The role of particle distribution in the dielectric response of epoxy–boron nitride nanocomposites

I. A. Tsekmes · R. Kochetov · P. H. F. Morshuis ·
J. J. Smit

Abstract In this study, three different techniques are used for the production of epoxy-boron nitride nanocomposites in an attempt to evaluate the role of particle dispersion and distribution in the dielectric response of nanocomposites. Although the produced nanocomposites have a different particle distribution which is evaluated with a scanning electron microscopy analysis, they exhibit the same trend and similar dielectric response. The slight differences between the samples are plausibly caused by the different amount of water content rather than the particle distribution. The presence of water inside the samples is evaluated with a thermogravimetric analysis including also an analysis with a mass spectrometer. Finally, it is proposed that the dielectric response of the nanocomposites is mainly dictated by two competing mechanisms, namely polymer re-organization and water uptake, and it is suggested that high levels of reproducibility can be achieved when the particles are effectively dispersed in the polymer matrix regardless the particle distribution.

I. A. Tsekmes (✉) · R. Kochetov · P. H. F. Morshuis ·
J. J. Smit
Department of Electrical Sustainable Energy, TU Delft,
Mekelweg 4, 2628 CD Delft, The Netherlands
e-mail: i.a.tsekmes@tudelft.nl

R. Kochetov
e-mail: r.kochetov@tudelft.nl

P. H. F. Morshuis
e-mail: p.h.f.morshuis@tudelft.nl

J. J. Smit
e-mail: j.j.smit@tudelft.nl

Introduction

Epoxy composites exhibit a unique behavior regarding their dielectric response [1–6]. Nanocomposites at relatively low filler concentrations, i.e., less than 1 vol%, they show a relative permittivity which is lower than that of both the polymer and filler. As the filler concentration increases, the permittivity of nanocomposites can be higher than would be expected from the rule of mixture for the respective combination of filler and base material. The trend which epoxy nanocomposites exhibit, indicates that at least two competing mechanisms are involved; one is related to the decrease of the relative permittivity and the other one to the increase. It seems that the former prevails at low fill grades, whereas the role of the latter becomes more important at higher filler concentrations.

The decrease in the relative permittivity of epoxy composites indicates that the introduction of surface-modified fillers is capable of affecting the polymer properties in the vicinity of the particles [7]. However, the way in which the particles interact with the polymer is not well defined. It is speculated that particle dispersion and distribution significantly influence the behavior of polymer composites. If particle dispersion and distribution are of vital importance for the performance of epoxy nanocomposites, then, there should be significant differences between samples with different distribution and dispersion of particles. The term dispersion describes the extent to which nanoparticles can be separated from each other, while the term distribution refers to the spreading of particles inside the polymer matrix.

In this study, three different ex situ techniques, namely speedmixer, solvent, and nanomizer technique, are used for preparing epoxy−boron nitride (E-hBN) nanocomposites, and the role of particle distribution in their dielectric
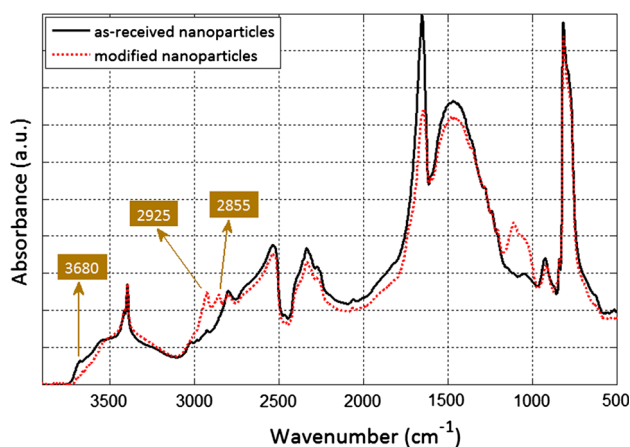
Fig. 1 Infrared spectra of as-received and surface modified-hBN nanopowder at 20 °C

response is evaluated. The three techniques lead to a different particle distribution, while the particles are well dispersed in all three cases. The results suggest that the dielectric response of the nanocomposites is mainly dictated by the filler content rather than the particle distribution. Furthermore, two main mechanisms are considered for explaining the dielectric response of the nanocomposites, i.e., matrix re-organization and water uptake.

Experimental

Materials

The base material used in this study was a type of epoxy resin consisting of bisphenol-A diglycidyl CY225 and anhydrite hardener HY225. As a filler, hBN nanoparticles with an average particle size of 70 nm were used (supplied by mkNANO). The particle size ranges from 30 to 300 nm. All particles were modified with (3-Glycidyloxypropyl)trimethoxysilane (EPPS) to improve the adhesion between the polymer matrix and fillers. EPPS was supplied by Sigma-Aldrich and the corresponding empirical formula is $C_9H_{20}O_5Si$. The particles were modified using 3 wt% of EPPS. Prior to the modification, the particles were dried at 140 °C and dispersed in ethanol by means of an ultrasonic bath for approximately 1 hour.

EPPS is chemically bonded to the surface of the nanoparticles due to the reaction of hydroxyl groups on the inorganic particles with alkoxy groups of EPPS. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used to evaluate the reaction of hydroxyl groups on the inorganic particles with the alkoxy groups of EPPS. Therefore, the spectra of as-received and modified-hBN nanoparticles were obtained and compared (Fig. 1). It

is observed that both spectra contain the characteristic bands of hBN [8]. In the case of as-received particles, the peak at 3680 cm^{-1} is ascribed to the free hydroxyl (OH) stretching vibrations of the B-OH surface groups. This peak is not included in the spectrum of surface modified particles indicating the successful reaction between EPPS and OH groups. Furthermore, in the case of modified particles, the presence of EPPS is observed at 2925 and 2855 cm^{-1}. These peaks correspond to asymmetrical CH_3 stretching and symmetrical CH_2 stretching, respectively. Both of these groups are included in the chemical structure of EPPS.

Synthesis techniques

Three different ex situ techniques were used for the nanocomposite production. The first technique includes the dispersion of particles in a solvent (ethanol) by means of an ultrasonic bath and evaporation of ethanol before further proceeding with the synthesis process. The second method includes the direct dispersion and distribution of particles in epoxy with the use of a suitable mixing device. Finally, in the third method the modified particles are again directly mixed with epoxy with the use of another device.

A prior investigation on nanocomposite production showed that the use of an ultrasonic bath is an effective way of dispersing particles [1]. Therefore in the solvent technique, the mixture of modified nanoparticles and ethanol is subjected to an ultrasonic bath for approximately 1 hour. Once the particles are dispersed in ethanol, epoxy is added to the solution. Afterward, the solution is heated to 105 °C in order for ethanol to be evaporated. The evaporation of ethanol requires several hours of heating, while the weight of the solution is closely monitored to realize the completion of the ethanol evaporation. During the evaporation procedure, it is important to maintain the dispersion of particles; therefore, a magnetic stirrer is used. Then, the appropriate amount of hardener is added to the solution and a high shear mixer at 5000 rpm for 15 min is used. The material is cast in aluminum molds and cured at 140 °C for 3 h. Afterward, the samples are post-cured at 120 °C for 16 h. It should be mentioned that prior to the curing process, the material is degassed under vacuum (0.01–0.1 mbar) for at least 2–2.5 h to get rid of the trapped air.

