Synthesis of polymer-derived graphene/silicon nitride-based nanocomposites with tunable dielectric properties

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Within the present work, reduced-graphene oxide (rGO)/silicon nitride (Si_3N_4) nanocomposites were prepared upon pyrolysis of a graphene oxide (GO)-filled polysilazane. The novel preparative approach consists in the synthesis of the polysilazane in the presence of different concentrations of GO, yielding a homogeneous GO/polysilazane composite which was subsequently thermally converted in Ar atmosphere into rGO/ Si_3N_4 nanocomposites. Hot-pressing of the obtained nanocomposite powders delivered monolithic rGO/ Si_3N_4 . All prepared samples exhibited the presence of homogeneously dispersed rGO phase within an amorphous or crystalline silicon nitride matrix, as for the as-prepared and hot-pressed samples, respectively. An increasing amount of rGO in the nanocomposites was found to gradually suppress the crystallization of the silicon nitride matrix into α - Si_3N_4 . Moreover, depending on the volume fraction of the graphene phase in the ceramic nanocomposites, different dielectric properties were observed, indicating a facile preparative method to produce materials with tunable electromagnetic waves (EMW) behavior.

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1. Introduction

EM absorbing and shielding materials are utilized to provide protection against EM interference (EMI) as well as EM pollution. The primary strategy to provide EM shielding is to use EM reflective materials, typically metals. EM absorbing materials are needed in anechoic chambers and stealth ships/planes and should have electric and/or magnetic dipoles, which interact with the EM field and attenuate the incident EM waves. Ferrites and metal powders, which produce large electric and magnetic loss, are normally used in this area.¹⁾ Recently, electrical insulating polymers, which are EM transparent, were combined with carbon-based fillers to provide EM absorbing and shielding low density composites with outstanding mold ability and processability.²⁾ Furthermore, composites consisting of polymers and carbon-based fillers such as carbon nanotubes (CNTs) or graphene have tailorable complex permittivity and electrical conductivity.³⁾ However, these polymer composites have their intrinsic disadvantages. They cannot be used in structural applications at high temperature and harsh environments, due to their low decomposition temperature. In contrast, nanocomposites consisting of carbon-based fillers dispersed within a EM transparent ceramic matrix (e.g., Si_3N_4) may provide great effectiveness in the X-band as well as exceptional stability at high-temperatures and in harsh environments.⁴⁾

Rather few papers have been reported on graphene/ceramic composites. Among those, most of the studies focused on the effect of the graphene phase on the mechanical properties of the composites. Thus, it was shown that the fracture toughness of

Si_3N_4 was improved by $\sim 235\%$, i.e. from 2.8 to 6.6 MPa $\text{m}^{1/2}$, at only 1.5 vol% loading of graphene.⁵⁾ Also the fracture toughness of alumina was significantly improved (as with 53%) upon loading with 2 wt% graphene.⁶⁾ Regarding the functional properties, enhanced electrical conductivity as well as a rather small percolation threshold ($< 3 \text{ vol}\%$) were reported for graphene/alumina composites.⁷⁾ However, the dielectric properties of graphene-containing ceramic composites have been rarely studied.⁸⁾ Similar to graphene/polymer composites, an improved electrical conductivity of graphene-containing ceramic composites may lead to an increase of the dielectric constant and dielectric loss, which makes graphene/ceramic composites suitable in applications which require EM shielding materials.

The main objective of this work was to synthesize graphene/ Si_3N_4 nanocomposite ceramics from a GO-filled preceramic polymer via polymer-derived ceramics route. For this purpose, the synthesis of the preceramic polymer was performed in the presence of highly dispersed GO, yielding a homogeneous GO/polysilazane composite which was subsequently thermally converted (Ar, 1100°C) into graphene/silicon nitride. The prepared nanocomposites were investigated concerning dc and ac conductivity.

