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Electromagnetomechanical coupling response of plastoferrites

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The impetus of this work was to investigate the electromagnetic and tensile properties of several commercially available plastoferrites (PFs) at ambient conditions. The approach involved selection of a set of PFs, and measuring their complex effective permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ under uniaxial stress at microwave frequencies in the range 0.1–4.5 GHz at room temperature. The ε spectra have been analyzed for intensively strained PFs up to 3%. Comparing the experimental ε values against several dielectric relaxational behaviours, we find that the main physics cannot be understood with a single relaxation mechanism. More importantly we show that the ε measurements under stress can be explained in terms of a Gaussian molecular network model in the limit of low stress. The present results have important applications in magnetoactive smart composite materials, e.g. flexible circuit technology in the electronics industry (sensors, actuators and micromechanical systems), functionalized artificial skin and muscles for robotic applications.

Key words: *plastoferrite; effective permittivity; microwave spectroscopy*

1. Introduction

Plastoferrites (PFs) are thermosetting polymers filled with ferrite particles. Ferrites are widely used for components in high-frequency electronic devices, taking advantage of their high initial permeability, and high electrical resistivity. On the one hand, the ferrite (e.g., $Ba_3Co_2Fe_{24}O_{41}$) is a soft magnetic material with a planar anisotropy, having a relatively high resonant frequency and high permeability. On the other hand, the hexaferrite (e.g., $BaFe_{12}O_{19}$) has a high saturation magnetization and a strong uniaxial anisotropy leading to low permeability and very high resonant frequency. PF is a composite having constituents with highly dissimilar mechanical properties: polycrystalline ferrites have the density of about 5 g/cm^3 and a longitudinal modulus of the

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order of 100 GPa, whereas a typical epoxy has a low density of about 1 g/cm^3 and a longitudinal modulus of a few GPa. These large differences can result in complex behaviour under tensile stress, particularly at higher loadings of ferrite. PFs are distinguished from other magnetic materials by their useful applications in a wide variety of fields such as microwave absorbers and flexible magnets. In addition, the mouldability of these composites into complex shapes is another advantage, and the properties of this class of filled polymers may be valuable to several related industries due to the versatile engineering and cost effectiveness.

On the experimental front, we note that there is no plethora of experimental and theoretical studies on the magnetization mechanisms and permeability behaviour in these materials. Along with technological interest in the magnetic properties of PF, there are also fundamental reasons for being excited about them. PFs are interesting partly because they are a class of composite materials that provide materials scientists an interesting opportunity for furthering our understanding of multifunctional materials. Moreover, the possibility in changing the grain size such as it matches with relevant fundamental length scales associated with exchange and dipolar coupling is one of the several issues that need to be addressed in regard to the aforementioned microwave applications. The electromagnetic wave transport properties of particulate composites are different in striking ways from those of the bulk counterparts. Tensile stress in these materials is complicated by the complex evolution of microstructure. Although there have been several attempts to develop the magneto-mechanical coupling characteristics of PFs, the progress of these methods has been impeded by the lack of precise experimental electromagnetic data, and general factors characterizing and explaining their polarization and magnetization are not well understood. One such factor is the elasticity network which strongly governs the physical/mechanical properties in the end use.

Rubber and particle-filled polymeric resins are large polymeric solid networks formed when polymers in the molten state are randomly cross-linked by permanent bonds and polymer chains are attached to the surface of particles. These materials are much more flexible than ordinary crystalline solids and, moreover, may remain in the linear viscoelastic regime even in response to deformations increasing their dimensions far beyond their original, unstrained, size. Such a behaviour is attributed to the elasticity network structure of these materials and to the fact that the elastic restoring forces are of entropic origin. Considerable scientific debate has taken place over the last decades regarding the structure and properties of the elasticity network [3, 4], and e.g. [5]. The simplest theory of rubber elasticity which captures these essential physical features is the Gaussian molecular network model (GMNM) [3, 4]. This model assumes that the configurations of the polymer chains are independent of each other, and neglects the excluded volume interactions between the monomers. With these simplifying assumptions, one can treat a polymer network as an ideal one. However, in filled polymers, the network strands are very short and do not necessarily resemble ideal Gaussian springs. Nevertheless, there is experimental evidence that the GMNM of the elasticity network may be an appropriate model when a macroscopic large network spans the system [4, 6].

