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# Electrical properties of C/C and C/C–SiC ceramic fibre composites

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## Abstract

The electrical properties of carbon/carbon (C/C) and carbon/carbon–silicon carbide (C/C–SiC) ceramic composites were measured. The results show that the capacitance decreases rapidly with an increase in frequency and it becomes constant above a frequency of 500 kHz, whereas the dissipation factor increases with increasing frequency. C/C–SiC composites give higher value than C/C composites due to the presence of microcracks.

*Keywords:* Carbon ceramic composites; C/C; C/C–SiC; Electrical capacitance

## 1. Introduction

Ceramic matrix composites (CMC) have many potential applications as high-temperature structural components, because of their high strength at elevated temperature, low density, superior toughness and wear resistance. Originally, demands in space and aeronautics technology played the decisive role in the development of ceramic matrix composites. High specific characteristics and extreme temperature resistance are important in selection criteria for materials used in jet engines and thermal protection systems of new spacecraft and rockets. Among CMC, carbon fibre reinforced silicon carbide composites (C/SiC) have been extensively investigated and received certain practical applications. Within the last few years, the properties and the manufacturing methods of ceramic matrix composite (CMC) materials have been improved, so that the industry in general can share the profits of this new class of materials. C/C–SiC composites exhibit improved mechanical and thermal performance characteristics such as low density, high strength-to-weight ratio and wear resistance. It has been found wide applications in the field of aerospace and aeronautics industry for rocket nozzles and re-entry thermal protection shields of space vehicles. Ceramic brake discs and heat insulating materials are used in automotive industry because of their low cost manufacturing methods [1,2]. Further, SiC-based ceramics are known to exhibit excellent oxidation characteristics related to the formation of a protective silica scale (passive regime), which slows down inward diffusion of oxygen. Significant research is going on for the development of porous materials. Some of the porous material includes; graphite/carbon foam, ceramic foam and porous conducting paper for electrodes of fuel cells, etc. However, Si–SiC porous ceramic is derived from C/C–SiC composites, which exhibit superior performances over the conventional porous materials [3]. Silicon infiltrates into the cracks arising from the pyrolysis of carbon fibre reinforced matrix composite and form layers of protective segments over the carbon fibres resulting in the retardation of oxidation in C/C–SiC composite, when subjected to the high-temperature environments. The carbon fibres that run through the C/C–SiC laminate are not completely covered by the silicon carbide/free silicon in the longitudinal direction of the fibres [4,5]. The above-mentioned facts of the C/C–SiC ceramics are difficult to obtain (Table 1). Hence, a controlled oxidation of the C/C–SiC composite in an oxidizing atmosphere should result in the oxidation of the carbon fibres only leaving behind a network of channels, resulting from depletion of carbon throughout the entire composite, forming a highly porous structure [6–8].

Ceramic composites are potential materials in the field of electrical and optoelectrical applications. Among passive electronic components, capacitors are of much importance for integrated circuits, because a large number of capacitors are used in electronic systems for various functions, such as signal de-coupling, switching noise suppression, filtering, and tuning.

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Table 1
Constituents of C/C–SiC ceramics along with their oxidation temperatures and oxidation products.

| Constituent | Oxidation temperature (°C) | Oxidation products |
|---|---|---|
| Carbon (C) | Above 400–450 °C | $CO_2$ |
| Silicon carbide (SiC) | Rapidly above 1200 °C | $SiO_2$, $CO_2$ |
| Silicon (Si) | Rapidly above 870 °C | $SiO_2$ |

Consequently, the high-dielectric constant materials are required for making embedded capacitors for integrated electronic devices. On the other hand, combinations of dielectric and mechanical properties are hard to achieve in a one-component material. Pure polymers are easy to process into mechanically robust components but generally suffer from a low dielectric constant. At the same time typical high-dielectric constant materials, such as ferroelectric ceramics are brittle and require high-temperature processing, which is often not compatible with current circuit's integration technologies. The ideal solution would be a high-dielectric constant material that is mechanically robust and processable at ambient temperatures. This has raised a great interest in hybrid materials, such as ferroelectric polymer/ceramic composites, that may combine desired properties of the components [9–11].