In the case of the speedmixer technique, modified particles are not dispersed in ethanol but instead, they are directly mixed with epoxy. The mixing of the two materials is performed with the use of speedmixer DAC 150.1 FVZ. Epoxy and dry surface-modified nanoparticles are mixed for 15 min. Afterward, the proper amount of hardener is added to the mixture and the material is mixed for another 5 min. During the whole mixing process, balls of zirconia with a diameter of 1.95 mm are used to achieve a

Table 1 Produced nanocomposites

Sample	Synthesis technique	Filler content (vol%)
Neat epoxy	–	0
E-hBN_02	Speedmixer	0.2
E-hBN_06	Speedmixer	0.6
E-hBN_1	Speedmixer	1
E-hBN_5	Speedmixer	5
E-hBN_02 S	Solvent	0.2
E-hBN_1 S	Solvent	1
E-hBN_5 S	Solvent	5
E-hBN_02 N	Nanomizer	0.2
E-hBN_05 N	Nanomizer	0.5
E-hBN_1 N	Nanomizer	1
E-hBN_5 N	Nanomizer	5

homogeneous dispersion and distribution of nanoparticles. Finally, the mixture is degassed under vacuum and cast in molds. The curing and post-curing process is the same as in the solvent technique.

Finally, the nanomizer technique includes first the dispersion of modified nanoparticles in epoxy by means of an ultrasonic bath for 15 min. Then, epoxy and particles are stirred with a rotational speed of 2000 rpm using mixer ARE 250 Thinky for 45 min. Afterward, the mixture is subjected to a dispersion process called nanomizer. Nanomizer forces agglomerations to break and leads to a good dispersion and distribution of the particles in the polymer matrix due to the ultrahigh pressure of 200 MPa and the narrow aperture (170 µm). The mixture of epoxy and particles is passed through the nanomizer ten times. Then, the proper amount of hardener is added to the mixture and the material is mixed with the mixer for 15 min. The composite is degassed under vacuum and cast in molds. The samples are cured at 140 °C for 3.3 h and post-cured at the same temperature for 72 h. All produced nanocomposites are presented in Table 1.

Measuring setups and sample characterization

The dielectric response of the specimens was determined with the use of a fully automated Alpha-A dielectric analyzer from Novocontrol. The amplitude of the applied voltage was 3 V_{rms} and the sample was placed in a cryogenic cell in which the temperature could be controlled in the range between −20 and 60 °C. The accuracy of the measurements can be significantly affected by a number of error sources such as bad contacts and thickness variation [9]. In order to ensure a good contact between the samples and external electrodes, gold electrodes were deposited on both sides of the samples. Furthermore, the error in thickness determination was estimated by calculating twice the average thickness of a sample and comparing the difference in the results. Each average thickness was calculated based on five values. The maximum error due to thickness variation is expected to be less than 2 %.

The distribution and dispersion of particles in the samples were evaluated with a scanning electron microscope (FEI Strata DB 235) which combines a field emission scanning electron column and a focused ion beam. The latter was used for milling the samples and preparing cross sections. The distribution and dispersion of particles were evaluated using 2D images and visual inspection. Evaluating the particle distribution based only on 2D images is not a straightforward procedure and thus, we used two different locations of a sample to increase the validity of the results. At both locations, a similar particle distribution is observed. Finally, it should be noted that there are several methods for quantifying the particle distribution such as the nearest-neighborhood distance method or Monte Carlo method. However, the low contrast between the particles and matrix in the images hindered the use of such a method. The low contrast makes impossible for a software to accurately detect all particles, especially the smallest ones, in order to further proceed with the analysis.
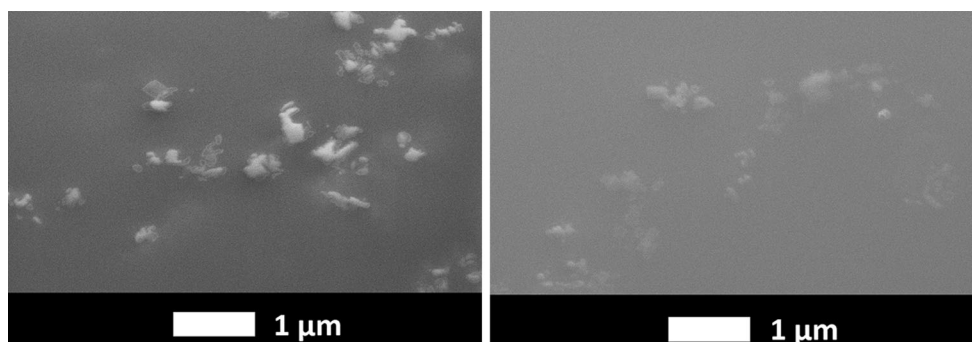
Fig. 2 SEM analysis of E-hBN_1

Results

The results of SEM analysis are presented in Figs. 2, 3, 4, 5, 6, and 7. In each figure, two different locations of a sample are shown. As observed, the particles are effectively dispersed with all three techniques. Even in areas where the particles seem to be agglomerated, they are separated from each other. However, the distribution of the particles with the solvent technique is not as homogeneous as with the other two techniques. At 5 vol% filler content, the dispersed particles tend to be organized into groups which are distributed inside the polymer matrix. On the contrary, speedmixer and nanomizer technique exhibit a better particle distribution but nanomizer technique slightly outperforms speedmixer technique.

