Composites Part B 96 (2016) 231–241

Contents lists available at ScienceDirect

Composites Part B

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

Conductive carbon black/magnetite hybrid fillers in microwave absorbing composites based on natural rubber

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ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form
12 March 2016
Accepted 14 April 2016
Available online 21 April 2016

Keywords:
A. Polymer-matrix composites (PMCs)
A. Hybrid
B. Electrical properties
B. Magnetic properties

ABSTRACT

The study presents the microwave properties of natural rubber based composites in the 1–12 GHz frequency range as determined by the conductive carbon black/magnetite hybrid fillers obtained by impregnation at different ratios between carbon and magnetite phase. It has been established that, the changes in the investigated properties exhibit a resonance character in the 3–9 GHz range and are caused by alternations both of frequency and the ratio between the hybrid phases. The real and imaginary parts of permittivity and permeability, dielectric and magnetic loss angle tangent and conductivity have been also determined. The composite comprising a hybrid filler whose carbon:-magnetite phase ratio is 90:10 has turned to be the most successful. The good microwave characteristics of the composite are related to the dielectric and magnetic losses, as well as to the achieved optimal permittivity of the composite at the given ratio of the carbon and magnetite phase. The percent content of the conductive filler has a significant impact upon EMI SE of the composites. The introduction of Fe_3O_4 into the hybrid filler has a crucial role for decreasing the reflection by the composites surface.

1. Introduction

The main principles for developing microwave absorbing composites involve [1]: (i) finding a suitable dielectric matrix and a suitable conductive filler or a system of fillers; (ii) ensuring interaction between the composite and microwaves in the entire volume of the composite; (iii) ensuring that the matrix insulates completely the filler particles from each other and (iv) usage of functional fillers with high dielectric and magnetic loss values.

The main requirements for such kind of composites are minimum reflection and maximum absorption of the electromagnetic (EM) energy. The ideal absorber has a broad frequency range of the absorbing energy, excellent weather stability characteristics, reliability and capability to perform in a large temperature range. Most of the present-day microwaves absorbing composites are produced of a dielectric rubber matrix and specific functional fillers. Those fillers - carbon black, graphite, active carbon, short carbon or metal fibers, micro- and nanosized metal powders - possess high values of the imaginary part of the complex permittivity and/or permeability and absorb high frequency energy [2–8]. For the past few years, the composites containing both dielectric and magnetic fillers have been a well-considered topic in the field of electromagnetic interference (EMI) shielding and radar absorbing materials (RAM) [9–14]. As the EM field has both an electric and magnetic component, it is obvious that both dielectric and magnetic materials are effective for the absorption of microwave radiation. Therefore it has been of interest to combine components of high dielectric and magnetic losses into a hybrid filler what opens new opportunities of preparing modern microwave absorbers of specific properties.

F. Meng et al. [15] reported a hybrid microsphere, Fe-phthalocyanine oligomer/Fe_3O_4 that showed the maximum

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http://dx.doi.org/10.1016/j.compositesb.2016.04.039
1359-8368/

reflection of −31.1 dB at 8.6 GHz. R. Che et al. [16] also reported maximum reflection of −18 dB at 9.0 GHz for nanocomposites containing CNT–$CoFe_2O_4$ hybrids, whereas, the maximum reflection for CNT and $CoFe_2O_4$ was −6.0 dB and −8.3 dB, respectively. Obviously, the combination of a dielectric material with the hybrid filler comprising a dielectric and a magnetic component has lower reflection than the filler comprising any of the particular components.

In the last years electrically conductive carbon black (CCB) has received special attention in the manufacture of some polymer composites. The composites are used in applications like shielding of electrical cables, special electrical parts in cars, and in electrodes for fuel cells [17]. CCB is characterized by a very high specific surface area and by a very high electrical conductivity, uncharacteristic of the classical types of furnace carbon black (N550, N330, N220, etc.).

Magnetite, a member of spinel group, was chosen due to its low toxicity and great stability at high temperature [18]. On the other hand, magnetite crystal structure follows an inverse spinel pattern with alternating octahedral and tetrahedral–octahedral layers. It is known, that the octahedral sites in magnetite structure contain ferrous and ferric species. The electrons coordinated with these iron species are thermally delocalized and migrate within the magnetite structure causing high conductivity exchange constants: ranging from −28 J K to 3 J K between tetrahedral/octahedral sites and octahedral/octahedral sites, respectively [19]. Resultant conductivities range from 10^{-5}–10^{-4} S/m. Magnetite's Curie temperature is observed at 850 K. Below the Curie temperature, magnetic moments on tetrahedral sites, occupied by ferric species, are ferromagnetically aligned while magnetic moments on octahedral sites, occupied by ferrous and ferric species, are antiferromagnetic and cancel each other; such combined behavior is termed ferromagnetic [19]. The said above allows the conclusion that the CCB-magnetite hybrid filler will exhibit both high dielectric and high magnetic losses what will ensure good microwave properties of the composites comprising it.