2. Experimental procedure

2.1 Materials synthesis

GO was synthesized via the method reported by Marcano et al.⁹⁾ Thus, 3.0 g of graphite flakes were added to a 400 ml mixture of concentrated H_2SO_4 and HNO_3 (vol. ratio 9:1) and refluxed for 12 h at 50°C. The suspension was subsequently diluted upon pouring it onto 600 ml ice while 5 ml H_2O_2 was added at the same time. After multiple washing/centrifugation steps, the obtained material was vacuum-dried (10^{-2} mbar) at 55°C for 4 h. The reduction of GO was carried out through

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Table 1. rGO-Si₃N₄ samples prepared within the present study (the amounts of SiCl₄ and HMDS were constant, while the amount of GO varied)

Sample Code	Amount of SiCl ₄ [g]	Amount of HMDS [g]	Amount of GO [mg]
XF0			0
XF1			31
XF2	5	5.9	62
XF5			155
XF10			310

thermal pyrolysis in the atmosphere of Ar and N₂ at 1100°C with a heating rate of 100 K/h.

The synthesis of the polysilazane was performed by reacting SiCl₄ with HMDS. Thus, 5 g SiCl₄ were added dropwise to a solution of HMDS (5.9 g) in toluene (20 ml) in the presence of 5 ml of pyridine. The reaction solution was stirred at 0°C for 2 h, allowed to reach room temperature and stirred overnight before the solvent was removed in vacuum (10⁻² mbar, 40°C). The obtained solid, colorless powder was thermally treated at two different temperatures (700 and 1100°C) in Ar and N₂ atmosphere. One additional sample was heated to 1400°C in Ar atmosphere. The obtained ceramic samples are referred to as XF0_700Ar, XF0_1100Ar, XF0_700N₂, XF0_1100N₂ and XF0_1400Ar, respectively. Furthermore, a Si₃N₄-based monolithic sample (referred to as hot-pressed XF0) was prepared via hot-pressing of XF0_1100N₂ (45 MPa, 1600°C, N₂ atmosphere).

The synthesis of the polysilazane was additionally performed in the presence of different amounts of GO. Thus, in this case, SiCl₄ was added dropwise to HMDS solutions containing the dispersed GO phase. The GO/polysilazane composites were subsequently processed in a similar manner as the graphene-free materials. The obtained graphene/Si₃N₄ samples prepared within this study are listed in **Table 1**.

2.2 Materials characterization

Fourier transform infrared (FTIR) spectra were recorded on a Varian 670-IR spectrometer. X-ray diffraction (XRD) patterns were collected on a STOE STADI P transmission diffractometer with Mo K α radiation (17.5 keV, 0.709 Å). The XRD measurements on the monolithic samples were taken on a Bruker D8 Powder diffractometer with Cu K α radiation (8.05 keV, 1.57 Å). The data were collected over an incident angle (2 θ) range of 5 to 45° by using a step size of 0.2° and 20 s count time per measurement. Raman spectroscopy was performed with a LabRAM HR800 machine (Horiba Jobin Yvon) using He/Ne (633 nm) and Ar laser excitation (514 nm). Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and mass spectrometric analysis (MS) were carried out with a Netzsch STA 449 C Jupiter TA device. The elemental analysis (C, N, O) of the samples was performed on LECO C-200 and LECO TC-436 devices. The characterization of microstructure was performed with using a Philips XL30 FEG high-resolution scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy and a transmission electron microscope (TEM JEM-2100F, JEOL, Co. Ltd., Japan) operated at 200 kV. For the TEM observation, the samples were grinded into fine powders and dispersed in ethanol (>99.5%, Junsei-Chemical Co. Ltd., Japan) using an ultrasonic bath. A small amount of the suspension was caught from the top of solution and dropped on a thin carbon film supported by Cu grid. The residual open porosity as well as the density of the monolithic samples prepared upon hot-pressing were assessed

using the water immersion method. The relative permittivity and electrical conductivity of the monolithic samples were measured by means of impedance spectroscopy with an Alpha-A13 Analyzer in the frequency range of 1 to 10⁷ Hz.

3. Results and discussion

In order to understand the properties of resulting rGO-Si₃N₄ nanocomposite, the components rGO and Si₃N₄ resulted from the thermal decomposition of GO and the polysilazane respectively, were analyzed individually. A special attention for accorded to the synthesis of silicon nitride from a highly cross-linked polysilazane produced via a reaction of SiCl₄ with HMDS.

