect. It has been found that the constant-viscosity effect of MBT on high-performance NR is as same as that of normal NR. When the dosage of MBT reaches 0.15% wt, the reaction between sulfhydryl and aldehyde groups in MBT has reached the optimal effect; that is, the constant viscosity effect has also reached the optimal performance of ozone aging. Increasing the content of MBT has little effect on the number of aldehyde groups.

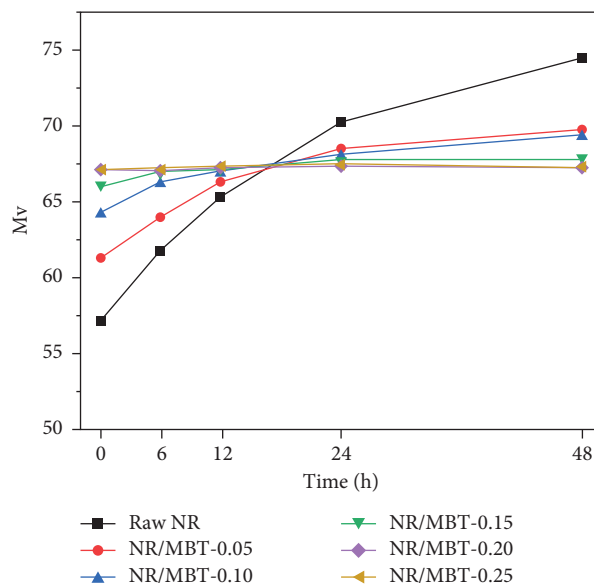


FIGURE 1: Mv_0 of NR with different contents of MBT during accelerated storage.

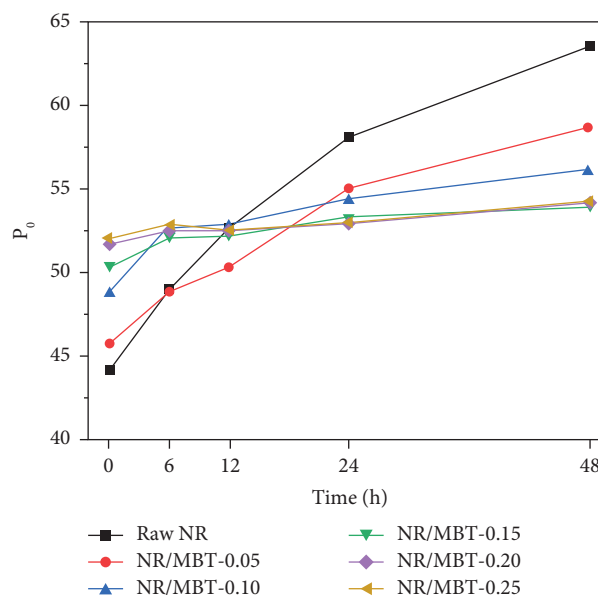


FIGURE 2: P_0 of NR with different contents of MBT during accelerated storage.

TABLE 1: The changes of storage hardening value before and after accelerated storage.

Sample	Mv_0	ΔMv	P_0	ΔP
Raw NR	57.4	17.8	44.1	19.5
NR/MBT-0.05	61.3	9.2	45.8	12.9
NR/MBT-0.10	64.5	6.8	48.7	7.3
NR/MBT-0.15	66.2	3.8	50.3	3.8
NR/MBT-0.20	67.2	0.9	51.7	2.5
NR/MBT-0.25	67.1	1.2	52.1	2.2

3.2. Infrared Spectroscopy Analysis of Constant Viscosity NR.

The Fourier transform attenuated the total reflection infrared spectrum of raw NR without MBT as shown in Figure 3. The characteristic peaks normally found in NR are identified in the figure and described in Table 2, respectively. Among them, the appearance of two weak peaks of C=O stretching vibration at 1736 cm^{-1} and C-H stretching vibration at 2725 cm^{-1} in the aldehyde group can prove the existence of the aldehyde group in the NR. The protein has an amide structure, which is mainly reflected in the characteristic absorption bands of amide I at 1654 cm^{-1} and amide II at 1541 cm^{-1} in the infrared [17, 18]. The characteristic absorption band of amide I overlaps with the C=C stretching vibration peak in the NR to be masked. The characteristic peak at 1542 cm^{-1} in the figure is the characteristic absorption band of amide II in protein, which proves the presence of protein in NR. There is a large O-H peak at 3300 cm^{-1} , which may be caused by the incomplete drying of the rubber.

