Chinese Journal of Chemical Engineering 23 (2015) 853–859

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Materials and Product Engineering

Modified graphite filled natural rubber composites with good thermal conductivity ☆

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ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 10 April 2014
Accepted 3 May 2014
Available online 31 January 2015

Keywords:
Graphite
Natural rubber
Thermal conductivity
Tire
Polyacrylate

ABSTRACT

The rubber composites with good thermal conductivity contribute to heat dissipation of tires. Graphite filled natural rubber composites were developed in this study to provide good thermal conductivity. Graphite was coated with polyacrylate polymerized by monomers including methyl methacrylate, *n*-butyl acrylate and acrylic acid. The ratios between a filler and acrylate polymerization emulsion and those between monomers were varied. Eight types of surface modification formulas were experimentally investigated. Modification formula can affect coating results and composite properties greatly. The best coating type was achieved by a ratio of 1:1 between methyl methacrylate and *n*-butyl acrylate. The coating of graphite was thermally stable in a running tire. Filled with modified graphite, the tire thermal conductivity reached up to 0.517–0.569 $W \cdot m^{-1} \cdot K^{-1}$. In addition, the mechanical performance was improved with increased crosslink density, extended scorch time and short vulcanization time.

1. Introduction

When a tire is in use, dynamic deformations caused by loss of hysteresis of vulcanized rubber composites lead to thermal energy production. In addition, the internal friction at the molecular level between filler–filler, filler–rubber and rubber–rubber networks, and the friction between tire and ground are the other two ways for thermal energy generation. Part of the energy is dissipated into the circumference; however, most of the energy causes heat buildup in the tire, accompanied by increased temperature. High temperature will result in degradation of mechanical performance, acceleration of fatigue damage, oxidation and heat-degradation of the rubber, and most seriously, puncture of the tire. Therefore, in order to enhance the tire durability, much effort has been made to lower the temperature of a running tire.

There are three ways to dissipate the thermal energy. One is to enhance the heat exchange on the tire surface. The second is to decrease the heat generation in the tire. And the third way is to transfer the generated heat from inside to outside. Much research works on thermal conductivity of rubber composites have been done [1–8], however, there are rather few reports dealing with the applications in tires [9–11]. Wang *et al.* [9] indicated that nano-zinc oxide could not only reinforce ethylene propylene diene monomer (EPDM) but also improve thermal conductivity significantly, and the composites could serve in dynamic conditions with longer expected service life. Das *et al.* [10] achieved a good dispersion of multi-walled carbon nanotubes in a rubber blend by a novel mixing approach and studied properties of the composite. The theoretically predicted thermal conductivities of isolated tubes could not be transferred into rubber-based composites in practice. The large surface area of the carbon nanotubes led to a strong phonon boundary scattering, which resulted in poor thermal conductivity of composites. Li *et al.* [11] studied the thermal conductivity of emulsion polymerized styrene–butadiene rubber (ESBR) vulcanizate filled with alumina, zinc oxide, carbon nanotubes and silicon carbide. The result showed that the thermal conductivity of ESBR vulcanizate filled with alumina or zinc oxide increased nearly linearly with increasing loading when the filler loading exceeded 20 phr, where phr is defined as the grams of filler added into 100 g of matrix; The ESBR vulcanizate filled with carbon nanotubes had the highest thermal conductivity at a given filler loading in comparison with composites filled with alumina or zinc oxide. At a given loading of 100 phr, the ESBR vulcanizations filled with two different silicon carbide particle sizes of 1–3 μm and 5–11 μm at a mass ratio of 1:1 had the highest thermal conductivity in comparison with the vulcanizations filled with only one kind of silicon carbide. Natural rubber is widely used in tire industry. Enormous studies have been focused on the mechanical properties of natural rubber based compounds. However, few studies address thermal conductivity. The present authors [12–14] studied the thermal conductivity of carbon black filled natural rubber composites; however, thermal conductivity enhancement of the reinforcing filler was limited.

☆ Supported by the National Natural Science Foundation of China (51076070, 51276091), the Natural Science Foundation of Shandong Province (ZR2012EEQ017), and the Research Award Fund for Outstanding Young Scientists in Shandong province (BS2012CL014).
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http://dx.doi.org/10.1016/j.cjche.2014.05.022
1004-9541/

Graphite, as one of the main forms of the sixth element in the Periodic Table of Elements, is abundantly available in nature. The π orbital distributed over the entire graphene sheet makes it thermally and electrically conductive. The thermal conductivity of graphite is about 209.34 $W \cdot m^{-1} \cdot K^{-1}$, which is three orders of magnitude of that of pure rubber. Therefore, if graphite filler is used in natural rubber with good dispersion, it surely can greatly enhance the thermal conductivity of the rubber. Wang [15] concluded that for tread rubber of radial tires, graphite could be used instead of silica, and it was possible to maintain a certain level of main properties of the compounds and vulcanizate. However, there are no detailed reports about graphite filled tire rubber for thermal conductivity improvement up to now.

