

Effects of Dibutyltin Dilaurate and Epoxidized Soya Bean Oil on the Thermal Stability of Chlorinated Natural Rubber from Latex

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ABSTRACT: The effects of dibutyltin dilaurate (DBTL) and epoxidized soya bean oil (EBO) on the dehydrochlorination reaction of chlorinated natural rubber (CNR) from latex were studied by the measurement of the HCl evolving rate during the thermal degradation of CNR and by the determination of the amounts of cyclic conjugated dienes that formed on the CNR molecular chains. During the early stage of the thermal degradation of CNR at 150°C, HCl was eliminated, and the cyclic conjugated dienes formed on the CNR molecular chains. Under the effects of DBTL and EBO, the HCl evolving rates during the early stage of the thermal degradation of CNR were reduced, whereas the amounts of cyclic conjugated dienes formed on the CNR molecular chains were increased. Under the effects of mixtures from

the compounding of DBTL with barium stearate or 2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol) as well as the compounding of EBO with 2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol), not only the HCl evolving rate from CNR but also the formation of cyclic conjugated dienes decreased, and this indicated that the compounded mixtures had synergistic functions against the thermal degradation of CNR. However, the mixture from the compounding of EBO with barium stearate had no synergistic effect on increasing the thermal stability of CNR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1986–1991, 2006

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

INTRODUCTION

Chlorinated natural rubber (CNR), a kind of white, powder product, can be prepared from latex directly by the proper control of the chlorination reaction conditions and the improvement of the stability of natural rubber latex with a nonionic surfactant.^{1–3} Because the chlorination involves a number of side reactions, CNRs are complex structures and show poor thermal stability. 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.⁴ Studies of the thermooxidative degradation of CNR from latex have indicated that the thermal degradation of CNR mainly is a dehydrochlorination (DHC) reaction and that 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.⁵ Therefore, delaying the DHC reaction is the key to improving the thermal stability of CNR.

A chlorine-containing polymer such as poly(vinyl chloride) (PVC) also easily suffers from poor heat stability and HCl released from the DHC reaction, and this leads to severe discoloration and the loss of mechanical properties.^{6–8} Organotin as a highly efficient stabilizer against PVC degradation has become increasingly apparent. Most of the stabilizers in general use have structures of the type $R_nSnX_{(4-2)n}$, where R is normally an alkyl group, usually methyl, butyl, or octyl, and X is one of a large number of saturated or unsaturated carboxylates or mercaptid derivatives.⁹ Probably the most widely used stabilizer falling into this category is dibutyltin dilaurate (DBTL). In practice, compounds that have been shown to have low efficiency when used as a single organotin component appear to have greatly improved performance when compounded as part of a synergistic mixture. Epoxy compounds, of which epoxidized soya bean oil (EBO) is a typical example, are frequently used as costabilizers with metal carboxylates, and their presence induces high long-term stability by delaying the onset of the blackening of PVC. As the costabilizer of zinc stearate, the main function of EBO seems to be a

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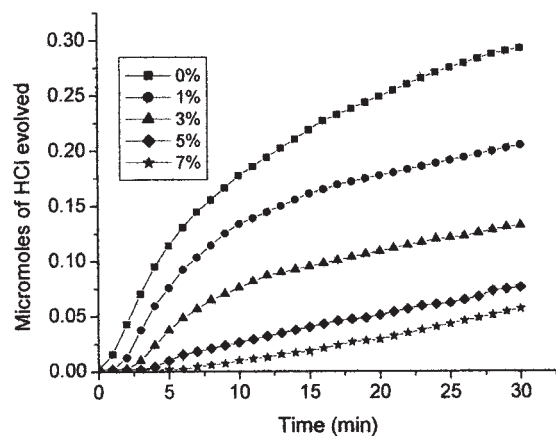


Figure 1 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of DBTL.

reaction with $ZnCl_2$, which delays the catalytic degradation of the Lewis acid.¹⁰ In this study, by the measurement of the evolving rate of HCl during the early stage of the thermal degradation of CNR and by the determination of the amounts of the cyclic conjugated dienes formed on the degraded CNR molecular chains during the early stage of the thermal degradation of CNR, the effects of DBTL and EBO as well as their compounded mixtures with barium stearate ($BaSt_2$) and 2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol) (antioxidant 2246) 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).

