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Thermodynamics favoured preferential location of nanoparticles in co-continuous rubber blend toward improved electromagnetic properties

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ABSTRACT

Engineered blend structure with tailor-made distribution of nanoparticles is the prime requisite to obtain materials with extraordinary functional properties. Here, preferential location of carbon black (CB) has been achieved in a binary elastomeric bend based on natural rubber (NR) and epoxidized natural rubber (ENR). Meticulous investigation has been conducted via thermodynamic, microscopic and electromagnetic analysis in order to illustrate the morphology-promoted performance behaviors. It is found that the filler-rubber interfacial tensions difference induces the preferential localization of CB in NR/ENR blend, thus endowing the composites with lower electrical percolation (2.11 vol.%), higher microwave absorption capacity (−19.31 dB) and broader effective absorption bandwidth (2.96 GHz). Such improved electromagnetic properties are ascribed to the higher conduction loss, stronger dielectric relaxation and more interface scattering of CB/NR/ENR composites.

1. Introduction

With the increasing use of wireless telecommunication systems and high frequency circuit devices such as mobile phones, radar and satellite broadcast systems, electromagnetic interference and radio frequency interference emitted by these electronic devices have been found to be a novel pollution [1]. Therefore, more and more attention has been paid to finding suitable microwave absorbing (MA) materials to prevent this phenomenon [2], which is generally controlled by two main factors. One is primarily dominated by reflection when free electrons or holes can carry the mobile charge in shield and interact with the electromagnetic field. In this context, metals are of primary interest as MA materials [3,4], but they suffer from miscellaneous inconveniences including cumbersome processing methods, poor flexibility, high weight and susceptibility to corrosion. As an alternative, absorbers-filled polymer composite has been gained considerable research attention owing to their high strength to weight ratio, good processability, structural flexibilities, and corrosion resistance [5–7]. To date, many efforts have been made to carbon-based materials in the MA field, particularly for carbon nanotube, graphene and fullerene composites [8,9]. However, their practical applications are restricted due to the complicated preparation processes, difficulty in un-entanglement or exfoliation, high cost and so

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on.

Alternatively, carbon black (CB) can be massively used as MA fillers due to its sufficiently light, excellent electrical property, cheap and good absorption performance in higher frequency ranges [10]. It is reported that polyaniline composites with 20–30 wt.% CB exhibit good absorption performances over a broadband range of 2–4 GHz [11]. CB/hydrogenated acrylonitrile–butadiene rubber composites has the minimum reflection loss (RL) of −13.1 dB and the −10 dB absorption bandwidth of 2.9 GHz [12]. CB-incorporated nitrile rubber composites exhibit enhanced microwave absorption and broaden band width, as well as a shift of an absorption peak towards the low frequency regime and decrease in the thickness of absorber with increase in CB concentration [13]. Moreover, the microwave absorbing performance of CB/rubber composites can be enhanced by incorporating magnetic and dielectric fillers [14]. However, CBs is not an attractive MA nanofillers due to the extremely high loading (> 40 wt.%) required to achieve adequate RL that is suitable for commercial applications. High concentration of the CBs would impair the mechanical properties, processing ability, cost of the composite. Therefore, a revolutionary change is in dire need of formulating MA materials at lower fillers content.

Recently, preferential localization of nanofillers in co-continuous blends provides an alternative approach toward improving nanofillers filling efficiency, thus achieving improved electrical and thermal properties [15,16]. Thermodynamically, the nanofillers usually tend to locate within the one of the phases or interphase of the blends due to the interfacial interaction difference between nanofillers and components. Wu et al. have designed CB/acrylonitrile-butadienestyrene (ABS)/polyamide 6 (PA6) composite with a low percolation threshold of 2 phr (means per hundred rubber) CB, which is much lower than that of pure ABS (8 phr) and PA6 (25 phr) matrix [17]. Shape-dependent preferential localization of carbon-based nanofillers in immiscible poly(styrene acrylonitrile)/polycarbonate blend during melt mixing have been also investigated by Göldel et al. The results indicate that nanofillers with low aspect ratios have higher stability in the blend phase than those with high aspect ratio [18]. Although different aspects have been well-investigated for enhancing functional properties of composites with preferential location of nanofillers, few study has been concerned with enhancing electromagnetic performance.