Dielectric and material properties of composite materials are routinely interpreted within the frame of EM theories. The importance of this issue manifests itself in a large area of research, the theory of composites, and a huge literature that cannot be cited here. The basic idea is to describe the system by a simple average permittivity (or magnetic permeability) and is based on a self-consistent procedure in which a grain of one of the constituents is assumed to have a convenient shape (usually taken as spherical or ellipsoidal) and to be embedded in a (homogeneous) EM whose properties are determined self-consistently [1, 2, 8–12]. This requires that the wavelength λ of the electromagnetic radiation probing the system has to be larger than a typical scale of length ξ that characterizes the inhomogeneities in the material. In the corresponding frequency region, the scattering effects from the heterogeneities are avoided. Actually, if one considers a mixed medium consisting of two constituents, each of which is characterized by a bulk (scalar) relative permittivity ε_i and relative permeability μ_i, there are at least three long wavelength (quasistatic) conditions:

$$\lambda >> 2\pi \frac{\xi}{c}\sqrt{\varepsilon_i \mu_i}, \quad i = 1,\, 2 \quad \text{and} \quad \lambda >> 2\pi \frac{\xi}{c}\sqrt{\varepsilon\mu}$$

where c denotes the velocity of light in free space. For instance, the length scale of the dispersed phase in PFs is typically of the order of1 μm, whereas the smallest length scale, d, of the part manufactured from the polymer filled system is much larger, e.g. a few mm. If the above conditions were not satisfied, there would be the possibility that internal structure of the medium could diffract as well as refract radiation. In the microwave wavelength range, d and ξ are far smaller than λ. Continuing with our studies of tension-strained filled polymers [7], we recently discovered that the peak position (gyromagnetic resonance) of the spectrum of the imaginary part of the effective complex permeability of a PF at the microwave frequency is shifted towards higher frequencies in response to an external stress. Moreover, the paucity of experimental data on the electromagnetic of PFs, together with a desire to understand the physics of the frequency shift observed in this system has motivated our interest in additional experimental study.

The present work was undertaken to extend the understanding of the physical mechanisms that underlie the dielectric and magnetic behaviours of PFs. To do so, we choose models with the smallest number of parameters that allows one to study the phenomena of polarization and magnetization in PFs. Practical and predictive modelling of PFs to evaluate their magneto-mechanical coupling behaviour is a tough challenge and has still fallen behind applications and empirical description of their behaviour. There are ample motivations for developing a theory to understand, control and hence utilize the electromagnetomechanical coupling characteristics of soft composite materials. One potential interest is the development of flexible substrate. Flexible circuit technology attracts much attention in the electronics industry for portable applications because the flexible substrate can be rolled, bent, and folded to fit a limited space where required. Two other potential applications deal with the design of functionalized artificial skin and muscles for robotics.

Guided by the results obtained in [7], the scope of the current study is to continue that work and to contribute in understanding the coupling between elasticity network of the polymer matrix and the effective dielectric and magnetic behaviors of PFs in the microwave range of frequencies. In this paper, we present a detailed investigation of the effective permittivity measured in the microwave range of frequencies. Three types of PFs were chosen to provide a reasonable comparative set of electromagnetic and magnetic parameters. We also present models describing the effective material properties and determine model parameters to fit the data. The difference in electromagnetic response between two states of PFs, i.e. magnetized vs. demagnetized, is also investigated. We hope that this characterization of PFs can provide valuable information for PF design.

2. Experimental

Epoxy-based plastoferrite composite formulations (designated samples PF1-PF3 in the present investigation) had different commercial origins and were used as received. These typical PFs (see Table 1) contain 30 vol. % of ferrite. These materials consist of micrometer size grains that are uniformly and randomly dispersed in an amorphous epoxy resin matrix.

Table 1. Specifications of the PF materials examined in the current study

Sample	Manufacturer	Type of a polymer[a]	Glass transition temperature[b] T_g [K]	Type of ferrite[a]	Fraction of ferrite [vol. %]	Average grain size diameter [μm]
PF1	Walker Braillon Magnetics	epoxy resin	271	$SrFe_{12}O_{19}$ hexaferrite	ca. 30	0.98
PF2	Euromag		279	Sr hexaferrite		0.94
PF3	Arelec		285	hexaferrite		0.97

[a]From the manufacturer product literature.

[b]Data obtained as a result of modelling from the current (SEM, XRD, and DMA) measurements.

The ferrite particles were imaged on a 100 keV Hitachi F-3200N scanning electron microscope. Cross-sectional micrographs on different regions of PF samples were taken to quantify the degree of polydispersity in size and shape. The microstructure was digitized directly from micrographs to capture the grain morphology. As seen in the selected area SEM of Fig. 1, the ferrite grains are completely buried in an amorphous matrix.