3.1 Preparation and characterization of rGO

FTIR spectroscopy was used to assess the as-prepared GO [**Fig. 1(a)**]. Absorption bands at 3420 (OH), 1720 (C=O), 1220 (C–O) and 1100 cm⁻¹ (C–O–C) indicate the successful preparation of GO.¹⁰⁾

Figure 1(b) shows the XRD pattern of the prepared of GO. The interlayer spacing of the prepared GO was found to be 0.920 nm, which is significantly higher than that of graphite (0.335 nm)¹¹⁾ and reveals that the GO prepared in this work was highly oxidized. The thickness of the GO crystallites was estimated by the Scherrer's equation to be ca. 11.6 nm. Thus, it is estimated that the prepared GO crystallites consist in average of ca. 12–13 graphene sheets.

Thermogravimetric analysis of GO coupled with in situ MS was carried out under argon up to 1400°C (**Fig. 2**). GO shows a slight mass loss from room temperature to 100°C, followed by a remarkable mass loss up to 250°C. At higher temperature, the mass of GO further decreases. The mass loss up to 100°C is due to the elimination of inter-lamellar water, whereas the major mass loss up to 250°C is assigned to the release of oxygen functionalities in GO. Thus, the mass loss in this temperature range is accompanied by the release of gaseous CO, CO₂ and H₂O.¹²⁾ At higher temperatures a steady mass loss is recorded, which indicates a further reduction of GO. Thus, the release of amount of CO₂ and CO has been detected up to 700 and 900°C, respectively. This has been attributed to the sublimation or removing of the damaged/oxidized graphitic regions.^{13),14)}

Thermally reduced graphene (rGO), which was obtained via thermal treatment of GO at 1100°C (in Ar/N₂ atmosphere), was studied by FTIR and Raman spectroscopy (**Fig. 3**). The FTIR spectrum of rGO [**Fig. 3(a)**] indicates the almost complete removal of hydroxyl as well as carboxyl groups (elimination of absorption bands at 1740, 1230 and 3200–3300 cm⁻¹); whereas some residual epoxy groups are left. Moreover, the absorption band at 1630 cm⁻¹ (C=C) also vanished in the FTIR spectra of rGO.^{15),16)}

The GO and rGO samples were also investigated by Raman spectroscopy, which is a very sensitive technique in order to evaluate the nano/microstructure of carbon-based materials and consequently provide valuable information about their ordering, hybridization, defect state etc. The first order Raman spectrum of sp² carbon exhibits a band of E_{2g} symmetry, which relates to bond stretching of sp² carbon pairs contained in rings or chains. This band is called G band and appears at around 1575–1595 cm⁻¹. Disordered or nanostructured carbon-based materials, which might contain also some amount of sp³ hybridization, exhibit additional bands in their first order Raman spectrum, such as a band of A_{1g} symmetry, which relates to breathing modes of sp² carbon atoms within rings (so-called D band; its position depends on the laser wavelength; ca. 1350 cm⁻¹ at 514.5 nm), a

Fig. 1. FTIR spectrum (a) and XRD pattern (b) of the as-prepared GO.

Fig. 2. TG (black line) and QMID (quasi multiple ion detection, colored curves) ion current curves during the heat treatment of GO in argon.

band related to C–C sp^3 vibrations (ca. 1150–1200 cm^{-1} ; A_{1g} symmetry, T band), a D'' band (ca. 1500 cm^{-1} , related to amorphous carbon), as well as a D' band (E_{2g} symmetry, ca. 1620 cm^{-1} , disordered graphitic lattice related to surface graphene layers)^{17),18)}. Figure 3(b) shows the Raman spectra of GO and two rGO samples (as-prepared upon thermal treatment of GO

Fig. 3. FTIR (a) and Raman (b) spectra of GO and rGO obtained upon heat treatment in nitrogen (GO_1100N₂) and argon (GO_1100Ar) atmosphere.Table 2. Raman graphitization indices (L_a , L_{eq}) for the as-prepared GO and rGO

	I_D/I_G	A_D/A_G	L_a [nm]	L_{eq} [nm]
GO	1.59	2.57	1.57	2.04
rGO_1100N ₂	1.87	2.73	1.50	2.34
rGO_1100Ar	1.90	2.74	1.59	2.27

in N₂/Ar atmosphere), which exhibit two main bands, at 1580 and 1360 cm^{-1} . An additional band at ca. 2700 cm^{-1} , which is referred to as 2D band (second order band), can also be observed in the Raman spectra in Fig. 3(b).

