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Comparison effects of lanthanum stearate and antioxidants in epoxidized natural rubber

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Abstract: This work studied possibilities of using lanthanum stearate (LaSt) as an antioxidant in epoxidized natural rubber containing 25 mol.% expoxidation (ENR25) compounds. For comparison purposes, two commercial antioxidant 4010NA and MB were also used. The influence of LaSt, antioxidant 4010NA and MB on cure characteristics, mechanical properties, crosslink density, hot air aging and thermo-oxidative degradation were studied. The results indicated that the incorporation of LaSt and antioxidants could accelerate the vulcanization of ENR. The ENR vulcanizates with antioxidant MB had better mechanical properties than 4010NA and LaSt. Compared with antioxidant 4010NA and MB, the ENR25 vulcanizates with the addition of LaSt exhibited the best hot air aging resistance and thermo-oxidative stability.

Keywords: lanthanum stearate; antioxidants; ENR25; thermal degradation; hot air aging resistance; rare earths

The epoxidized natural rubber (ENR) have become a research focus due to good anti-wet skid resistance and rolling resistance of ENR[1], which is a promising rubber in the application of the green tire. However, ENR exhibits poor aging resistance because of the ring-opening reaction of epoxide groups in the aging of ENR[2]. Currently, adding a base[3] or antioxidant[4] may stop or delay the process of the aging for ENR, but it can sacrifice the other properties, such as processing safety[2], mechanical properties[5]. In particular, traditional antioxidant may produce carcinogens or the rubber products discoloration[6]. Recently, our previous research results show that rare earth stearate exerts better protective effect in the hot air aging for ENR[7,8]. In the present study, the comparative study of LaSt and traditional antioxidant, viz., 4010NA, MB, on curing characteristics, crosslinking density, mechanical properties, and hot-air aging of ENR vulcanizates was carried out.

1 Experimental

1.1 Materials

ENR 25 having 25 mol.% of epoxidation was supplied by Agricultural Product Processing Research Institute (APPRI), China. LaSt was supplied by Inner Mongolia Haohai Chemicals Company (P.R.C.). Other compounding ingredients such as antioxidant 4010NA, MB, zinc oxide, stearic acid, N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), sulfur were of commercial grades and used without further purification.

1.2 Preparation of samples

The base formulation for the rubber compound was (phr): ENR25, 100; stearic acid, 2; zinc oxide, 5; TBBS, 1.5; sulfur, 1.5; antioxidant or LaSt 1.

ENR25 compounds were prepared in an open two-roll mill in accordance with ISO 2393:1994. The ENR compounds were vulcanized at 150°C for optimum curing time in a press.

1.3 Characterization

Vulcanizing conditions (time and temperature) were previously determined by an Alpha moving die rheometer (MDR 2000). Curing rate index (CRI) was evaluated according to the following equation:

$$\mathrm{CRI}=\frac{1}{T_{90}-T_{S1}}\times 100 \quad (1)$$

where T_{S1} is the scorch time. Tensile properties were measured on universal material testing machine (Instron3365, U-CAN, Taiwan, China) according to ISO 37-1977, with type 5 test specimens. Tear strength was measured following the ISO 816-1983. Shore hardness was measured according to ASTM D-2240.

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The crosslinking density was determined on the basis of the rapid solvent-swelling measurements (toluene during 72 h at room temperature) by application of the Flory-Rhener equation[7]:

$$\gamma = \frac{-[\ln(1-V_r)+V_r+\chi V_r^2]}{V_s \times (V_r^{1/3}-V_r/2)} \quad (2)$$

where γ is crosslinking density, V_r is the volume fraction of rubber in the swollen network, χ is the interaction parameter, and V_s is the molar volume of the solvent.

A UA-2071A aging oven (U-CAN technology Co., LTD, Taiwan, China) was used to carry out the hot air aging test at 100 ºC for 24 h. The mechanical properties after hot air aging were tested in the same way as in tensile tests, and then the percentage retention of tensile strength and elongation at break for ENR vulcanizates were calculated. The aging coefficient was calculated according to the following expression:

$$\text{Retention} = \frac{\text{Values after aging}}{\text{Values before aging}} \times 100\% \quad (3)$$

The thermogravimetry analysis was carried out with a NETZSCH simultaneous thermal analyzer (STA449, made in Germany). The reaction environment is air with a flow rate of 50 mL/min. The samples were heated from 30 to 600 ºC at a heating rate of 20 ºC/min.