The complex impedance of the sample with the real and imaginary components can be written as [12]

$$Z' = Z\cos\varphi, \tag{1}$$

$$Z'' = Z\sin\varphi. \tag{2}$$

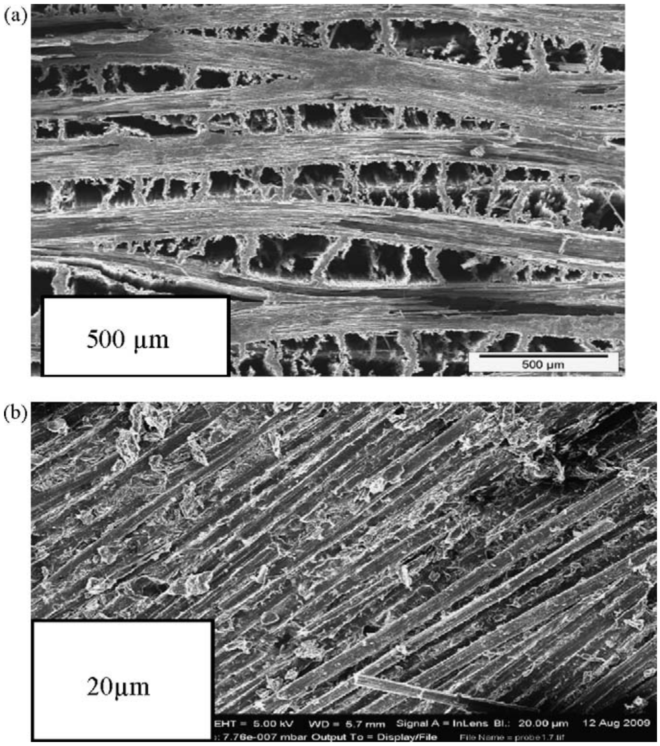

Fig. 1. Scanning electron micrograph showing the (a) large amounts of porosity appeared in C/C–SiC composite during pyrolysis process and (b) carbon fibres pullout and debonded from carbon matrix even after dense populations of C/C composites.

The dielectric constant $\varepsilon'$ and the dielectric loss $\varepsilon''$ of the sample are calculated from the following equations:

$$\varepsilon' = Z'2\pi fC_0Z^2, \tag{3}$$

$$\varepsilon'' = Z''2\pi fC_0Z^2, \tag{4}$$

where $f$ is the frequency of the applied ac electric field and $C_0$ is the capacitance of the two plates of the cell without sample given by

$$C_0 = \varepsilon_0\frac{A}{d}, \tag{5}$$

where $A$ is the disc area and $d$ is the distance between the two plates. The ac conductivity of the sample is calculated from the following equation:

$$\sigma AC = 2\pi f\varepsilon_0\varepsilon'', \tag{6}$$

where $f$ is the natural frequency.

The relaxation time ($\tau$) is given by

$$\omega_{\max}\tau = 1, \tag{7}$$

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}, \tag{8}$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}, \tag{9}$$

where $M'$ and $M''$ are the real and imaginary electrical modulus.