The local infrared spectra at $2800\text{ cm}^{-1}\sim 1500\text{ cm}^{-1}$ of the samples such as raw NR, NR/MBT-0.05, NR/MBT-0.10, NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25 with and without MBT are shown in Figure 3, respectively. As shown in Figure 3, the addition of MBT would have no effect on the content of the C=C double bond in the six samples, prepared from the same batch of latex. The influence of the MBT on the characteristic peak of C=C is negligible. Therefore, this characteristic peak can be used as the base peak. It can be found more intuitively that after adding MBT, the protein amide II absorption band near 1542 cm^{-1} of NR is obviously enhanced, and the position is shifted. The introduction of proteases in the production of high-performance NR would promote the decomposition of proteins, while the addition of MBT may cause an inhibitory effect on this process. Therefore, the NR/MBT-0.25 of NR with MBT added is of more protein than the raw NR. Furthermore, the addition of MBT in rubber may bring disadvantages to the solidifying and producing processes, which would show adverse impact on the high performance of rubber to some extent.

The decrease of C=O and C=C stretching vibration peaks at 1736 cm^{-1} and 1663 cm^{-1} , respectively, was not obvious. As presented in Figure 3, for the aldehyde group, the variation of the two characteristic peaks can be determined based on the area ratio of the C-H characteristic peak at 2725 cm^{-1} to the C=C characteristic peak at 1663 cm^{-1} and the aldehyde group at 1736 cm^{-1} . The area ratio of the C=O characteristic peak to the C=C characteristic peak at 1663 cm^{-1} is calculated and compared [19, 20].

$$\begin{aligned} \frac{\text{NR}}{\text{MBT}-0.05}: \frac{A_{2725\text{cm}^{-1}}}{A_{1663\text{cm}^{-1}}} &= 0.052, \\ \frac{A_{1736\text{cm}^{-1}}}{A_{1663\text{cm}^{-1}}} &= 0.038, \\ \frac{\text{NR}}{\text{MBT}-0.25}: \frac{A_{2725\text{cm}^{-1}}}{A_{1663\text{cm}^{-1}}} &= 0.044, \\ \frac{A_{1736\text{cm}^{-1}}}{A_{1663\text{cm}^{-1}}} &= 0.032. \end{aligned} \quad (1)$$

It was calculated that the addition of MBT weakened the relative intensity of the aldehyde-based characteristic peak in the rubber. It can be speculated that the MBT added would prevent the cross-linking reaction of the aldehyde group during storage by reacting with the aldehyde group in the molecular chain of rubber, thereby inhibiting the occurrence of storage hardening. Of course, the occurrence of storage hardening will also be affected by other factors. The influence of the reaction between the thiol group and the aldehyde group in MBT is mainly considered.

3.3. Ozone Aging Resistance Analysis of Constant-Viscosity Vulcanizate.

The NR vulcanizate samples with different viscosity agent contents in the samples of raw NR, NR/MBT-0.05, NR/MBT-0.10, NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25 were subjected to ozone aging resistance test under the temperature of 40°C , humidity of 65%, and ozone concentration of 100 ppm. The ozone aging resistance of the sample can be compared using the time when the surface of the sample begins to crack, as shown in Table 3. The high-performance NR without the constant-viscosity agent of MBT begins to crack on the surface after an ozone aging time of 240 min, which is much later than that of normal NR, meaning that the high-performance NR own an obviously better ozone aging resistance by itself. The addition of a constant-viscosity agent has a certain improvement for the ozone aging resistance of rubber at low contents. For NR/MBT-0.15 with the MBT content of 0.15%, the crack began to appear after aged for 300 minutes, which was the latest, exhibiting the best ozone aging resistance. Then, with the continuous increase of MBT content, the ozone aging resistance decreased. When the MBT content reached to 0.25%, the ozone aging performance of NR/MBT-0.25 was below that of the raw NR without MBT.

The microphotograph of the rubber after ozone aging for 6 hours is shown in Figure 4, and the magnification is 20 times. Under the same aging time, the cracks in the NR/MBT-0.15 and NR/MBT-0.20 are shorter, narrower, and fewer than those of the others. It is investigated that the NR/MBT-0.15 has the best ozone aging resistance. Although the crack in NR/MBT-0.10 is dense, the crack length is short, due to the unconnection of the cracks. Compared with raw NR, the fine cracks in NR/MBT-0.05 are fewer and shorter, indicating that a small amount of MBT added has a certain improvement effect on the ozone aging resistance of rubber. Combined with the occurrence time of cracks [21–23], it can be found that the ozone aging resistance in each group of samples is NR/MBT-0.15 > NR/MBT-0.20 > NR/MBT-0.10 > NR/MBT-0.05 > raw NR > NR/MBT-0.25.

