Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 34, No. 2, Feb. 2016, P. 221
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Reinforcement of natural rubber latex with silica modified by cerium oxide: preparation and properties

ZHANG Fuquan (张福全)[1], LIAO Lusheng (廖禄生)[1], WANG Yongzhou (王永周)[1], WANG Yueqiong (汪月琼)[1], HUANG Honghai (黄红海)[1], LI Puwang (李普旺)[1,*], PENG Zheng (彭 政)[1,*], ZENG Rizhong (曾日中)[2]

(1. Chinese Agricultural Ministry Key Laboratory of Tropical Crop Product Processing, Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, China; 2. Agriculture Ministry Key Laboratory of Biology and Genetic Resources of Rubber Tree, Rubber Research Institute, Chinese Academy of Tropical Agricultural Sciences, Danzhou 571731, China)

Received 18 August 2015; revised 25 November 2015

Abstract: Variable masses of nano cerium oxide (CeO_2) were added into nano silica (SiO_2) to prepare the well-dispersed SiO_2-CeO_2 suspension (SiO_2-CeO_2), cetyltrimethyl ammonium bromide (CTAB) was used to adjust the compatibility of SiO_2-CeO_2 with rubber matrix, then SiO_2-CeO_2 modified by CTAB and curing formulas were mixed with fresh natural rubber (NR) latex to prepare NR/SiO_2-CeO_2 nanocomposites that contained 0–10 parts of CeO_2 by a new emulsion compounding method. The morphologies, cure characteristics, mechanical properties and thermal-oxidative stability of NR/SiO_2-CeO_2 nanocomposites were investigated. The results revealed that the presence of CeO_2 in NR/SiO_2-CeO_2 nanocomposites was favorable for enhancing the interaction between NR matrix and fillers, helped to get smaller SiO_2-CeO_2 particles with narrower particle size distribution, further improved the crosslink densities and mechanical properties of NR/SiO_2-CeO_2 nanocomposites vulcanizates. Meanwhile, the addition of CeO_2 increased the active energy at least 4.66%, obviously improved the thermal-oxidative aging-inhibiting properties of NR/SiO_2-CeO_2 nanocomposites. Additionally, nanocomposites containing CeO_2 promoted T_g shift to high temperature direction, causing the nanocomposites featured higher tanδ at 0 ºC and lower tanδ at 60 ºC and exhibited comparable wet grip and lower rolling resistance when NR/SiO_2-CeO_2 nanocomposites were used in tire tread compound.

Keywords: cerium oxide; silica; natural rubber latex; emulsion compound; reinforcement; aging-inhibiting property; glass transition temperature; rare earths

SiO_2 filled non-polar polymer, e.g., NR, offers many advantages, e.g., improvement of mechanical properties[1,2], especially tensile strength and tear strength, also increases the compound adhesion in multi-component products such as tires owing to its nanoscale dimension and high specific surface area. The biggest challenge for silica reinforcement is its strong tendency to agglomerate and poor dispersion in rubber matrix when using dry compounding technology, i.e., through the heterodromous inward rotation of two hollow rollers, forming strong shear force to realize the dispersion of nanofiller in rubber matrix. Therefore, bis-(3-triethoxysilylpropyl) tetrasulfide (Si69) was added during compounding procedure[3,4], which can accelerate the reaction of silica with the polymer chains via participation in the vulcanization reaction or sulfur crosslink process. However, this technology has not been applied successful in NR industrial, especially "Green tire"[5] due to the significantly negative impact on tear resistance and result in substantial deterioration of the cut-chip properties for tires[6]. Additionally, great permanent set, low modulus, bad thermal aging property and poor processing safety are also a couple of outstanding issues that must be solved urgently.

Rare earth compound has particular function in polymer process and applications on account of its special electronic configuration and strong surface activity, for example, improved cross action, accelerated sulfuration reaction, etc. Ultrafine nano CeO_2 powder is a particularly important rare earth material that has been extensively applied in glass, ceramics, catalyst and so on[7–9], because of the high surface-to-volume ratio and quantum-size effect. The study of CeO_2 application in rubber has also been reported. Su et al.[10] reported that the heat stability of silicon rubber increased as filled with CeO_2. Li et al.[11] studied the uniaxial ratchetting behaviour of cerium oxide filled vulcanized natural rubber by cyclic asymmetric stress-controlled experiments, considering that cerium oxide filled vulcanized NR exhibits obvious ratchetting behaviour under cyclic asymmetric loading.

Foundation item: Project supported by the Special Fund for Agro-scientific Research in the Public Interest, Ministry of Agriculture of the People's Republic of China (201403066), Natural Science Foundation of Hainan Province (20155198), and the Fundamental Research Funds for Rubber Research Institute, Chinese Academy of Tropical Agricultural Science (1630022014014)

* **Corresponding authors:** PENG Zheng, LI Puwang (**E-mail:** zpengcatas@126.com, puwangli@163.com; **Tel.:** +86-759-2286933, +86-759-2202603)

DOI: 10.1016/S1002-0721(16)60017-0

The ratchetting strain increases with increase of mean stress or the decrease of stress rate. However, the study is few on the whole.

There has been considerable scientific interest in researches of rubber nanocomposties containing only single filler, relatively little attention is paid to the rubber nanocomposites containing binary even more types of fillers. The nano CeO_2 particles coated on surface of fillers should be active due to its nanoscale dimension and surface property and reactivity. In this article, nano CeO_2 modified SiO_2 filled NR was prepared using a new emulsion compounding method. The morphology, cure characteristic, mechanical property and thermal-oxidative stability of nanocomposites were studied in this work.

