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Prevention of oxide aging acceleration by nano-dispersed clay in styrene-butadiene rubber matrix

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ABSTRACT

In order to minimize the oxidative degradation of SBR at high temperature, the nano-dispersed clay layers were introduced by using the SBR/clay (100/80) nanocompound to prepare SBR/clay/carbon black (CB) nanocomposites, then the effects of nano-clay on the properties of SBR nanocomposites are investigated. The clay layers and CB are uniformly dispersed in the SBR matrix at nano-scale. The mechanical properties of the SBR/clay/CB nanocomposites mostly decrease with the increase of clay loading, however, with the increase of clay loading, the change rate of the mechanical properties of the nanocomposites decreases and the aging coefficient of the nanocomposites rises, and the length and depth of the cracks of the aged nanocomposites after bending decrease, which means that the clay layers can provide the nanocomposites excellent thermal aging resistance and heat resistance. The experiment of aging with air and without air proved the importance of oxygen during rubber aging process. The FTIR spectra show the generation of oxygen-containing group on the external surface of the nanocomposites during aging. The DSC results indicate the differences between the internal layer and the external layer of the aged nanocomposites.

1. Introduction

In recent year, it has been found that clay filled polymer composites often exhibit remarkable improvement of mechanical, thermal and physicochemical properties when compared with pure polymer and their conventional microcomposites [1–7]. The clay mostly used is montmorillonite (MMT) which is composed of regular staking of two-dimensional plate like layers bound together with weak inter-atomic forces and belongs to the general family of 2:1 layered silicates. These layered silicates have attracted great attention of researchers because of their low cost, abundance and high aspect ratio. Nevertheless, exploiting more excellent properties of the polymer/clay nanocomposites and find out optimum application fields is of great importance, which could speed up the development and application of the nanocomposites.

Oxidative aging of rubber is one of the most serious problems in rubber industry because the absorption of a small amount of oxygen causes considerable deterioration in the physicomechanical properties of rubber [8]. Depending on the structure of rubber materials, the deterioration leads to chain scission, crosslinking or formation of oxygen containing functional groups in the polymer chain or as degradation products [9]. The aging process involves the oxidation of rubber chains by molecular oxygen in a free radical process which can be catalyzed by oxygen, ozone, heat, or mechanical stress, etc. Fortunately, several reports have shown that presence of nanoclay improves the thermal property of polymer [10–16]. Bhowmick et al. have done extensive work to improve the thermal stability of polymers like polybutadiene rubber (BR), acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), fluoroelastomer (FKM), and hydrogenated nitrile rubber (HNBR) by using different types of nanoclay [17–20]. Lewicki et al. investigated the aging behavior of polysiloxane/clay nanocomposites by degradative thermal analysis, and found that a more thermodynamically stable polymer-filler network was formed [21]. Chen et al. found that the coexistence of clay and carbon nanotube could form compact char layers with better barrier property thus

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improved the thermal stability of HNBR [22]. Most of the studies believed that the formation of rubber/clay nanocomposite affects the thermal behavior of the matrix because well dispersed nanofillers result in the modification of their degradation pathways. However, very few studies have reported the optimum application fields of the rubber/clay nanocomposites.

The heat-resisting conveyer belt is widely used in industry for transporting high-temperature and heavy materials, such as sintering ore, concrete clinker, limestone, inorganic fertilizer, and so on. It is comprised of a thermally stable skeleton layer and a heat-resistant rubber cover. For the rubber cover materials, there exists a very serious problem which is aging and degradation during the long-term application, especially in harsh conditions. It is noteworthy that the materials transported on the heat-resisting conveyor belt during the production are very hot, 400–600 °C in general, or more than 800 °C in extreme cases. Therefore, the heat-resisting conveyor belt should be long-term served at the temperature of around 100 °C, and require very good mechanical properties, outstanding aging resistance, and especially excellent heat-resistance. Styrene butadiene rubber (SBR) [23] is a general-purpose synthetic rubber with high filler loading capacity; good flex resistance, crack-initiation resistance and abrasion resistance, which make it a candidate for heat-resisting conveyer belt. However, like other unsaturated rubbers, it is highly susceptible to degradation due to the presence of double bonds in the main chain.

In this paper, in order to minimize the oxidative degradation of SBR during the operation at high temperature, the nano-dispersed clay layers were introduced to the SBR matrix, and clay filled SBR nanocomposites combined with carbon black (CB) were developed. The effects of clay and CB on the properties of SBR were evaluated, including mechanical properties, thermal aging property and the resistance to high temperature aging, and then the mechanism of the good resistance to high temperature aging via introducing nano-dispersed clay layers to rubber matrix was proposed by virtue of FTIR and DSC characterization. We believe that the SBR/clay/CB nanocomposites were good candidate for the heat-resisting conveyer belt.

