

Effects of Stearates on the Thermal Stability of Chlorinated Natural Rubber from Latex

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ABSTRACT: The effects of stearates on the dehydrochlorination (DHC) reaction of chlorinated natural rubber (CNR) from latex were studied by the measurement of the HCl evolving rate during the early stage of the thermal degradation of CNR and by the determination of the amounts of cyclic conjugated dienes formed on the CNR molecular chains. During the early stage of the thermal degradation of CNR at 150°C, HCl was eliminated from the CNR molecular chains, and the cyclic conjugated dienes were formed on the CNR molecular chains. Under the effects of barium stearate, lead stearate, cadmium stearate, and calcium stearate, the HCl evolving rates of CNR were reduced, whereas the

amounts of cyclic conjugated dienes that formed on the CNR molecular chains were increased. When zinc stearate was added, because of the formation of ZnCl₂, which was an active catalyst of the DHC reaction of CNR, both the HCl evolving rate from CNR and the formation of cyclic conjugated dienes were increased. The results indicate that the addition of stearates can reduce the thermal stability of CNR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1981–1985, 2006

Key words: halogenated; rubber; stabilization; UV-vis spectroscopy

INTRODUCTION

Chlorinated natural rubber (CNR), a kind of white, powder derivative product of natural rubber (NR), can be prepared by a solution or latex process. In a typical solution process, chlorination is carried out in solution by the dissolution of NR into CCl₄. Because the molecular chains of NR are in unfolding states in the solution, the chlorination reaction of NR can proceed more easily, and the structures and properties of the product are more homogenized and unanimous accordingly.^{1–3} However, the traditional CCl₄ solution process has been prohibited in many countries because it has defects such as high equipment investment, the serious problem of environmental pollution, and harmfulness to the health of workers. This ensures that the production of CNR from latex has vast vistas. By the proper control of the chlorination reaction conditions and the improvement of the stability of the NR latex with a nonionic surfactant, the chlorination of NR is available in latex directly.^{4–6} Because NR exists in the form of colloid particles in latex, the chlorination reaction, which is concentrated mainly on

the outer parts and then gradually into the inner parts of the rubber particles, is difficult to conduct. Besides, the nonrubber contents, which are about 5% of the rubber hydrocarbon in the latex, can affect the chlorination more or less. Therefore, there are certain side reactions occurring in the chlorination of NR from latex, which lead to the structural complexity and poor thermal stability of CNR. Fourier transform infrared (FTIR) analyses of the structures of CNRs from solution and latex processes have demonstrated that the main abnormal groups existing on the molecular chains of CNR from latex are carboxyl groups, whereas those on the molecular chains of CNR from solution are mainly hydroxyl groups.⁷ Although detailed structures of CNR are not available presently, many authors believe that there are quite a number of six-member rings existing on the CNR molecular chains at random.⁸ Studies of the thermooxidative degradation of CNR from latex by the use of thermogravimetric analysis, coupled with FTIR spectroscopy, ultraviolet–visible spectroscopy, and difference FTIR, have indicated that the thermal degradation of CNR mainly is a dehydrochlorination (DHC) reaction with a little oxidative scission of the molecular backbones, and the conjugated polyenes are formed on the molecules of CNR. During the early stage of the thermal degradation of CNR, only HCl is released, and this leads to severe discoloration.⁹ Therefore, the delay of the DHC reaction is the key to improving the thermal stability of CNR.

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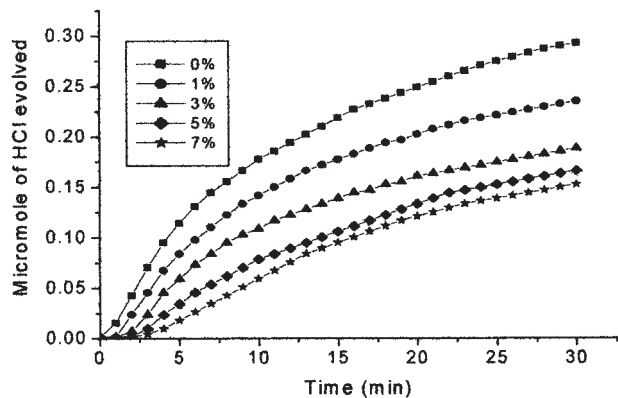


Figure 1 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of BaSt₂.