The dielectric response of the nanocomposites is presented and compared to that of neat epoxy in Figs. 8, 9, and
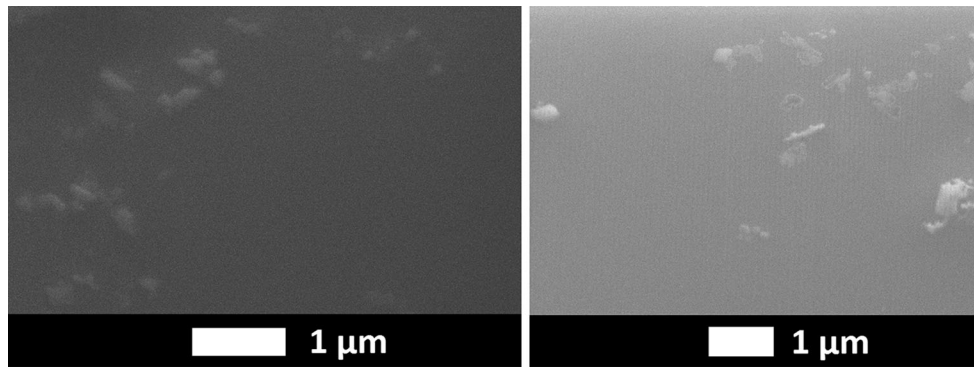
Fig. 3 SEM analysis of E-hBN_1 S
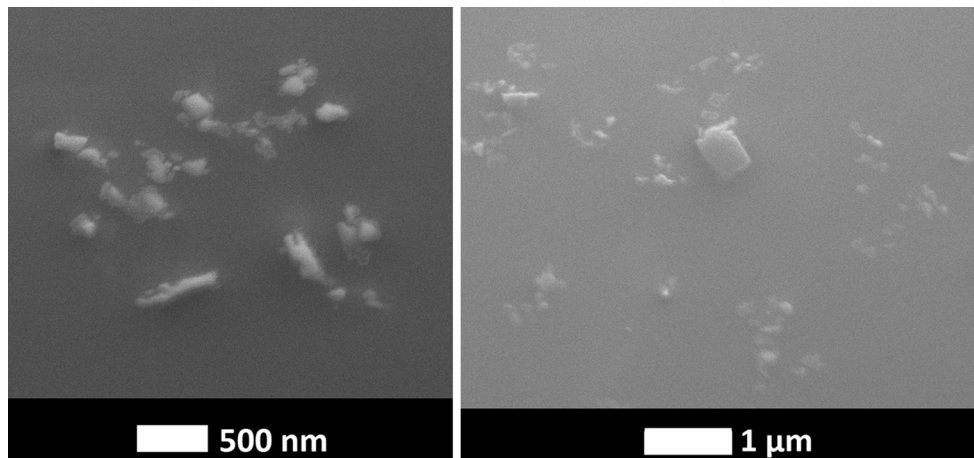
Fig. 4 SEM analysis of E-hBN_1 N
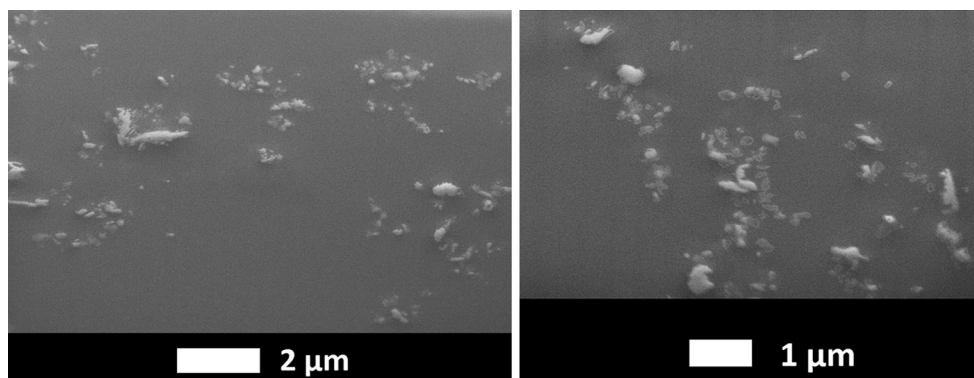
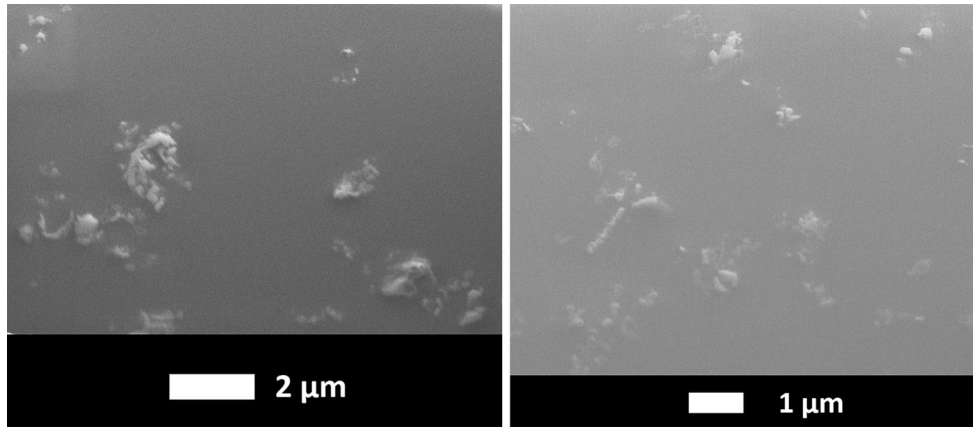**Fig. 5** SEM analysis of E-hBN_5
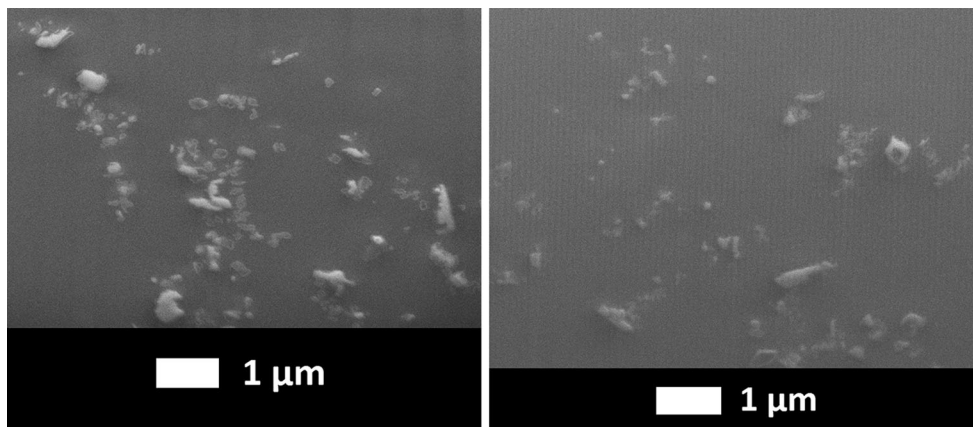
Fig. 6 SEM analysis of E-hBN_5 S

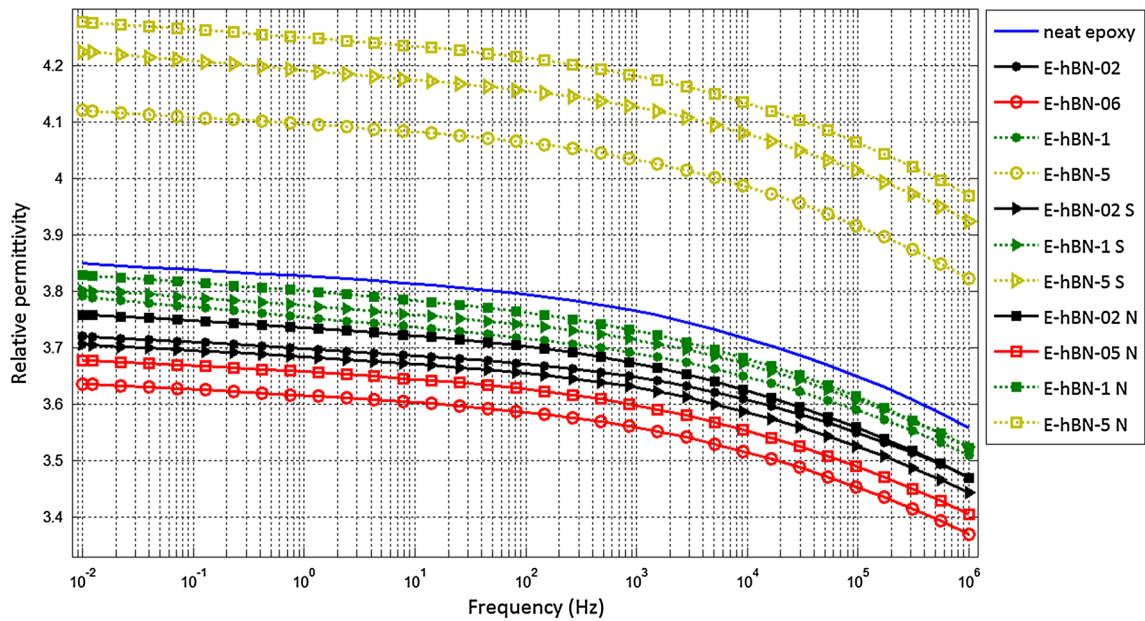
Fig. 7 SEM analysis of E-hBN_5 N

Fig. 8 Real part of the complex permittivity of neat epoxy and all produced nanocomposites at 20 °C