Theoretically, the functional properties of composites are stemmed form the geometrical or connectedness of infinite nanofillers network [19]. It is believed that preferential distribution of nanofillers can endow blend-based composites with better electromagnetic performance. The work of Bose and coworker have confirmed this, in which dielectric/magnetic nanoparticles were incorporated in different phase of polycarbonate/poly(vinylidene fluoride) blend, providing many folds microwave absorption than when they were localized in the same or in both the phases [20]. However, it is difficult to identify whether the synergistic effect is derived from the preferential distribution of nanofillers. Moreover, Sundararaj's research have revealed that addition of 5 vol.% SBS can change the morphology of poly(propylene)/polystyrene blend with high structure carbon black, but there is not enhancement in electromagnetic interference shielding performance [21]. Therefore, the relationships between preferential location of nanofillers and its effect on the electromagnetic properties have not been fully understood on a scientific base, and a detailed analysis on rubber-based system is still lacking.

Natural rubber (NR) is one of the most important rubber in terms of versatility and application volume owing to its superior strength, elasticity, flexibility, etc. Epoxidized natural rubber (ENR), derived from natural rubber latex after being treated with peroxide, has different characteristics, especially in affinity with nanofillers [22]. Le and his co-worker have illustrated the influence of polarity NR on CB Localization in its blends with styrene butadiene rubber [23,24]. Here, the morphology, electrical conductivity, dielectric and microwave absorbing performance of CB filled NR, ENR and NR/ENR (50/50, wt./wt.) binary blends were systematically investigated. Due to the different interfacial energy between nanofillers and rubber matrices, the location of CB in NR/ENR blends can be thermodynamically tuned. Therefore, the NR/ENR blends with preferential location of CB demonstrate tailorable electromagnetic properties. A possible structure-promoted attenuation mechanism is also proposed.

2. Experimental

2.1. Materials

NR and ENR containing 50 mol.% (mole percentage) epoxide groups were provided form our pilot-plant, both of NR and ENR share the same density of 0.91 g/cm^3. CB nanoparticles were purchased from Ebory Chemical Co., Ltd (Tianjin, P.R. China). According to the manufacturer, CB has the electrical conductivity of 2.5×10^{-2} S/cm and the surface area of 420 m^2/g. Vulcanizing compounding ingredients including sulfur, zinc oxide, stearic acid, 2-mercaptobenzimidazole (antioxidant MB) and n-*tert*-butylbenzothiazole-2-sulphenamide (accelerant NS) are analytical grade and used as received without further purification.

2.2. Composites preparation

Both the pure rubber and their composites with CB were prepared by a standard mixing/curing procedure. Take the CB-filled NR composites for example, NR 100.0 g, zinc oxide 5.0 g, stearic acid 2.0 g, and antioxidant MB 2.0 g were first blended using a two-roll mill with a friction ratio of 1:1.35. Then, various CB ranging from 0–15.82 vol.% (volume percentage, based on neat rubber matrices) were incorporated into the above blend and mixed until almost well dispersed. Thereafter, accelerant NS 0.7 g and sulfur 2.2 g were added and further blended for 3 min. Room temperature (below 60 °C) was maintained during the milling process to avoid early cross-linking reaction. Having been stayed for 24 h, the mixed compound was vulcanized (12.5 MPa, 140 °C) into specific shape for an optimum time (about 20 min) which was determined by a disc rheometer (MDR 2000, Alpha, USA). According to the matrix used (NR, ENR and NR/ENR), the prepared composites were designated as CB/NR, CB/ENR and CB/NR/ENR, respectively.