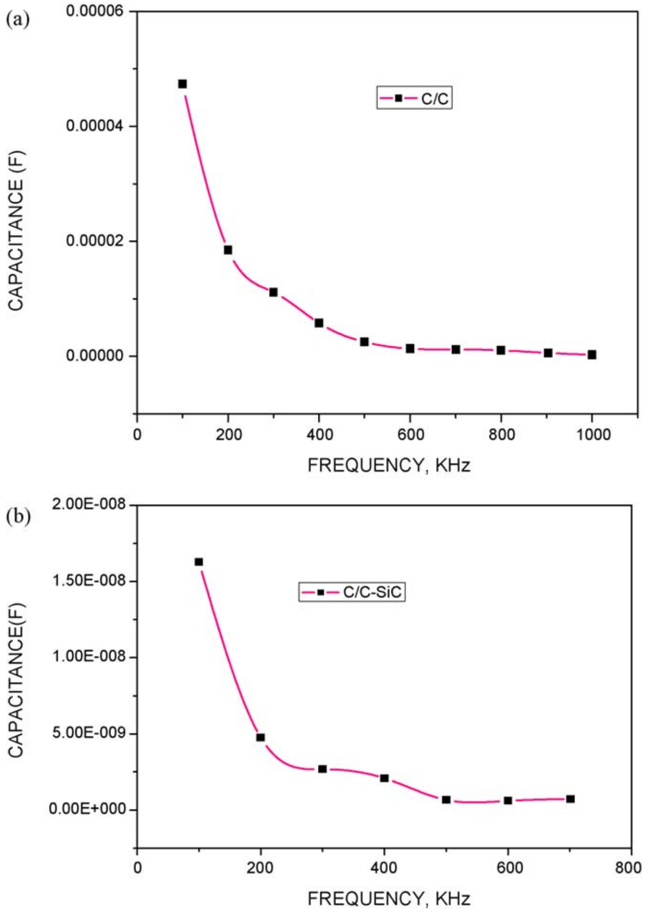

Fig. 2. Variation of capacitance with frequency of (a) C/C composite and (b) C/C–SiC composite.

The ratio of the power dissipated in the test material to the power applied equal to the tangent of the loss angle, or the cotangent of the phase angle. The dissipation factor can be calculated using:

$$D = \tan\delta = \cot\theta = \frac{1}{2\pi f R_p C_p} = \frac{\varepsilon''}{\varepsilon'}, \tag{10}$$

where $\delta$ is the loss angle, $\theta$ is the phase angle, $f$ is the frequency, $R_p$ is the equivalent parallel resistance, and $C_p$ is the equivalent parallel capacitance.

In the present work, electrical conductivity of C/C and C/C–SiC composites was studied. The electrical observations were taken at the frequency range to see the conductive behaviour of C/C and C/C–SiC composites. The microstructural behaviour of both ceramic composites was observed by the scanning electron microscope to verify the effect of frequency on electrical conductivity.

## 2. Experiments

### 2.1. Materials

Carbon/carbon–silicon carbide composite (C/C–SiC) was manufactured by liquid siliconising infiltration (LSI) method. The cross-ply carbon fibres were 2D stacked and impregnated with phenolic resin using hand-laying procedures. The mould was then warm pressed, cured and post-cured in a vacuum oven to obtain the carbon fibre reinforced plastic composites (CFRP). The open porosity of the matrix was nearly about 1% at this step. The CFRP's were thermally treated in inert atmosphere to 900 °C and then in vacuum up to 1650 °C. This process results in a shrinkage the polymer matrix by evolving mainly, CO, $CO_2$ and $H_2O$ and yields carbon/carbon composites with an interconnecting pore structure, which can be described as a translaminar crack pattern. The open porosity at this stage was about 20%. The manufacturing C/C–SiC composite involves melting of silicon, which infiltrates into the cracks/pores of the porous C/C laminate preferably along the fibre direction, and reacts with carbon to form silicon carbide. In case of 2D reinforcements and high fibre matrix bonding, layers of SiC occur around segments of carbon fibres resulting in an internal volumetric protection. The processing of Si–SiC porous ceramics involves the addition of an oxidation step to the LSI process. Usually, the LSI process gives C/C–SiC composites containing significant amount of unreacted free carbon together with unreacted free silicon. C/C–SiC ceramics were oxidized in ambient air/oxygen. However, the temperature to which the samples were subjected and the holding times play an important role. The following table lists the oxidation temperatures and the evolved products of the various constituents of C/C–SiC composites.