10. The nanocomposites with low filler concentrations (≤ 1 vol%) exhibit a lower relative permittivity (ε') compared to neat epoxy. On the contrary, the nanocomposites with 5 vol% have a higher ε' with respect to neat epoxy. Given that the relative permittivity of epoxy (≈ 3.82 at 1 Hz and 20 °C) is lower than that of boron nitride (BN) (≈ 4) [10], one would expect that the nanocomposites exhibit an ε' between that of epoxy and BN. However, the nanocomposites exhibit an unexpected decrease in the relative permittivity which has already been reported in literature [11]. The decrease can be attributed to the surface modification of the particles as the chemical bonding between the particles and polymer chains results in the immobilization of the latter in the vicinity of the particles

and thus in a decrease of the relative permittivity [12]. However, the relative permittivity of the samples increases as the filler concentration increases; all nanocomposites with 5 vol% filler concentration show a higher ε' compared to neat epoxy.

The imaginary part of the complex permittivity can be divided into two parts, i.e., low and high frequencies. The nanocomposites which exhibit a lower ε' than neat epoxy, have also lower losses at high frequencies. This can be an indication that the polymer chains in the proximity of the particles immobilize suppressing the β-relaxation process. At low frequencies, there are small differences between neat epoxy and nanocomposites which depend on the filler content. Nanocomposites with 1 vol% concentration or

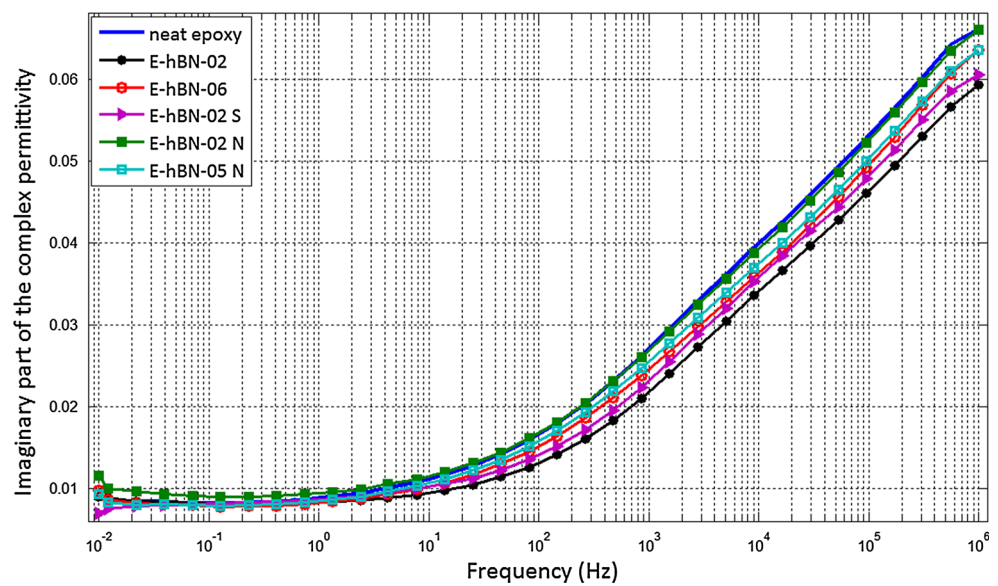Fig. 9 Imaginary part of the complex permittivity of neat epoxy and nanocomposites with <1 vol% fill grade at 20 °C

Fig. 10 Imaginary part of the complex permittivity of neat epoxy and with ≥ 1 vol% fill grade at 20 °C
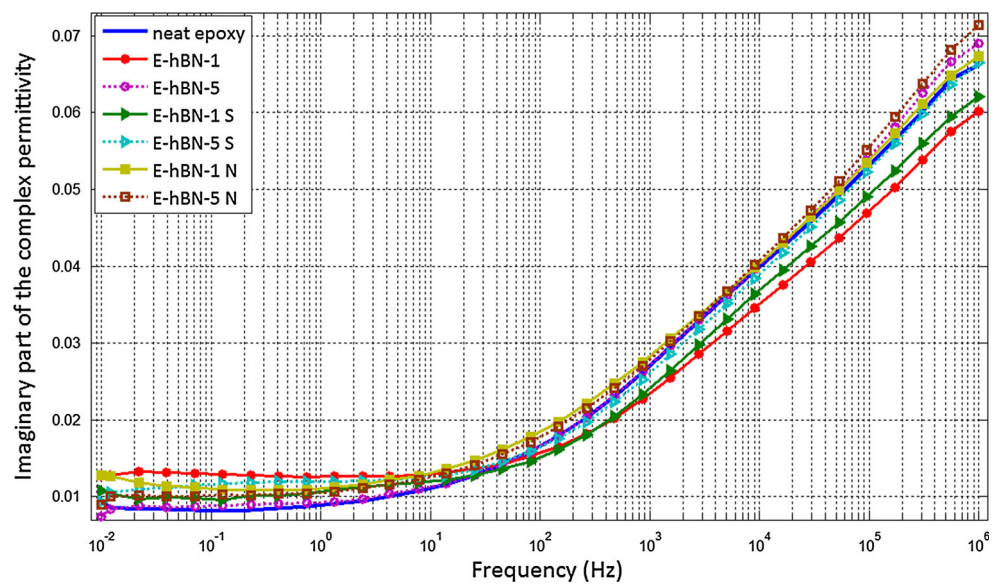
Fig. 11 Relative permittivity of neat epoxy at 20 °C, *meas1* dry sample, *meas2* vacuum storage for 15 months, *meas3* exposed to ambient conditions for 41 h, *meas4* vacuum storage for 3 days, *meas5* exposed to ambient conditions for 5 days
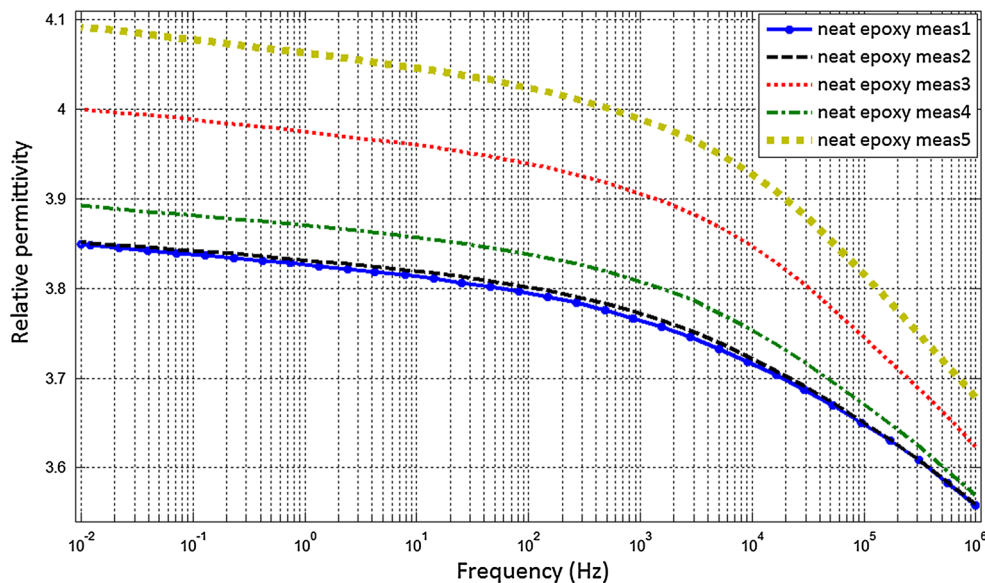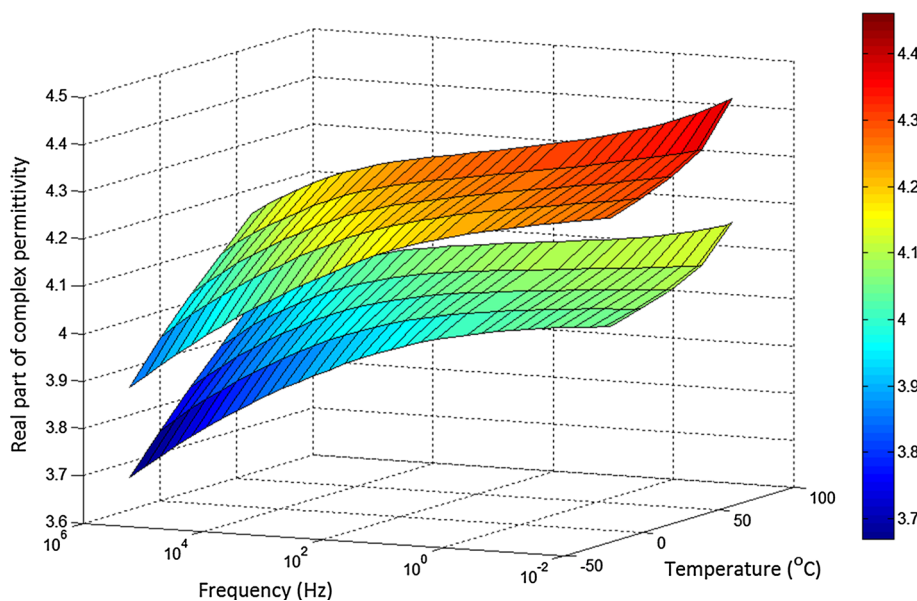