Table 2 summarizes some Raman graphitization indices such as the intensity ratio of the D and G modes (I_D/I_G , A_D/A_G), the lateral cluster size L_a [$L_a = 4.4(A_D/A_G)^{-1}$ nm]^{19),20)} as well as the parameter L_{eq} which describes the average continuous graphene length including tortuosity and is defined cf. $L_{eq} = 8.8(A_{2D}/A_G)^{-1}$ nm.²¹⁾

As shown in Fig. 3(b), the thermal reduction of GO induces an increase of the I_D/I_G ratio from 1.59 (in the as-prepared GO) to 1.87 and 1.90 in rGO obtained in N₂ and Ar atmosphere, respectively (see Table 3). Interestingly, the values of L_{eq} are only slightly larger than those of L_a , indicating that probably the

Fig. 4. FTIR spectrum of XF0 and of the resulting silicon nitride ceramics synthesized upon pyrolysis at different temperatures in Ar and N₂ atmospheres.

size of the rGO sheets is rather small. However, the equations used for the estimation of L_a and L_{eq} have large uncertainty for $L_a/L_{eq} < 5 \text{ nm}^{22}$) and consequently the values of L_a and L_{eq} must be treated carefully, as they usually are strongly underestimated (please see the discussion on the TEM data below).

3.2 Preparation of silicon nitride

Hexamethyldisilazane (HMDS) was reacted with tetrachlorosilane in the presence of catalytical amounts of pyridine. The novel preceramic polymer was characterized by FTIR spectroscopy (see XF0 in Fig. 4). The strong absorption peak at 3380 cm^{-1} is assigned to the N–H stretch vibrations. The absence of a double peak in the N–H absorptions area indicates that there are no $-\text{NH}_2$ groups present in the precursor. The absorption bands at $2900\text{--}2955 \text{ cm}^{-1}$ as well as 1409 cm^{-1} are attributed to C–H bonding. Si–CH₃ stretch vibrations are also confirmed by the absorption at 1250 cm^{-1} . Additionally, very strong bands related to Si–N–H, Si–N–Si as well as Si–C were identified at 1160, 907 and 823 cm^{-1} , respectively. Additionally, an absorption band at 1026 cm^{-1} was analyzed and assigned to Si–O–Si groups and is related to slight contamination of the precursor with oxygen during the synthesis procedure.

The polymer-to-ceramic transformation of the prepared polysilazane was assessed by TGA/DTA (Fig. 5). The ceramic yield of the preceramic polymer was 47% and the ceramization process presents three main decomposition steps. The first step (mass loss of ca. 24 wt%) occurs at ca. 200°C and is predominantly caused by the evaporation of low weight molecules (oligomers); their presence can be explained by the fact that the synthesized polysilazane is probably not highly polymerized and additionally does not exhibit cross-linkable substituents such as Si–H or vinyl groups. The second step (mass loss ca. 24 wt%) occurs between 200 and 700°C and mainly relies on transamination processes and the release of hydrocarbons (i.e., CH_4), as detected by in situ MS (not shown here). At higher temperatures, a third mass loss step was determined and it relates to the release of ammonia and methane.

Fig. 5. TG (black line) and DTA (red line) curves during the thermal treatment of XF0 in argon atmosphere.

The XRD patterns of the XF0-based samples prepared upon pyrolysis in argon atmosphere at 1100, 1400 and 1600°C , are illustrated in Fig. 6. XF0_1100 was found to be X-ray amorphous; whereas the samples prepared at 1400 and 1700°C exhibited the presence of $\alpha\text{-Si}_3\text{N}_4$ as crystalline phase.

3.3 Synthesis and characterization of rGO/Si₃N₄ nanocomposites

The rGO-containing Si₃N₄ nanocomposites were prepared from precursors synthesized upon mixing GO with HMDS and SiCl_4 in the presence of pyridine. FTIR spectroscopy results (see Supporting Information) revealed no significant differences between the GO-containing precursors and the neat polymer. Whereas the FTIR spectra of the rGO/Si₃N₄ samples obtained upon pyrolysis show the presence of an absorption band assigned to Si–O–Si units, which probably relate to the interface bonding between the rGO phase and the silicon nitride matrix.