Antioxidant 2246, $BaSt_2$, DBTL, and EBO, 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

The samples were obtained by the mixing of DBTL or EBO (1, 3, 5, or 7 g) into CNR (100 g). The compounded samples were obtained by the mixing of DBTL (0.5 g) or EBO (0.5 g) together with $BaSt_2$ (0.5 g) or antioxidant 2246 (0.5 g) into CNR (100 g). Each sample was thoroughly mixed in a mortar, and 1 g of the resulting fine powder was used for the investiga-

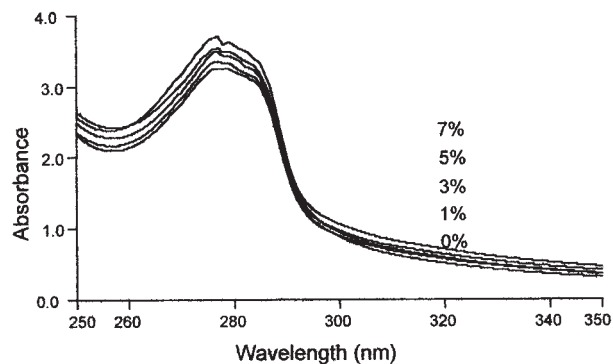


Figure 2 UV-vis spectra of CNR degraded in the presence of DBTL.

tion. Each sample was determined three times, and if the results differed obviously, the ingredients were reblended with CNR.

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. 11. 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

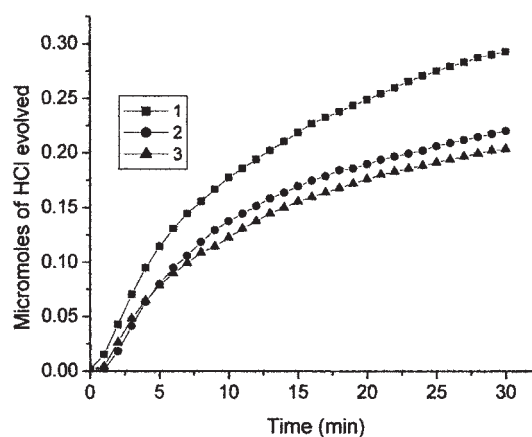


Figure 3 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of DBTL and $BaSt_2$: (1) the HCl evolving rate of the control, (2) the mean value of the HCl evolving rate of CNR when DBTL and $BaSt_2$ are used as single components, and (3) the HCl evolving rate of CNR when DBTL and $BaSt_2$ are used as a compounded mixture.

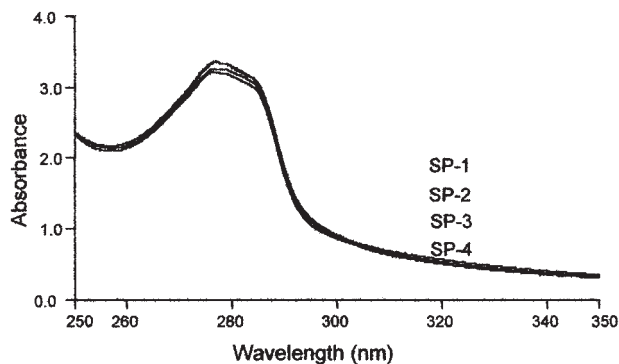


Figure 4 UV-vis spectra of CNR degraded in the presence of DBTL and BaSt₂ at 150°C: (SP-1,SP-2) the spectra of CNR degraded in the presence of DBTL and BaSt₂ individually (they nearly overlap each other), (SP-3) the spectrum of the control, and (SP-4) the spectrum of CNR degraded in the presence of a compounded mixture of DBTL and BaSt₂.