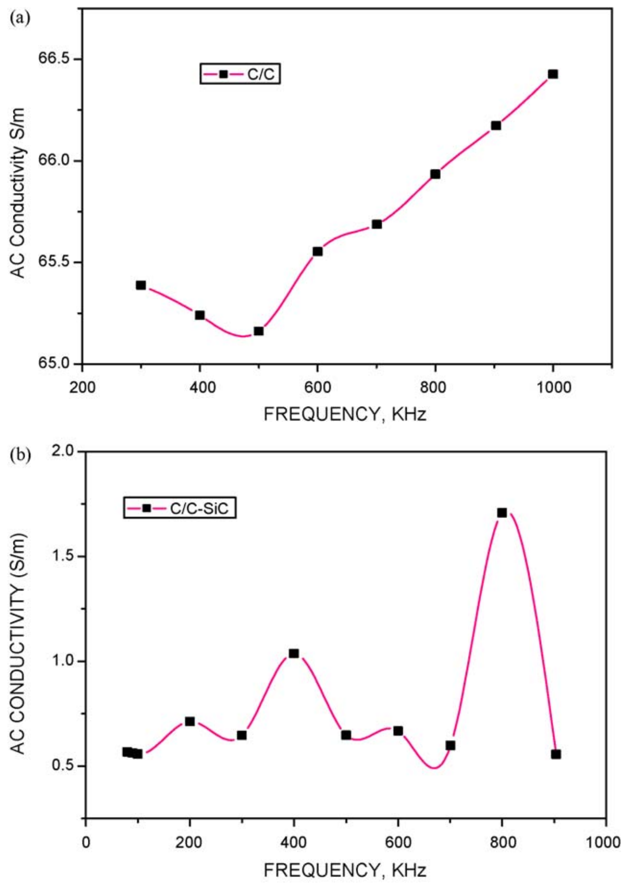

Fig. 3. Variation of AC conductivity with frequency of (a) C/C composite and (b) C/C–SiC composite.

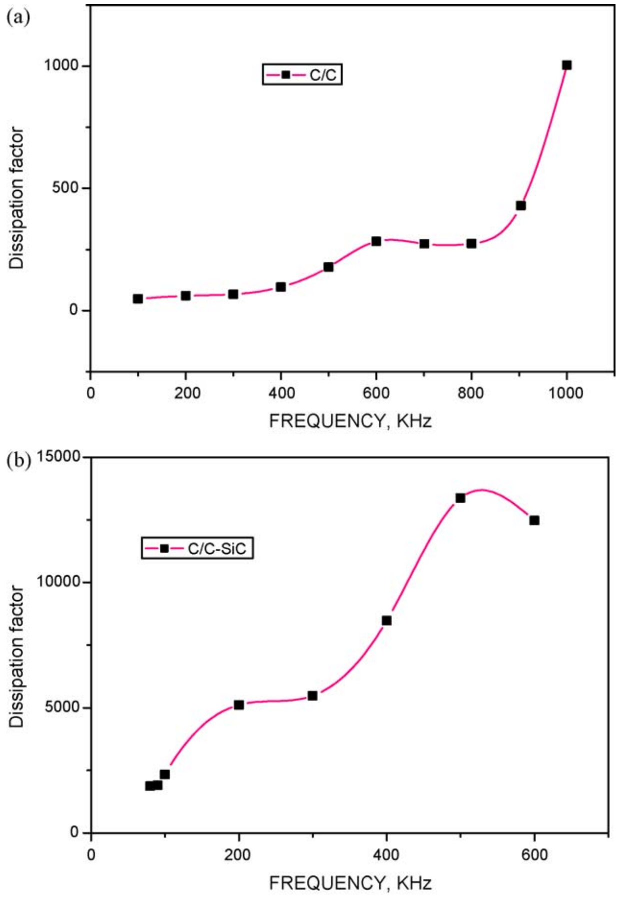

Fig. 4. Variation of dissipation factor with frequency of (a) C/C composite and (b) C/C–SiC composite.