In addition to the high thermal conductivity of graphite, the graphene sheets can easily slide with each other due to the weak van der Waals forces between the graphite layers. Therefore, the graphite has a soft and lubricating nature, which attributes to the relatively poor reinforcing properties of graphite for polymer. Li *et al.* [16], Zhao [17] and Tang *et al.* [18] pointed out that the graphite as a filler in conjunction with carbon black incorporated in rubber could improve the mechanical properties. The thermal conductivity of the composites would be better than that of the composites using graphite as a filler alone. Thus, graphite in conjunction with kinds of carbon black can improve the thermal conductivity of natural rubber on the basis of maintaining a certain level of mechanical properties.

Graphite exists as a layered material in its bulk state. Because of the high surface energy, graphite particles are easy to come together to form aggregates. As a filler, in order to utilize graphite efficiently, it is necessary to separate and disperse its layers in a polymeric matrix. Broadly, two methods are adopted. One is to form graphite intercalation compounds (GIC) [19] by intercalating various atoms, molecules, metal complexes and salts between the expanded graphene sheets. Another is surface treatment of the graphite [16,20–22].

Propylene ester copolymer emulsion is an emulsion polymerization product of acrylate or methyl propylene esters with other vinyl monomers. At present, methacrylic acid ester copolymer emulsion, vinyl acetate/methyl acrylate copolymer emulsion, and styrene/methyl acrylate copolymer emulsion are widely used. Because the acrylic ester contains functional groups of ester, carboxyl and hydroxyl, it has strong polarity, and thus has good adhesive properties with various substances. In addition, the acrylic emulsion bears good weather resistance, heat resistance and oil resistance, and it is non-toxic, easily synthetic, of non-environmental pollution and so on, and thus it is widely used [23–25]. If graphite particles are coated with polyacrylate in natural rubber, aggregation among the particles will be hindered for the reduction in potential energy of the surface. Therefore, the filler can achieve good dispersion in a rubber matrix, and then enhance the thermal conductivity of rubber.

The present study reported graphite filled natural rubber composites with good thermal conductivity. The graphite was coated with polyacrylate by the method of emulsion polymerization to achieve good dispersion in the rubber matrix and eight schemes of graphite coating were investigated. In order to obtain certain mechanical properties, carbon black N660 and acetylene black were incorporated as fillers together with graphite and the acetylene black was also good for thermal conductivity enhancement. The curing characteristics, thermal conductivity and mechanical properties of the rubber composites were discussed in detail.

2. Experimental

2.1. Materials

Natural rubber (GB1NR, China) was supplied by Hainan Natural Rubber Co., Ltd. (Hainan, China). The graphite (industrial-grade) used in the study was microcrystalline graphite with an average diameter of 15 μm. Carbon black N660 with a specific surface area of 33,000 $m^2 \cdot kg^{-1}$ and acetylene black with a specific surface area of 78,000 $m^2 \cdot kg^{-1}$ were used. Emulsifiers OP-10 and sodium dodecyl sulfate (SDS, $C_{12}H_{25}$–OSO_3Na), and monomers methyl methacrylate (MMA, $C_5H_8O_2$), *n*-butyl acrylate (BA, $C_7H_{12}O_2$), diethylene glycol diacrylate (DEGDA, $C_{10}H_{14}O_5$), acrylic acid (AA, $C_3H_4O_2$) and initiator potassium persulfate ($K_2S_2O_8$) were analytically pure.

2.2. Surface modification

Polymerized acrylate monomers were used to coat graphite in order to improve its dispersion in the matrix and ensure good interface between the filler and matrix. The choice of monomers was very important for properties of polymer emulsion, thereby affecting the coating effect. MMA was used as hard monomer, BA was used as soft monomer, and AA was used as function monomer. According to the ratios between hard and soft monomers, and between the filler and acrylate polymerization emulsion, eight kinds of surface modification schemes are listed in Table 1.

Table 1
Mass fraction of the components for the graphite modification

	1#	2#	3#	4#	5#	6#	7#	8#
Graphite/acrylate polymerization emulsion	10:1	5:1	10:1	5:1	10:1	5:1	10:1	5:1
MMA mass fraction/%	78	78	58	58	63	63	48	48
BA mass fraction/%	15	15	30	30	30	30	45	45
DEGDA mass fraction/%	5	5	10	10	5	5	5	5
AA mass fraction/%	2	2	2	2	2	2	2	2
$K_2S_2O_8$mass/g	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

The surface modification of graphite was carried out as follows: (1) water and emulsifiers OP-10 and SDS were mixed in a flask with four necks; (2) monomers were added to the mixture and emulsified for 20 min; (3) graphite was added in the mixture to emulsify for 40 min accompanied by very slowly stirring; (4) the mixture was heated up to 60 °C followed by stirring for 20 min; (5) the emulsion was heated up to 80 °C, then part of the initiator was put in, and the temperature was maintained for approximately 2 h for the reaction in the mixture; (6) the remaining amount of the initiator was added to continue the reaction for another 2 h; and (7) the mixture was cooled down followed by filtration and drying.

2.3. Sample preparation

The weight fractions of the components for rubber composites are shown in Table 2.

Table 2
Sample composition

Materials	Mass composition/g
Natural rubber	100
Sulfur	2.6
Stearic acid	2
Zinc oxide	5
N660	20
Acetylene black	15
Graphite	30