The impact of MBT on ozone aging resistance is a complex process. The reaction between MBT and NR is connected to the NR molecular chain. The sulfur atom in MBT has an empty d orbital to capture electrons. Ozone has a strong oxidizing power during the ozone aging, and will attack sulfur atoms preferentially, reaching a stable state after losing electrons [24]. Therefore, the addition of MBT has an advancing effect on ozone-aging performance. Moreover, MBT itself acts as a vulcanization accelerator to

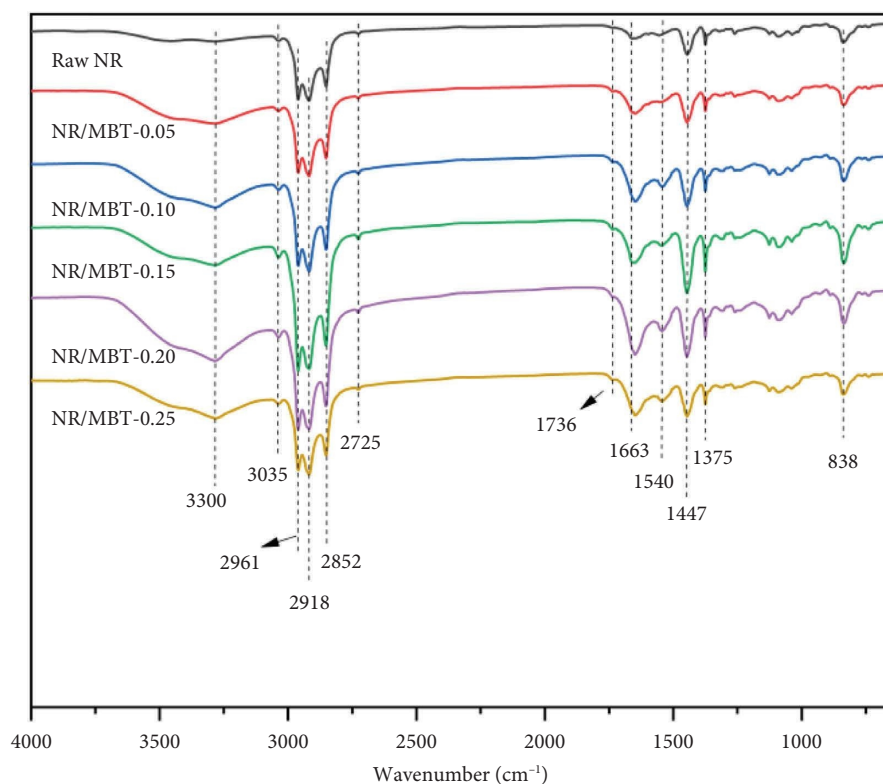


FIGURE 3: Effect of MBT in ATR-FTIR.

TABLE 2: FTIR characteristic peaks of NR.

Wave (cm^{-1})	Characteristic peaks	Wave (cm^{-1})	Characteristic peaks
3300	O-H stretching vibration and stretching vibration	1663	C=C stretching vibration
3035	Unsaturated hydrocarbon C-H stretching vibration	1542	Protein amide II absorption band
2960, 2915, 2852	Saturated hydrocarbon C-H stretching vibration	1447, 1375	C-H in-plane bending vibration
2725	Aldehyde C-H stretching vibration	890	C-H bending vibration outside the plane of 3,4 structure
1736	Aldehyde C=O stretching vibration	838, 740	C-H bending vibration outside the plane of the 1,4 structure

TABLE 3: The first cracking time of constant-viscosity rubber.

Sample	Raw NR	NR/MBT-0.05	NR/MBT-0.10	NR/MBT-0.15	NR/MBT-0.20	NR/MBT-0.25	Normal
Time of cracking (min)	240	250	285	300	260	210	60~120

promote the cross-linking, which reduces the double bonds in the molecular chain of NR after vulcanization and enhances ozone aging performance. Studies have found that amino acids in the decomposition products of proteins would contribute to the cross-linking of rubber vulcanization, allowing more double bonds to participate in the vulcanization, leaving fewer double bonds and improving the ozone aging performance. Amine groups can also take part in the ozone reaction, forming amine oxygen compounds on the surface to slow the occurrence of ozone aging on the surface of the gel [12, 25]. The excessive addition of

MBT will inhibit the breakdown of protein, resulting in the reduction of ozone aging performance for rubber. Therefore, the effect of MBT added is comprehensive on the ozone aging resistance of high-performance NR.