A chlorine-containing polymer such as poly(vinyl chloride) (PVC) also easily suffers from poor heat stability and HCl liberated from the DHC reaction, and this leads to severe discoloration and the loss of mechanical properties.^{10–12} The metal carboxylates that have played such important roles in the development of PVC are molecules having the general formula (RCO₂)₂M, where M is cadmium, zinc, barium, lead, or calcium and R is a linear or branched alkyl group, often a stearate. These stearates are commonly added to protect PVC from thermal degradation.^{13,14} In this study, by the measurement of the evolving rate of HCl during the initial stage of the thermal degradation of CNR and by the determination of the amounts of the conjugated double bonds that formed in the degraded CNR, the effects of barium stearate (BaSt₂), lead stearate (PbSt₂), cadmium stearate (CdSt₂), calcium stearate (CaSt₂), and zinc stearate (ZnSt₂) on the thermal stability of CNR were investigated.

EXPERIMENTAL

Materials and reagents

CNR, a white, powder product with a chlorine concentration of 64%, was prepared by a latex process and was supplied by the Chlorinated Natural Rubber Plant at the Agricultural Product Processing Research Institute of the Chinese Academy of Tropical Agricultural Science (Zhanjiang, Guangdong, People's Republic of China).

BaSt₂, PbSt₂, CdSt₂, CaSt₂, and ZnSt₂, chemically pure reagents, and tetrahydrofuran (THF), an analytically pure reagent, were obtained from Shanghai Chemical Co. (Shanghai, People's Republic of China).

Preparation of the samples

Each stearate (1, 3, 5, or 7 g) was added to CNR (100 g) by thorough mixing in a mortar, and 1 g of the result-

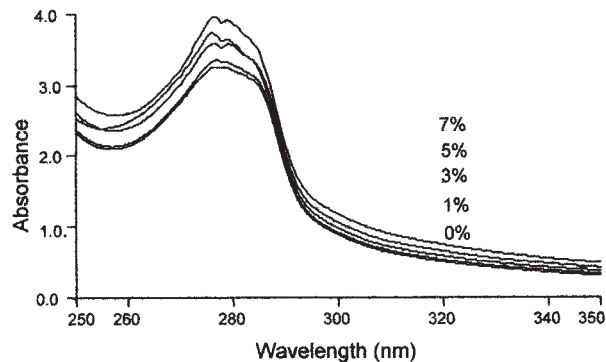


Figure 2 UV-vis spectra of CNR degraded in the presence of BaSt₂.

ing fine powder was used for the investigation. Each sample was determined three times to ensure that the stearate was mixed into CNR homogeneously.

Measurement of the HCl evolving rate

The apparatus for the measurement of the evolving rate of HCl from CNR was installed with reference to ref. 15. The CNR sample (1 g) was put into a U-type glass reaction vessel, and the lower part of the vessel was immersed in a thermostat containing glycerol to degrade the sample at 150°C for 30 min. The HCl that evolved from the sample was carried into the distilled water (1000 mL) with nitrogen (45 mL/min). The micromoles (M_m) of HCl were calculated from a predetermined standard curve by the measurement of the variations of the electrical conductivity (ρ) of distilled water. The ρ values were read on a model DDS-307 conductometer from Shanghai Precision & Scientific Instrument Co., Ltd. (Shanghai, People's Republic of China). By the measurement of the ρ values of a standard HCl solution, the relationship between M_m of HCl and ρ , obtained by linear regression, can be expressed as follows:

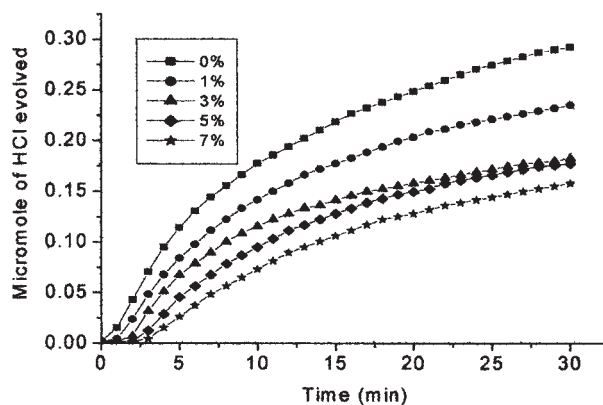


Figure 3 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of PbSt₂.

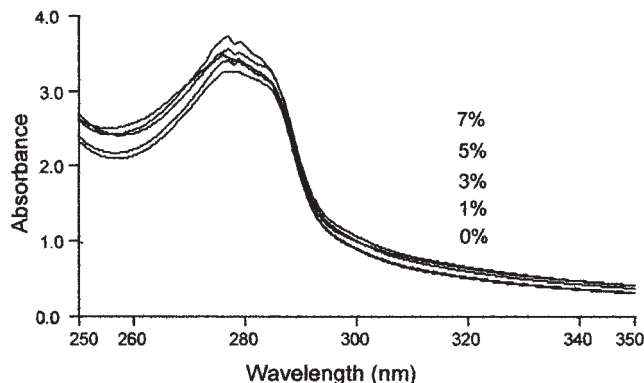


Figure 4 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of CaSt₂.

$$M_m = 2.7465 \times 10^{-6} \times \rho + 1.6601 \times 10^{-6} \quad (1)$$

UV-vis spectroscopy analysis

The degraded samples (residues) were dissolved in THF at a concentration of 1.0 mg/mL and then scanned from 200 to 600 nm on a PerkinElmer Lamda 35 ultraviolet-visible spectrophotometer (Shelton, CT). A reference cell loaded with THF was used to eliminate any signals due to the solvent itself.

RESULTS AND DISCUSSION

The effects of BaSt₂ on the evolving rate of HCl from CNR during the early stage (30 min) of the thermal degradation of CNR at 150°C are shown in Figure 1. Under the effects of BaSt₂, the induction time during which no detectable amounts of HCl could evolve from CNR was prolonged slightly, and M_m of evolved HCl decreased gradually with increases in BaSt₂.

Figure 2 presents the UV-vis spectra of the corresponding degraded CNR dissolving in THF. Because

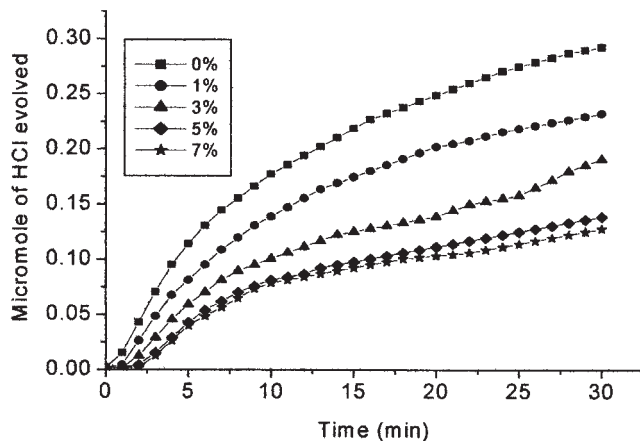


Figure 5 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of CdSt₂.

