

Novel nonammonia preservative for concentrated natural rubber latex

Ting Wang,^{1,2} Hong-Xing Gui,² Wen-Fei Zhang,^{1,2} Ke-Xi Zhang,¹ Wei-Qiang Yu,² Yi-Min Li,² Ri-Zhong Zeng,³ Mao-Fang Huang²

¹College of Materials and Chemical Engineering, Hainan University, Haikou 570228, China

²Agricultural Product Processing Research Institute, CATAS, Zhanjiang 524001, China

³Rubber Research Institute, Chinese Academy Of Tropical Agricultural Sciences, Danzhou 571737, China

Correspondence to: H.-X. Gui (E-mail: guihongxing@263.net)

ABSTRACT: A derivative of *sym*-triazine (HTT) was chosen as a new nonammonia preservative for concentrated natural rubber latex (CNRL) in place of NH₃-TT/zinc oxide (ZnO). The preservation effects of the HTT for CNRL, drying characteristics, mechanical properties, and cytotoxicity of the vulcanized natural rubber (NR) film were investigated. The results show that the CNRL was preserved steadily for more than 6 months with 0.3% HTT, and the volatile fatty acid number, viscosity, and mechanical stability of CNRL all met the requirements of ISO 2004:2010(E). The drying characteristics of the vulcanized NR film preserved by HTT retained no change compared with those of the film preserved by NH₃-TT/ZnO. The tensile strength and elongation at break of the vulcanized NR film preserved by HTT were 32.17 MPa and 853.80%, respectively; these were very similar to those of the film preserved by NH₃-TT/ZnO, whereas the tear strength reached 68.43 kN/m, and this was much higher than that by NH₃-TT/ZnO. The results of the cytotoxicity and dermal irritation tests prove that HTT is not especially harmful to humans. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41749.

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INTRODUCTION

Natural rubber latex (NRL) can easily become unstable because of the action of bacteria. The spoilage of rubber latex will affect the stability and processability of NRL and the mechanical properties of raw rubber. Therefore, it is necessary to add some fungicide to maintain the stability of NRL during the preservation and transportation process. Currently, ammonia and its composite preservation system, ammonia plus tetramethyl thiuram disulfide/zinc oxide (ZnO), are treated as main preservatives in NRL and concentrated natural rubber latex (CNRL). However, ammonia produces volatility and irritation, corrodes equipment, and harms workers' health. At the same time, the addition of tetramethyl thiuram disulfide and ZnO not only brings about adverse effects to CNRL processing but also produces toxic nitrosamine substances at a high temperature. Therefore, researchers have been looking for nonammonia preservatives of CNRL to replace ammonia and NH₃-tetramethyl thiuram disulfide/ZnO in industry. Since the 1940s, various preservatives, including sodium pentachlorophenol, formaldehyde, and orthoboric acid, were developed continuously. Sodium pentachlorophenol, formaldehyde, and orthoboric acid are limited in use in industry because of their toxicity. In recent

years, Wang *et al.*¹ adopted ammonium carbonate as a main preservative to save NRL and achieved a good performance. However, the dosage of ammonium carbonate was as high as 1.8 wt % NRL. In addition, ammonium carbonate will generate carbon dioxide bubbles, which is harmful to NRL. Surapich *et al.*² developed chitosan and its derivative preservatives to save NRL. The expensive price of chitosan derivatives limits their popularization. In another study of Surapich,³ zinc sulfate was tested as a secondary preservative for NRL with a low concentration of ammonia. With the use of 0.03% zinc sulfate, latex was successfully preserved for more than 1 month in a 0.30% ammonia concentration. It is an attractive alternative preservative, but the environmental irritation problem brought by ammonia has still not been eliminated. At the same time, several patents have reported new natural rubber (NR) preservatives, such as lauricidin Beka100⁴ made by Med-Chen Labs, Inc., and hydrophobically modified saccharide.⁵

A derivative of *sym*-triazine (HTT) is a water-soluble antimicrobial agent.⁶ It is effective against both Gram-positive and Gram-negative bacteria. At higher concentrations, it is also effective against fungi. So far, HTT, which is nonvolatile, has been widely used in metal-working fluids, aqueous-based paints, coatings,

