



Synthesis and antioxidative properties in natural rubber of novel macromolecular hindered phenol antioxidants containing thioether and urethane groups



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ABSTRACT

Two novel macromolecular hindered phenol antioxidants containing thioether and urethane groups were synthesized by the combination of thiol-acrylate Michael addition and nucleophilic addition. First, a hindered phenol with hydroxyl (GM-ME) was synthesized by Michael addition between 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylphenyl) methyl-4-methylp-henyl acrylate (GM) and 2-mercaptoethanol (ME). Then macromolecular antioxidants GM-ME-IPDI and GM-ME-TDI were obtained after GM-ME reacted with isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI), respectively. The structures of the macromolecular antioxidants were confirmed by FT-IR, ¹H NMR and MALDI-TOF-MS. TG analysis showed that the thermal stability of the GM-ME-IPDI and GM-ME-TDI were higher than that of the GM. The oxidation induction time (OIT) and accelerated thermal aging tests of natural rubber vulcanizates showed that the thioether and urethane groups of GM-ME-IPDI and GM-ME-TDI played an important role in improving antioxidative efficiency. In addition, it was found that the urethane group connected with benzene ring had better antioxidative ability than that connected with alicyclic ring.

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1. Introduction

To improve the aging resistance of polymers, antioxidant is an essential additive, especially for rubber materials which contain a number of C=C unsaturated bonds [1–3]. However, most antioxidants are the compounds with low molecular weight, and easily migrate to the surrounding media during polymer processing and long-term service, which leads to the decrease of antioxidative efficiency and the pollution of surrounding environment, especially in packaging materials for food and medicine [4–7].

In order to overcome the problem, two important ways have been developed. One way is to immobilize reactive antioxidants onto solid supports, such as silica, carbon nanotube [8–15]. It not only can obviously improve the extraction resistance of the obtained antioxidant, but also increase the reinforcing effect of solid supports for the polymer. For example, Gao et al. [15] prepared a nanosilica-immobilized antioxidant (AO-AEAPS-silica) using aminosilane coupling (AEAPS) and reactive antioxidant 3,5-di-tert-

butyl-4-hydroxycinnamic acyl chloride (AO-Cl) as bridging agent and functional monomer, respectively. It was found that the antioxidative efficiency and water extraction resistance of AO-AEAPS-silica were higher than those of the corresponding low molecular counterpart (AO) under the same molar concentration of the phenolic moiety, and its dispersion state of AO-AEAPS-silica in polyethylene was better than neat nanosilica. However, compared with the organic antioxidant, there is some aggregation of AO-AEAPS-silica, which may have an adverse effect on the antioxidative property.

Another way is to prepare macromolecular antioxidants, which are usually obtained by radical polymerization of hindered phenol containing vinyl group or grafting reactive antioxidants onto polymer chain. The previous reports showed that the macromolecular antioxidants own excellent migration and extraction resistances due to the high molecular weight [16–24]. However, the content of antioxidative moiety of obtained macromolecular antioxidant is relatively low due to the introduction of polymer chain, resulting in low antioxidative efficiency. To improve the antioxidative efficiency, it is wise to prepare macromolecular hindered phenol antioxidant containing secondary antioxidative groups (thioether and phosphites) [25–28]. In addition, the structure of

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macromolecular antioxidant, such as molecular weight, distribution of antioxidative group, is difficult to control by radical reaction. Therefore, a new method to prepare macromolecular antioxidant is urgently required.

Thiol-acrylate Michael addition has desirable features, such as mild reaction conditions, simple reaction process, high selectivity and efficiency [29,30]. More importantly, the thioether, a secondary antioxidative group owning a good synergistic effect with hindered phenol [28], can be introduced into the obtained compound. In addition, reaction between –OH group and –NCO group to prepare macromolecular antioxidant is attractive because it is not affected by antioxidative group and easy to obtain products with controllable structure. With the above considerations, two novel macromolecular hindered phenol antioxidants with thioether and urethane groups were synthesized by the combination of thiol-acrylate Michael addition and nucleophilic addition in this study. First, a hindered phenol with hydroxyl group (GM-ME) was obtained by thiol-acrylate Michael addition between 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylphenyl) methyl-4-methylphenyl acrylate (GM) and 2-mercaptoethanol (ME), then two macromolecular hindered phenol antioxidants with thioether and urethane groups, GM-ME-IPDI and GM-ME-TDI, were obtained after GM-ME reacted with isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI), respectively. Their structures were characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (^1H NMR) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). In addition, antioxidative abilities of the GM-ME-IPDI and GM-ME-TDI in natural rubber (NR) were evaluated by accelerated thermal aging and oxidation induction time (OIT) tests, and their possible antioxidative mechanisms during NR degradation were also proposed.