The synthesized rGO/SiN_x nanocomposites were characterized by transmission electron microscopy (TEM). Figure 7 displays TEM micrographs of XF10 prepared upon pyrolysis at 1100°C .

The ceramic nanocomposite seems to be rather amorphous. The TEM micrographs indicate the presence of randomly oriented, well exfoliated and distributed rGO, which are uniformly embedded within the ceramic matrix. Additionally, some amount of mesopores was also identified within the microstructure of the nanocomposites. According to the high-magnification TEM micrographs Fig. 7(b), the rGO nanoparticles consist of 8–10 graphene layers. This result agrees well with that obtained from the XRD data of the as-prepared GO, thus indicating that the pyrolysis process did not significantly affect its stacking number. The interlayer distance in the rGO particles was determined to be 0.37 nm, which is larger than the interlayer distance in graphite (i.e., 0.335 nm) but significantly shorter than that found in the as-prepared GO (0.855 nm). Moreover, the rGO precipitations were found to be highly wrinkled (see Fig. 7) and have aspect ratios in the range of 20 to 40.

The chemical composition of the rGO/SiN_x samples prepared upon pyrolysis at 1100°C in N₂ atmosphere is shown in Table 3. The samples exhibit the presence of relatively large amounts of oxygen, which relies on the use of GO for the preparation of the nanocomposites. Moreover, the carbon content in the GO-free silicon nitride was negligible; whereas the C content in the rGO/SiN_x nanocomposites increases as the amount of GO is increased, indicating GO as being the source for the carbon content in the nanocomposites.

Table 3. Chemical composition of the as-prepared rGO-Si₃N₄ samples (1100°C, N₂ atmosphere)

Name	Si [wt%]	C [wt%]	N [wt%]	O [wt%]	Empirical Formula	Phase Composition [vol%]			
						Si ₃ N ₄	SiO ₂	Si	rGO
XF0	59.27	0.10	24.67	15.96	Si ₁ N _{0.83} O _{0.47} C _{0.004}	50.91	42.33	6.76	0
XF1	65.85	1.06	27.62	11.47	Si ₁ N _{0.93} O _{0.34} C _{0.04}	60.38	27.85	10.20	1.56
XF2	63.12	1.72	26.04	9.12	Si ₁ N _{0.83} O _{0.25} C _{0.06}	57.84	20.58	19.13	2.45
XF5	58.62	2.53	18.56	20.29	Si ₁ N _{0.64} O _{0.61} C _{0.10}	37.84	44.22	14.48	3.46
XF10	54.38	5.24	23.89	16.49	Si ₁ N _{0.88} O _{0.53} C _{0.22}	49.81	37.57	5.14	7.47

Fig. 6. XRD patterns of XF0 prepared upon pyrolysis at 1100, 1400 and 1600°C in argon atmosphere.

From the chemical composition of the prepared nanocomposites, the volume fraction of rGO was estimated. As shown before, the interlayer distance in the rGO particles was 0.37 nm. Considering the density of rGO being inversely proportional to the interlayer distance, the density of rGO in the as-prepared rGO/Si₃N₄ nanocomposites was estimated to be 1870 kg/m³ [cf. $\rho_{rGO} = (\rho_{Graphite} \cdot d_{Graphite}) / d_{rGO}$]. The volume fractions of rGO in the prepared nanocomposites were evaluated upon considering the matrix material consisting of Si₃N₄ (density 3200 kg/m³), SiO₂ (2200 kg/m³) and excess silicon (2300 kg/m³) and are listed in Table 3.

The rGO/Si₃N₄ samples prepared upon pyrolysis at 1100°C were hot-pressed at 1600°C in nitrogen atmosphere to prepare monolithic rGO/Si₃N₄ nanocomposites. The Raman spectra are shown in Fig. 8. The sample XF0 shows the presence of absorption bands in the range of 400 to 1000 cm⁻¹ [Fig. 8(a)] which were assigned to α-Si₃N₄.²³⁾ In the Raman spectra of the rGO-containing nanocomposites, i.e. XF5 and XF10, the typical absorption bands of carbon (D, G and 2D bands) can be also identified and were assigned to the rGO phase.