3.4. Mechanical Properties of High-Performance Constant-Viscosity NR. There are excellent mechanical properties and high tensile strength of high-performance NR. Before and after the accelerated storage experiments were conducted, the mechanical properties of the high-performance

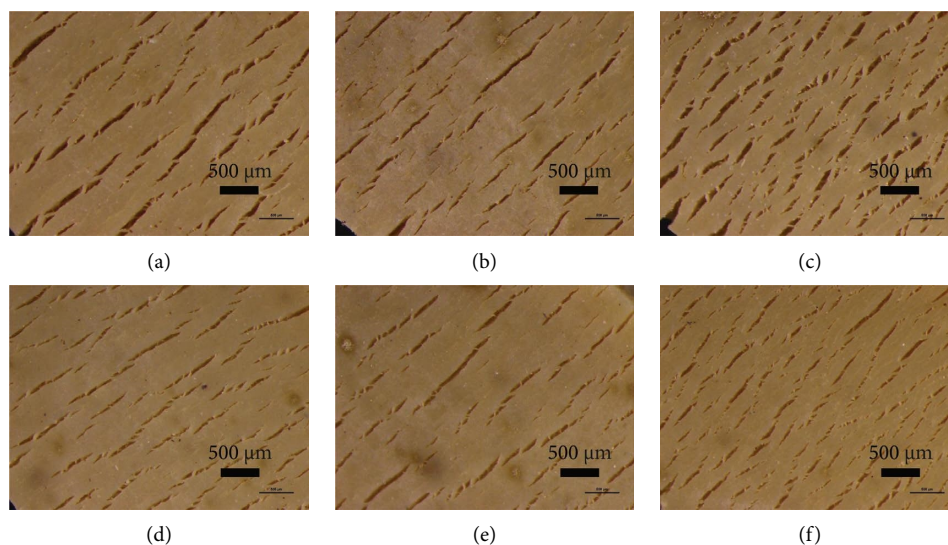


FIGURE 4: The digital sight of rubber after ozone aging for 6 h: (a) raw NR, (b) NR/MBT-0.05, (c) NR/MBT-0.10, (d) NR/MBT-0.15, (e) NR/MBT-0.20, and (f) NR/MBT-0.25.

TABLE 4: The mechanical properties of NR before and after accelerated storage.

Sample	Tensile strength (MPa)	Initial		Accelerated storage of 24 h		
		Elongation %	Stress at 300% (MPa)	Tensile strength (MPa)	Elongation %	Stress at 300% (MPa)
Raw NR	28.21	882.9	1.37	24.62	804.8	1.07
NR/MBT-0.05	28.29	878.1	1.38	25.34	785.8	1.11
NR/MBT-0.10	27.25	794.7	1.41	26.26	744.8	1.21
NR/MBT-0.15	27.84	821.8	1.60	27.45	785.6	1.47
NR/MBT-0.20	27.70	788.9	1.54	27.56	744.8	1.42
NR/MBT-0.25	28.09	792.2	1.62	27.94	739.2	1.53

TABLE 5: The mechanical properties of NR before and after ozone aging.

Sample	Tensile strength (MPa)	Initial		Ozone aging of 24 h		
		Elongation %	Stress at 300% (MPa)	Tensile strength (MPa)	Elongation %	Stress at 300% (MPa)
Raw NR	28.21	882.9	1.37	8.51	678.7	0.71
NR/MBT-0.05	28.29	878.1	1.38	9.32	659.8	0.73
NR/MBT-0.10	27.25	794.7	1.41	11.65	654.0	0.83
NR/MBT-0.15	27.84	821.8	1.60	13.63	650.4	1.16
NR/MBT-0.20	27.70	788.9	1.54	12.81	628.8	1.05
NR/MBT-0.25	28.09	792.2	1.62	13.37	619.9	1.22

gels with different contents of MBT in sample were performed. As shown in Table 4, the addition of a constant-viscosity agent has a little effect on the tensile strength of high-performance NR, while a certain effect of maintaining the performance on the NR before and after accelerated storage. After 24 hours of accelerated storage, the tensile strength of raw NR without MBT declined by 3.59 MPa, but the tensile strength of raw NR with MBT decreased less noticeably. It was demonstrated that the constant-viscosity agent worked during the accelerated storage, so that the tensile properties of the stored sample were well maintained. Similarly, the constant-viscosity effect of MBT could be found from the change of the tensile strength before and

after storage with a value of 300%, which may be resulted from the reaction of MBT with NR.

