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Dielectric properties of BN modified carbon fibers by dip-coating

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Abstract

Continuous and uniform boron nitride (BN) coatings were synthesized on carbon fibers by dip-coating and their microstructure, chemical composition and dielectric properties were investigated. Results show that the as-prepared coatings are composed of phase mixture of *h*-BN and amorphous *t*-BN. The oxidation property of the BN modified carbon fibers is improved with higher initial and final oxidation temperatures. Both the real (ε') and imaginary part (ε'') of permittivity of the BN modified carbon fibers decrease significantly compared with the pure carbon fibers. The decrease of ε' can be mainly attributed to the absence of dielectric relaxation effect, while the decrease of ε'' can be ascribed to the large decrease in electrical conductivity. The decreasing permittivity leads to increase of microwave impedance which is beneficial for electromagnetic matching. With improved impedance match and still relatively high ε'', the BN modified carbon fibers exhibit a promising prospect as microwave absorbing materials.

Keywords: B. Fibers; C. Dielectric properties; D. Nitrides

1. Introduction

In recent years, microwave absorbing materials have attracted considerable attentions because of their wide applications in civil and military fields [1–5]. An ideal microwave absorbing material should possess the advantages of low density, thin thickness, light weight, wide bandwidth, preferred physical–mechanical properties, low cost and can be operated simply [6,7]. Carbon fiber based composites with light weight, high strength and excellent electrical property, have been found to be fascinating candidates for microwave absorption materials [8–10]. However, the low electrical resistivity ($10^{-3}\,\Omega\,cm$) of carbon fibers results in strong reflecting electromagnetic waves. Many treatments have been applied to enhance the absorbing property of the carbon fibers, including decreasing the carbonization temperature and changing the cross-section shape and size of carbon fibers. Specially, to coat carbon fibers with a layer of magnetic metal, ferrites or oxides has been proved as an effective way [11–15]. However, with relatively heavy density, magnetic metal, ferrites and oxides are unable to dissipate electromagnetic energy in high temperature environment due to their low curie temperatures. Boron nitride (BN) has low density, high electrical resistivity, good anti-oxidation property, extremely low dielectric constant (5.16) and dielectric loss (0.0002) [16–18]. It is an ideal alternative for carbon fiber coating material to satisfy the requirements of lighter weight, thinner thickness, and chemical and temperature resistances for microwave absorption materials. It is therefore believed that the carbon fibers modified with BN coatings could be promising candidates for microwave absorbing materials.

Chemical vapor deposition (CVD) is the primary process to prepare BN coatings on fibers [19–21]. However, the requirement of some hazardous and expensive chemical precursors, such as BCl_3 and NH_3, to produce BN coatings by CVD process limits its application. Dip-coating process, which is known for simple operation, low cost and might obtain uniform coatings on fibers, and more importantly, the use of harmless raw materials (boric acid and urea) had been successfully applied to prepare BN coatings on fibers [22,23].

In this study, BN coatings were synthesized on carbon fibers by dip-coating in boric acid and urea solutions

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followed by nitridation at a nitrogen atmosphere. The microstructure and chemical compositions of the fiber coatings were investigated. In particular, the dielectric properties of the BN modified carbon fibers which were rarely reported before, to the best of our knowledge, were evaluated in the present study.

2. Experimental

2.1. Sample preparation

The PAN-based carbon fibers (T700, 12 K, Toho Tenax, Inc.) with 7 μm average diameter and 10 cm length were used as the substrates for dip-coating. Boric acid (reagent grade, Xilong Chemical Co., Ltd., Shan'tou China) and urea (reagent grade, Xilong Chemical Co.) were employed as boron and nitrogen sources of BN, respectively. Firstly, the carbon fibers were immersed in acetone for 24 h and cleaned ultrasonically with distilled water, then dried at 120 °C for 2 h. Secondly, the obtained carbon fibers were dipped in the precursor solution with boric and urea (1:3, wt. ratio) dissolving in non-aqueous ethanol. After being vibrated ultrasonically for 15 min, the pretreated carbon fibers were drawn from the solution and dried at room temperature. Thirdly, the precursor coated fibers were placed in a carbon crucible positioned in a vacuum furnace before nitridized at 800 °C for 4 h under a nitrogen atmosphere. The heating and cooling rate were 5 °C/min. Finally, the BN coatings were synthesized on carbon fibers. Fig. 1 shows the formation process of BN coating on carbon fiber schematically.