Fig. 12 Relative permittivity of sample E-hBN_5#1; *upper part* first measurement, *lower part* re-measurement after being stored for 6 months under vacuum

higher, exhibit slightly higher losses than neat epoxy. The slight increase in losses can be either due to a higher dc-conductivity or/and the presence of limited amount of humidity.

Discussion

The results on the dielectric response of E-hBN nano-composites exhibit the same behavior regardless the synthesis technique and thus the particle distribution. All produced composites up to 1 vol% fill grade, show a lower relative permittivity than neat epoxy. However, at 5 vol%

filler concentration the permittivity of nanocomposites is higher than that of the base material. The small differences in the dielectric response of the samples produced with different techniques can also be attributed to a different amount of water presence rather than the particle distribution, as even a limited amount of water uptake can significantly affect the dielectric response of nanocomposites.

Epoxy resin is susceptible to water uptake but the location of trapped water cannot be easily determined. Water usually exists in two forms; free and molecularly dispersed throughout the matrix [13]. Free water may accumulate in voids or areas with low cross-linking density. However, water molecules can also be bound to epoxy

depending on the affinity between water molecules and polymer matrix [14]. Inclusion of water can significantly affect the dielectric response of epoxy (Fig. 11) and composites based on epoxy (Fig. 16) [13, 15–17]. In the case of polymer composites, the surfaces of particles are also places where water can be trapped, especially when nanosized fillers of hydrophilic nature are used. Surface modification of nanoparticles can help alter the nature of the particles to hydrophobic but it cannot be totally efficient.

In Figs. 12, 13, 14, and 15, the dielectric response of epoxy−hBN nanocomposites with 5 vol% filler concentration (speedmixer technique) is presented. Two samples of the same batch (E-hBN_5#1 and E-hBN_5#2) were measured before and after drying them. Sample E-hBN_5#1 was measured immediately after its production, whereas sample E-hBN_5#2 was exposed to ambient conditions for several days prior to the first measurement. The upper graphs in Figs. 12, 13, 14, and 15 are the results of the first measurements.

Fig. 13 Imaginary part of the complex permittivity of sample E-hBN_5#1; *upper part* first measurement, *lower part* re-measurement after being stored for 6 months under vacuum
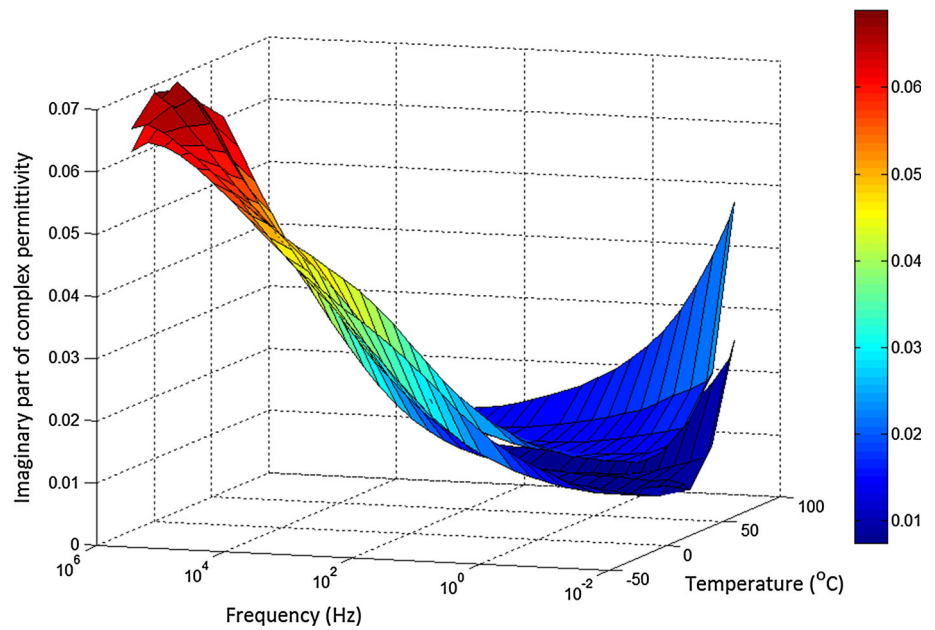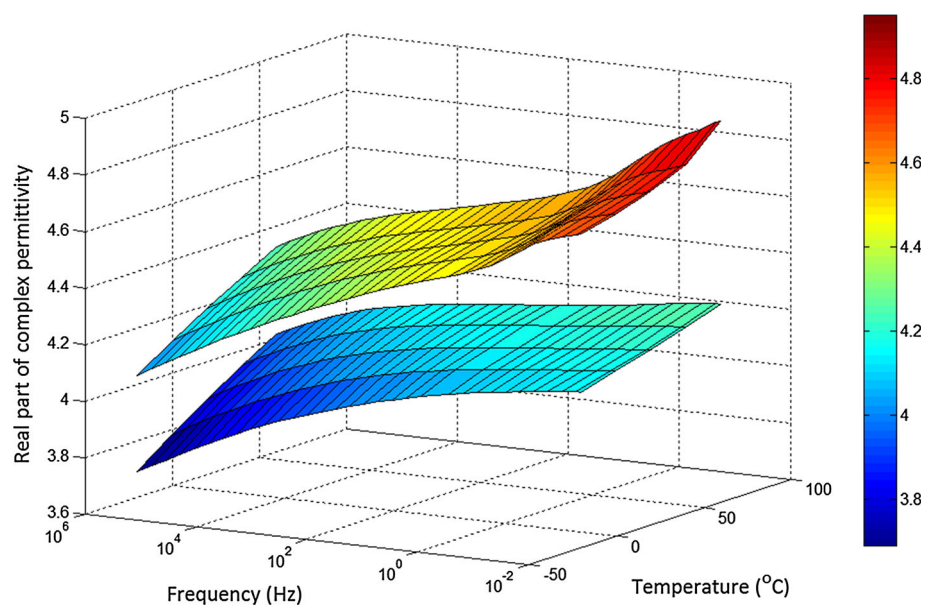