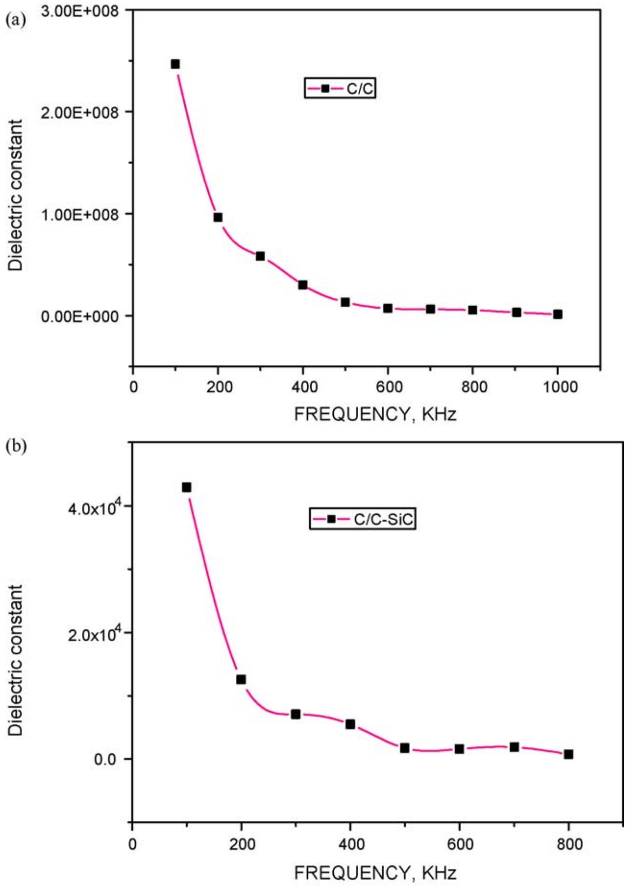

Fig. 5. Variation of dielectric constant with frequency of (a) C/C composite and (b) C/C–SiC composite.

C/C–SiC was fabricated in the form of rectangular plates of 3 mm nominal thickness. C/C–SiC is a tough ceramics. The investigations refer to cross-woven (0°/90°) C/C–SiC composites with high tenacity (HTA) carbon fibre ($\Phi = 7\ \mu m$) as reinforcement, and the matrix was silicon carbide. The volume fractions are 60% carbon fibre, 38% silicon carbide and 2% silicon. Large amounts of microcracks appeared during the pyrolysis step of LSI technique [4], as can be seen from Fig. 1(a).

A processing route of yarn method was used to produce the carbon/carbon (C/C) rectangular plates of 3 mm thickness, fibre orientation of 0°/90° and 50% volume fraction. Polyacrylonitrile (PAN) based high modulus (HTA) carbon fibre (Torayca M40) was used because of good properties at high temperature. Fractograph shows that most of the fibres are pullout and debonded from the matrix [4] as can be identified from Fig. 1(b).

### 2.2. Impedance tests

The electrical conductivity was carried out under stationary heat flow conditions using a HP 428a Impedance Analyser at room temperature. The specimens were prepared in the form of plates having 8 mm × 8 mm × 3 mm dimensions. Specimens were coated by silver for better conductivity between probes and specimen. Electrical conductivity was measured in the range of frequency 100 kHz to 2 MHz and other properties were obtained by using Eqs. (1)–(10).

## 3. Results and discussion

The electrical conductivity, capacitance, dissipation factor, dielectric constant, dielectric loss, real and imaginary moduli, and real and imaginary impedances were plotted versus frequency as shown in Figs. 2–10. A plot of capacitance versus frequency for the C/C and C/C–SiC composites is shown in Fig. 2(a) and (b).

It can be seen from the figures that the capacitance decreases with increase in frequency. But, C/C composite gives higher value of capacitance than the C/C–SiC composite, because C/C composite resulted in higher AC conductivity compared to C/C–SiC composite (Fig. 3(a) and (b)) due to better interface coherence between fibres and matrices. Also, conductivity fluctuated in C/C–SiC composite with the increase of frequency due to presence of microcracks.

Fig. 4(a) and (b) indicates that the dissipation factor increases very rapidly with the increase of frequency in both composites. This may be related to a possible increase in the number of conduction paths created between the fibres and matrices, which accumulates in the composite and decreases the width of the potential barriers within the bulk region of high