The ozone aging test can be carried out to evaluate the ozone aging resistance based on the cracking time, surface morphology, and the retention of tensile properties for the sample after aging. Before and after ozone aging for 24 h, the mechanical properties of high-performance NR with different contents of MBT added are shown in Table 5. The tensile strength retention rate of each sample before and after ozone aging was calculated separately and used as a criterion to evaluate the ozone aging resistance. The corresponding values were 30.16%, 32.94%, 42.75%, 48.96%, 46.24%, and 47.60% of raw NR, NR/MBT-0.05, NR/MBT-

0.10, NR/MBT-0.15, NR/MBT-0.20, and NR/MBT-0.25, respectively. These results indicated that the addition of MBT had a certain enhancement to the ozone aging resistance of the rubber. When the amount of MBT is above 0.15%, the retention rate of NR increased more than 45%, exhibiting a favorable ozone aging resistance.

4. Conclusion

In this paper, the effects of addition and specific dosages of the constant-viscosity agent on the ozone aging performance of NR were analyzed and investigated briefly. The data of the accelerated storage experiment showed that when the amount of the constant-viscosity agent reached 0.15% or more, the changes of the processing properties such as Mooney viscosity and Wallace plasticity during storage hardening were successfully solved, achieving a good constant-viscosity effect. The infrared analysis data confirmed that MBT eliminated the intermolecular crosslinking during storage by reacting with the aldehyde group in advance, thus preventing the occurrence of storage hardening and proving the important role of the aldehyde group in the storage hardening phenomenon. The initial tensile strength of the NR was not influenced much by the addition of the constant-viscosity agent and stable at about 28 MPa. However, the tensile strength of the rubber without the constant-viscosity agent was decreased by 3.59 MPa after storage, while the rubber maintained the original high tensile strength after adding the constant-viscosity agent. It is found that with the increasing contents of MBT, the ozone aging resistance of rubber shows a process of initial increasing and subsequent decreasing. With the MBT dosage of 0.15%, the ozone aging resistance of the NR/MBT-0.15 reached the best. Although the effect of MBT added on the ozone aging resistance of NR is comprehensive, this work provided a certain value for the actual production of NR and suggested a potential application in preventing NR hardening and cracking during storage and use.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Juan Zhou wrote the original draft and investigated the study. Peng Deng reviewed and edited the article. Hongxing Gui proposed the methodology and reviewed and edited the article. Junxiao Xu proposed the methodology and performed data curation. Jianhe Liao reviewed and edited the article and supervised the study. Aiwu Ding performed formal analysis and contributed to project administration.

Acknowledgments

This study was financially supported by the Major Project of Hainan Province (nos. ZDKJ2021045 and ZDKJ2016020-3).

