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The effect of new ferrite/kaolin pigment on the properties of acrylonitrile–butadiene rubber composites

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ABSTRACT

This work presents the preparation of rubber compounds containing new ferrite pigment for making new elastomeric magnetic composites with good properties and high savings. The pigment incorporated in this work is a new ferrite/kaolin core–shell pigment which contains a thin shell of ferrites not exceeding 10–15% of the whole pigments deposited on kaolin surface representing the core and comprises 85–90% of the pigment. These pigments have concomitant savings and are advantageous of combining the properties of both its components and overcoming their deficiencies. The evaluation of these new magnetic fillers influence on curing characteristics, physical–mechanical and magnetic properties will be estimated; these rubber ferrite composites have the advantage of easy mouldability and flexibility. Also, the effect of loading on the cure characteristics, physical–mechanical and magnetic properties of these rubber ferrite/kaolin composites will be evaluated. The study showed that, the tensile strength and elongation at break of the composites increased up to 50 parts per hundred rubber (phr) of ferrite and then decreased at higher loading whereas the hardness was increased gradually with increasing of ferrite/kaolin loadings. The magnetic tests showed that the saturation magnetization (M_s) and not the coercivity (H_C) is the dominant factor which affects the energy loss in the rubber composites.

1. Introduction

Rubber ferrite composites are composites containing ferrite pigments as one of the constituents and natural or synthetic rubber as the base matrix. In these composites, the magnetic filler as well as the polymer affects the processability and other physical properties of the final product. The physical and chemical properties of the magnetic composites will possibly be influenced by the interactions between the ferrite and the matrix. Incorporation of ferrites in elastomeric matrices leads to the formation of rubber ferrite composites (RFCs) [1]. An appropriate selection of magnetic filler and matrix can result in (RFCs) with required properties for different applications. Nowadays, more and more attention is given to the preparation and study of elastomeric composites with magnetic properties [2].

Ferrites remain one of the best magnetic materials ever discovered and cannot be easily replaced by any other magnetic material because they are cheap, stable and have a wide range of technological applications [3,4], so they are still widely used wherever the product cost is a major consideration [5]. Recently, transition metal ferrite have found great concern because of their unique properties that enable them to be used in fields as magnetic storage, catalysts, and magnetic refrigeration systems [6]. The effect of the filler structures usually depends greatly on their shape, particle size, and particle shapes of mineral fillers [7].

Kaolin is a versatile industrial mineral, which is known for its availability [8], low price, light color, and special stratified structure [9]; allowing them to be used in a multiplicity of industries because of their unique physical and chemical properties [10]. Kaolin adds strength, abrasion resistance, rigidity to rubber and it can provide excellent reinforcement after being treated [11].

Hybrid or core–shell pigments are new trend of pigments that contain more than one component chemically deposited on each other. These components are of high savings, since they contain low concentration of an effective pigment not exceeding 15–20% of the whole compound deposited on a cheap core which is the main constituent comprising 80–85% of the new core–shell compound. These new pigments have concomitant savings besides imparting new properties that combines their individual counterparts and overcoming the deficiencies that can be found in them

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Table 1
Chemical composition of Egyptian kaolin.

Component	wt.%
Al_2O_3	50.54
SiO_2	31.48
Fe_2O_3	2.26
TiO_2	1.87
MnO	0.01
P_2O_5	0.90
Na_2O	0.01
CaO	0.66
MgO	0.10
K_2O	0.07

individually. In this study, the shell composition is different ferrites (Zn, Mg and Zn·Mg ferrite), while the core is kaolin. These shells will have the piriority in the interaction with the rubber matrix, but still the core has its effect. These new core–shell pigments have approved direct effect in changing the mechanical, rheometric and magnetic properties of rubber composites than those containing the individual components of these pigments.

This work forms part of a comprehensive study focusing on the preparation of rubber-composites containing new core–shell ferrite/kaolin pigments, and studying the physical properties (curing, mechanical, rheometric and magnetic properties) of these pigmented rubbers as a function of ferrite/kaolin pigments content.

