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Antioxidative behavior of a novel samarium complex in styrene-butadiene rubber/silica composites

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The focus of this study was on the thermo-oxidative aging resistance of a new rare earth complex, samarium lysine dithiocarbamate (Sm-LDC), in the styrene-butadiene rubber (SBR)/silica composites. The anti-aging behavior of SBR/silica composites with Sm-LDC, as well as several common commercial antioxidants, was systematically investigated by oxidation induction time (OIT), mechanical testing, crosslink density determination, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), and thermo-gravimetric analysis (TGA). The results demonstrated that Sm-LDC significantly improve the thermo-oxidative stability of SBR/silica composites and protect the composites against the thermo-oxidative aging more effectively than the widely used antioxidant 4010NA and antioxidant MB in rubber industry. It could be attributed to the synergistic effect between dithiocarboxyl groups and samarium ions in Sm-LDC, which can high-efficiently decompose the hydroperoxide and scavenge the oxy radicals, respectively. Besides, the results of whiteness and yellowness index (*Y.I.*) analysis indicated that Sm-LDC can hardly cause discoloration to the SBR/silica composites and is better than the recognized light-colored antioxidant MB in the aspect of color. This research might open up new opportunities for preparing highly thermo-oxidative aging-resistant rubber composites without color contamination.

1. Introduction

Styrene-butadiene rubber (SBR), as one of the most widely used synthetic rubber, has become fantastically attractive and increasingly important for academia and the applied polymer industry [1–4]. SBR doesn't belong to self-reinforcing rubbers and usually behaves the poor physical and mechanical properties, failing to meet the demands for practical application. Therefore, SBR must be reinforced before use and the introduction of nano-filler into rubber is a significantly efficient and practical method to prepare the enhanced rubber composites [5], further expanding the application field of rubber materials. For instance, SBR/silica composites have been increasingly used in high-performance tires or "green tires", where silica is incorporated to SBR for enhancing the mechanical properties and reducing the rolling resistance of the composites [6]. However, the existence of high level unsaturated carbon-carbon double bonds and active allylic hydrogens in its molecular chains makes SBR easily attacked by oxygen during service [7], especially under conditions of heat, pressure, light, etc. [8], which extremely deteriorates the mechanical and thermal properties and greatly shortens service life of SBR/silica composites. Thus, the performance of thermo-oxidative aging resistance is of key importance for the long-term industrial applications of SBR/silica composites. To date, some different approaches have been proposed to improve the thermo-oxidative aging resistance, and the addition of chemical antioxidants seems to be the most convenient and effective ways to prevent or delay the thermo-oxidative aging of rubbers [9,10].

Recently, it has been reported that rare earth complexes show great scavenging effects on free radicals and have strong protective ability in the process of thermo-oxidative aging of polymer composites owing to the large number of unoccupied orbits of rare earth ions [11–18]. Xie prepared a series of rare-earth complexes with 2-mercaptobenzimidazole and the results revealed that those complexes have remarkable effect in binding and inactivating the oxy radicals to discontinue autocatalytic chain reactions and retard

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the aging process of natural rubber (NR) vulcanizates [11,12]. Luo and co-workers declared that the addition of neodymium stearate (NdSt) prominently improves the thermal and thermo-oxidative stability of epoxidized natural rubber (ENR25) vulcanizates because the unoccupied orbits in rare earth Nd can capture the free radicals and stabilize the epoxide groups [13]. Zhong found that the vitamin C-lanthanum complex (VC-La) can offer SBR/silica composites with more comprehensive protection against aging than some commercial antioxidants due to the scavenging effect of rare earth ions on free radicals [14]. Moreover, some researchers demonstrated that many kinds of lanthanum complexes presented a significantly improvement of stabilization efficiency for polyvinyl chloride (PVC) at high temperature in air [15–17]. In summary, coordination compounds consisting of rare earth metals and certain organic ligands containing O, S and N atoms could provide excellent protective effects to restrain the process of thermo-oxidative aging of polymer composites [18,19]. On the other hand, it has been proved that sulfur compounds, such as metal dithiocarbamates, can effectively decompose the hydroperoxide generated from the oxidation degradation of rubber to inhibit the autocatalytic, free radical chain reactions [20,21].