Figure 9 shows the XRD patterns of the hot-pressed monoliths. All samples show the presence of α-Si₃N₄. In the XRD patterns of rGO-containing samples, two additional reflections were observed at 15.2 and 16.84°, whose assignment was not possible yet.

Note that no crystalline SiC was present in the hot-pressed rGO/Si₃N₄ samples, indicating that the reaction of the rGO phase with Si₃N₄ to form β-SiC and gaseous N₂ is suppressed. Additionally, the crystallinity of the samples XF0, XF1 and XF2 was found to be significantly higher as that in XF5 and XF10, indicating that the rGO phase suppresses the crystallization of Si₃N₄ ceramics. This is in agreement to observations made in

Fig. 7. Typical TEM micrographs of as-prepared XF10. The marked region in (a) is shown magnified in (b).

polymer-derived ceramics (i.e., SiCN materials), which were also shown to have an improved crystallization resistance at high-temperatures as the fraction of the segregated carbon phase increases.^{24),25)}

The TEM image of hot-pressed XF10 is shown in Fig. 10. The presence of α-Si₃N₄ nanocrystals with an average size of 10 nm can be clearly seen and thus supports the results obtained via XRD. Moreover, the tortuous rGO phase which in some regions consists of just 2 graphene layers can also be observed, indicating the successful preparation of a Si₃N₄ nano composites containing a well dispersed graphene-like phase.

The skeletal density and the open porosity values for the prepared hot-pressed samples are summarized in Table 4, indicating rather high porosity in all monolithic samples. This is obviously related to the very low self-diffusion coefficients in the silicon nitride matrix. Despite the obtained samples were not dense, they were used for the assessment of their dielectric properties (the effect of porosity on the electrical conductivity and dielectric constant was taken into account though).

The dc electrical conductivity of the hot-pressed samples was assessed. The electrical conductivity σ has been defined as the inverse of the electrical resistivity (ρ), i.e. $\sigma = (1/\rho)$, whereas ρ relates to the resistance R and the sample dimensions cf. $\rho = R(A/l)$. The values of the electrical conductivity of the hot-pressed samples are listed in Table 5.

The rGO-free Si₃N₄ monolith (i.e., XF0) has an electrical conductivity of 1.09×10^{-11} S/m, which is similar to reported

Fig. 8. Raman spectra of XF0 (a), XF1 (b), XF5 (c) and XF10 (d) prepared upon hot-pressing at 1600°C in N₂ atmosphere.

Fig. 9. XRD patterns of hot-pressed XF0, XF1, XF2, XF5 and XF10.

values for Si₃N₄-based ceramics.²⁶⁾ Upon increasing the volume fraction of rGO, the electrical conductivity increases significantly. For instance, the electrical conductivity of XF5 (3.46 vol% rGO) was found to be 1.9×10^{-5} S/m and thus six orders of magnitude higher than that of the rGO-free Si₃N₄. Whereas XF10 exhibited an electrical conductivity of 2.64×10^{-1} S/m (Fig. 11).

Despite the fact that the rGO phase is well distributed within the Si₃N₄ matrix material, the percolation threshold in the prepared rGO/Si₃N₄ nanocomposites is estimated to be in the range of 2 to 7 vol%, which is relative large in comparison to those of other reported graphene-based composites material.²⁷⁾ This probably might rely on the small aspect ratio of the rGO phase.

Fig. 10. HR-TEM micrograph of hot-pressed XF10, showing the presence of α-Si₃N₄ nanocrystallites and well-dispersed few-layer rGO.

Table 4. Porosity and skeletal density of hot-pressed Si₃N₄ and rGO/Si₃N₄ samples

Sample	Porosity [%]	Skeletal Density [kg/m ³]
XF0	32.9	1780
XF1	42.4	1540
XF2	25.9	1850
XF5	38.6	1690
XF10	44.6	1550

Figure 12 shows the relative complex permittivity ε (both the real and the imaginary part, cf. $\varepsilon = \varepsilon' + i\varepsilon''$) and the dielectric loss $\tan \delta$ for the hot-pressed Si₃N₄ and rGO/Si₃N₄ samples as functions of the frequency (the frequency range was from 1 and

Table 5. Electrical conductivity of the hot-pressed rGO/Si₃N₄ samples

Sample	Volume fraction [%]	Electrical conductivity [S/m]
XF0	0	1.09E-11
XF1	1.56	1.54E-11
XF2	2.45	1.18E-10
XF5	3.46	1.88E-5
XF10	7.47	2.64E-1

Fig. 11. Electrical conductivity of the hot-pressed rGO/Si₃N₄ samples as a function of the volume fraction of the rGO phase.