Table I. Formulation of the Nonammonia CNRL Formulation for the Samples

Sample	HTT (% w/w)	SDS (% w/w)	KOH (%w/w)
H1	0.3	0.1	0.05
H2	0.3	0.1	0.1
H3	0.3	0.2	0.05
H4	0.3	0.2	0.1
H5	0.3	0.3	0.05
H6	0.3	0.3	0.1

latex emulsion products, and so on.⁷ The environmental irritation problem can be effectively solved by the use of HTT. In addition, compared with the ammonia system, the acid dose can be reduced when NRL is coagulated. Hence, HTT was chosen to replace NH₃-TT/ZnO as a new preservative. In this study, the effects of HTT on the preservation of CNRL, film formation, drying, and mechanical properties of vulcanized NR films and their toxicity were studied. We laid a foundation for exploring an efficient and economic preservative of NRL with no ammonia. As NRL is a complex system, the mechanism of HTT is still unknown. Further study is needed to explain the deep mechanism.

EXPERIMENTAL

Materials

The NRL was supplied by Gaozhou Rubber Processing Center (Maoming, China). HTT was provided by Zhejiang Shengshi Jiahua Biotechnology Co., Ltd. (Zhengzhou, China).

Preparation of the CNRL Samples

A concentration of 0.15% HTT was added to a certain amount of NRL, and CNRL was obtained after centrifugation. Other reagents were added, according to Table I, to obtain the CNRL samples.

Preparation of the Pre vulcanized CNRL

The CNRL was heated to 40°C, and the ingredients were added to CNRL according to the following formula (w/w): CNRL, 100; KOH, 0.1; pereg-O, 0.1; sulfur, 1.0; ZDC, 0.5; and ZnO, 0.4. The compound was stirred slowly for 2 h at 60°C to obtain the pre vulcanized CNRL.

Preparation of the Vulcanized NRL Film

A certain amount of pre vulcanized CNRL was poured onto a clean glass plane and dried at room temperature. We took it off when it was transparent and had leached for 24 h. We took it out to obtain the vulcanized NRL film.

Measurement and Characterization

Tests for CNRL. Four properties of CNRL, including the volatile fatty acid number (VFA No.), mechanical stability test (MST) results, viscosity, and pH value, were tested every month regularly during the storage period of CNRL. The VFA No. and MST were determined according to GB/T 8292-2008 and GB 8301-2008, respectively. The viscosity and pH value were examined with a Brookfield viscometer and an OHAUS ST10 pH meter, respectively.

FTIR Spectroscopy Analysis. A GXI Fourier IR spectrometer was adopted to determine the IR absorption spectrum of the vulcanized NR films. The detection area ranged from 4000 to 370 cm⁻¹ with a resolution of 4 cm⁻¹, and the detection lasted for 32 times.

Mechanical Properties. The tensile properties and tear strength of the vulcanized NRL films were measured with a UT-2080 electronic tensile testing machine (U-CAN Co., Chinese Taiwan) according to GB/T 528-2009 and GB/T 529-2009, respectively.

Crosslinking Density Analysis. The crosslinking density was examined by an XLDS-15 NMR crosslinking density analyzer. The magnetic strength was 0.35 Tesla, the frequency was 15 MHz, and the test temperature was 60°C.

Dynamic Mechanical Analysis (DMA). The DMA of vulcanized NRL films was carried out with a DMA242 dynamic mechanics analyzer (Netzsch, Germany). The vibration frequency was 5 Hz, and the testing temperature ranged from -120 to 100°C and was increased at a heating rate of 5°C/min.

Thermogravimetry (TG) Analysis. The TG analysis of the NRL films was conducted on an STA 449 thermal analyzer with the temperature increasing from 50 to 600°C at a rate of 10°C/min and in air with a gas flow rate of 50 mL/min.

Drying Tests. A certain amount of pre vulcanized CNRL was used to pour onto a clean glass plane. We dried it at room temperature and leached it for 24 h. Then, it was dried at 80°C with a 841Y-2 thermostatic blast drying oven. We weighed the vulcanized NRL film during the drying course until it had a constant weight.

Dermal Irritation and Cytotoxicity Tests. The dermal irritation test was conducted with a skin patch, and we compared the results with medical heat-vulcanized silicone rubbers. Healthy New Zealand rabbits were chosen as the testing animals. The contact time lasted for 24 h. We observed erythema and edema in the contacting part after 24, 48, and 72 h, respectively. L929 mouse fibroblasts were used, and the extracting liquid method [dimethylthiazol diphenyltetrazolium (MTT) test] was adopted in the cytotoxicity test.