Fig. 14 Relative permittivity of sample E-hBN_5#2; *upper part* first measurement after exposing the sample to ambient conditions, *lower part* re-measurement after thermal treatment

In order to dry the samples, sample E-hBN_5#1 was stored under vacuum for a long period of time (6 months), while sample E-hBN_5#2 was thermally treated at 100 °C for 24 h and 140 °C (vacuum) for 10 days. In Figs. 12, 13, 14, and 15, it can be observed that the whole spectrum of the dielectric response is affected by the humidity including both the real and imaginary part of the complex permittivity. In the second sample where a larger amount of water is expected due to the exposure to ambient conditions, the influence on the dielectric response is more pronounced especially at low frequencies. After drying the samples both the relative permittivity and losses decreased.

Comparing the dielectric response of the dry samples (Figs. 16, 17), it is observed that they show a similar behavior. Actually, the first sample, which was not thermally treated, shows a lower relative permittivity and lower losses than the second sample. So, it seems that the further polymerization of the sample due to the thermal treatment does not significantly contribute to its dielectric response. The difference between the samples after drying them can be attributed to the presence of a limited amount of water in the second sample which still affects its dielectric response but not in a pronounced way. In Fig. 16, the relative permittivity of sample E-hBN_5#2 exhibits a

Fig. 15 Imaginary part of the complex permittivity of sample E-hBN_5#2; *upper part* first measurement after exposing the sample to ambient conditions, *lower part* re-measurement after thermal treatment
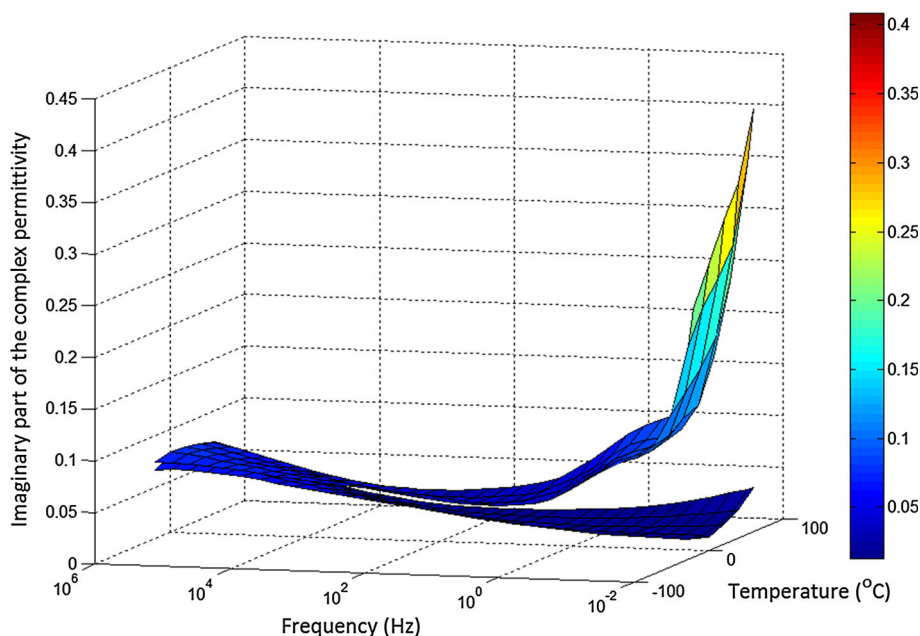