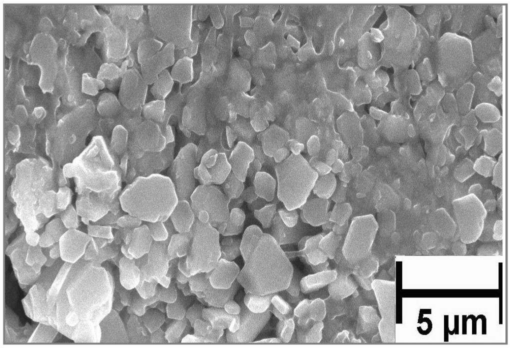

Fig. 1. Cross-sectional SEM images of a typical sample belonging to experimental series of PFs. The composite microstructure (PF3) is a three-dimensional assemblage of ferrite grains, bonded by an epoxy resin matrix

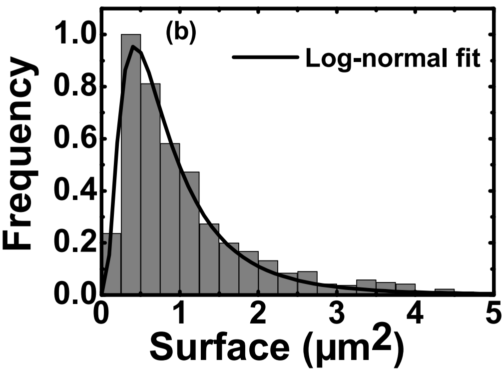

Fig. 2. Corresponding surface area distribution of ferrite grains (thousands in each characterization). The fitting results (solid line) have shown that a log-normal distribution of grain surfaces is a good approximation of the surface area profile. As a result, we obtained an average and variance of size (assuming that the grains have spherical shape) which are presented in Table 1

Most ferrite grains are approximately spherical. Each of the PFs studied was carefully characterized for ferrite grain projected surface and distribution. As illustrated by the histogram in Fig. 2, there is agreement between the (normalized) experimental surface area data and the calculated curve based on a log-normal grain surface distribution:

$$f(A) = \frac{1}{\sqrt{2\pi}\sigma A}\exp\left(-\frac{1}{2\sigma^2}\left(\log A - \log A_0\right)^2\right)$$

This distribution satisfies the properties: $\langle \log A \rangle = \log A_0$, and

$$\left\langle \left(\log A - \log A_0\right)^2 \right\rangle = \sigma^2$$

Assuming a spherical grain shape, it appears that the measured ferrite average grain size is about 1 μm for the PF samples chosen for the present study (Table 1). Some intergranular pores are present in all samples.

The electromagnetic characterization of PFs was performed by *in situ*, real-time measurement of the transmission/reflection coefficients of an asymmetric microstrip transmission line containing the sample during uniaxial tensile stress. Since the details of this method have been described elsewhere [7], we shall not repeat that derivation here, but simply give a brief description of the experiment. The experimental setup used for producing tensile loading was described in [7]. The rectangular-shaped samples (approximately $50\times3\times1.8$ mm^3) were mounted with clamped ends. The stress sequence employed in this work consisted in a series of step stress (0.5%) changes. The current method was employed to extract the effective complex (relative) permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ and (relative) permeability $\mu = \mu' - j\mu''$ of a composite sample from microwave measurement, where $j = \sqrt{-1}$. The measurement of the scattering parameters (S parameters) is achieved using a Agilent H8753ES network analyzer with SOLT calibration. The test device is used as Thru in the transmission connection. Control of data acquisition and data storage is accomplished with Labview 6.1 (National Instruments) graphical programming software operating in a Windows 2000 environment. The method enables us to calculate simultaneously ε and μ of the material over a frequency range of 0.1 MHz – 4.5 GHz from the measurement of the S_{21} and S_{11}. It was not possible to explore the ε and μ spectra at higher frequency because of the dimensional resonance mode arising at $\cong$ 6.5 GHz. An error analysis indicates modest uncertainties in ε' (<5%), ε'' (<1%), μ' (< 3%), and μ'' (< 1%) for the data. One further feature of the measurement system is worth commenting on. To obtain accurate measurements of ε and μ, it is particularly important to account for the residual air-gap between the sample and the line walls. On the one hand, the air space increases as the extension is increased. On the other hand, the gap is determined by the roughness of the surfaces of the measured samples. A static magnetic field can be applied perpendicular to the rectangular-shaped sample by an electromagnet. A Hall sensor is used to measure the field near the characterized sample.