1 Experimental

1.1 Materials

$Ce(NO_3)_3·6H_2O$ (ΣREO≥99.95%), 20–50 nm, and CTAB were purchased from Shanghai Sinopharm Chemical Reagent Company. Fresh natural rubber latex (NRL), the dry rubber content is 26.55%, the ammonia content is 0, supplied by Guangdong Shuguang Farmer, China. SiO_2, AEROSIL VN3, was supplied by EVONIK industries AG. All those above were used the primary starting materials. Other chemical reagents, such as ammonia water ($NH_3·H_2O$), zinc oxide (ZnO), stearic acid, sulfur and accelerator 1,3-diphenylguanidine (DPG) were of commercial grade and used without further purification.

1.2 Sample preparations

(1) SiO_2 (30 g) after being dried at 100 ºC for 2 h in a vacuum oven and distilled water (200 mL) were added into a container, the mixture was conducted under high-shear homogeneous mixing for 15 min to obtain stable SiO_2 emulsion, then SiO_2 emulsion was heated to 100 ºC.

(2) 2.3 mL 0.5 mol/L aqueous $Ce(NO_3)_3·6H_2O$ and 0.5 g hot CTAB were simultaneously added into SiO_2 emulsion above, after that, $NH_3·H_2O$ was used to adjust the value of pH to 10, then $Ce(NO_3)_3·6H_2O$ would transform to $Ce(OH)_3$ and coated on surface of SiO_2 particles. The reaction mixture was filtered and the solid were washed with lots of distilled water. The product was dried in vacuum oven and finally ground into fine powder SiO_2-CeO_2.

(3) Powder SiO_2-CeO_2 mentioned above, 6 g ZnO, 2.5 g stearic acid and 2 g DPG were added into 376.65 g NRL with low-shear agitation for 0.5 h to form NRL/SiO_2-CeO_2 mixture, 1.5 g sulfur was added into NRL/SiO_2-CeO_2 mixture under stirring followed, then the mixture was extremely slowly poured into self-made glass plate with volume of 25 mm×20 mm×2 mm without bubble, horizontally placed at room temperature to obtain coagulated NR/SiO_2-CeO_2 sheets. The sheets were finally conducted in an electric constant temperature drying oven at 70 ºC for 6 h. Thus, the NR/SiO_2-CeO_2 nanocomposite, named 30/0.5, was obtained which actually contained 30 parts by weight (phr) SiO_2, 0.5 phr CeO_2, 6 phr ZnO, 2.5 phr stearic acid, 2 phr DPG, 1.5 phr sulfur relative to 100 phr of NR.

The samples, named 30/0, 30/1, 30/3, 30/5 and 30/10 were also prepared according to the steps above. The differences between samples were the variable volume of aqueous $Ce(NO_3)_3·6H_2O$ added in step (2).

1.3 Characterizations

The crosslink density was tested using an equilibrium swelling measurement by help of Flory-Rehner equation[12]. The samples were cut into dimensions of approximately 1 cm×1 cm×2 mm, and were swollen in toluene. The samples were weighted (W_b, g), and then swollen up to equilibrium at room temperature for 48 h. Then excess surface liqiud was removed from the swollen samles by "pat drying" quickly. The samples were weighed (W_a, g) immediately and dried in an oven to remove all the solvent and reweighed (W_d, g). The calculation of volume fraction of rubber in the swollen gel (φ_r, %) is given by Eq. (1),

$$\varphi_r = \frac{W_b\varphi\dfrac{1-\alpha}{\rho_r}}{W_b\varphi\dfrac{1-\alpha}{\rho_r}+\dfrac{W_a-W_d}{\rho_s}} \quad (1)$$

where, φ (%) is the weight fraction of actual rubber in crosslinked sheet, α (%) is the weight loss of the rubber during swelling, ρ_s (g/cm^3) is the density of the solvent (toluene: ρ_s = 0.872 g/cm^3), ρ_r (g/cm^3) is the density of the rubber (NR: 0.92 g/cm^3).

After φ_r was determined, the network chain density (n_{sw}, mol/cm^3), often loosely referred to as crosslink density, was calculated using the modified Flory-Rehner equation based upon the phantom model[13] as expressed by Eq. (2),

$$n_{sw} = \frac{1}{M_c} = -\frac{\ln(1-\varphi_r)+\varphi_r+\chi\varphi_r^2}{\rho_r\varphi_s\left(1-2/f\right)\varphi_r^{1/3}} \quad (2)$$

where, M_c (g/mol) is the network chain molecular weight, χ is the solvent-rubber interation, φ_s (cm^3/mol) is the molar volume of the solvent (toluene: 106.2 cm^3/mol), f=4, the functionality of the crosslinks.

Curing property, accurately weigh 4.8 g sample, was tested using an MDR2000 Rheometer at 70 ºC.

The mechanical property measurement was performed with an Instron IX3365 Universal materials testing machine according to GB/T 528-2009 (equal to ISO 37: 2005).

Dynamic mechanical property was measured over a German NETZSCH 242C dynamic mechanical analyzer (DMA). The testing was carried out at tension condition under temperature rising rate of 5 ºC/min ranging from