Research Article

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Influence of L-quebrachitol on the properties of centrifuged natural rubber

<https://doi.org/10.1515/epoly-2021-0042>

received April 01, 2021; accepted May 01, 2021

Abstract: Nonrubber components (NRCs) play an important role in the outstanding mechanical property of natural rubber (NR). The main inositol component of NRCs in natural rubber latex (NRL) is L-quebrachitol. In this study, the influence of L-quebrachitol on the properties of centrifuged natural rubber (CNR) was investigated. The NRL was centrifuged twice to remove most of the NRCs. After that, L-quebrachitol was added in the latex with per hundreds of rubber (phr) vary from 0% to 0.8%, and the vulcanized CNR were prepared. It is shown that the properties of vulcanized CNR were greatly changed, with T_{90} reduced from 19 to 15 min, the tensile strength increased from 5 to 9 MPa, T_g reduced by about 2°C, and the ability for strain-induced crystallization was enhanced. It was proved by FTIR results that L-quebrachitol was linked to the CNR crosslinking network with ester bond.

Keywords: natural rubber, non-rubber components, L-quebrachitol, centrifuged natural rubber, vulcanization network

1 Introduction

NR is a kind of natural biosynthetic macromolecule. The NR from *Hevea brasiliensis* has been widely used in military and life for decades due to its excellent mechanical properties that include both outstanding toughness and extraordinary strength. More research has been done to study why NR as a natural product has such unique mechanical properties (1–3). As a comparison, synthetic polyisoprene (PI) has the same polymerization unit as the hydrocarbon chain of NR but has totally different mechanical behaviors. In terms of toughness, NR is five times larger than highly *cis* PI (4–6). This phenomenon is attributed to NRCs by many studies (7,8). There are four main types of NRC in NR. They are proteins, lipids, carbohydrates, and inorganic salts. Raw NR consists of 94 wt% polyisoprene, 3 wt% fatty acids, 2.2% proteins, approximately 1 wt% carbohydrates, and others (9–11). These carbohydrates are inositol and sugars, including L-quebrachitol, sucrose, glucose, galactose, fructose, raffinose, and pentoses (12–14). L-Quebrachitol is the most abundant saccharides in the serum with 1.5 wt% (15).

NRCs have a major contribution to the superior mechanical properties of NR according to various studies. Protein can provide a naturally occurring sacrifice bond in natural rubber, which ultimately results in the excellent fatigue resistance of natural rubber (2). Protein also plays an important role in the structure of the natural rubber crosslinking network. After deproteinization, the end groups of the rubber chain are not bound and more entanglement occurs, which is conducive to stress-induced crystallization (SIC) (3). Fatty acids were reported to have a plasticizing effect and nucleating effect on the crosslinking network and accelerate the effect on the crystallization behavior of NR (16). Metal ions with vacant orbitals like Fe^{3+} , Cu^{2+} , and Zn^{2+} can form a coordinate bond with O and N atoms and increase the strength and act like a sacrificial bond (17,18). Glucose was reported to reduce the crosslinking density, as well as tensile and dynamic properties of vulcanized

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rubber (19). Although, much work has been done on the effect of NRCs on natural rubber (2,7,8,16,18,20–22), no work has been done on the effect of L-quebrachitol on the properties of natural rubber.

To understand the role that L-quebrachitol plays in vulcanized NR, in this study, most of the NRCs were removed by high-speed cryogenic centrifugation and different compositions of L-quebrachitol were added to the centrifuged NRL. After that, CNR was obtained by air drying and vacuum drying, and then, vulcanized CNR is obtained by mixing and vulcanization. The curing, mechanical, thermal, SIC behaviors, and chemical bonding were examined by various manners.

2 Materials and methods

2.1 Materials

Fresh NRL with the dry content of 31% was purchased from Jinlian rubber factory of China Hainan Natural Rubber Industry Group Co., Ltd. Sodium dodecyl sulfate (SDS), zinc oxide, sulfur, stearic acid, and 2-mercaptobenzothiazole (MBT) were provided from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Silica gel powder with a specific surface area of 300–450 m²/g and, 0.8–1.0 mL/g pore volume was provided by Qingdao Ocean Chemical Co., Ltd. L-Quebrachitol was extracted from NRL with optical purity of 98.8%.