Fig. 16 Relative permittivity comparison between thermal treatment (sample E-hBN_5#2) and vacuum storage (sample E-hBN_5#1) at 20 °C
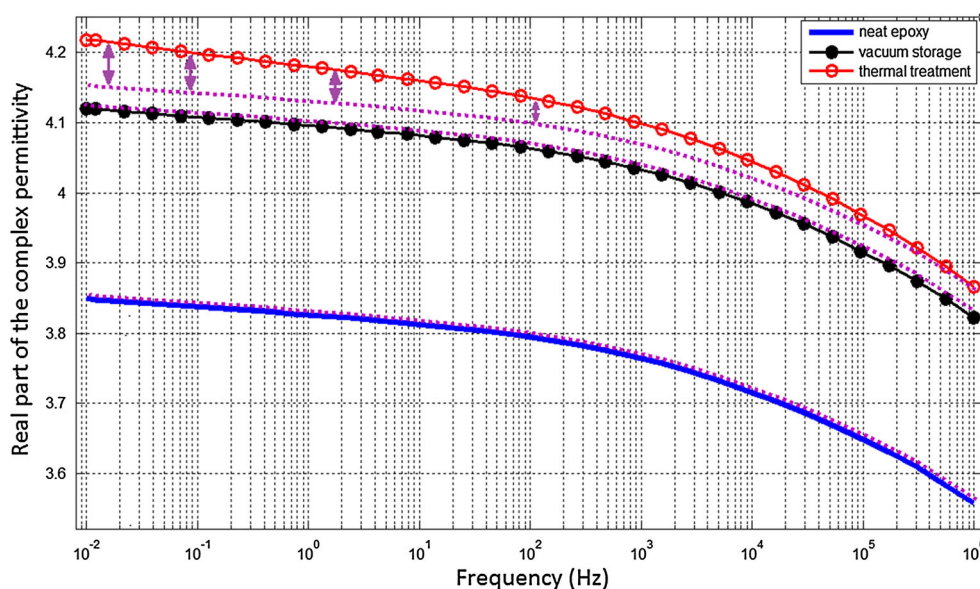
Fig. 17 Comparison of losses between thermal treatment (sample E-hBN_5#2) and vacuum storage (sample E-hBN_5#1) at 20 °C
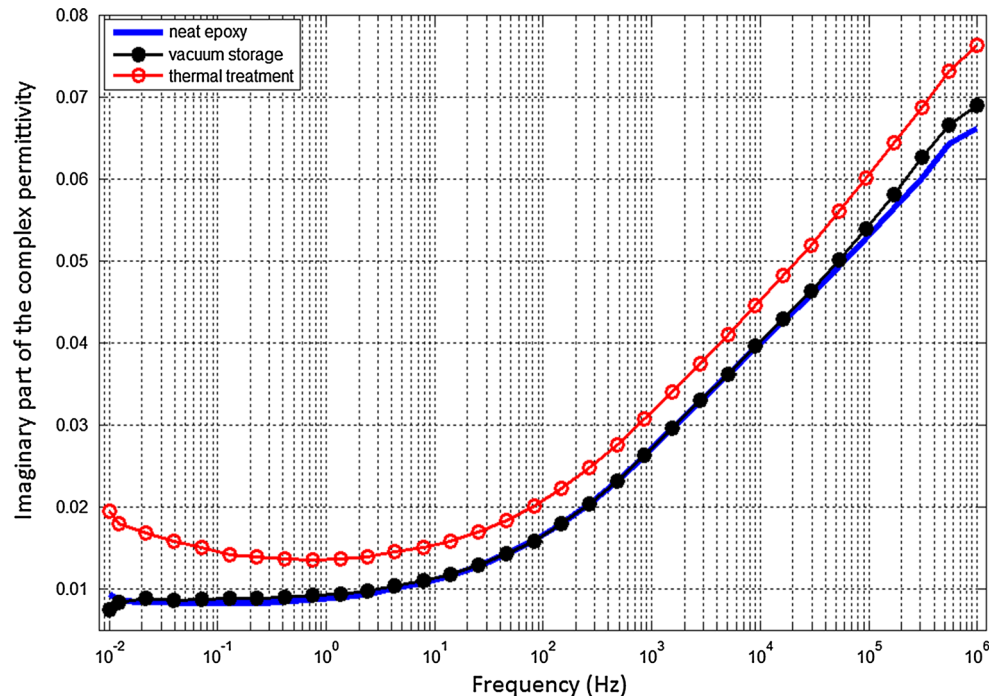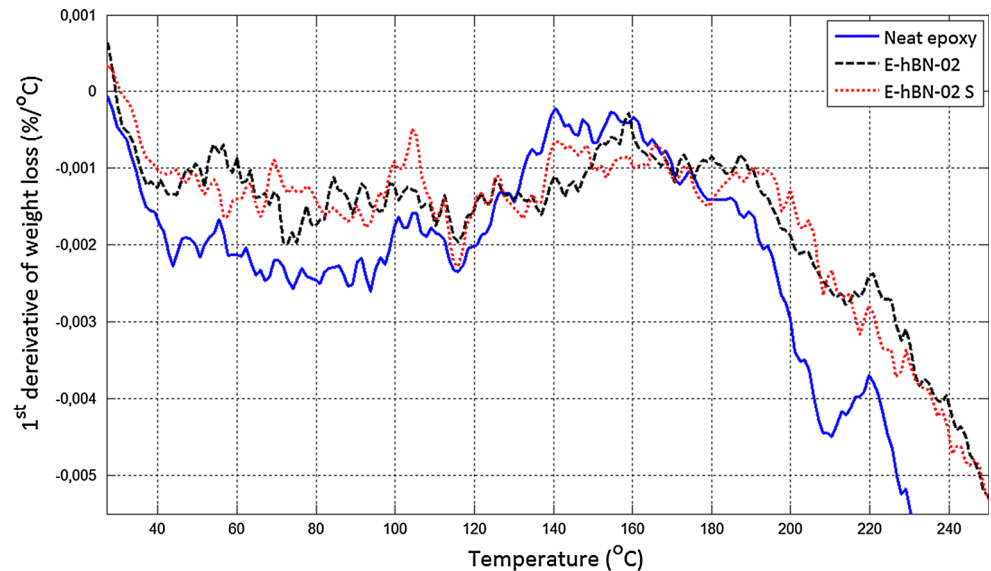

Fig. 18 TGA analysis of the samples with 0.2 vol% filler concentration

greater slope than those of neat epoxy and sample E-hBN_5#1, especially at low frequencies (the purple dashed line is used as a reference). The different slope indicates the water influence.

The effect of water uptake on the dielectric response of polymer nanocomposites can be minimized and almost eliminated to an extent to which water influence is not obvious anymore. However, the possibility that some water is still present inside the composites cannot be ruled out. Bound water molecules cannot be easily removed. The samples with 5 vol% filler concentration exhibit a relative

permittivity higher than four which cannot be explained based only on the relative permittivity of neat epoxy and hBN given that the filler concentration is relatively low. It is possible that a limited amount of water still affects the dielectric response but not in a pronounced way. In order to evaluate the water content of E-hBN nanocomposites, a Thermogravimetric analysis (TGA) was performed on neat epoxy and six nanocomposites. The analyses were performed under helium atmosphere.

With a heating rate of 5 °C/min, the first derivative of the weight loss is plotted and presented in Figs. 18, 19

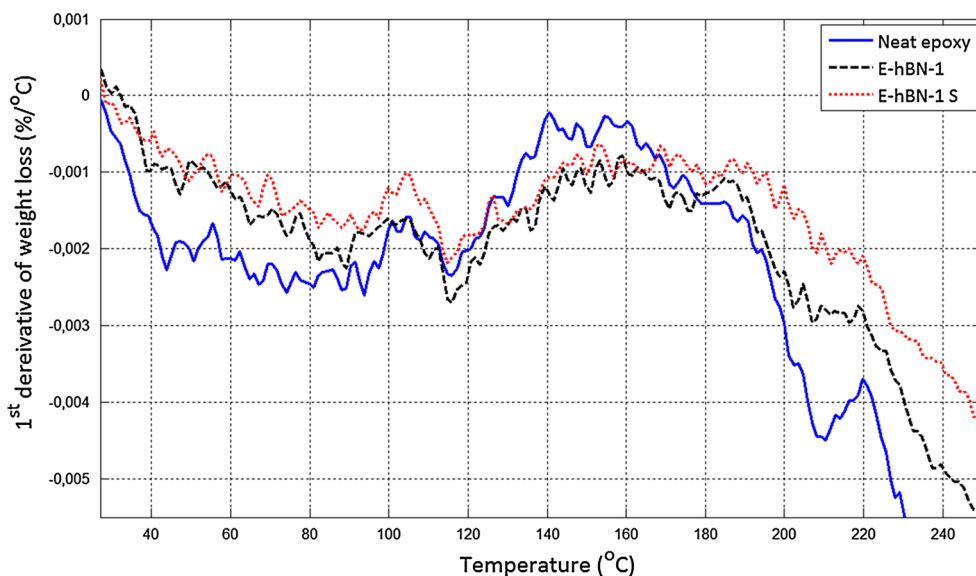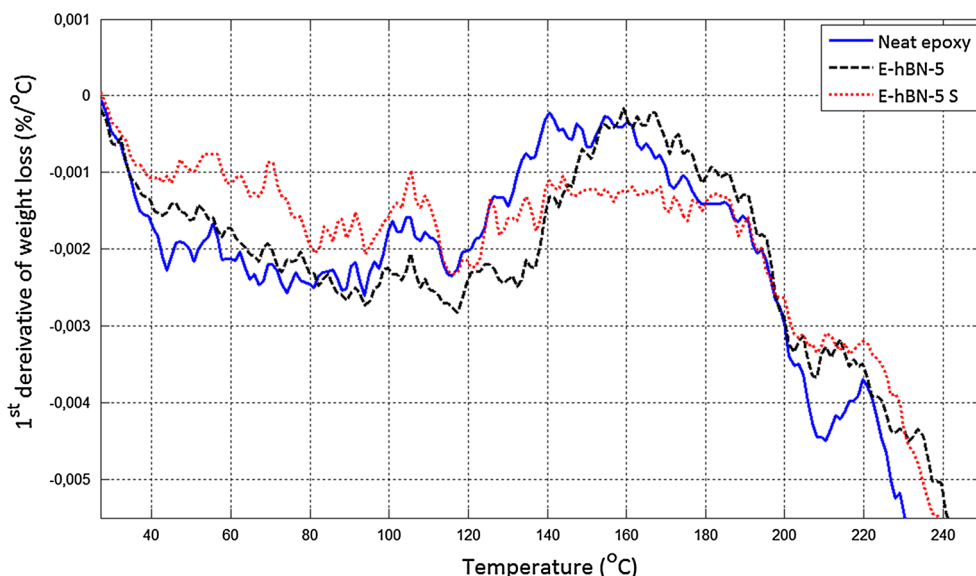**Fig. 19** TGA analysis of the samples with 1 vol% filler concentration