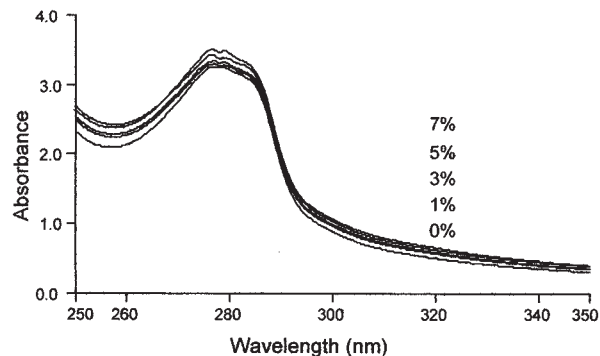


Figure 6 UV-vis spectra of CNR degraded in the presence of PbSt₂.

the differences among the absorbance intensities of the spectra are not obvious, only the spectra from 250 to 350 nm are presented. The main absorbance peak appears at about 280 nm for the degraded CNR containing BaSt₂ or not and indicates the formation of conjugated carbon-carbon double bonds on the CNR molecular chains. However, under the effect of BaSt₂, the absorbance intensities of the degraded CNR in THF increased gradually. Although the evolving rates of HCl from CNR decreased gradually, the amounts of the conjugated double bonds that formed in the degraded CNR increased with an increase in the BaSt₂ dosages. Besides, the appearance of a doublet or triplet on the UV-vis spectra of the degraded samples indicated different substituting groups on the conjugated double bonds.

The HCl evolving rates during the early stage of the thermal degradation of CNR under the effects of PbSt₂, CdSt₂, and CaSt₂ at 150°C are shown in Figures 3, 5, and 7, respectively. Figures 4, 6, and 8 are the UV-vis spectra of the corresponding degraded CNR dissolving in THF. It is obvious that the effects of PbSt₂, CaSt₂, and CdSt₂ on the DHC reaction of CNR are in accord with that of BaSt₂. However, the effects of CaSt₂ on the DHC of CNR were relatively low when the amounts of CaSt₂ increased, in comparison with

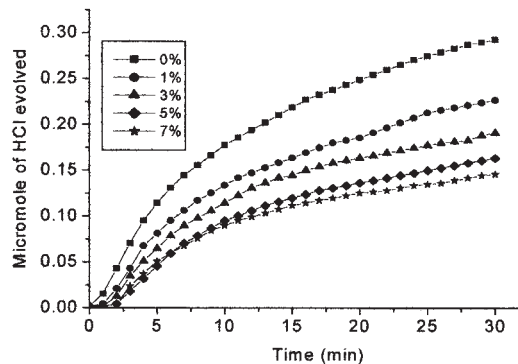


Figure 7 UV-vis spectra of CNR degraded in the presence of CaSt₂.

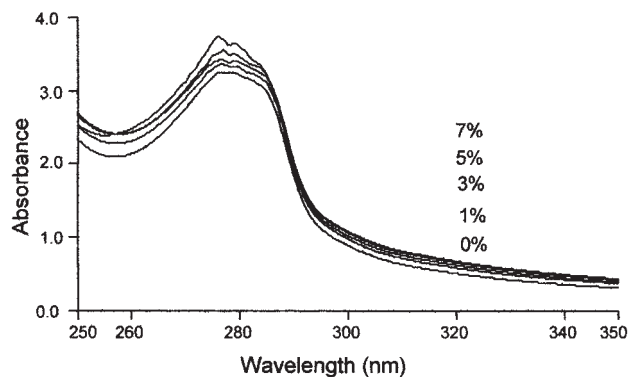


Figure 8 UV-vis spectra of CNR degraded in the presence of CdSt_2 .

the other stearates. With the addition of CaSt_2 , CNR easily coagulated during the thermal degradation, and this led to the release of HCl unanimously.