2.2 Sample preparation

2.2.1 L-Quebrachitol extraction

Figure 1 shows the extraction process map of L-quebrachitol. In this study, the extraction process imitated the general processing method in the rubber latex factory. The acid serum was obtained through acid coagulation of NRL with slightly overdosed acetic acid. The acid serum was treated with quick lime to neutralize the excess acid. The reduced pressure distillation was introduced to remove all the water after the acid–base neutralization, and the white powder was obtained. The white powder was shattered and immersed in ethanol, and solid–liquid extraction was performed. The sugar solution was obtained after filter paper filtration. The solution was further purified with a silica gel column, and the impurities that is difficult to pass through the column

Figure 1: Extraction process map of L-quebrachitol.

was removed. L-Quebrachitol crystal was obtained through evaporation, concentration, cooling, and crystallization.

2.2.2 CNR preparation

Fresh NRL was first filtrated with gauze and diluted to 30% dry content with pure water. SDS was then added in the latex with 0.5% of the mass of dry content. The latex was then agitated at 300 rpm for 0.5 h and then centrifuged with GL-21M refrigerated high-speed centrifuge at 12,000 rpm for 1 h. The upper layer cream was obtained and redissolved to 30% dry content in pure water, then 0.5% SDS was added, and the solid substance was crushed and stirred until completely dissolved. The latex was centrifuged twice. The cream was obtained and redissolved in water, and CNR latex was prepared. Different dosing (0%, 0.2%, 0.4%, 0.6%, and 0.8% phr) of L-quebrachitol was added in five sets of CNR latex and stirred for 4 h, and then the membrane was dried for 48 h and vacuum dried for 12 h. The samples were named CNR-0, CNR-0.2, CNR-

0.4, CNR-0.6, and CNR-0.8, respectively, corresponding to the CNR with the addition of different dosing of L-quebrachitol.

2.2.3 Vulcanized CNR preparation

Vulcanized CNR was prepared through mill mixing and vulcanization. The mill mixing was performed utilizing XK-230 open mill mixing. The compositions of vulcanized CNR are presented in Table 1. T_{90} was measured through MDR-2000E rheometer, and vulcanization was performed utilizing XLB25-D press vulcanizer. The vulcanization time is T_{90} .

2.2.4 Thermal oxygen aging CNR preparation

Thermal oxygen aging CNR was prepared through BHO-401A high temperature aging chamber. The aging process was performed under the condition of 100°C for 24 h.

2.3 Characterization

The optical purity of L-quebrachitol was determined with ATR-W2 HHW5 Polarimeter at 24°C, 40% RH. Waters 2695 high-performance liquid chromatography (HPLC) was also utilized to confirm that the L-quebrachitol was pure. The optical purity was calculated using the following equation:

$$\text{optical purity} = \frac{\alpha(\text{crude L-quebrachitol})}{\alpha(\text{standard L-quebrachitol})} \times 100\%. \quad (1)$$

The vulcanization process was characterized with MDR-2000E at 145°C. Mechanical properties were characterized with GOTECH AI-3000 tensile testing machine. Uniaxial tensile measurements were performed at room

temperature with a strain rate of 500 mm/min. The sample for stretch testing was prepared: a dumbbell-shaped thin strip with central dimensions of $25 \times 6 \times 4$ mm.

Differential scanning calorimeter (DSC) characterization was performed with METTLER TOLEDO DSC822e under N_2 atmosphere, from -75°C to 220°C , 10 K/min. Thermogravimetric differential thermal analysis (TG-DTA) characterization was performed using METTLER TOLEDO 1/1000LF under N_2 atmosphere, from 25°C to 600°C , 10 K/min. Attenuated total reflection infrared spectroscopy (ATR) characterization was performed with PERKIN ELMER spectrum one under room temperature.

3 Results and discussion

3.1 Extraction and determination of L-quebrachitol

The L-quebrachitol extracted from NRL was tested on polarimeter and HPLC. Polarimeter results proved the extraction successful to have L-quebrachitol with optical purity of 98.8%. Further evidence from HPLC shown in Figure 2 coincided with the polarimeter test that the L-quebrachitol was very pure.