2. Experimental details

2.1. Materials

Egyptian kaolin used in this work is a product of El-Nasr Company, Egypt. It has chemical formula: $Al_2O_3{\cdot}SiO_2{\cdot}2H_2O$ and its chemical composition is given in Table 1 as determined by XRF analysis. It has specific gravity 2.6, its loss on ignition is 14% max, oil absorption 55 (g/100 g), and pH 6–7.

- Acrylonitrile butadiene rubber (NBR) containing 32% acrylonitrile content with specific gravity 1.17 + 0.005 was supplied from Bayer AG, Germany.
- N-cyclohexyl-2-benzothiazole sulphenamide (CBS), a pale gray powder, with specific gravity of 1.27–1.31 at room temperature (25 ± 1 °C), melting point 95–100 °C.
- Zinc oxide and stearic acid were used as activators with specific gravity at 15 °C of 5.55–5.61 and 0.90–0.97, respectively.
- Elemental sulfur, fine pale yellow powder, with specific gravity of 2.04–2.06 at room temperature was used as vulcanizing agent.
- Dioctyl phthalate (DOP) as plasticizer with density 0.991 g/ml and boiling point = 384 °C, was supplied by Aldrich Company, Germany.

All the rubber ingredients were of commercial grades, purchased from Aldrich Co., Germany.

2.2. Pigment preparation

First kaolin was calcined at 600–800 °C; the formed kaolinite (calcined kaolin) species were then impregnated in nitrate solutions of different cations of Zn, Mg and Fe. The cations were prepared as single and double ferrites, i.e. Zn, Mg and Zn·Mg ferrites. These solutions were stirred for one hour to confirm homogeneity of the formed ferrite precursor's distribution on kaolin surface, then the stirred paste was left to dry at 300 °C, then after that grinding was done. After grinding, the formed paste was calcined at 1000 °C, where the ferrite containing different cations are now deposited on kaolin surface. The prepared ferrite was deposited according to the ratio 2X:6Fe.

The pigments are prepared according to the following scheme;

$$\text{Kaolin} \underset{600-800\,^{\circ}\text{C}}{\overset{\Delta}{\rightarrow}} \text{m-kaolinite } (\text{Al}_2\text{Si}_2\text{O}_5)^+ \cdot (\text{OH})_4^- \quad (1)$$

$$\text{X(NO}_3)_2 + \text{Fe}_2\text{O}_3/\text{kaolin} \underset{1000\,^{\circ}\text{C}}{\overset{\Delta}{\rightarrow}} \text{XO/kaolin} + 2\text{NO}_2 \quad (2)$$

$$\text{XO/kaolin} + \text{Fe}_2\text{O}_3 \rightarrow \text{XFe}_2\text{O}_4/\text{kaolin} \quad (3)$$

where X is Zn, Mg, and Zn·Mg.

2.3. Rubber compounding

The formulations of nitrile–butadiene rubber (NBR) compounds are presented in Table 2. The compounds were prepared in two roll-mixing mills (outside diameter 470 mm, working distance 300 mm, speed of slow roll 24 rpm and fraction ratio of (1:1.4) in accordance with ASTM: D3182-07. The rubber compounds were vulcanized in an electrically heated hydraulic press at 162 ± 1 °C and a pressure of about 4 MPa for the optimum cure time (Tc_{90}) as determined for each compound in Fig. 3, previously determined from Monsanto Rheometer.

Table 2
Formulations of NBR compounds.

Compound no. ingredients (phr)[a]	NBR	30 K	50 K	70 K	30ZnFe/K	50ZnFe/K	70ZnFe/K	30MgFe/K	50MgFe/K	70MgFe/K	30(Zn·Mg)Fe/K	50(Zn·Mg)Fe/K	70(Zn·Mg)Fe/K
NBR	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
DOP[b]	3	3	3	3	3	3	3	3	3	3	3	3	3
CBS[c]	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Kaolin	–	30	50	70			–	–	–	–	–	–	–
Zn ferrite/kaolin	–	–	–	–	30	50	70	–	–	–	–	–	–
Mg ferrite/kaolin	–	–	–	–	–	–	–	30	50	70	–	–	–
Zn–Mg ferrite/kaolin	–	–	–	–	–	–	–	–	–	–	30	50	70

[a] Part per hundred parts of rubber.
[b] Dioctyl phthalate.
[c] N-cyclohexyl-2-benzothiazole sulphenamide.