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:

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

Ultraviolet-visible (UV-vis) spectroscopy analysis

The degraded samples (residues) were dissolved in THF at a concentration of 1.0 mg/mL and then

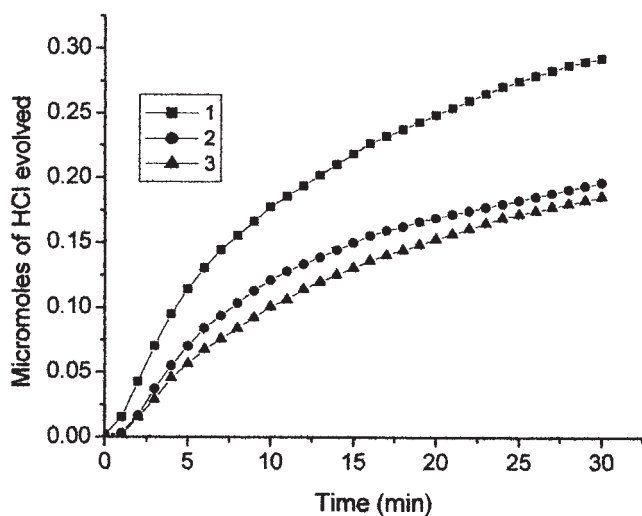


Figure 5 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of DBTL and antioxidant 2246: (1) the HCl evolving rate of the control, (2) the mean value of the HCl evolving rate of CNR when DBTL and antioxidant 2246 are used as single components, and (3) the HCl evolving rate of CNR when DBTL and antioxidant are used as a compounded mixture.

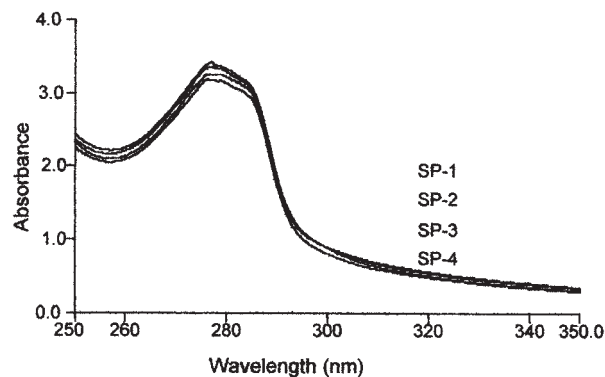


Figure 6 UV-vis spectra of degraded CNR in the presence of DBTL and antioxidant 2246: (SP-1,SP-2) the spectra of CNR degraded in the presence of DBTL and antioxidant 2246 individually, (SP-3) the spectrum of the control, and (SP-4) the spectrum of CNR degraded in the presence of a compounded mixture of DBTL and antioxidant 2246.

scanned from 200 to 600 nm on a PerkinElmer Lambda 35 UV-vis spectrophotometer (Shelton, CT). A reference cell loaded with THF was used to eliminate any signals due to the solvent itself.

RESULTS AND DISCUSSION

Effect of DBTL on DHc of CNR

The effects of DBTL 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 DBTL, the induction time at which the detectable HCl gas began to evolve from CNR during the thermal degradation of CNR was delayed slightly, and M_m of evolved HCl decreased gradually with increases of DBTL. Figure 2 presents the UV-vis spectra of the corresponding degraded CNR dissolving in THF. Because the differences among the absor-

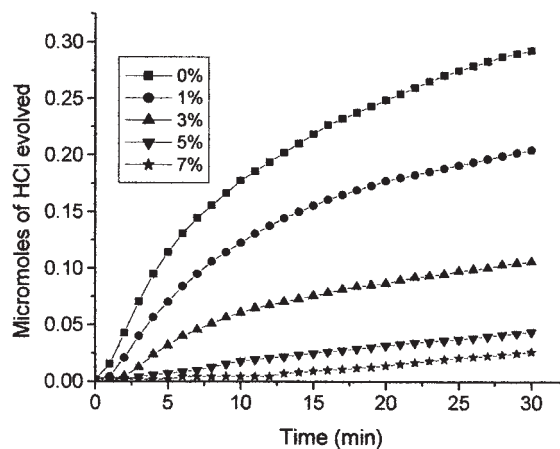


Figure 7 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of EBO.

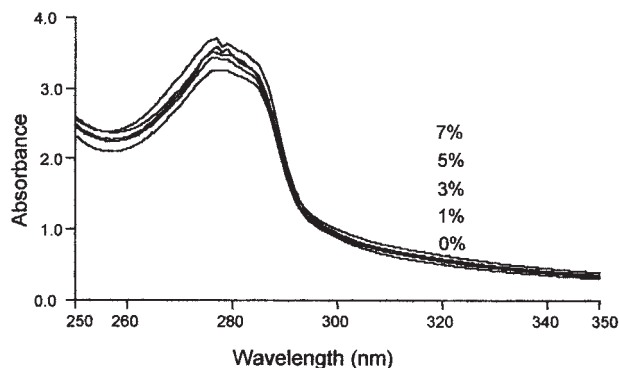


Figure 8 UV-vis spectra of CNR degraded in the presence of EBO.

balance intensities of the spectra are not obvious, only the spectra from 250 to 350 nm are presented. The main characteristic absorbance peak appears at about 280 nm for the degraded CNR containing DBTL or not and indicates the formation of conjugated carbon-carbon double bonds on the CNR molecular chains. However, under the effect of DBTL, the absorbance intensities of degraded CNR 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 DBTL dosage.