3.2 Curing behavior

Figure 3 shows the vulcanization curve of CNR with different components of L-quebrachitol. As shown in the figure, the overall curve of CNR-0.8 is higher than that

Figure 2: HPLC results of L-quebrachitol solution and solvent.

Table 1: CNR curing formula

Ingredient	phr
CNR	100
Stearic acid	0.5
ZnO	6
MBT	0.5
Sulfur	3.5

Figure 3: CNR vulcanization curve of different components of L-quebrachitol.

of CNR-0. The data at the initial point of the curves suggest that L-quebrachitol increases the torque of the unvulcanized CNR from 0.014 to 0.113 dN m. This may attribute to the increasing physical crosslinking points created by L-quebrachitol. The maximum torque is increased from 1.54 to 2.10 dN m with the content of L-quebrachitol increased from 0 to 0.8 phr. The slope of the curve becomes steeper, indicating that the rate of vulcanization has increased, whereby the T_{90} is reduced from 19.2 to 15.2 min. The accelerated rate of vulcanization may be attributed to the coordination bond between L-quebrachitol and ZnO improved the dispersion of ZnO.

The mechanical properties of CNR were improved with the addition of L-quebrachitol, and the initial torque, the maximum torque, and the rate of vulcanization have also increased.

3.3 Mechanical properties

Figure 4 shows the tensile strength and elongation at break of CNR with different amounts of L-quebrachitol. The figure also shows that the tensile strength of the sample decreases when the content of L-quebrachitol increased from 0% to 0.2% phr, while the tensile strength of the samples showed a significant increasing trend when the supplemental amount of L-quebrachitol was 0.2–0.8% phr. The tensile strength increased from 5 to 9 MPa. From CNR-0 to CNR-0.6, the elongation at break decreased from 1,031% to 948%. From CNR-0.6 to CNR-0.8, the elongation at break increased from 948% to 986%. The overall decreasing trend of elongation at break may be attributed to the early occurrence of strain-induced crystallization induced by L-quebrachitol. The

Figure 4: Tensile strength and elongation at break of vulcanized CNR by adding different components of L-quebrachitol.

increasing trend of elongation at break from CNR-0.6 to CNR-0.8 may be related to the significantly improved crosslinking network by L-quebrachitol that extended the stretching capacity of vulcanized CNR. L-Quebrachitol had a great influence on the mechanical properties of CNR, which was greatly improved.

3.4 Aging properties

Figure 5 shows the comparison of the tensile strength and elongation at break of vulcanized CNR before and after aging with different contents of L-quebrachitol. After aging treatment, the elongation at break decreased significantly by about 200%. The tensile strength increased when the phr of L-quebrachitol was 0–0.6. This indicated that the aging treatment broke the polymer chain of CNR and reduced the average length of the polymer chain and thus increased the strain-induced crystallization and reduced the elongation at break. Compared with the L-quebrachitol content of 0–0.8, the retention of elongation decreased from 76% to 72%. From a perspective of mechanical behavior, adding L-quebrachitol is not conducive to the aging resistance of CNR.

3.5 Cross-linking density

Figure 6 shows the cross-linking density of vulcanized CNR with different phr of L-quebrachitol. As show in the figure, the cross-linking density does not change significantly, and the test data fluctuate from 10.0 to 10.7 kg/mol. In general, with the increase of the phr of L-quebrachitol, the cross-linking density trends to increase.

Figure 5: Comparison of tensile strength and elongation at break of vulcanized CNR before and after aging with different contents of L-quebrachitol.

Figure 6: Cross-linking density of vulcanized CNR with different phr of L-quebrachitol.

3.6 Glass transition temperature

Figure 7 shows DSC patterns of vulcanized CNR with different phr of L-quebrachitol. After the addition of

Figure 7: DSC of vulcanized CNR with different phr of L-quebrachitol.