2.2. Characterization

The morphology and structure of BN coatings were characterized by scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, JEOL 2010F). The chemical compositions of the coatings were analyzed by Fourier transform infrared spectroscopy (FI-IR, IS10, Thermo scientific) and X-ray photoelectron spectroscopy (XPS, K-Alpha 1063) with Al Kα radiation. The oxidation resistance of the pure and BN modified carbon fibers was studied in air up to 1200 °C with a DTA/TGA instrument (STA 409PC, NETZSCH). The complex permittivity (ε', ε'') of the pure and BN modified carbon fibers was measured by the coaxial line method in a frequency range of 2–18 GHz using a network analyzer (AV3618). For the permittivity measurement, the fibers were cut into short fragments (2–3 mm in length) and mixed with paraffin through ultrasonic agitation. The weight fraction of fibers in paraffin was 20%. The mixtures were then pressed into a ring with 7.0 mm outer diameter, 3.0 mm inner diameter and 2 mm thickness.

3. Results and discussions

3.1. Morphology and chemical composition of the coating

To investigate the effect of dip-nitridation cycles on the surface morphology of the fiber coatings, one, two and three cycles were applied, respectively. Fig. 2 shows the surface morphologies of as-prepared coatings synthesized with different dip-nitridation cycles. It can be seen that the coating surface changes significantly with increasing dip-nitridation cycles. For one dip-nitridation cycle, a discontinuous coating was obtained on the surface of carbon fibers composed of large amount of separated film pieces (Fig. 2(a)). For two cycles, the fiber surface is covered by a smooth and uniform coating, as shown in Fig. 2(b). For three cycles, the coating presents a relative rough surface with parts of the coating peeling from the fibers (Fig. 2(c)). During the synthetic process, the coating will suffer a tensile stress due to the volume contraction from the evaporation transformation of organic materials and the

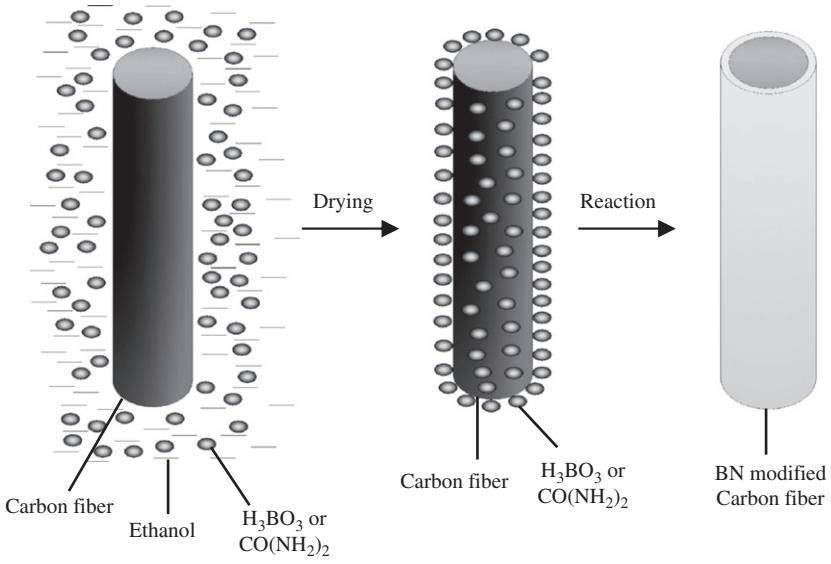

Fig. 1. Schematic diagram of the formation process of BN coating on carbon fiber.