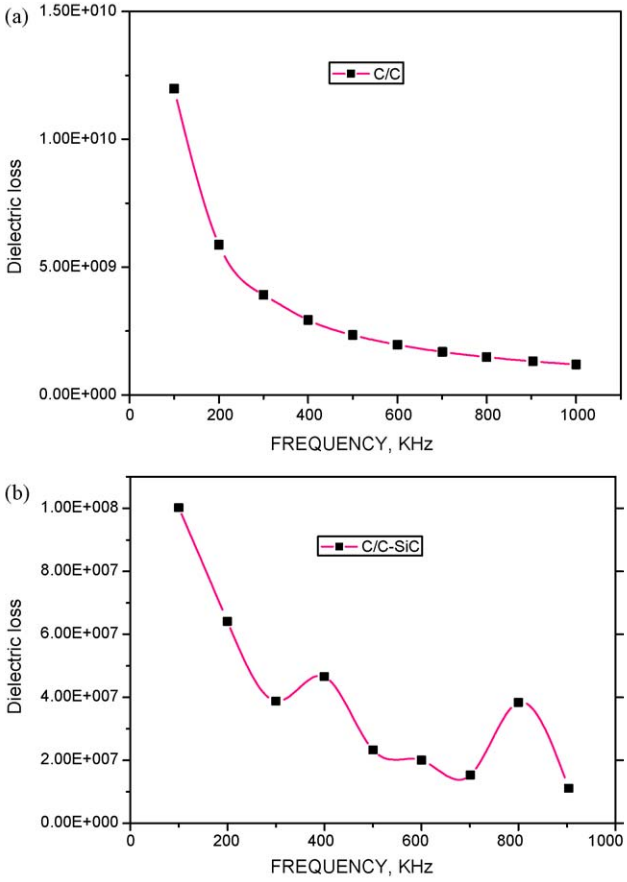

Fig. 6. Variation of dielectric loss with frequency of (a) C/C composite and (b) C/C–SiC composite.

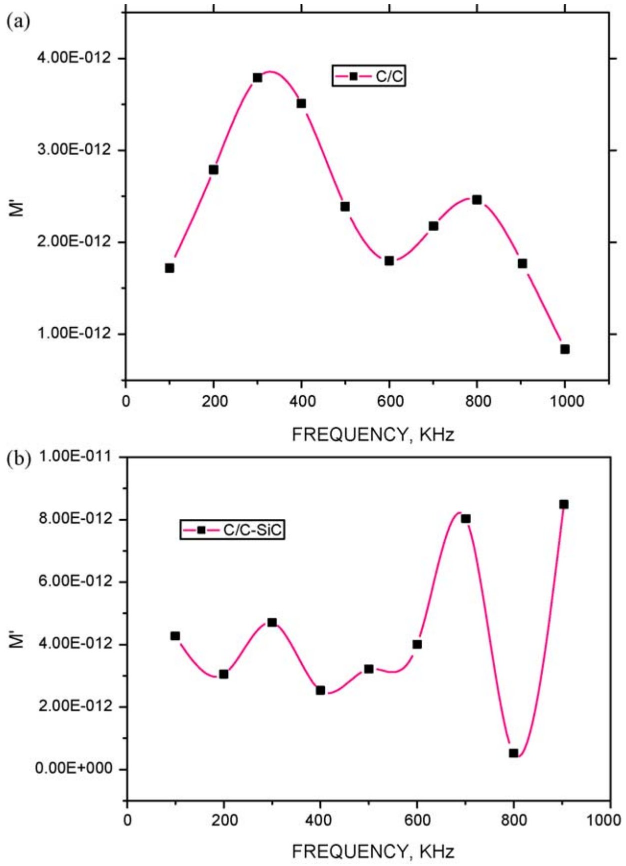

Fig. 7. Variation of real electrical modulus with frequency of (a) C/C composite and (b) C/C–SiC composite.