Figures 3 and 4 illustrate the effects of the compounded mixture of DBTL (0.5 g) and BaSt₂ (0.5 g) on the HCl evolving rates during the thermal degradation of CNR at 150°C and the UV-vis spectra of the corresponding residues. Under the effect of the compounded mixture of DBTL and BaSt₂, the HCl evolving rate from CNR decreased and was even lower than

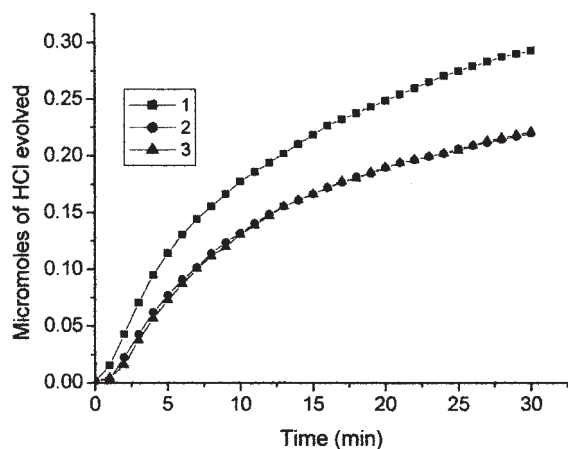


Figure 9 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of EBO and BaSt₂: (1) the HCl evolving rate of the control, (2) the mean value of the HCl evolving rate of CNR when EBO and BaSt₂ are used as single components, and (3) the HCl evolving rate of CNR when EBO and BaSt₂ are used as a compounded mixture.

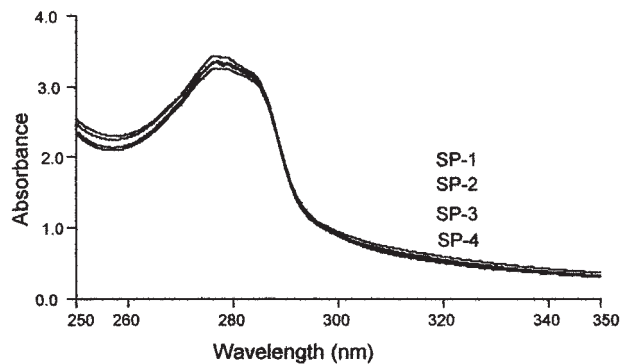


Figure 10 UV-vis spectra of degraded CNR in the presence of EBO and BaSt₂: (SP-1, SP-2) the spectra of CNR degraded in the presence of EBO and BaSt₂ individually, (SP-3) the spectrum of the control, and (SP-4) the spectrum of CNR degraded in the presence of a compounded mixture of EBO and BaSt₂.

the mean value of the HCl evolving rates from CNR when they were used as individual components. Obviously, under the effect of the compounded mixture of DBTL and BaSt₂, not only the HCl evolving rate but also the amounts of conjugated double bonds that formed on the CNR molecular chains during the early stage of the thermal degradation of CNR at 150 were reduced, and this indicated that the compounded mixture of DBTL and BaSt₂ had a synergistic effect against the thermal degradation of CNR.