L-quebrachitol with the content of 0.8 phr, the T_g shifted left from -53.8°C to -55.6°C , indicating that the addition of L-quebrachitol promoted the rubber crosslinking network. In the vulcanized CNR crosslinking network, crystallization of the chain segments at a lower temperature can be attributed to a shorter average chain length. L-Quebrachitol can promote the crosslinking and increase the density of crosslinking, so that the T_g decreases.

3.7 Thermal stability

Figure 8 shows that at about 200°C , samples begin to lose weight. The thermal decomposition of the compound began at about 350°C , and the chemical bonds began to break. In a nitrogen atmosphere, the temperature at which the cracking of natural rubber begins at 350°C . The addition of L-quebrachitol did not increase the pyrolysis temperature. The thermal decomposition properties of natural rubber were not affected by L-quebrachitol.

3.8 Strain-induced crystallization

Figure 9 is a comparison of 300% and 700% constant extensional stresses. With the increase of the phr of L-quebrachitol, the difference between the tensile strength of 700% and 300% elongation increased. This indicates that L-quebrachitol can promote stress-induced crystallization in the crosslinking network of vulcanized CNR during the stretching process. This explains the reinforcing effect of L-quebrachitol on CNR.

In the process of stretching, the rubber molecular chain will form an orientation along the stretching

Figure 8: TG-DTA thermogravimetric diagram of vulcanized CNR of different phr of L-quebrachitol.

Figure 9: Stress at 300% and 700% elongation of vulcanized CNR.

direction, which will make the rubber chain more orderly, lead to the decrease of entropy, and then promote crystallization (23). Such crystals include both fibrous and lamellar (24). These crystals are very small, usually only about 10 nm (1,25,26). In the material, these crystals can play the role of nano filler or physical crosslinking points to improve the mechanical strength of the material. It has been reported that glucose acts as a lubricant to reduce the Mooney viscosity of unvulcanized NR (19). It can be speculated that in the process of stretching, the permanent deformation is accompanied by the breaking of chemical bonds, and the L-quebrachitol breaks out of the control of the ester bond, acting as lubrication, making orientation faster and easier.

3.9 Bonding analysis

Figure 10 shows the stretching vibration peak of C=O of ester bond at 1,735/cm of FTIR spectra. The figure shows

that there is no infrared absorption peak when the addition amount of L-quebrachitol was 0, but the infrared absorption peak appeared after adding L-quebrachitol.

Figure 10: FTIR spectra of C=O stretching vibration peak of ester bond.

This indicates that L-quebrachitol is linked to CNR cross-linking network by the ester bond.

4 Conclusion

L-Quebrachitol plays an important role in NR crosslinking network through esterification and Maillard reaction with protein amino acids. This includes making T_g of vulcanized CNR move to a lower temperature, improving the cross-linking density, improving the tensile strength, and promoting the strain-induced crystallization. FTIR shows that the signal peak of the ester bond appeared after the addition of L-quebrachitol. This shows that L-quebrachitol linked to CNR crosslinking system by forming ester bonds with proteins. The data from NMR cross-linking density analyzer showed that the crosslinking degree of rubber was improved after the addition of L-quebrachitol. The data from the tensile tester showed that the tensile strength of the vulcanized CNR was increased from 5 to 9 MPa after the addition of L-quebrachitol. The 700% modulus data showed that the addition of L-quebrachitol improved the ability of strain-induced crystallization of vulcanized CNR. It is concluded that the addition of L-quebrachitol to the CNR vulcanization system can promote cross-linking, promote vulcanization, promote strain-induced crystallization, and reduce the T_g and aging resistance.

Funding information: This research was funded by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDC06010100), Key-Area Research and Development Program of Guangdong Province (2020B020217003), and Major Science and Technology Plan Projects of Hainan Province (ZDKJ2016020).

Author contributions: Benxiang Hu: investigation, writing – original draft, writing – review and editing, methodology, formal analysis, experiment, data analysis, and plotting; Ming-Chao Luo, Yan-Chan Wei, Gui-Xiang Liu: data analysis and writing – review and editing; Yuanbing Zhou, Yanfang Zhao, Shuangquan Liao: writing – review and editing.

Conflict of interest: The authors state no conflict of interest.

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