Figure 9 shows the effect of ZnSt_2 on the HCl evolving rate during the early stage of the thermal degradation of CNR at 150°C . The evolving rate of HCl from the sample containing 1% ZnSt_2 was faster than that of the control sample. When the dosage of ZnSt_2 was as high as 3%, the evolving rate of HCl was so fast that it was difficult to determine, and the residue became dark black in 3 min. Therefore, only the evolving rate curve of HCl from the CNR sample containing 1% ZnSt_2 is presented in Figure 9. Figure 10 illustrates the spectra of the degraded samples containing 1 and 3% ZnSt_2 . The residue of the sample containing 3% ZnSt_2 was obtained by the degradation of the sample at 150°C for 3 min. Obviously, under the effects of ZnSt_2 , the amounts of the conjugated double bonds formed on the CNR molecular chains increased. However, the absorbance intensities of the sample degraded under the effect of ZnSt_2 did not increase greatly in comparison with

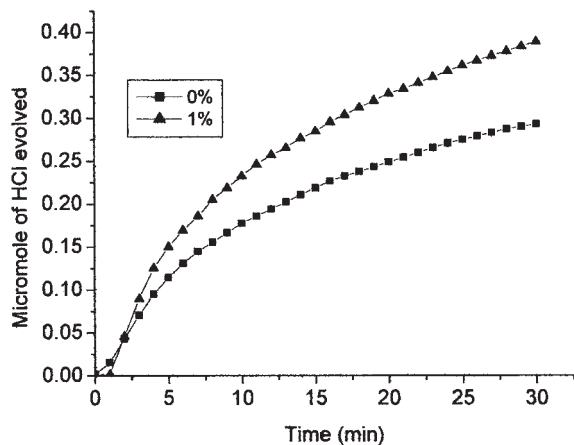


Figure 9 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of ZnSt_2 .

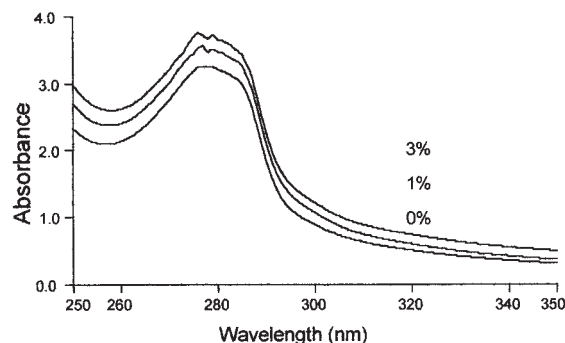


Figure 10 UV-vis spectra of CNR degraded in the presence of ZnSt_2 .

that of the control. This can be explained by the incomplete solvability of the residue in THF.

The DHC reaction of PVC most probably proceeds by a chain mechanism involving radical intermediates. Its degradation occurs by autocatalytic DHC initiated at the labile sites in the polymer chains, such as the branching,¹⁶ chloroalkyl group,^{17,18} peroxide residue,¹⁹ oxygen-containing group,²⁰ and head-to-head structures.²¹ The primary degradation product HCl has been shown to have a catalytic effect on the DHC reaction of PVC. Because the main backbone structures of PVC are straight chains and HCl can be easily eliminated through a zipper DHC reaction, conjugated polyene sequences, $(-\text{C}=\text{C}-)_n$, with n ranging from 3 to 15, are formed. Therefore, acting as thermal stabilizers, the stearates can stabilize PVC by adsorbing HCl formed during the initial stage of thermal degradation and/or replacing the labile chlorine atoms through esterification of the polymer. The HCl acceptor abilities of the stearates are the basis of their establishing function, and the esterification of the polymer to form PVC-stearate esters could be at least equally as important as HCl acceptors.

The DHC reaction of CNR, however, is different from that of PVC. Because of the complexity of the chlorination reaction of NR in latex, the detailed structures of CNR have not been determined at present. However, from the studies of some researchers,^{2,8} the following chlorination reaction scheme of NR in latex and possible structure of CNR have been suggested (Figure 11).