Figures 5 and 6 show the effect of DBTL compounded with antioxidant 2246 on the HCl evolving rates and the formation of cyclic conjugated double bonds during the thermal degradation of CNR at 150°C, respectively. Similar performances of the com-

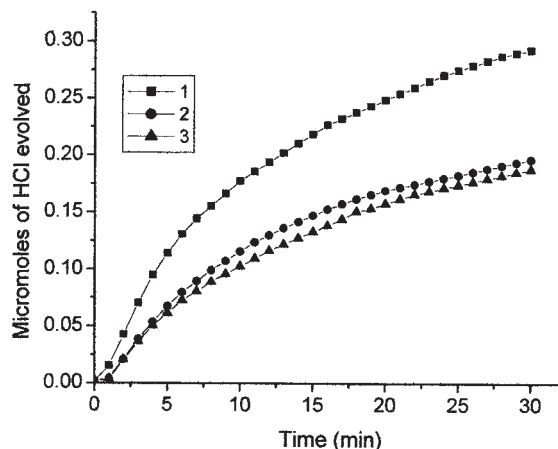


Figure 11 HCl evolving rates during the thermal degradation of CNR at 150°C in the presence of EBO and antioxidant 2246: (1) the HCl evolving rate of the control, (2) the mean value of the HCl evolving rate of CNR when EBO and antioxidant 2246 are used as single components, and (3) the HCl evolving rate of CNR when EBO and antioxidant 2246 are used as a compounded mixture.

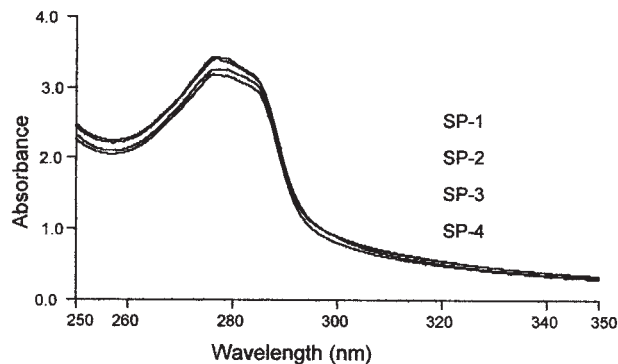


Figure 12 UV-vis spectra of degraded CNR in the presence of EBO and antioxidant 2246: (SP-1,SP-2) the spectra of CNR degraded in the presence of EBO and antioxidant 2246 individually, (SP-3) the spectrum of the control, and (SP-4) the spectrum of CNR degraded in the presence of a compounded mixture of EBO and antioxidant 2246.

pounded mixture of DBTL with antioxidant 2246 on the DHC reaction of CNR were observed, and this indicated that the compounded mixture of DBTL and antioxidant 2246 also had a synergistic effect on the thermal stability of CNR.

Effect of EBO on DHC of CNR

The effects of EBO 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 7. Figure 8 presents the UV-vis spectra of the corresponding degraded CNR dissolving in THF; only the spectra from 250 to 350 nm are presented. The effects of EBO on the DHC reaction of CNR during the early stage of thermal degradation at 150°C are similar to those of DBTL.

Figure 9 illustrates the effect of EBO compounded with BaSt₂ on the HCl evolving rates during the thermal degradation of CNR at 150°C. Under the effect of the compounded mixture of EBO and BaSt₂, the HCl evolving rate from CNR was not further reduced and almost equaled the mean value of the HCl evolving rates when they were used as individual components. The amounts of conjugated double bonds that formed on the corresponding degraded CNR molecular chains

were still more than those of the degraded control (see Fig. 10). This indicated that the compounded mixture of EBO and BaSt₂ had no synergistic performance against the thermal degradation of CNR.

However, under the effect of the compounded mixture of EBO and antioxidant 2246, the HCl evolving rate from CNR decreased and was even lower than the mean value when they were used as single components (see Fig. 11), and the amounts of conjugated double bonds that formed on the CNR molecular chains during the early stage of the thermal degradation of CNR at 150 were also reduced (see Fig. 12); this indicated that the compounding of EBO and antioxidant 2246 had synergistic efficiency against the thermal degradation of CNR.

During the early stage of thermal degradations of both PVC and CNR, HCl is eliminated from the polymer chains, and the conjugated double bonds form on the residual polymer molecular chains through the DHC reaction. However, the DHC mechanisms seems different from each other. The DHC reaction of PVC with straight molecular chains most likely proceeds by a chain mechanism involving radical intermediates. The primary degradation product HCl has been shown to have a catalytic effect on the DHC reaction of PVC, and this leads to the elimination of HCl through a zipper reaction and the formation of conjugated polyene sequences, $(-[\text{C}=\text{C}]-)_n$, with n ranging from 3 to 15. The DHC reaction of CNR, however, seems different from that of PVC. In our previous article, we reported that cyclic conjugated dienes such as structure B or structure C might possibly be formed through the DHC reaction during the early stage of the thermal degradation of CNR (see Fig. 13); therefore, the DHC reaction of CNR cannot proceed by a zipper reaction to form a conjugated polyene, $-\text{[C=C]}-$, with $n > 3$.