2. Experimental

2.1. Materials

SBR1502 was purchased from Jilin Rubber Co. Ltd., Jilin Province, China. SBR latex (with 23% styrene and 22.4% solid content) was supplied by Jilin Petrochemical, China. Clay (sodium-montmorilionite) with cation exchange capacity of 93 meq./100 g was supplied by Liufangzi Clay Factory, Jilin, China. CB (N330) was obtained from Tianjin Haitun Co. Ltd., China. Other ingredients were purchased from the chemical reagent shop of Beijing.

Table 1
Formulations of the SBR compound.

Ingredients	Amount (phr[a])						
	C0	C10	C20	C30	C40	C50	C60
SBR	100	100	100	100	100	100	100
Clay	0	10	20	30	40	50	60
CB	60	50	40	30	20	10	0
Zinc oxide	10	10	10	10	10	10	10
Stearic acid	3	3	3	3	3	3	3
NOBS[b]	0.8	0.8	0.8	0.8	0.8	0.8	0.8
CZ[c]	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DTDM[d]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD[e]	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Antioxidant 4010NA[f]	2	2	2	2	2	2	2

[a] Parts per hundred parts of rubber.
[b] N-oxidiethylene-2-benzothiazolyl sulfonamide.
[c] N-cyclohexyl-2-benzothiazole sulfonamide.
[d] 4′,4′-Dithiobis-morpholine.
[e] Tetramethyl thiuram disulfide.
[f] N-isopropyl-N′-phenyl-p-phenylene dianime.

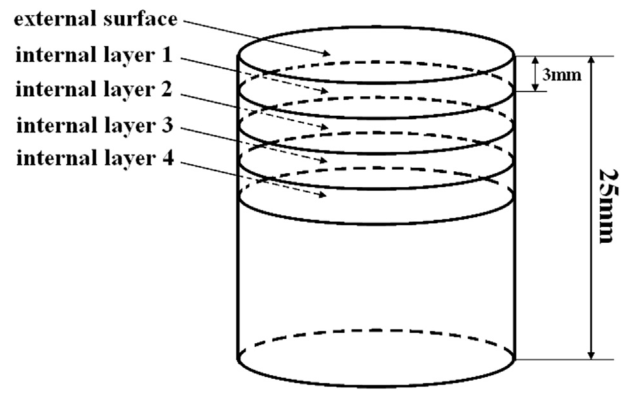

Fig. 1. The cylinder sample and the sampling points.

2.2. Processing and specimen preparation

SBR/clay (100/80) nanocompound was prepared via latex compounding method by Liufangzi Clay Factory, Jilin, China. The clay was first dispersed in deionized water at a concentration of 2% with vigorous stirring until an aqueous suspension of clay was obtained. Then, a given amount of SBR latex was incorporated into the above aqueous suspension and stirred for 20 min. After that, the mixture was slowly poured into the intensively agitated electrolyte solution(1 wt% calcium chloride aqueous solution) for co-coagulating. The co-coagulated compounds were washed with water until neutral, and then dried at 50 °C for 24 h.

CB and other ingredients were mixed into SBR1502 or SBR/clay nanocompound in an open two-roll mill at room temperature, according to the formulations for compounds shown in Table 1. Then the compounds were vulcanized at 150 °C in a standard mould. The vulcanizates were referred to as SBR/clay/CB nanocomposites.

2.3. Characterization

X-ray diffraction (XRD) analyses were carried out using a diffractometer (D/Max-III C, Rigaku, Japan) with CuKα radiation operating at 40 kV and 200 mA, at a scan rate of 1.00° min^{-1}.

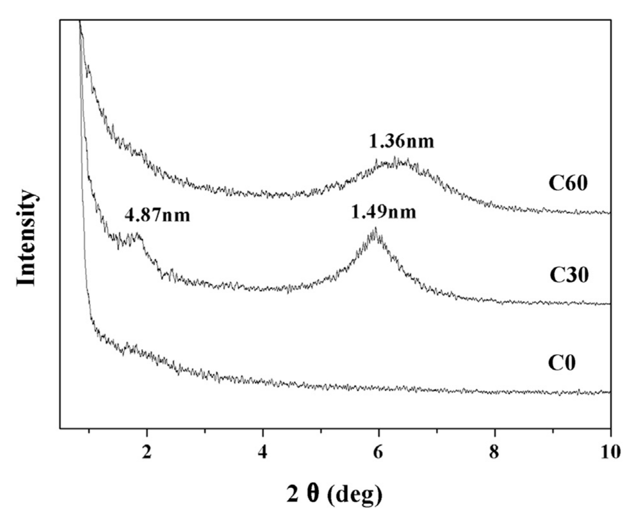

Fig. 2. XRD curves of SBR/clay/CB nanocomposites.