RESULTS AND DISCUSSION

Effect of HTT on the Preservation of CNRL

As shown in Figure 1(a), the bacteria continued to breed and break down carbohydrates, and various short-chain acids were obtained. The VFA No. showed an increasing tendency in the preservation process. The VFA No. of high ammonia (HA) was lower than those of H1, H3, and H5 (KOH = 0.05%) and higher than those of H2, H4, and H6 (KOH = 0.05%), as shown in Figure 1(a). In Figure 1(b), H5 and H6 show an over stability because of a high surfactant concentration of 0.3% SDS. Both ammonia and HTT were alkaline, and the addition of ammonia or HTT made the proteins and lipoids on the surface of the rubber particle hydrolyzed. Protein hydrolysates, which are amino acids, made the MST results decline. Whereas lipid hydrolysates, a higher fatty acid soap, cause the MST results to increase. During the process of saving CNRL for 120 days, the lipid hydrolysis rate was faster, but the hydrolysis of protein was slower. The MST

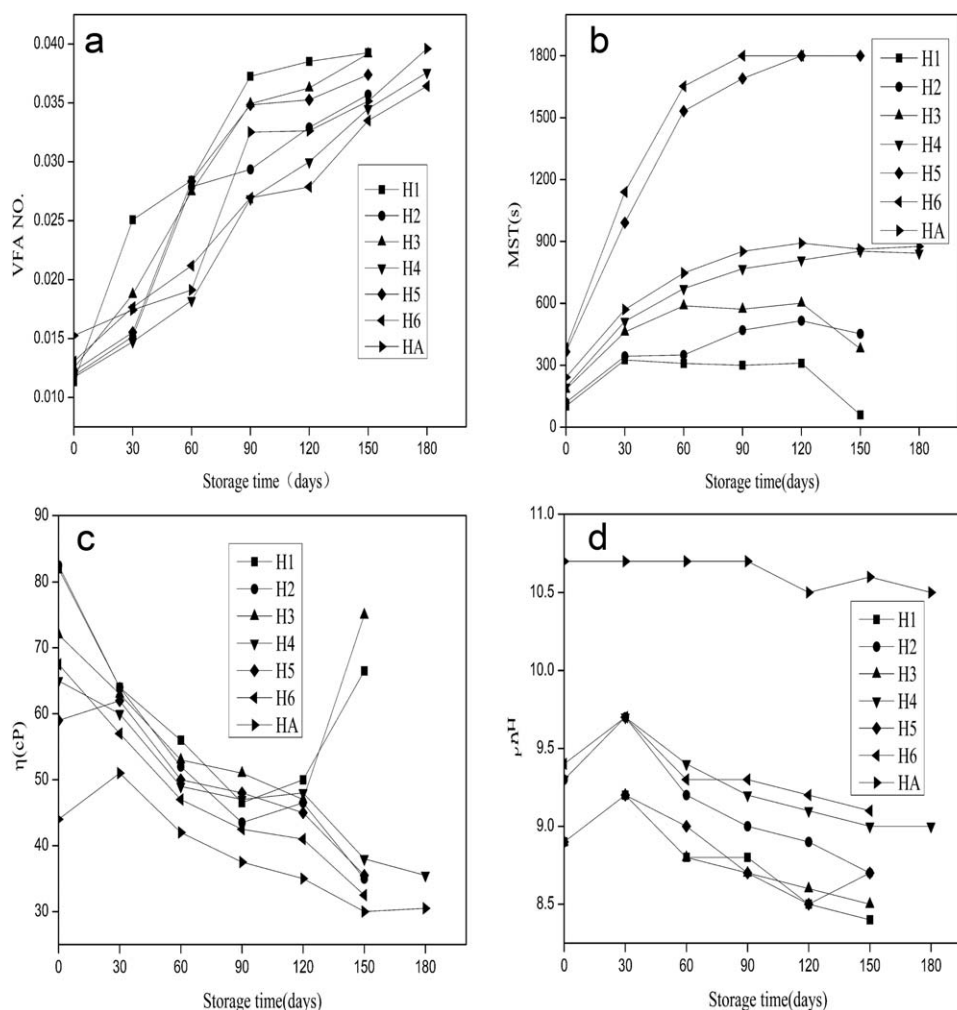


Figure 1. Properties versus the storage time of the CNRL: (a) VFA No., (b) MST, (c) viscosity, and (d) pH versus storage time of CNRL. η is the viscosity of CNRL.

results of H1, H2, and H3 began to decline when the rubber latex was stored for 120 days. The MST results of H4 were consistent with those of HA during the storage process and was above 650 s when the H4 was stored for 60 days.

