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Full Length Article

Enhanced interfacial interaction and antioxidative behavior of novel halloysite nanotubes/silica hybrid supported antioxidant in styrene-butadiene rubber

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A novel antioxidant (HS-s-RT) to improve the mechanical properties and anti-aging performance of styrene-butadiene (SBR) composites was prepared by antioxidant intermediate p-aminodiphenylamine (RT) grafting on the surface of halloysite nanotubes/silica hybrid (HS) via the linkage of silane coupling agent. The analysis of SEM and rubber processing analyzer (RPA) demonstrated HS-s-RT was uniformly dispersed in SBR, and stronger interfacial interaction between HS-s-RT and SBR was formed. Consequently, SBR/HS-s-RT composites have improving mechanical properties. Furthermore, the test of the retention of mechanical properties, Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR), and oxidation induction time (OIT) showed HS-s-RT can effectively improve the anti-aging effect of SBR composites than corresponding low molecular-weight antioxidant N-isopropyl-N′-phenyl-4-phenylenediamin (4010NA). Then, the mechanism of thermo-oxidative aging of SBR/HS composites was also investigated, and the superior antioxidative efficiency is attributed to the uniform dispersion and excellent migration resistance of HS-s-RT. Hence, this novel antioxidant might open up new opportunities for the fabrication of high-performance rubber composites due to its superior anti-aging effect and reinforcement.

1. Introduction

Elastomers with high extensibility, excellent insulation, super water and gas blocking performances, and abundant sources have been widely used for the production of large quantities in the industrial fields, such as the automobile, aviation, navigation and so forth [1–3]. However, elastomers, especially with unsaturated carbon–carbon bonds like SBR, are easy to oxidize under air, leading to the deterioration of mechanical performance and reduced service life. Until now, elastomers aging remains a noteworthy critical problem for scientific and industrial researchers [4–6]. With the goal of suppressing the aging, antioxidants are always regarded as the most effective additive to protect elastomers from getting sticky, hardening and chalking. Unfortunately, antioxidant is vulnerable to diffusing and migrating towards the surface of elastomers products due to its low molecular weight and easy volatile performance [7–9]. Recently, the idea of supporting rubber additives on the inorganic filler has been largely propagated in rubber industry [10]. Especially, the preparation of novel antioxidants with good migration fastness has attracted a lot of attentions from scientists and researchers [11]. Guo et al. [12] fabricated silica-based immobile antioxidant RT-silica with antioxidant intermediate p-aminodiphenylamine (RT) grafting on silica, revealing that RT-silica possesses better antioxidative and anti-migratory efficiency. Zhong et al. [13] synthesized a novel antioxidant HNTs-s-MB by 2-mercaptobenzimidazole (MB) grafting on the surface of halloysite nanotubes (HNTs) to improve the antioxidative efficiency and mechanical performances of NR composites. Yang et al. [14] prepared a rare-earth complex La-GTDC chemically bond to the SiO_2 particles through hydrogen bonds and coordination bonds, indicating La-GTDC could largely improve mechanical properties and antioxidative effect of SBR/SiO_2 composites. Consequently, grafting antioxidants on the inorganic filler can not only endow elastomers with great excellent anti-aging performance, but also significantly improve the interfacial interaction between filler and polymer matrix.

Besides, as one of the important part of nanocomposites industry, nano hybrid filler/polymer materials have been a popular research topic [15–17]. By means of combing two and more

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traditional filler materials via physical or chemical bonding, nano hybrid fillers are formed and have confirmed their feasibility for utilization in a variety of polymer applications such as rubber and plastic industry [18–20]. A nanoscale hybrid filler comprising single-walled carbon nanotubes and graphite nano platelets was reported to provide a synergistic effect in the enhancement of thermal conductivity of epoxy composites [21]. Kumar et al. [22] fabricated a new hybrid structure of filler through multi-walled carbon nanotubes (MWCNTs) decorated by TiO_2 nanoparticles, which significantly improved the dispersion of MWCNTs in the epoxy matrix. In recent years, HNTs with large length-diameter ratio and nano-tubular structures has been served as reinforced fillers and sustained release carrier for drugs, catalyst in many fields [23–25]. However, owing to the smooth surface of HNTs, the poor engagement between HNTs and matrix remains intricate problem [26,27]. In our previous work, a novel kind of nano hybrid HNTs-g-Silica (HS) has been prepared by the methods of electrostatic self-assembly and in-situ growth of silica particles on HNTs surface [28,29]. It has been found that the rough surface and large specific area could improve the dispersion of HS and the interfacial interaction between HS and unsaturated polyester resin. Significantly, HS would be a promising functionalized filler candidate due to the abundant active hydroxyl and rigid surface of HS, which makes it possible to chemically supporting polymer addictives. To our best knowledge, HS grafted aromatic amine as immobilized antioxidant has never been employed in SBR.

Herein, RT was used as an interfacial modifier for the nano hybrid (HS) and novel immobilized antioxidant (HS-s-RT) was formed. The effect of HS-s-RT on the mechanical properties and anti-aging efficiency for SBR composites were fully investigated. The uniform dispersion of HS-s-RT and enhanced interfacial interaction between HS-s-RT and SBR gave a rise to mechanical properties for composites. Besides, HS-s-RT showed excellent thermal oxidative stability and superior anti-aging efficiency for SBR composites by comparison with low molecular-weight 4010NA.

2. Experiment

2.1. Materials

SBR (1502) was offered by Guangzhou Institute of Rubber Products. Halloysite nanotubes (HNTs) were purchased from Henan, China and purified according to the relevant method [30]. N-isopropyl-N′-phenyl-p-phenylenediamine (4010NA), Zinc oxide (ZnO), Stearic acid (SA), 4-aminodiphenylamine (RT), accelerator N-cyclo-hexylbenzothiazole-2-sulphenamide (CZ), and insoluble sulfur (S) were industry grade products and used as received. γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH-560) was produced by Sinopharm chemical reagent Co., Ltd., China. Tetraethoxysilane (TEOS) and absolute ethanol were analytical reagent supplied by Damao Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Preparation of HS and HS-s-RT

HS was synthesized by the sol–gel method according to our previous study [29]. The preparation of HS-s-RT is illustrated in Fig. 1. Typically, 10 g of HS powder was scattered in 350 ml of absolute ethanol and pre-treated for 15 min by ultrasonic disperser. Then 2 g of KH-560 was added into the suspension and stirred for 4 h at 90 °C. The product was filtered and washed with absolute ethanol. The modified HS (m-HS) was dried in a vacuum oven at 70 °C for 24 h.

2.0 g of RT and obtained m-HS (10 g) were added into 350 ml of absolute ethanol and stirred for 8 h at 70 °C. The products were washed by absolute ethanol to remove any un-reacted RT and dried in a vacuum oven at 70 °C to get the sample (HS-s-RT).

2.3. Preparation of SBR/HS composites

The composition of all rubber compounds is summarized in Table 1. The content of 4010NA was determined by the residues

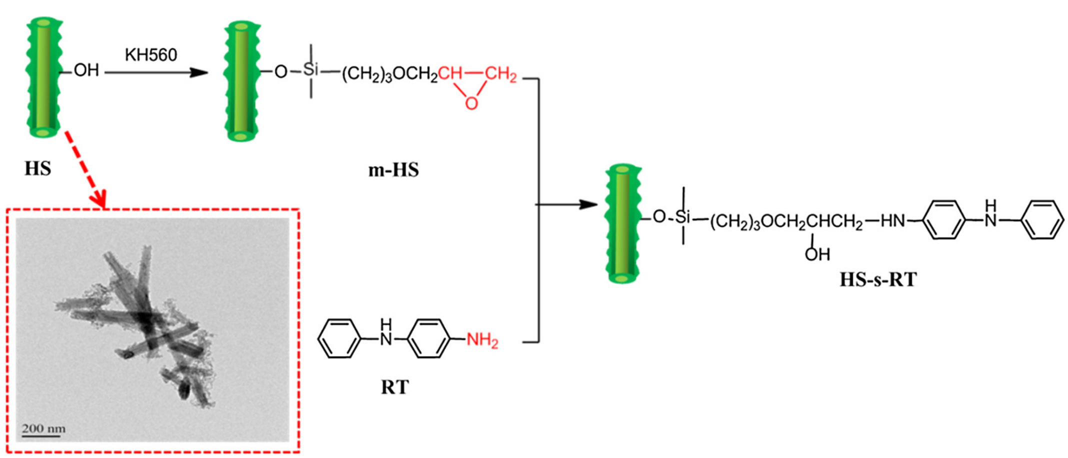

Fig. 1. Synthesis route of HS-s-RT.

Table 1
Composition of SBR/HS composites.

Samples	Component (phr)						
	SBR	Filler	ZnO	SA	4010NA	CZ	S
SBR	50	–	2.5	1	–	1	0.8
SBR/HS/4010NA	50	15(HS)	2.5	1	0.15	1	0.8
SBR/m-HS/4010NA	50	15(m-HS)	2.5	1	0.15	1	0.8
SBR/HS-s-RT	50	15(HS-s-RT)	2.5	1	–	1	0.8