Cyclic structure E distributes at random along the straight chains of CNR. During the early stage of the thermal degradation of CNR, cyclic conjugated dienes such as structures F and G might be formed from the DHC reaction (Figure 12). Because of the $n \rightarrow \pi$ conjugation between the conjugated double bonds and the lone-pair electron of conjoined chlorine, the $\pi \rightarrow \pi^*$ transition energy is reduced, and so the UV-vis absorbance wavelength (λ_{max}) of conjugated diene migrates from 217 to about 280 nm. According to Woodward's

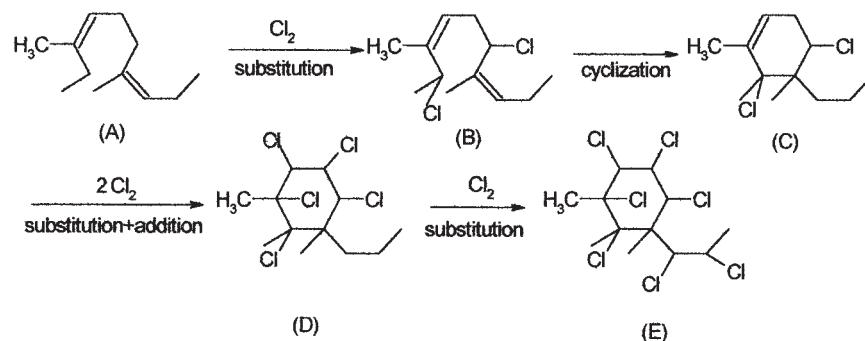


Figure 11 Scheme of the chlorination of NR.

rule, λ_{\max} of cyclic conjugated dienes of F and G is 278 and 288 nm, respectively. The formation of structures F and G makes the DHC reaction of CNR unable to proceed by a zipper reaction to form a conjugated polyene, $-\text{[C=C]}-$, with $n > 3$.

During the thermal degradation of CNR in the presence of stearates, because of the steric hindrance, it seems impossible for the stearic acid ion being attached onto the cyclic structure of CNR to form CNR-stearate esters; therefore, the replacement of labile chlorine atoms from structure E by stearic acid ion is not available. The main functions of BaSt_2 , PbSt_2 , CdSt_2 , and CaSt_2 on CNR are to react with HCl; this can accelerate the elimination of HCl from CNR molecular chains, leading to an increase in the formation of structures F and G, and also can reduce the HCl evolving rate.

During the thermal degradation of CNR in the presence of ZnSt_2 , the product ZnCl_2 from the reaction between ZnSt_2 and HCl can catalyze the DHC of CNR and lead to the HCl evolving rate increasing greatly. This effect of ZnSt_2 on CNR is similar to its effect on PVC. During the thermal degradation of PVC containing CdSt_2 , the effect of CdSt_2 on the thermal stability of PVC is similar to that of ZnSt_2 because the effect of CdCl_2 on the DHC reaction of PVC is similar to that of ZnCl_2 . However, during the thermal degradation of CNR containing CdSt_2 , different phenomena were observed. With an increase in the dosage of CdSt_2 , M_w of evolved HCl decreased.

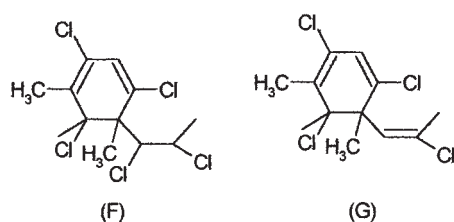


Figure 12 Possible structures of conjugated double bonds formed on CNR molecular chains.

CONCLUSIONS

During the early stage of the thermal degradation of CNR at 150°C , HCl is eliminated from CNR molecular chains, and cyclic conjugated dienes are formed on the CNR molecular chains. Under the effects of BaSt_2 , PbSt_2 , CaSt_2 , and CdSt_2 , the HCl evolving rates of CNR can be reduced, whereas the amounts of cyclic conjugated dienes formed on the CNR molecular chains are increased. During the thermal degradation of CNR in the presence of ZnSt_2 , the evolving rate of HCl increases greatly, and the amounts of cyclic conjugated dienes formed on CNR molecular chains also increase. The results indicate that the additions of stearate can reduce the thermal stability of CNR.

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