Fig. 20 TGA analysis of the samples with 5 vol% filler concentration

and 20. The results show that there is a consistent difference between neat epoxy and nanocomposites. The latter show a greater weight loss in the temperature range of 110–170 °C. The difference increases as filler concentration increases and it can be attributed to the larger amount of water presence. In order to evaluate the presence of water, a TGA with a mass spectrometer under argon atmosphere with a heating rate of 10 °C/min was carried out on sample E-hBN_5 (Fig. 21). At 150 °C, water started coming out of the sample. It should be noted that the system detects water with a time delay; therefore, water starts to get out of the sample at a lower temperature which cannot be exactly determined. Based on the consistent behavior of nanocomposites, it can be claimed that nanoparticles can favor the adsorption of water even
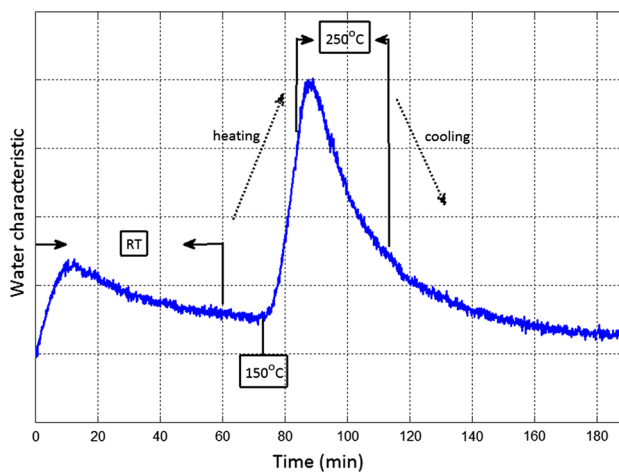

Fig. 21 TGA with a mass spectrometer for sample E-hBN_5

if they are surface modified. The amount of water cannot be accurately detected but it seems to be limited.

Conclusion

The first important outcome of this study is that the dielectric response of the produced nanocomposites shows a consistent behavior which follows the same trend. At low filler concentrations, the relative permittivity of the nanocomposites decreases with the increase of the filler content. However, after a critical filler concentration, their relative permittivity starts increasing. The minimum relative permittivity for these nanocomposites can be achieved when the filler concentration is nearly 0.6 vol%. In order to explain the trend of epoxy nanocomposites two mechanisms are considered, namely re-organization of the polymer matrix and water uptake. The former justifies the decrease in the relative permittivity whereas the latter is used to explain the increase. There was an extensive discussion about the role of water uptake in the performance of polymer composites, and it was shown that nanoparticles are susceptible to moisture even if their surface is chemically modified. Therefore, in polymer nanocomposites, the surfaces of the particles can constitute additional trap sites for water.

As far as the particle dispersion is concerned, it is difficult to evaluate its role because all three techniques result in an effective dispersion of particles. However, it can be suggested that the particle distribution does not play an important role in determining the dielectric response of the nanocomposites. The differences in the dielectric response which are observed between the three techniques are quite small and they can also be caused due to the different amount of water inclusion. Therefore, it can be concluded that the distribution of well-dispersed particles inside epoxy does not significantly affect the dielectric response of nanocomposites; the trend remains the same regardless the particle distribution. The results suggest that high levels of reproducibility can be achieved as soon as the particles are effectively dispersed.

References

1. Kochetov R (2012) Thermal and electrical properties of nanocomposites, including material processing. PhD Dissertation, Delft University of Technology
2. Andritsch T (2010) Epoxy based nanocomposites for high voltage dc applications. PhD Dissertation, Delft University of Technology
3. Singha S, Thomas MJ (2008) Dielectric properties of epoxy nanocomposites. IEEE Trans Dielectr Electr Insul 15:12–23
4. Krivda A et al (2012) Characterization of epoxy microcomposite and nanocomposite materials for power engineering applications. IEEE Electr Insul Mag 28:38–51
5. Nelson JK, Hu Y (2005) Nanocomposite dielectrics—properties and implications. J Phys D 38:213–222
6. Heid TF, Freebody N, Frechette MF, Couderc H, Vanga C, David E, Vaughan AS (2013) Dielectric properties of epoxy/BN micro- and meso-composites: dielectric response at low and high electrical field strengths. IEEE Conference on Electrical Insulation, 25–29
7. Todd MG, Shi FG (2003) Characterizing the interphase dielectric constant of polymer composite materials: effect of chemical coupling agents. J Appl Phys 94:4551–4557
8. Nyquist RA, Kagel RO (1971) Infrared spectra of inorganic compounds. Academic Press, San Diego
9. Kochetov R, Tsekmes IA, Morshuis PHF, Smit JJ (2014) Inaccuracies in the dielectric permittivity due to thickness variation. IEEE Conference on Electrical Insulation, 55–58
10. Lipp A, Schwetz KA, Hunold K (1989) Hexagonal boron nitride: fabrication, properties and applications. J Eur Ceram Soc 5:3–9
11. Kochetov R, Andritsch T, Morshuis PHF, Smit JJ (2012) Anomalous behaviour of the dielectric spectroscopy response of nanocomposites. IEEE Trans Dielectr Electr Insul 19:107–117
12. Andritsch T, Kochetov R, Morshuis PHF, Smit JJ (2011) Proposal of the polymer chain alignment model. IEEE Conference on Electrical Insulation and Dielectric Phenomena, 624–627
13. Maxwell IA, Pethrick RA (1983) Dielectric studies of water in epoxy resins. J Appl Polym Sci 28:2363–2379
14. van der Wel GK, Adan OCG (1999) Moisture in organic coatings—a review. Prog Org Coat 37:1–14
15. Zhang C, Stevens GC (2008) The dielectric response of polar and non-polar nanodielectrics. IEEE Trans Dielectr Electr Insul 15:606–617
16. Kochetov R, Andritsch T, Morshuis PHF, Smit JJ (2011) Impact of postcuring and water absorption on the dielectric response of epoxy-based composites filled with MgO nanoparticles. IEEE Conference on Electrical Insulation and Dielectric Phenomena, 342–345
17. Zou C, Fothergill JC, Rowe SW (2008) The effect of water absorption on the dielectric properties of epoxy nanocomposites. IEEE Trans Dielectr Electr Insul 15:106–117