Except for H1 and H4, the viscosities of the other HTT samples and HA sample declined with increasing storage time [Figure 1(c)] because of the formation of higher fatty acid soaps. As

shown in Figure 1(d), the increase in the VFA No. resulted in the decline of pH, and HTT broke down slowly during the preservation process because HTT was a slow-release bactericide. As a result, the pH value of HA showed little variation over the storage time. However, the pH value of the HTT samples decreased after they increased first.

Compared with the preservation properties of the HTT formulation, the indicators of H4 were in line with national standards. H4 and HA were adopted to compare the differences in the various properties of the vulcanized NRL films. H4 was substituted by HTT in the following experiments.

Crosslinking Density and Mechanical Properties of the Vulcanized NRL Films

Table II shows a comparison of the crosslinking density parameters between the HTT- and HA-vulcanized NRL films, where physical crosslinking resulted from mutual entanglements of the polymer chains and chemical crosslinking was generated by chemical reactions. In Table II, M_c is the average molecular weight between two crosslinking points, and $A(M_c)$ is the fraction of the network chain in the crosslinking polymer.⁸

Table II. Crosslinking Density of the Vulcanized NR Films

Parameter	HTT	HA
Total crosslinking density (10^{-5} mol/cm ³)	10.12	10.50
Chemical crosslinking density (10^{-5} mol/cm ³)	7.31	8.23
Physical crosslinking density (10^{-5} mol/cm ³)	7.01	6.52
M_c (kg/mol)	9.38	9.05
$A(M_c)$ (%)	92.25	91.13

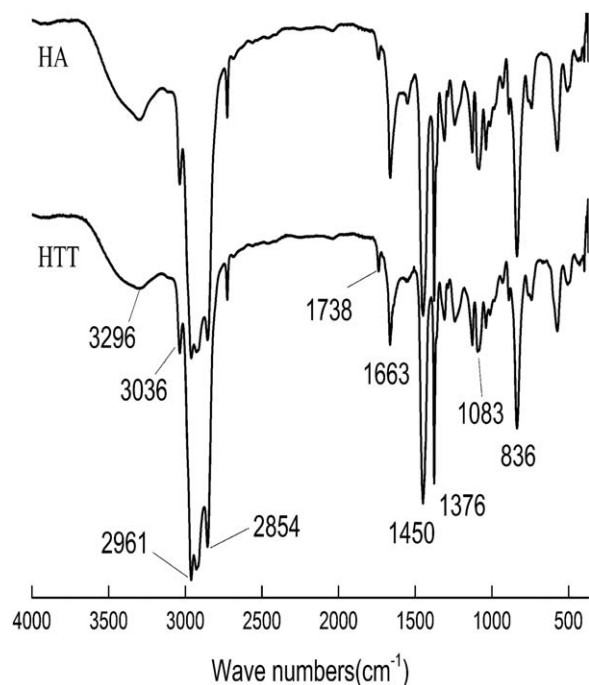
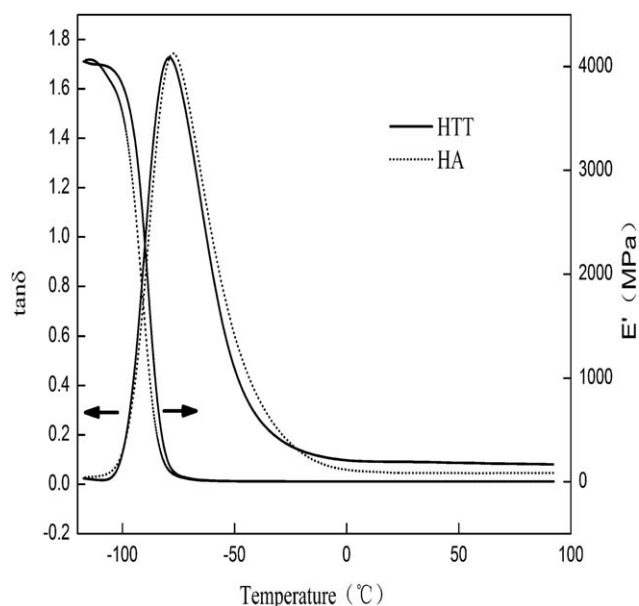
Table III. Mechanical Properties of the Vulcanized NR Films