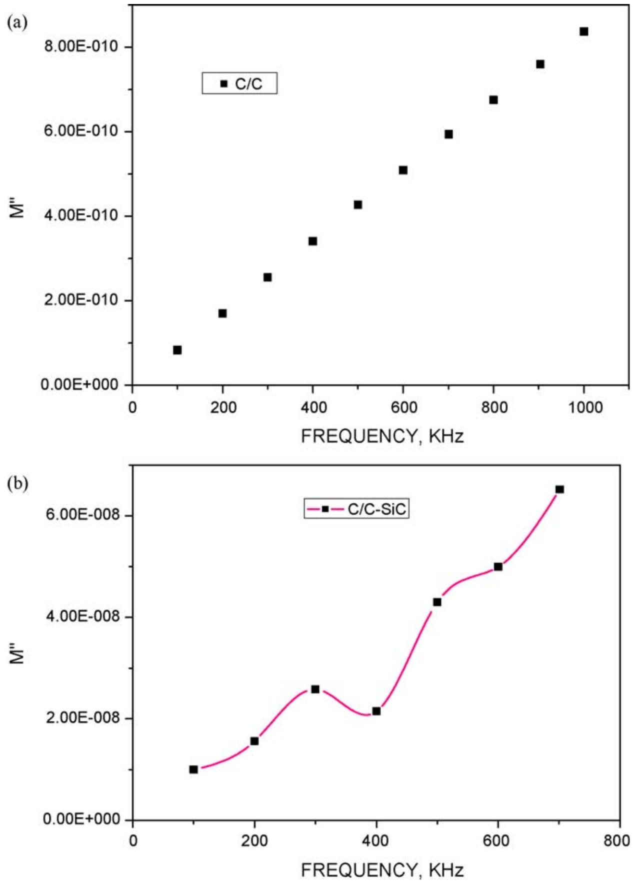

Fig. 8. Variation of imaginary electrical modulus with frequency of (a) C/C composite and (b) C/C–SiC composite.

conductivity [6]. Therefore, more charge carrier may be able to 'hop' by tunnelling, resulting in the decrease in bulk resistance. It can be observed that dielectric constant and dielectric loss give higher values at about 100 kHz frequency for C/C and C/C–SiC composites, as shown in Figs. 5 and 6.

After 100 kHz frequency, dielectric constant and dielectric loss decreases gradually with the increase of frequency. This may be associated with Maxwell–Wagner mechanism (interfacial space charge) and the electrode polarization effect. At low frequencies, accumulations of electronic impurities and space charges also have a similar effect [7]. These effects cause large and rapid increase in the dielectric constant and dielectric loss for both composites. It can be observed that dielectric constant and dielectric loss give increase in dielectric constant and dielectric loss appeared due to orientation of dipoles, increased segmental mobility of composites.

Fig. 7(a) shows that real electrical modulus in C/C composite increases with increase of frequency up to 350 kHz and then decreases till 600 kHz frequency. The increase and decrease tendency of real electrical modulus reverted because of distortion in electrical path, whereas, real electrical modulus in C/C–SiC composite fluctuates with increase of frequency due to irregularity of electrical continuity, as shown in Fig. 7(b). Because, LSI process gives C/C–SiC composites containing significant amount of unreacted free carbon and silicon, which change the electrical properties of ceramic composites.

On the other side, imaginary electrical modulus increases linearly with the increase of frequency in both the composites, as can be seen from Fig. 8(a) and (b). These indicate that the ceramic composite materials are electrically equivalent to network that reduces to a pure resistance. The distance of the intersection from the origin represents the resistive bulk resistance. Also, it can be seen that lower value of resistivity in C/C composite corresponds to better electrical conductivity. This may be related to a possible increase in the number of conduction paths created between the fibre and matrix.

Generally, the ac electrical conductivity is attributed to the electronic interaction process and formation of conductive network takes place in the composites. The electric charges flow more rapidly through hopping or tunneling mechanisms. The C/C composite exhibited a large increase in electrical conductivity compared to the C/C–SiC composite, because addition of silicon in C/C–SiC composite increases the interface strength [4]. Therefore, in the range of the percolation threshold the electrical conductivity of the composites is anisotropic. Fig. 3(a) and (b) makes these phenomena more clear when measuring the conductivity. Over the whole frequency range the composites are conductive.

## 4. Conclusions

Based on the experimental observations with the C/C and C/C–SiC composites, following conclusions can be drawn:

Capacitance decreases with increase of frequency but conductivity and dissipation factor increases with the influence of frequency for both the composites.

Dielectric loss and dielectric constant of both composites increases rapidly with increase of frequency. This shows that as the frequency is raised, the interfacial dipoles have less time to orient themselves in the direction of the alternating field and to forming clusters of fibres and matrices. The imaginary electrical modulus increases linearly due to increase of frequency whereas real electrical modulus reduces with the frequency for both the composites.

The overall performance of capacitance and conductivity are possible due to transfer of electron through the carbon fibre, carbon matrix and silicon carbide phases.

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