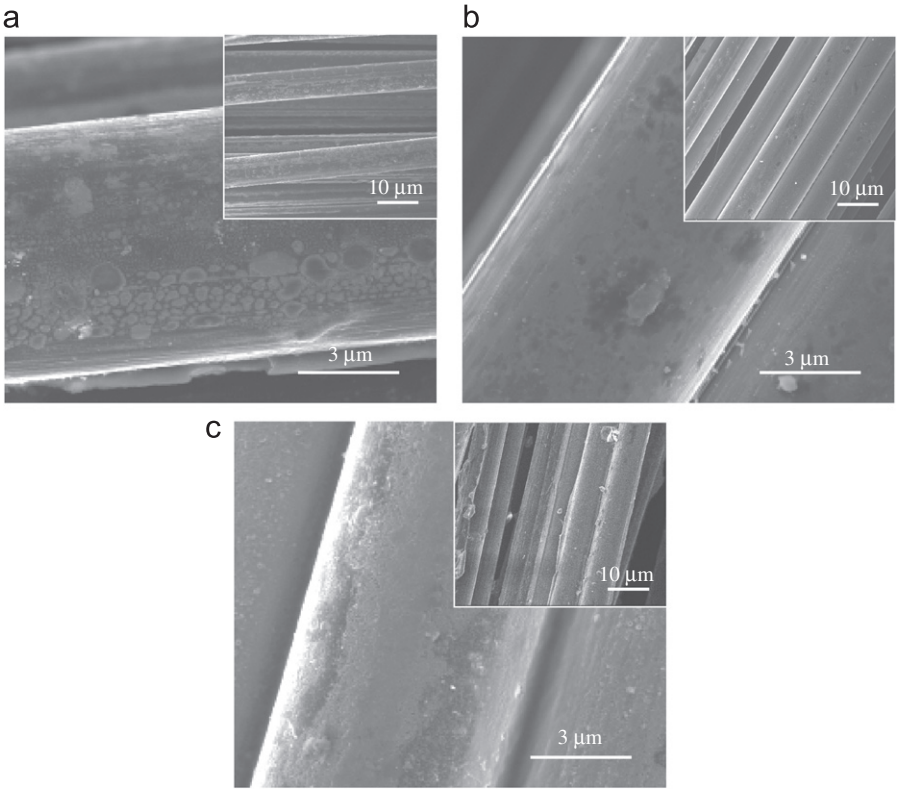

Fig. 2. The Surface morphologies of as-prepared coatings synthesized with different dip-nitridation cycles.

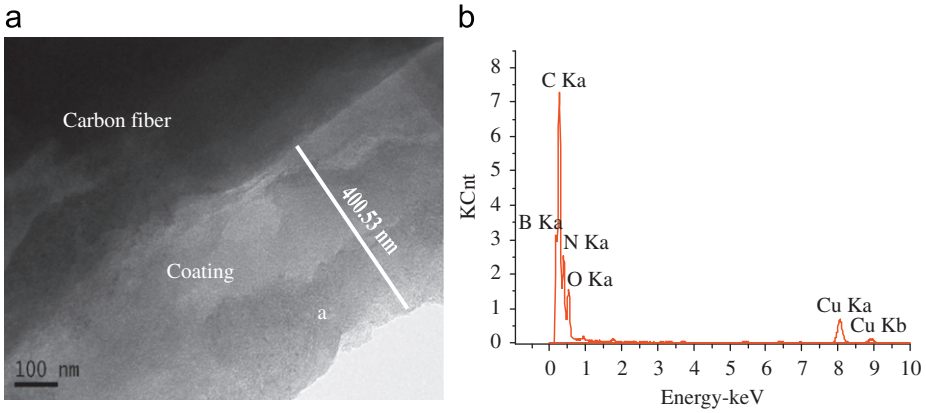

Fig. 3. (a) TEM image and (b) energy dispersive spectroscope (EDS) spectrum of the coating synthesized on fiber surface with three cycles.

mismatch of thermal expansion coefficients between the coating and the carbon fiber. Once the stress reaches a critical value, the interfacial debonding between the coating and fiber occurs, which is responsible to the peeling of coating.

Fig. 3 shows the TEM image and energy dispersive spectroscope (EDS) spectrum of the coating synthesized on fiber surface with three cycles. As shown in Fig. 3(a), two regions with distinct contrast can be observed: the dark region and the bright region. In addition, a continuous interface can be distinguished clearly between the two regions. The EDS results obtained from the bright region show the existence of C, B, N, O and Cu elements (Fig. 3(b)), indicating the formation of coating. The presence of Cu peaks can be attributed to the reflection of the sample holder. Moreover, the coating is uniform with a thickness of about 400 nm and exhibits good adhesion to the carbon fiber.