2. Experimental

2.1. Materials

2-Tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylphenyl) methyl-4-methylphenyl acrylate (GM) was kindly donated by Guangzhou Research Institute of Synthetic Material, China. 2-Mercaptoethanol (ME) and toluene diisocyanate (TDI) were purchased from Chengdu Gray West Chemistry Technology Co. Ltd., China. Isophorone diisocyanate (IPDI) was obtained from BASF Co. Ltd., Germany. Dibutyltin dilaurate (DBTDL) was purchased from GE Co., USA. Triethylamine (TEA) and toluene were obtained from Guangzhou Chemical Reagent Factory, China, and dried by 4A molecular sieves for two weeks before use. Natural rubber (NR, SCR5) was supplied by Hainan Natural Rubber Co. Ltd., China. Zinc oxide (ZnO), stearic acid, sulphur, N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), dibenzothiazyl disulfide (MBTS) and calcium carbonate were supplied by Guangzhou Longsun Technology Co. Ltd., China.

2.2. Synthesis of macromolecular hindered phenol antioxidant

The synthetic methods of the hindered phenol with alcoholic hydroxyl (GM-ME) and two macromolecular hindered phenol antioxidants containing thioether and urethane groups (GM-ME-IPDI, GM-ME-TDI) are described below. The chemical structures and synthetic routes of GM-ME, GM-ME-IPDI and GM-ME-TDI are showed in Fig. 1. All the processes were carried out in nitrogen atmosphere.

2.2.1. GM-ME

2-Tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylphenyl) methyl-4-methylphenyl acrylate (7.9 g, 0.02 mol) and 2-

mercaptoethanol (3.12 g, 0.04 mol) were dissolved in 50 g toluene. A solution of triethylamine (0.081 g, 0.8 mmol) as catalyst in 10 g toluene was added dropwise to the above solution at 50 °C. The mixture was kept stirring for 5 h, and then purified by rotary evaporation under reduced pressure at 90 °C for the removal of solvent, catalyst and excess 2-mercaptoethanol. After cooled to room temperature, white GM-ME was collected.

2.2.2. GM-ME-IPDI

GM-ME (4.73 g, 0.01 mol) and isophorone diisocyanate (1.11 g, 0.005 mol) were dissolved in 20 g toluene. A solution of dibutyltin dilaurate (0.63 g, 0.1 mmol) as catalyst in 10 g toluene was added dropwise to the above solution at 60 °C. The mixture was kept stirring for 5 h. Then white powder of GM-ME-IPDI was obtained after the removal of solvent by rotary evaporation under reduced pressure at 70 °C and dried in vacuum at 70 °C for 8 h.

2.2.3. GM-ME-TDI

GM-ME (4.73 g, 0.01 mol) and toluene diisocyanate (0.87 g, 0.005 mol) were dissolved in 20 g toluene. A solution of dibutyltin dilaurate (0.63 g, 0.1 mmol) in 10 g toluene was added dropwise to the above solution at 50 °C. The mixture was kept stirring for 4 h. Then white powder of GM-ME-TDI was obtained after purification as described in Section 2.2.2.

2.3. Preparation of NR vulcanizates

NR vulcanizates were prepared by mixing NR with the other ingredients via a two-roll mill (XK-168, Dongguan Lina Machinery Industrial Co., Ltd., China). First, NR was passed through the roller eight times with a nip gap of about 0.5 mm, and then the compounds were obtained after the other ingredients including stearic acid, ZnO, antioxidant, CBS, MBTS, calcium carbonate and sulphur were added into the NR by the conventional method. After the compounds were left for 24 h at room temperature, they were cured at 143 °C for optimum curing time (t_{90}) which was obtained using a rheometer (MR-C3, Ruidayuchen Co. Ltd., China). The formulations of the NR vulcanizates are given in Table 1.

2.4. Characterization

Fourier transform infrared (FT-IR) spectrum was recorded by a Bruker Tensor 27 spectrometer (Germany) in the range of 4000–400 cm^{-1} . Proton nuclear magnetic resonance (^1H NMR) spectrum was obtained in a Bruker Avance DMX400 spectrometer (Germany) using CDCl_3 as solvent and tetramethylsilane as internal standard. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis was performed on a Bruker-Autoflex III Smartbeam by using polystyrene as the internal standard, 2,5-dihydroxybenzoic acid as matrix, sodium iodide as cationizing agent. Thermal gravimetric analysis (TGA) was carried out on a TG 209 F3 thermogravimeter (Netzsch, Germany) from 30 to 800 °C at a heating rate of 20 °C min^{-1} under air atmosphere.

2.5. Oxidation induction time (OIT) test

The OIT measurement was performed on a TA Q20 DSC (TA Instrument, USA) according to the standard method (ISO 11357-6, 2008). The samples were first held at 60 °C for 3 min with a nitrogen flow of 50 mL min^{-1} . Subsequently, the samples were heated to 170 °C at a rate of 20 °C min^{-1} . After reaching 170 °C, the samples were held for another 3 min. At this point, the gas was switched to oxygen at a flow rate of 50 mL min^{-1} . The oxidation of the samples were observed as a sharp increase in heat flow due to the

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