Mechanical properties	HTT	HA
Elongation at break (%)	853.8	871.6
Tensile strength (MPa)	32.17	32.70
100% modulus (MPa)	0.61	0.65
300% modulus (MPa)	1.15	1.24
700% modulus (MPa)	11.29	13.70
Tear strength (MPa)	68.43	39.70

Table III shows the comparison of the mechanical properties between the HTT- and HA-vulcanized NRL films. The tensile strength was greatly influenced by the crosslinking density and molecular weight, and the total crosslinking density of the HTT films was lower than that of the HA films. After a comprehensive consideration of the two aspects, we observed that although the 700% modulus of HTT was lower, the other tensile properties, such as the elongation at break, tensile strength, 100% modulus, 300% modulus, and 500% modulus, were consistent with those of the HA ones. As the network fraction and average molecular weight of the HTT films were bigger, more tension was needed to tear the gap in the tear strength test. Therefore, the tear strength of HTT was nearly twice that of the HA sample.

IR Spectral Analysis

As shown in Figure 2, both HTT and HA showed the characteristic bands of isoprene units at 1663 and 836 cm^{-1} , which corresponded to C=C. The absorption bands at 2961 and 2854 cm^{-1} were due to the asymmetric and symmetric C—H, respectively. The absorption bands of —CH₃ and —CH₂ in the deformation vibration were near the waves of 1376 and 1450 cm^{-1} . The weak absorption bands at 1549 cm^{-1} were due

**Figure 2.** IR spectra of the CNRL film.**Figure 3.** Dynamic mechanical data for the vulcanized films.

to the N—H and C—N stretching vibrations. This indicated that protein existed in the vulcanized NRL films, whereas the absorption band near 1738 cm^{-1} was the stretching vibration peak of the carbonyl group.^{9,10} The HTT- and HA-vulcanized films almost shared an identical FTIR spectra. This illustrated that the new preservative HTT did not react with NR molecules, and it did not remain in the vulcanized NRL films.

DMA

Figure 3 shows the DMA curves for the vulcanized HTT- and HA-persevered NRL films. We found that the storage modulus and loss index ($\tan \delta$) changing tendencies with temperature for the HTT and HA samples were similar. The total crosslinking density of the HTT sample was smaller, and the junction was lower. It met with less resistance when the molecular chains started to move. Hence, the HTT sample had a lower T_g and a lower internal friction.

TG and Derivative Thermogravimetry (DTG) Analysis

Figures 4 and 5 display the TG and DTG curves of the HTT- and HA-vulcanized NRL films, respectively. The results show that the TG and DTG curves for the HTT and HA samples were basically the same and demonstrated the same mechanism for their thermal degradation. There were two degradation stages for both the HTT- and HA-vulcanized NRL films.¹¹ The major degradation course occurred at 300–450°C and corresponded to the thermal oxidation degradation of rubber hydrocarbon. The second degradation course at 450–550°C corresponded to the thermal oxidation decomposition of the curing additives. As shown in Figure 5, the thermal oxidation degradation temperatures of the HTT and HA samples were the same, and the weight loss rate for HTT was lower than that of HA, but the weight loss of HA was more evident after the degradation temperature.

Drying Characteristics of the Vulcanized NRL Films

As shown in Figure 6, the vulcanized HTT and HA NRL films exhibited the same drying regularity: the moisture ratio (M_R)

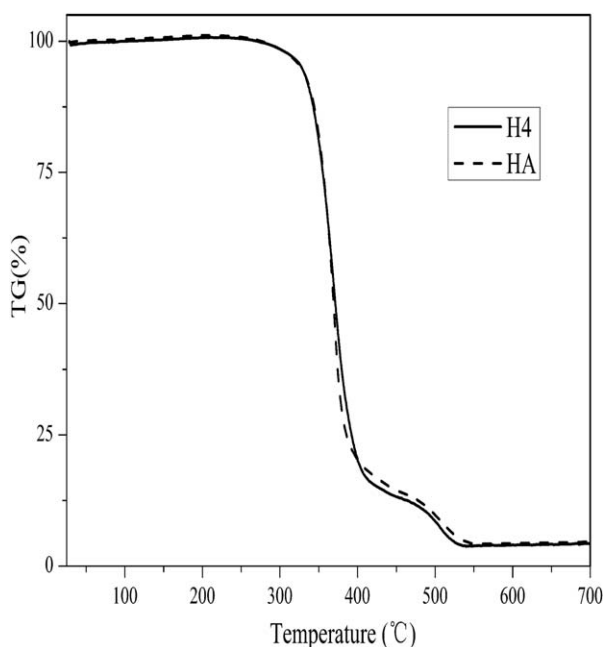


Figure 4. TG curves of the thermal oxidation degradation for the vulcanized films.

decreased with prolonged drying time. In this study, a first-order kinetics model was used to analyze the drying kinetics and obtain the drying rate constant:

$$\frac{dx}{dt} = -kt \ln \frac{x - x_e}{x_0 - x_e} = -kt$$

where x is the ratio between the mass of water and solid at one point in the drying process; x_e is the ratio between the mass of

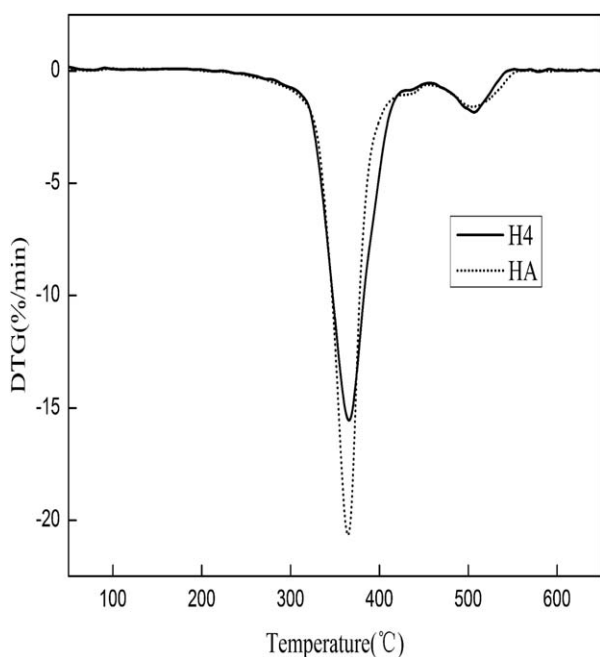


Figure 5. DTG curves of the thermal oxidation degradation for the vulcanized films.

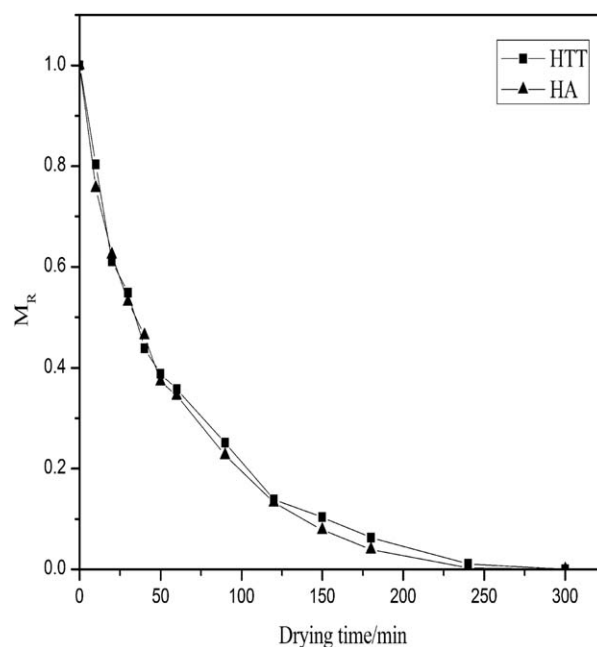


Figure 6. Drying curves of the vulcanized films.

water and solid at equilibrium condition; t is the drying time; x_0 is the ratio between the mass of water and solid at initial state; k is the drying rate constant.