Fig. 4 shows the FT-IR spectra of the carbon fibers with and without coating. It is shown that from the coated fibers, the two absorption bands are detected around 800 and 1380 cm^{-1} corresponding to the B–N bond bending vibration [24,25], indicating the formation of hexagonal BN (*h*-BN) [18] and turbostratic BN (*t*-BN) with amorphous structure [22], respectively. For better identification of the chemical compositions, XPS spectra were recorded

from the coating surface, shown in Fig. 5. The Survey XPS spectrum reveals the presence of boron, nitrogen, oxygen and carbon. Fig. 6 shows the XPS fitted spectra of B 1s and N 1s for coating. As shown in Fig. 6(a), there are two peaks centered at 190.9 eV and 192.1 eV in the B 1s spectra. The one located at 190.9 eV corresponds to the B–N bonding [26], while the other one at 192.1 eV indicates the existence of oxynitrides (BO_xN_y) with B_2O_3 species in the coating [27], which results from the incomplete reaction for the low reaction temperature. Simultaneously, the fitted N 1s spectra present two peaks centered at 398.4 eV and 398.9 eV (Fig. 6(b)). The former is assigned to the N–B bonding and the later to the N–C bonding [28]. In addition, the presence of O peaks in the as-prepared coating (as shown in Fig. 3(b) and Fig. 5) can be attributed to the contribution of B–O bonding of BO_xN_y and adsorbed oxygen. Combining the TEM and FT-IR results, it can be concluded that BN coatings are successfully prepared on carbon fibers by the dip-coating.

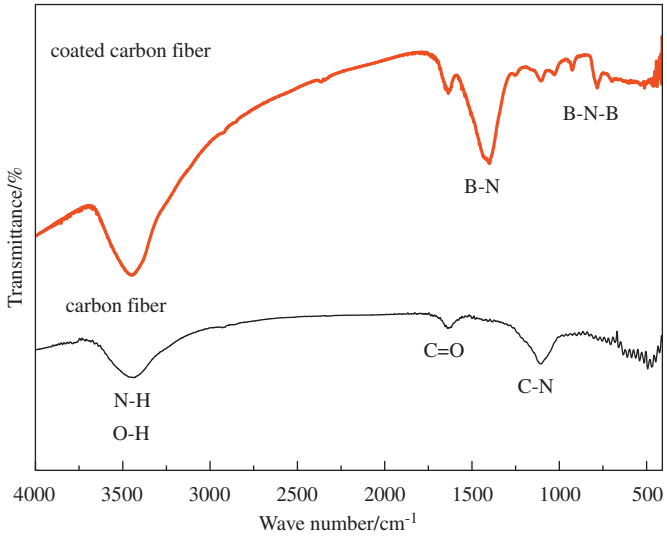

Fig. 4. FT-IR spectra of the carbon fibers with and without coating.

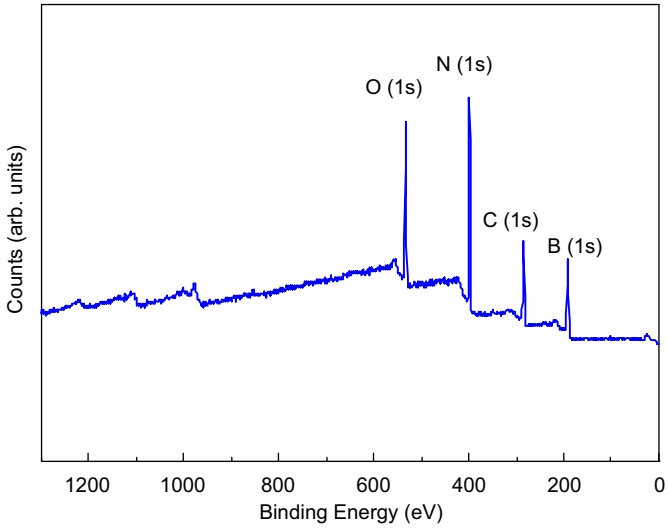

Fig. 5. Survey XPS spectra of the coatings on carbon fibers.