Acting as a thermal stabilizer, DBTL can stabilize PVC by adsorbing the HCl formed during the early stage of thermal degradation, reacting with and stabilizing the labile chlorine atoms through esterification of the polymer, and interfering with the chain mechanism [e.g., by scavenging reactive chain propagators, usually free radicals ($\text{Cl}\cdot$)].⁹

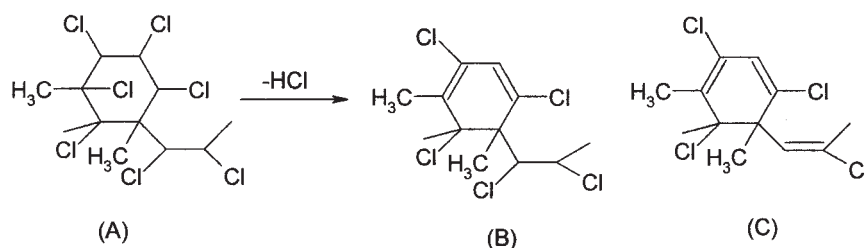
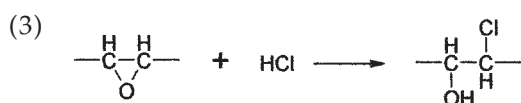


Figure 13 Possible scheme of cyclic conjugated dienes formed on CNR molecular chains.

During the thermal degradation of CNR in the presence of DBTL or EBO, because of the steric hindrance, it seems difficult for the lauric acid ion or EBO molecule to be grafted onto the molecular chains of CNR; therefore, the replacement of labile chlorine atoms from structure A by the lauric acid ion or EBO is not available. It is most likely that the main effect of DBTL or EBO on CNR is to react with HCl; this can accelerate the elimination of HCl from CNR molecular chains, leading to an increase in the formation of structures B and C, and can reduce the HCl evolving rate:



We have reported the effects of transition-metal ions on the thermal stability of CNR. The transition-metal ions, especially low-valence ions (e.g., Cu^{+1}), can accelerate the DHC reaction, resulting in a great decrease in the thermal stability of CNR.¹² Although it has not yet been confirmed, the DHC reaction of CNR most likely involves free-radical ($\text{Cl}\cdot$) propagation. When DBTL is compounded with BaSt_2 , by BaSt_2 and/or DBTL absorbing HCl and by DBTL scavenging the free radical ($\text{Cl}\cdot$) possibly, the compounded mixture appears to show a synergistic performance against the thermal degradation of CNR.¹³



The synergistic effect of the mixture from the compounding of DBTL or EBO with antioxidant 2246 on improving the thermal stability of CNR probably contributes to the free-radical scavenging behavior of the antioxidant. When EBO is compounded with BaSt_2 , the effect of the mixture on the DHC reaction of CNR is similar to the effects of the ingredients used individually. The reason is that the effects of both EBO and BaSt_2 on the DHC of CNR mainly are to react with HCl, and neither of the components interferes with the free-radical propagation.

CONCLUSIONS

By reacting with the HCl eliminated from CNR molecular chains during the early stage of the thermal degradation of CNR at 150°C, thereby reducing the evolving rate of HCl and increasing the formation of cyclic conjugated dienes on the CNR molecular chains, DBTL and EBO seem not to be sufficiently active to function as stabilizers in their own right.

Under the effects of mixtures from the compounding of DBTL with BaSt_2 or antioxidant 2246 as well as the compounding of EBO with antioxidant 2246, not only the HCl evolving rates during the thermal degradation of CNR but also the amounts of cyclic conjugated dienes that form on the CNR molecular chains can be reduced; therefore, the mixtures have been shown to have synergistic efficiency against the thermal degradation of CNR.

When EBO is compounded with BaSt_2 , the effects of the compounded mixture on the DHC of CNR are similar to those of the components used individually, and this indicates that the mixture has no synergistic effect on increasing the thermal stability of CNR.

The DHC of CNR during the early stage of thermal degradation most likely involves free-radical propagation, and the scavenging of free radicals seems to be one of the main ways of improving the thermal stability of CNR.

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