Therefore, rare earth complex composed of samarium (Sm) and dithiocarbamate are expected to have good thermo-oxidative aging resistance due to the presence of dithiocarboxyl groups and Sm ions. In present work, a novel rare earth complex, samarium lysine dithiocarbamate (Sm-LDC), was prepared in our laboratory. The effect of Sm-LDC on the thermo-oxidative aging resistance of SBR/silica composites was systematically investigated by differential scanning calorimetry (DSC), accelerated thermal-oxidative aging tests, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) and thermo-gravimetric analysis (TGA) to obtain some insight into the anti-oxidative mechanisms of Sm-LDC. Besides, the discoloration of SBR/silica composites with Sm-LDC was also studied by whiteness and yellowness index (*Y.I.*) analysis in comparison to some commercial antioxidants.

2. Experimental

2.1. Materials

The rare-earth complex, samarium lysine dithiocarbamate (Sm-LDC), was prepared according to our previous work [22] and dried in a vacuum oven overnight at 40 °C before use. The structural formula of Sm-LDC was shown in Fig. 1. Styrene-butadiene rubber with styrene content 23.5 wt% (SBR-1502), precipitated silica and rubber ingredients such as zinc oxide (ZnO), stearic acid (SA), *N-tert*-butyl-benzothiazole-2-sulphenamide (NS), 2,2′-dibenzothiazole disulfide (DM), *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (antioxidant 4010NA), 2-mercaptobenzimidazole (antioxidant MB), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (antioxidant RD) and sulfur (S) were generously donated by Dongguan First Rubber & Plastic Technology Co. Ltd, Guangdong, China. All the rubber additives were commercial grade and used as received.

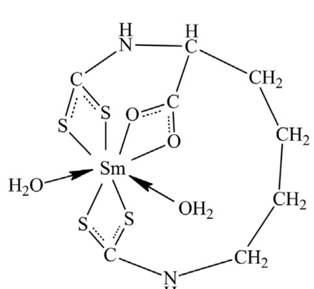

Fig. 1. The structural formula of Sm-LDC.

2.2. Preparation of SBR/silica composites

The composition of SBR/silica composites was as follows (phr, parts per hundred of rubber): SBR, 100; silica, 30; ZnO, 5; SA, 2; NS, 2; DM, 0.5; antioxidant, 2 and S, 2. The sample names appearing in the figures and tables of this article represent the SBR/silica composites with different kinds of antioxidants. For example, the sample name “MB” represents SBR/silica composites with antioxidant MB, and the sample name “Blank” represents SBR/silica composites without antioxidant. To obtain the sheets of SBR/silica composites, SBR and silica were first compounded with rubber additives in the order of ZnO, SA, antioxidant, NS, DM and S under 10 min in an open mill at room temperature, and then the SBR compounds were placed at room temperature overnight. Finally, SBR compounds were vulcanized in an electrically heated press (Ke Sheng Industrial Co. LTD., Dongguan, China) at 160 °C for the optimum cure time (T_{90}) previously determined by U-CAN UR-2030SD Oscillating Disc Rheometer (ODR) instrument.

2.3. Preparation of silica/antioxidant model compounds

To study the effect of silica on the thermo-stability of antioxidants during the rubber vulcanization more clearly, the antioxidants and silica powders were employed to prepare the silica/antioxidant model compounds. The samples of silica/antioxidant model compounds were prepared by a vulcanizing press machine (Ke Sheng Industrial Co. LTD., Dongguan, China) at a setting time of 15 min under 160 °C using the mixture of antioxidant and silica powders.

2.4. Characterization

2.4.1. Oxidation induction time (OIT) test

The determination of oxidation induction time (OIT) was conducted with a TA Q20 Differential Scanning Calorimetry (DSC) Instruments according to the standard method (ISO 11357-6, 2008), which specified the gas flow and temperature ramping. The method used for the measurement is as follows: Firstly, the sample was held at 30 °C for 5 min with a nitrogen flow of 50 mL/min. Subsequently, the sample was heated to 180 °C at a rate of 20 °C/min under the nitrogen flow. When the sample was held for another 5 min, the gas was switched to oxygen at a flow rate of 50 mL/min. The oxidation of the sample was observed as a sharp increase in heat flow due to the exothermic nature of the oxidation reaction. The OIT was equal to the time interval from the initiation of oxygen flow to the onset point of exothermic peak. In order to ensure the accuracy of measurement, the onset point of exothermic peak was obtained by the analysis software of TA instruments.

2.4.2. Accelerated thermal-oxidative aging test

Accelerated thermo-oxidative aging test of rubber dumbbell samples was performed in an air-circulating oven from U-CAN Corporation at 100 °C following ASTM D 573. Tensile strength and elongation at break of the SBR/silica composites before and after aging were measured by a U-CAN electron tensile testing machine (U-CAN 2080) following ASTM D 412. Five tests of each sample were performed and the results were the statistical average of these five tests. The mechanical property retentions after aging were calculated according to the following equations: