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Effect and mechanism of iron oxide modified carbon nanotubes on thermal oxidative stability of silicone rubber

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ABSTRACT

To investigate the effects of iron (III) oxide attached on carbon nanotubes (CNTs) surface on the thermal oxidative stability of silicone rubber (SR), a series of iron oxide modified carbon nanotubes (γ-Fe_2O_3–CNTs) with different sizes or loadings of γ-Fe_2O_3 were prepared. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were performed to characterize the additives; by comparing the mechanical properties of SR composites after aging, the optimal experimental group was obtained. Besides, the action mechanism of γ-Fe_2O_3–CNTs on the thermal oxidative degradation of SR composite was studied by measuring the average molecular weight between crosslinking points (M_c) of SR before and after aging, as well as by detecting the degradation products of SR by thermogravimetric analysis/infrared spectrometry (TG–IR). The results indicated that γ-Fe_2O_3–CNTs could not only increase the initial formation temperatures of degradation products, but also decrease the concentrations of products from the oxidation and fracture of side chains of SR. All the above influences contributed to the improvement of the thermal oxidative stability of SR.

1. Introduction

Silicone rubber (SR) as one of the most important synthetic rubbers is known to exhibit excellent thermal oxidative stability over conventional carbon backbone rubbers [1,2], which can be ascribed to its special structure, such as high bond energy (443.7 kJ/mol) and high ionic character (about 51%) of Si–O bonds [3]. With the rapid development of science and technology, a demand for high performance silicone elastomer, especially for thermal resistant SR, has increased greatly [4,5]. In many researches, the thermal oxidative degradation of SR has been proposed following two-competing mechanisms: the molecular mechanism takes place with formation of cyclic oligomers, which can lead to loss of crosslink density if the cyclic fragments contain a long segment of the polymer backbone; and the radical mechanism occurs on Si–CH_3 side chains including oxidation and bonds scission, which is accompanied by crosslinking reactions with subsequent gelation [6–9].

In the past several decades, lots of methods have been taken to improve the thermal oxidative stability of SR [10–12]. Among them, adding thermal resistant additives is the most convenient and effective one. As a traditional and useful thermal resistant additive for SR, iron oxide has been widely investigated. Related researches indicated that the improved thermal oxidative stability of iron oxide/SR composite might be attributed to the following two aspects. One was the bonding of rubber chains to the surface of iron oxide particles, which prevented the formation of volatile oligomers and added stabilizing crosslinkings to the network [13]. The other was the formation of stable complexes between iron oxide and the reaction center of siloxane molecules, as well as by radical elimination coupled to Fe^{3+} reduction [14]. Except for iron oxide, carbon nanotubes (CNTs) have also attracted enormous attention since the discovery in 1991 [15–17]. Due to their strong radical accepting capacity, CNTs may interrupt chain propagation, leading to antioxidant effects in polymeric materials [18]. Shen et al. considered that CNTs in the composite acted as radical scavengers, delaying the onset of thermal degradation and hence improving the thermal stability of the polymers [19].

As an important CNTs modification method, metal oxides modified CNTs, especially iron oxide modified CNTs, are extensively investigated and reported by scientists [20,21]. In our previous research [14], we had found the presence of CNTs affected the crystalline form of attaching Fe_2O_3, which was changed from α to γ. When Fe_2O_3 modified CNTs (γ-Fe_2O_3–CNTs) were added into SR matrix, they could remarkably improve the mechanical properties of SR based composite after thermal oxidative aging; at the same addition amount, their effect was superior to CNTs, γ-Fe_2O_3, or a mixture of both. This phenomenon may be attributed to the

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synergistic effect of γ-Fe_2O_3 and CNTs. However, how to make the synergistic effect maximum and what the roles of γ-Fe_2O_3–CNTs play during the thermal oxidative degradation process of SR deserve to research deeply.

In this paper, by regulating the process of sol–gel reaction, a series of γ-Fe_2O_3–CNTs with different sizes or loadings of γ-Fe_2O_3 were prepared. Comparing the mechanical properties of SR composites after aging, the optimal experimental group was obtained with the maximum synergistic effect of γ-Fe_2O_3 and CNTs. In addition, thermogravimetric analysis/infrared spectrometry (TG–IR) was used to investigate the thermal oxidative degradation products of SR composites.

2. Experimental

2.1. Materials

Methylvinyl silicone gum (110-2; Mn, 5.0×10^5–7.0×10^5; vinyl group content, 0.15–0.18 mol%) was purchased from Bluestar Chengrand Chemical Co., Ltd. (Chengdu, China). Carboxylic CNTs (carboxyl ratio, 2.31 wt%; purity, >95%; diameter, 20–40 nm; length, 1–2 μm) were purchased from Shenzhen Nanotech Port Co., Ltd., China. Fumed silica (AS-380) was purchased from Shenyang Chemical Co., Ltd. (China). Hexamethyldisilazane, 2,5-bis(tertbutylperoxy)-2,5-dimethylhexane (DBPMH) and polyvinylsiloxane were all industrial products, and used as obtained. Other reagents were all of analytical reagents, and used as obtained.

2.2. Preparation of γ-Fe_2O_3–CNTs

The detailed fabrication of γ-Fe_2O_3–CNTs was carried out as described previously [14]. $Fe(NO_3)_3{\cdot}9H_2O$ was added into 200 ml of absolute ethanol and stirred until it was dissolved completely. This solution was added by 0.35 g of carboxylic CNTs, stirred, and sonicated for 3 h. Then surfactant sodium dodecylbenzenesulfonate (SDBS) was added and stirred, later, ammonia solution was added as a gelation agent and went on stirring. The mixture was filtered and washed by deionized water and then vacuum-dried at 60 °C for 72 h. The calcination of this powder was performed at 600 °C in a muffle furnace under argon atmosphere for 5 h, and then annealed, γ-Fe_2O_3–CNTs was obtained. During this process, the amount of surfactant SDBS and precursor $Fe(NO_3)_3{\cdot}9H_2O$ were adjusted to obtain a series of γ-Fe_2O_3–CNTs with different sizes or loading of γ-Fe_2O_3. The detailed recipes are listed in Table 1.

2.3. Preparation of SR based composites

Materials were milled on a two-roll mill (SR-160B, Guangdong Zhanjiang Machinery Factory, China). 100 phr (parts per hundreds of rubber) of silicone gum was encapsulated onto rollers. 40 phr of fumed silica, 10 phr of hexamethyldisilazane, 2.6 phr of polyvinylsiloxane were mixed in step by step. Then 3 phr of the prepared additives were added respectively. After being milled uniformly, 0.7 phr of DBPMH was added. The mixture was cured in a stainless steel mold at 180 °C under a pressure of 10 MPa for 10 min, and postcured at 200 °C for 4 h under ambient pressure for crosslinking.

2.4. Thermal oxidative aging experiment

The vulcanizates were aged in an air-blowing oven at 300 °C for 12 h.

2.5. Characterization

Transmission electron microscope (TEM, Tecnai G2 F20, Philips) was employed to detect the morphology of additives. The samples were prepared by dropping a sample suspension in ethanol onto a Cu grid coated with a carbon film.

X-ray diffraction (XRD) measurement was performed with a Rigaku DMAX-RC diffractometer (Japan) to determine the crystalline form of Fe_2O_3. Cu Kα radiation ($k = 0.15406$ nm) was used and the scanning rate was 2°/min with a generator voltage of 45 kV and current of 180 mA. XRD peaks were recorded from $2\theta = 20°$ to 80°.

The average molecular weight between crosslinks (M_c) of SR composites was measured by swelling experiment [22]. A certain amount of sample was immersed in 100 ml toluene for 72 h at 30 °C to attain equilibrium swelling, after the equilibrium swelling, the sample was taken out and the solvent was blotted from the surface of the sample and weighted immediately. M_c was calculated by the Flory-French Eq. (1):

$$M_c = \frac{-\rho_2 V_0 \varphi^{1/3}}{[\ln(1-\varphi) + \varphi + \chi\varphi^2]} \quad (1)$$

where V_0 is the molar volume of the solvent; χ is Flory–Huggins interaction parameter between polymer and solvent, here 0.465; φ is the volume fraction of SR in the swelling rubber, which can be obtained through Eq. (2):

$$\varphi = \frac{W_1/\rho_2}{[(W_2 - W_1)/\rho_1 + W_1/\rho_2]} \quad (2)$$

where ρ_1 and ρ_2 are the densities of toluene and SR, respectively; W_1 is the initial weight of SR composite and W_2 is the weight of swollen SR composite.

TG–IR of the samples was performed by a STA449F3 instrument (Netzsch, Germany) that was interfaced to a TENSOR27 FT-IR spectrometer (Bruker, Germany). About 20 mg samples were heated from 30 to 700 °C at a heating rate of 20 °C/min (air atmosphere, flow rate of 100 ml/min). The IR spectra were recorded in the range of 600–4000 cm^{-1} with a resolution factor of 4 cm^{-1} and averaging 16 scans.

The tensile testing of the samples which were dumb-bell shaped test specimens was performed at a crosshead speed of 500 mm/min by using a universal testing machine (M350-20KN, Testometric, UK) at room temperature. The tear testing was performed in the same condition except using right-angled test specimens. Five samples were tested for each composite, and the mean value was applied.

Table 1
Experimental formulation for preparing additives γ-Fe_2O_3–CNTs.

Materials/no.	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
$Fe(NO_3)_3{\cdot}9H_2O$ (g)	1.5	1.5	1.5	1.5	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
CNTs (g)	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
SDBS (g)	0.04	0.08	0.12	0.16	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
$NH_3{\cdot}H_2O$ (mL)	24	24	24	24	64	64	64	64	64	64	64	64