10⁷ Hz). Due to the fact that the frequency range used in this study does not correspond to that responsible for atomic and electronic polarization, their contribution to the dielectric behavior of the samples is frequency independent and negligible. Thus, it is considered that the permittivities measured in this work rely on space charge polarization phenomena. At 10 MHz, XF0 shows a real part permittivity value of 5, which is only slightly smaller than that of pure Si₃N₄.²⁸⁾ Upon incorporating rGO, the permittivity values slightly increase; whereas they significantly increase as the content of rGO reaches 3.46 vol% (as in XF5). The evolution of the dielectric properties in rGO/Si₃N₄ as a function of the rGO content shows a typical percolation transition behavior as it was observed for the electrical conductivity [Fig. 12(d)].

Thus, at low rGO loading, the relative permittivity is mainly determined by the insulating silicon nitride matrix. At higher rGO loading, the influence of the semiconducting rGO phase becomes significant and contributes to a significant increase of the permittivity.²⁹⁾ Consequently, the investigated nanocomposites might be described by a parallel resistor-capacitor system (rGO and Si₃N₄, respectively), with the rGO phase acting as conductive component. When the concentration of rGO is just below the percolation threshold value, the conductive clusters might form a so-called 'super capacitor network'³⁰⁾ within the insulating matrix material, leading to large values of the permittivity. Therefore, the real part of the relative permittivity of XF10 is as high as 102 and 68 at 1 and 10 MHz, respectively.

Near the percolation threshold value, conductor-insulator composites exhibits an intensive increase of the dielectric constant.³¹⁾ As shown in Fig. 12(d), the value of ϵ' in XF0, XF1 and XF2

Fig. 12. Real (a) and imaginary (b) parts of the permittivity (ϵ' and ϵ'' , respectively) as well as the dielectric loss $\tan \delta$ (c) of the hot-pressed rGO/Si₃N₄ monolithic samples as functions of the frequency; d) Real permittivity and dielectric loss (values as for 10 MHz) as well as the dc electrical conductivity of the rGO/Si₃N₄ monolithic samples as function of the rGO volume fraction - the grayish area represents the probable region of the percolation threshold in rGO/Si₃N₄.

almost remained unchanged, while the value for XF10 is one order of magnitude larger at 10 MHz. A similar trend has been observed for ε'' , as the value for XF10 at 10 MHz is several orders of magnitude higher than that of XF2. This result suggests that the percolation threshold of the rGO/Si₃N₄ composites might be located between XF5 and XF10 and thus is in agreement with the electrical conductivity data.

XF5 and XF10 also show high values for the imaginary part permittivity and for dielectric loss while XF0, XF1 and XF2 have small values of ε'' and $\tan \delta$. Thus, XF0, XF1 and XF2 are expected to exhibit a transparent behavior towards electromagnetic waves. Whereas XF5 should behave rather as an EM absorbing material and XF10 as an EM shielding material.

Considering the values of the real and imaginary permittivity as well as those of the dielectric loss, the dielectric properties of the prepared rGO/Si₃N₄ nanocomposites can be influenced by adjusting the rGO content and thus the presented nanocomposites are expected to show different behavior toward electromagnetic waves (EMW), depending of their rGO content.

4. Conclusion

The present work emphasizes a facile preparative access to rGO/Si₃N₄ nanocomposites from a polysilazane filled with different volume fractions of GO. Due to the fact that the synthesis of the polysilazane is performed in the presence of GO, the graphene-based phase is homogeneously dispersed within the microstructure of the resulting rGO/Si₃N₄ nanocomposites. Measurements of the dc and ac conductivity of monolithic rGO/Si₃N₄ samples indicate that the percolation threshold might be located between 2 and 7 vol% rGO. The prepared nanocomposites exhibit interesting dielectric properties which can be easily tuned upon adjusting their volume fraction of rGO.

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