References

- [1] Bristol, "The storage hardening of natural rubber," *Translation bundle of tropical crops*, no. 3, pp. 8–11, 1975.
- [2] B. C. Sekhar, "Degradation and crosslinking of polyisoprene in Hevea brasiliensis latex during processing and storage," *Journal of Polymer Science*, vol. 48, no. 150, pp. 133–137, 1960.
- [3] X. Wang, H. Pan, K. Yang, and P. Zhang, "Cracking, structural, and mechanical property changes of SIBR and related elastomers during the ozone aging process," *Polymer Degradation and Stability*, vol. 195, Article ID 109774, 2022.
- [4] S. Khan, D. Newport, and S. Le Calvé, "Gas detection using portable deep-UV absorption spectrophotometry: a review," *Sensors*, vol. 19, no. 23, p. 5210, 2019.
- [5] T. Zheng, X. Zheng, S. Zhan, J. Zhou, and S. Liao, "Study on the ozone aging mechanism of Natural Rubber," *Polymer Degradation and Stability*, vol. 186, Article ID 109514, 2021.
- [6] S. Snow, A. R. Henriquez, A. Fisher et al., "Peripheral metabolic effects of ozone exposure in healthy and diabetic rats on normal or high-cholesterol diet," *Toxicology and Applied Pharmacology*, vol. 415, Article ID 115427, 2021.
- [7] C. Scassellati, A. C. Galoforo, C. Bonvicini, C. Esposito, and G. Ricevuti, "Ozone: a natural bioactive molecule with antioxidant property as potential new strategy in aging and in neurodegenerative disorders," *Ageing Research Reviews*, vol. 63, Article ID 101138, 2020.
- [8] P. Deng, H. Wang, X. Yang, H. Ren, and Q. Jiao, "Thermal decomposition and combustion performance of high-energy ammonium perchlorate-based molecular perovskite," *Journal of Alloys and Compounds*, vol. 827, Article ID 154257, 2020.
- [9] H. Huang, B. Zhang, and W. Deng, "Constant viscosity characteristics of different NR constant viscosity stabilizers," *Chinese Journal of tropical agriculture*, vol. 30, no. 3, pp. 1–5, 2010.
- [10] P. Li, H. Wang, and J. Du, "Preparation of constant viscosity natural rubber by mercaptan," *Rubber reference material*, vol. 42, no. 5, pp. 40–43, 2012.
- [11] L. Chen and J. Liao, "The ozone aging properties of NR of different rubber strains," *Chinese Journal of Topical Crops*, vol. 37, no. 3, pp. 602–608, 2016.
- [12] Z. Li and Y. Zhao, "Study on physics-chemistry properties of the constant viscosity NR," *China Elastomerics*, vol. 12, no. 5, pp. 10–13, 2002.
- [13] M. Poikelispää, A. Shakun, and E. Sarlin, "Nano-diamond—carbon black hybrid filler system for demanding applications of natural rubber—butadiene rubber composite," *Applied Sciences*, vol. 11, no. 21, Article ID 10085, 2021.
- [14] B. Wang, G. Huang, and Y. Chen, "Properties and structure of natural rubber on ozone aging under different production process," *Chinese Journal of Topical Crops*, vol. 36, no. 7, pp. 1342–1347, 2015.
- [15] Z. Duan and J. Liao, "Effect of viscosity stabilizer 2-Mercaptobenzothiazole on properties of natural rubber," *China Rubber Industry*, vol. 60, no. 5, pp. 279–283, 2013.
- [16] H. Yu, Z. Zhang, and Q. Wang, "Preparation of constant viscosity natural rubber with mercaptan," *Kautschuk Gummi Kunststoffe*, vol. 64, no. 5, pp. 30–34, 2011.
- [17] N. Candau, E. Vives, A. I. Fernández, and M. Maspoch, "Elastocaloric effect in vulcanized natural rubber and natural/

- wastes rubber blends,” *Polymer*, vol. 236, no. 30, Article ID 124309, 2021.
- [18] P. Deng, P. Chen, H. Fang, R. Liu, and X. Guo, “The combustion behavior of boron particles by using molecular perovskite energetic materials as high-energy oxidants,” *Combustion and Flame*, vol. 241, 2022 Accepted, Article ID 112118.
- [19] R. R. Hampton, “Applied infrared spectroscopy in the rubber Industry,” *Rubber Chemistry and Technology*, vol. 45, no. 3, pp. 546–626, 1972.
- [20] W. Zhang, Y. Liu, H. Yang et al., “A validated high-performance liquid chromatographic method with diode-array detection for the estimation of xyloketal B in rat plasma,” *Journal of Chromatography, B: Analytical Technologies in the Biomedical and Life Sciences*, vol. 885-886, no. 6, pp. 24–29, 2012.
- [21] I.-O. Toma, S.-M. Alexa-Stratulat, P. Mihai, A.-M. Toma, and G. Taranu, “Experimental investigations on the long term material properties of rubberized portland cement concrete,” *Applied Sciences*, vol. 11, no. 22, Article ID 10868, 2021.
- [22] E. Contreras-Marín, M. Anguita-García, E. M. Alonso-Guzmán et al., “Use of granulated rubber tyre waste as lightweight backfill material for retaining walls,” *Applied Sciences*, vol. 11, no. 13, p. 6159, 2021.
- [23] S. Phomrak and M. Phisalaphong, “Lactic acid modified natural rubber-bacterial cellulose composites,” *Applied Sciences*, vol. 10, p. 3583, 2020.
- [24] R. Shaker and D. Rodrigue, “Rotomolding of thermoplastic elastomers based on low-density polyethylene and recycled natural rubber,” *Applied Sciences*, vol. 9, no. 24, p. 5430, 2019.
- [25] P. Deng, Q. Jiao, and H. Ren, “Synthesis of nitrogen-doped porous hollow carbon nanospheres with a high nitrogen content: a sustainable synthetic strategy using energetic precursors,” *Science of the Total Environment*, vol. 714, Article ID 136725, 2020.