3.2. TGA

Fig. 7 shows the TGA curves of the pure and BN modified carbon fibers. It is found that the pure carbon fibers were oxidized sharply around 560 °C and consumed thoroughly around 780 °C. However, no significant weight loss was observed for the BN modified fibers until 650 °C and the final oxidation temperature was increased to 1000 °C. In modified fibers, the weight loss caused by the carbon fibers oxidation is compensated by weight increase from the generation of oxidation products (B_2O_3) of the BN coating in the temperature range of 560–650 °C. Thus, no significant change is shown in TGA curve before 650 °C for the modified fibers. However, as the oxidation temperature increases above 650 °C, the tendency of the weight loss is similar with that of the pure carbon fibers as the BN coating has been oxidized completely before. It is worth noting that the oxidation rate of fibers in BN modified fibers is lower than that of pure carbon fibers in the temperature range of 560–1000 °C, which can be ascribed to the formation of liquid B_2O_3 film on the surface which acts as a diffusion barrier and prevents oxygen penetration [29]. As the temperatures further increase to 1200 °C, the BN modified fibers continue to lose weight slowly due to the evaporation of the liquid

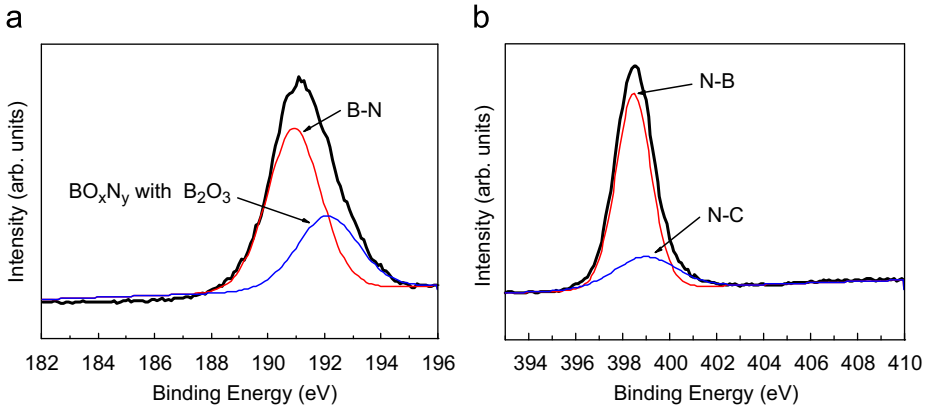

Fig. 6. The XPS fitted spectra of (a) B 1 s and (b) N 1 s for coating.

B_2O_3 film. Hence, the results indicate that the oxidation resistance of carbon fibers can be improved by modifying the surface with BN coatings. The initial and final oxidation temperatures of the BN modified carbon fibers are increased from 560 °C and 780 °C to 650 °C and 1000 °C, respectively. This leads to improved oxidation resistance in an oxygen environment for the BN modified carbon fibers.

3.3. Dielectric properties

Complex permittivity, $\varepsilon = \varepsilon' - j\varepsilon''$, is an important parameter to characterize the dielectric properties of materials. It is well-known that the real part (ε') of permittivity represents the ability of storing electromagnetic (EM) wave energy, while the imaginary part (ε'') represents the ability of dissipating EM wave energy [30]. Although high ε'' implies good microwave absorbing properties, excessively high permittivity is harmful to the impendence match and results in strong reflection and weak absorption [31]. Fig. 8 shows the real and imaginary parts of permittivity of the pure carbon fibers and BN modified carbon fibers synthesized with different cycles in the frequency range of 2–18 GHz. It can be found that the pure fibers show higher permittivity with ε' and ε'' values decrease as frequency increases. The permittivity of the BN modified fibers has a similar variation trend with the pure carbon fibers. But it is worth to note that both ε' and ε'' of the BN modified fibers decrease significantly in the frequency of 2–18 GHz compared with the pure fibers. With increasing synthesis cycles, ε' and ε'' decrease further, especially the imaginary part (ε''), which decreases dramatically from 166.1–37.7 to 23.6–12.9. These results demonstrate that by surface modification with BN coatings, the permittivity of carbon fibers can be significantly decreased, while the ε'' which represents dielectric loss remains relatively high. The lower permittivity is beneficial for impendence matching. Thus, the microwave absorption of the BN modified carbon fiber with improved impedance match will be improved. The wave impedance η can be calculated by the following relationship [32]:

$$\eta = Z_0\sqrt{\frac{\mu_r}{\varepsilon' - j\varepsilon''}} \tag{1}$$

where Z_0 is the characteristic impedance of free space, $\mu_r = \mu' - j\mu''$ is the complex permeability, ε' and ε'' are the real part and imaginary part of complex permittivity, respectively.