The impregnation method is the most used and common method for deposition of different phases upon a support or for future modification of compounds. Most often the materials subjected to impregnation are porous or such capable of forming a pseudoporous structure, e.g. materials built of aggregates or agglomerates. In the general case of impregnation the second phase is disposed from a precursor solution, then following a certain technological procedure (e.g. evacuation into a controlled closed vessel for a certain time), the impregnated materials undergo physical or chemical treatment – usually thermal activation. Having in mind the specifics of the impregnation technologies, we consider them to be very suitable for the synthesis of dual phase hybrid fillers.

The investigations performed previously [20] have revealed the elastomer composites comprising hybrid fillers based on N330 conventional carbon black and magnetite to possess microwave properties better than those of composites filled with a physical mixture of carbon black and magnetite.

Our hypothesis has been that a hybrid CCB/magnetite (M) filler would facilitate the preparation of composites possessing microwave absorbing properties better than those of composites containing standard furnace carbon black.

The most important matters of our interest have been to establish the influence of CCB/magnetite hybrid fillers, prepared by impregnation technology, as well as impact of the ratio between CCB and magnetite phases, on the electromagnetic parameters and microwave absorbing characteristics of natural rubber (NR) based composites. Finding answers to these questions is the purpose of the present investigation.

2. Experimental

2.1. Materials

Natural rubber (SMR 10) was purchased from North Special Rubber Corporation of Hengshui, Hebei Province, China. Other ingredients such as zinc oxide, stearic acid, N-tert-butyl-2-benzothiazolesulfenamide (TBBS, produced by Lanxess) and sulfur were commercial grades and used without further purification.

CCB (Printex XE2-B, produced by Orion Engineered Carbons) had particle diameter 18–30 nm, specific surface area (BET) 1003 m^2/g, oil absorption number 420 ml/100 g, iodine adsorption 1125 mg/g, vanadium, nickel and iron content approx. 5000, 2500 and 1800 ppm, respectively, sulfur content < 0.8% [21]. Magnetite containing 95–100% of Fe_3O_4 and 0–5% of silica, was purchased from Inoxia, UK.

2.2. CCB-magnetite hybrid fillers preparation

CCB 90, 70 and 50 g and 10, 30 and 50 g of magnetite were loaded into a ball mill, 1500 ml of ethyl alcohol were poured and the mixture was impregnated for 2 h. Ethyl alcohol was used to avoid eventual magnetite oxidation. The suspension thus obtained was dried at 50°C for 2 h. Then the temperature was raised to 150°C and the drying continued for 2 more hours till complete dryness of the compound. The yield was ground again in a ball mill for 2 h. After that the grind was loaded into the reactor (shown in Fig. 1) and heated under 10^{-2} mm Hg vacuum at 440 °C for 2 h. If necessary, the product was ground once more in a ball mill.

Three types of hybrid fillers were synthesized and denoted according to their carbon-magnetite phase ratios as: CCB/M-10: carbon:magnetite phase ratio 90:10; CCB/M-30: carbon:magnetite phase ratio 70:30; CCB/M-50: carbon:magnetite phase ratio 50:50.

2.3. CCB-magnetite hybrid fillers characterization

The following methods were used to characterize the filler:

Iodine adsorption number – according to ISO 15651/1-91.
Oil absorption number – according to Bulgarian State Standard 9665:1976.
Specific surface area – calculated according to BET method [22].
Mesopore volume – calculated by Gurvich rule [23–25].

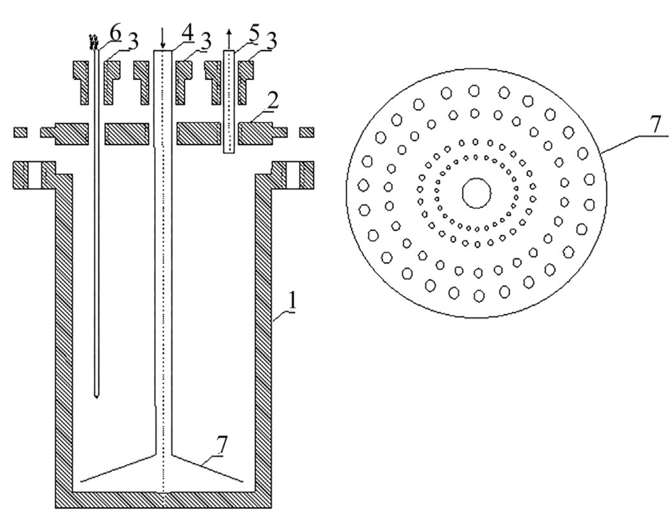

Fig. 1. Design of the reactor used: 1 – reactor vessel, 2 – top (sealing flange), 3 – sealing nuts, 4 – gas inlet, 5 – gas outlet, 6 – thermocouple, 7 – Buchner funnel.