2 Results and discussion

2.1 Cure characteristics

Fig. 1 shows the vulcanization curves of ENR25 compounds with LaSt and different antioxidants. To gain some important vulcanization parameters, the scorch time T_{S1} (a measure of scorch safety), optimum cure time T_{90}, and the difference between minimum and maximum torque (S_{max}–S_{min}) are determined from the curing curves, as given in Table 1. It is evident from Fig. 1 that the curing curves in the presence of antioxidant 4010NA and MB are obviously shifted toward the short time side, suggesting that the cure process of ENR is noticeably accelerated. The acceleration of vulcanization of

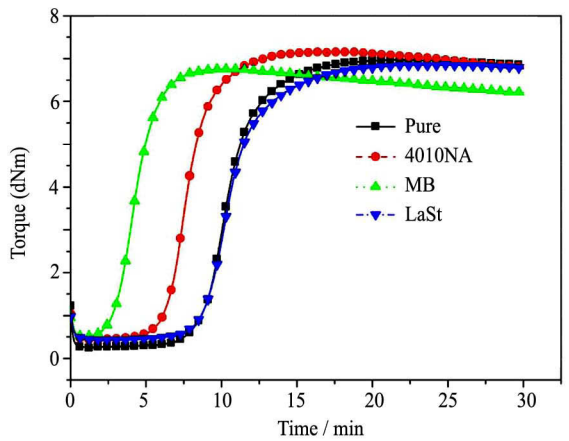


Fig. 1 Vulcanization curves of ENR25 with LaSt and different antioxidants

Table 1 Cure properties of the ENR25 with LaSt and different antioxidants at 150 ºC

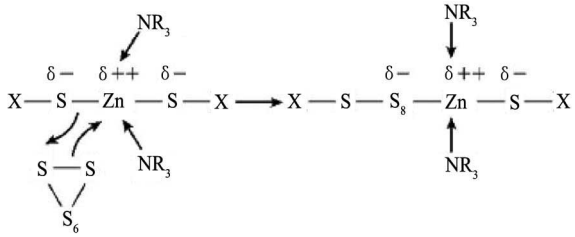
Antioxidant	Pure	4010NA	MB	LaSt
T_{S1}/ min	8.87	6.47	3.17	8.55
T_{90}/min	13.43	10.17	6.07	13.02
CRI/min^{-1}	21.93	27.03	34.48	22.37
S_{max}/(dNm)	6.98	7.17	6.76	7.03
S_{min}/(dNm)	0.25	0.42	0.50	0.44
S_{max}–S_{min}/(dNm)	6.73	6.75	6.26	6.59

ENR with 4010NA is attributed to the catalytic effect of the 4010NA (amine-based antioxidants) antioxidants in generating more active sulfurating agents for curing of ENR. The mechanism of 4010NA in catalyzing the formation of active sulfurating agent is shown in Scheme 1[9]. The external ligands formed by amines can occupy the vacant zinc orbitals. This occupation could weaken Zn-S binding, which results in increase of the nucleophilicity of the mercaptide sulfur atoms, thus facilitates the formation of the active sulfurating reagent.

The earlier studies showed that antioxidant MB only as accelerator has slight accelerating properties in natural rubber, is attributed to the absence of atomic grouping, —X—[11]—SH, in their azole ring[10] and to the high melting points (303 ºC). But the results in Table 1 show the opposite trend. It can be seen that the antioxidant MB gives the highest CRI. This may be possibly because of synergetic effect between the accelerator TBBS and antioxidant MB. As a result, MB shows the capacity of producing mercaptobenzimidazole radicals which could have abstracted α-allylic hydrogens from ENR, nor has it the ability to combine with S8 to form crosslink precursors.

However, the addition of LaSt shows slightly acceleration effect on the vulcanization of ENR. It may be because La can interact with S and N atom in the accelerator TBBS, which results in C–S and C–N bonds to be pulled long, and thus easier to fracture, therefore，the scorch time T_{S1} and curing time T_{90} for ENR compounds would be shortened in the process of ENR vulcanization[11], thus LaSt accelerates the vulcanization of ENR, but 0.5phr LaSt was used in this study, there is not enough La ion interacting with S and N atom in the accelerator TBBS, so the addition of LaSt can enhance the cure index of ENR.

From Table 1, It can be seen that T_{S1} (it was used to characterize the induction period) in the presence of an-



Scheme 1 Mechanism of 4010NA in catalyzing the formation of active sulfurating agent