Fig. 9 shows the microwave characteristic impedance of the pure carbon fibers and BN modified carbon fibers synthesized with different cycles in the measured frequency range. With the increase of synthesis cycles, the microwave impedance of the BN modified carbon fibers increases gradually compared with that of the pure carbon fibers. The increased microwave impedance of the BN modified carbon fibers is much closer to Z_0 (about 377 Ω) than that of carbon fibers without BN coating. Therefore, better electromagnetic matching can be obtained and more electromagnetic waves could enter into the BN modified carbon fibers and be dissipated.

According to the electromagnetic permittivity theory, the real part (ε') is related to polarization, and the imaginary part (ε'') represents dielectric loss correlating with electrical conductivity of a material [33]. Combined with the experimental results, higher real part (ε') permittivity of the pure carbon fibers can be mainly ascribed to

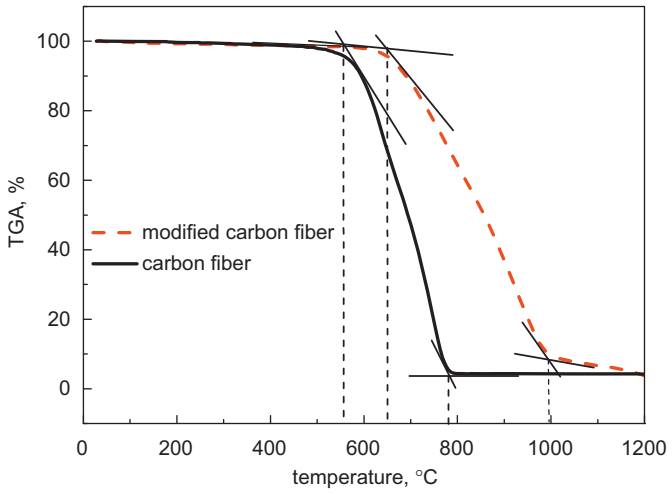

Fig. 7. TGA curves of the pure and BN modified carbon fibers, in air.

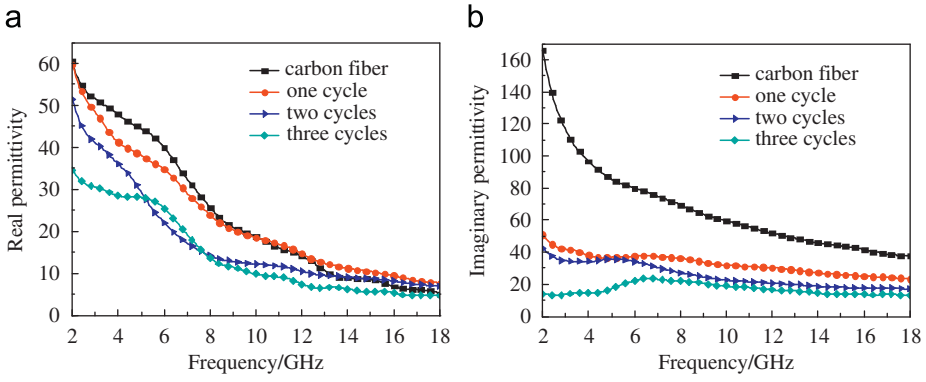

Fig. 8. The permittivity of the pure carbon fibers and BN modified carbon fibers synthesized with different cycles: (a) real permittivity and (b) imaginary permittivity.

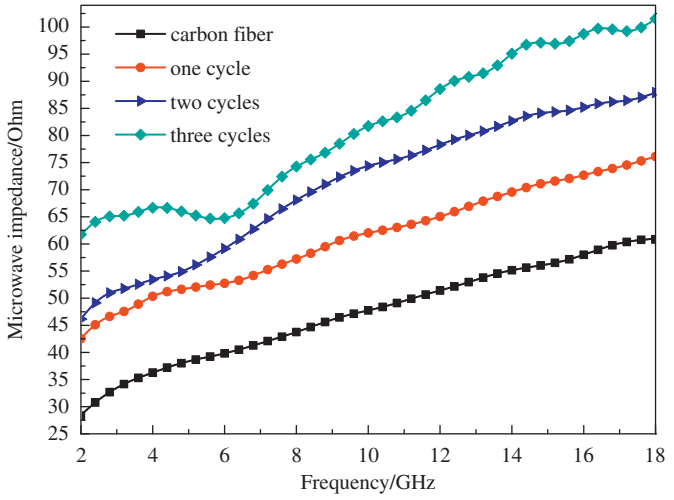

Fig. 9. The Microwave impedance of the pure carbon fibers and BN modified carbon fibers synthesized with different cycles.