The drying rate constant during the drying process was obtained by kinetic fitting;¹² the fitting results are shown in Table IV. As the molecular structure had a great effect on the drying properties of the vulcanized film, the hydroxyl group in the HTT molecules may mainly have affected the drying properties. However, as observed from the IR spectra results, a weak band appeared in the HTT FTIR figures, which was nearly the same as that appeared in the HA ones. This demonstrated that the hydroxyl group of HTT did not remain in the vulcanized films. As shown in the results of curve fitting, the pre-exponential factor and drying rate constant for the HTT and HA samples were very close. This demonstrated that the replacement of HA with HTT almost did not change the drying characteristic of the vulcanized NRL film.

Film-Forming Properties of CNRL

Figure 7 shows the products made of the HTT- and HA-vulcanized latexes. We found that the HTT and HA products both had no evident cracks or visible defects. There were no air bubbles or pinholes in the products, and the HTT products had good film-forming properties.

Table IV. Kinetic Fitting Results

Sample	Pre-exponential factor	Drying rate constant (min ⁻¹)	Correlation factor
HTT	0.9342	1.87×10^{-2}	0.9902
HA	0.9381	1.84×10^{-2}	0.9928

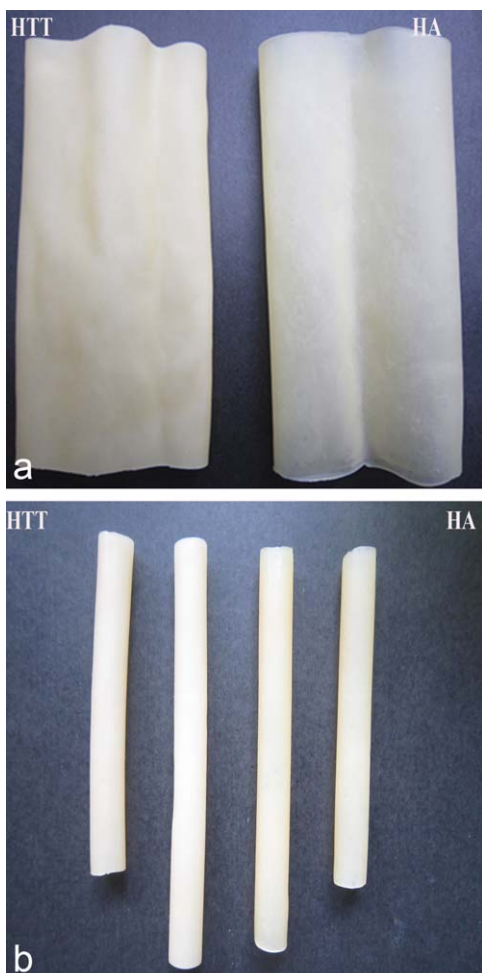


Figure 7. Vulcanized latex products. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dermal Irritation and Cytotoxicity Tests

Because of their direct contact with the human body, NRL products are required to have not only excellent physical properties but also good biological compatibility in case of the broadcast of viruses and allergies. The results of the dermal irritation and cytotoxicity tests (see Table V) show that the average dermal irritation scores of the HTT and HA films were zero; this illustrated that the HTT-vulcanized NRL film caused a tiny amount of irritation. The relative cell increments of HTT and HA were 19 and 18%, respectively; these values were still better than those in relevant reports about NRL products.¹³

CONCLUSIONS

In summary, an HTT preservation system with no ammonia effectively saved CNRL compared with an HA preservation. The VFA No. of HTT sample did not exceed 0.04, and the MST

Table V. Results of the Dermal Irritation and Cytotoxicity Tests

Item	Sample	Test result (%)	Conclusion
Dermal irritation test	HTT	0	Met the standard test
	HA	0	Met the standard
Cytotoxicity test	HTT	19	Grade four
	HA	18	Grade four

result was 650 s when the sample was saved for 180 days. The mechanical properties results of the HTT-vulcanized NRL film indicate that HTT did not react with rubber molecules, and its tear strength was nearly twice that of HA. The drying and film-forming properties illustrated that HTT did not affect the film formation. The dermal irritation and cytotoxicity tests showed that the HTT products did not irritate skin and should do no harm to the human body.

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