dielectric relaxation and space charge polarization between conductive fibers separated by the insulate matrix [34]. And higher imaginary part (ε'') of the pure carbon fibers can be mainly attributed to good electrical conductivity caused by the movement of free electrons in the disordered graphite layers in carbon fibers [8]. Moreover, with high fiber content (20 wt%) in the matrix, electric conducting networks can be easily formed as many fibers may contact with each other. The electric conducting networks lead to increasing electrical conductivity and result in high ε'' value of carbon fibers. By surface modified with insulative BN coating, the BN modified carbon fibers present a core–shell structure, and the conductivity of the BN shell is fairly low. Thus, the dielectric relaxation frequency of the BN modified carbon fibers is believed to be lower than 2 GHz [35] due to the core-shell structure or lower conductivity of fillers in composites which leads to a shift of dielectric relaxation frequency toward lower frequency [36,37]. Therefore, the real part (ε') of permittivity of the BN modified carbon fibers decreases due to the absence of dielectric relaxation effect. On the other hand, for carbon fibers coated with this insulating shell, the electric current flows only in the core which leads to distinctly decreased electrical conductivity of the BN modified carbon fibers. In addition, the distances between the conductive carbon fibers become farther with BN coating, and the fibers are isolated from each other physically. Thus, the formation of electric conducting networks in the BN modified carbon fibers can be effectively suppressed, which leads to electrical conductivity decrease. Therefore, the imaginary part (ε'') of permittivity of the BN modified carbon fibers decreases dramatically compared with that of the pure carbon fibers due to the great decrease in electrical conductivity. Since the space charge polarization of the BN modified carbon fibers caused by charge accumulation at the heterogeneous interface might be enhanced with the increase of interfaces, the decrease in ε' is lower than that of ε''. It is reported that even a thin insulating shell can reduce the permittivity of the core/shell structure significantly due to the resistivity increasing immensely [38,39]. With the shell thickness increase, the permittivity of the core/shell composites approach to the permittivity of the shell [40]. Therefore, both the real and imaginary parts of permittivity of the BN modified carbon fibers decrease gradually with increasing of synthesis cycles due to the increase of BN coating thickness [23]. The decrease of permittivity leads to increased permeability to permittivity ratio and thus increased microwave impedance based on Eq. (1). In addition, the ε'' (dielectric loss) of the BN modified carbon fibers remains high relatively. As a result, the reflection from the surface can be better restrained and much better microwave absorption property might be obtained for the BN modified carbon fibers.

4. Conclusions

In this study, BN coatings were synthesized on carbon fibers by dip-coating in boric acid and urea solutions followed by nitridation in a nitrogen atmosphere. Continuous and uniform coatings with a thickness of about 400 nm can be obtained with three dip-nitridation cycles. The as-prepared coatings are composed of phase mixture of *h*-BN and amorphous *t*-BN. By surface modification with BN coating, the oxidation resistance of the BN modified carbon fibers is improved due to the formation of a layer of liquid B_2O_3 film from BN coating oxidation which can prevent the carbon fibers from further oxidation. Both the real (ε') and imaginary part (ε'') of permittivity of the BN modified carbon fibers decrease significantly compared with the pure carbon fibers. The decrease of ε' is mainly resulted from the absence of dielectric relaxation effect caused by shifting dielectric relaxation frequency of the BN modified carbon fibers. The decrease of ε'' is attributed to the large decrease of electrical conductivity of the BN modified carbon fibers. The decreasing permittivity leads to increase of microwave impedance which is beneficial to electromagnetic matching. And thus the microwave absorption of the BN modified carbon fibers with still relatively high ε'' (dielectric loss) will be improved. In summary, this investigation suggests that high permittivity of carbon fibers can be adjusted with retaining relatively high ε'' by modifying the surface with BN coatings. Meanwhile, the oxidation resistance and electromagnetic matching of the BN modified carbon fibers can be improved. Thus, the BN modified carbon fibers exhibit a promising prospect as microwave absorbing materials. However, the detailed mechanism remains unclear and further study is still under way.

Acknowledgments

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