To understand the complex permittivity of these systems, the relative importance of polarization (ε'') and conduction ($\sigma_{dc}/(\varepsilon_0\omega)$) losses needs to be addressed. For this purpose, dc electrical measurements were carried out in capacitive configuration. All dc current–voltage I–V characteristics and contacts were Ohmic in the voltage range studied. Details of the circuit equipment and conditions for measuring the dc electrical conductivity σ_{dc} are given elsewhere [14]. Since the parameter $(\sigma_{dc}/(\varepsilon''\varepsilon_0\omega)) \ll 1$ in our samples under investigation ($\sigma_{dc}/(\varepsilon_0\omega) \approx 10^{-3}$ at 1 GHz, to be compared with the typical order of magnitude of ε'' of 10^{-2}), then we do not need to take into account any contribution of the static conductivity in the modelling of the imaginary part of the effective permittivity. This is consistent with recent work on the microwave absorbing properties of ferrite nanopowder dispersed in a polymer matrix [14]. The dc conductivity of the material is also important as it determines the extent of losses due to eddy currents. The skin depth being large compared to the sample size, the influence of eddy currents on the magnetic field is entirely negligible.

3. Results and discussion

The first set of results concerns the frequency dependence of the complex effective permittivity of a typical sample (PF1) in the demagnetized state. In Figure 3, we present two examples of ε' and ε'' to allow comparison at two different extension ratios ($\lambda = 1$ and $\lambda = 1.023$).

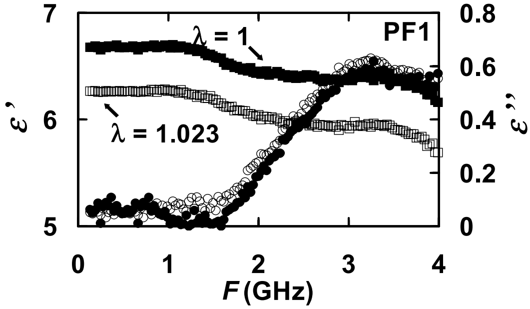

Fig. 3. Spectral dependence of the real and imaginary parts of the effective permittivity of PF1 for two values of the extension ratio λ; room temperature

Figure 3 illustrates the number of reproducible features generally found in all sets of results in this study. The observed dielectric response is complex and cannot be identified with a single relaxation mechanism. In the frequency range 0.1–4.5 GHz investigated, a single resonant peak at ≈ 3.5 GHz was observed which does not change with extension over the considered range of strain. It is attributed to Maxwell–Wagner (MW) interfacial polarization. Similar observations have been made for $Ni_{1-x}Zn_xFe_2O_4$ ferrite particles embedded in a butyl rubber matrix [15]. A decrease of ε' is observed as λ is increased, while ε'' is only slightly modified with increasing λ. The extension dependence of the change of sample dimensions relative to their respective initial value was characterized (not shown). The most striking feature of these experimental data is that the lateral dimensions cannot be adequately described as $\propto 1/\lambda^{1/2}$, that models the contraction of a volume invariant sample. This is attributed to much smaller Poisson s ratio $\nu \approx 0.3$ of the plastoferrite sample.

In keeping with our stated goal of developing an analysis for interpreting electromagnetic properties of PFs, the interpretation of the experimental data can now be tested with different relaxation models. Figure 4 shows representative plots of the imaginary (ε'') versus real (ε') part of the complex effective permittivity (Cole–Cole plot) at different frequencies. For a pure Debye-type response (see Appendix), the effect of grain and grain boundary can be modelled with parallel combinations of respective capacitance and resistance connected in series. Each resistance and capacitance combination is expected to exhibit a separate semicircle with different mean relaxation times. As shown in Fig. 4, the ε'' (ε') variations seem to deviate considerably from a perfect semicircle and appear to be stretched. This indicates a distribution in time constant characteristic of a material that exhibits a broad size distribution consistent with the SEM observations. We note that care is needed when comparing these experimental data with models that are customarily used to determine the relaxational behaviour of dielectric materials.

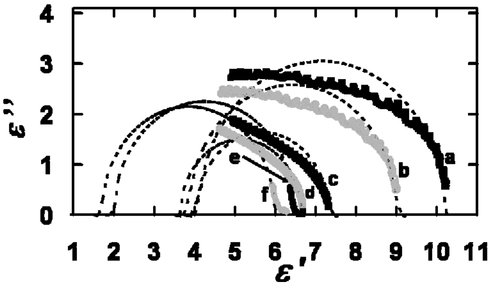

Fig. 4. Experimental and calculated effective (relative) permittivities of PFs for two values of λ: real part of the permittivity for PF1 (a), PF2 (c), and PF3 (e), imaginary part of the permittivity for PF1 (b), PF2 (d), PF3 (f). The dashed lines denote the results from the Debye model (Eq. (A1)); room temperature

It would be tempting to assign an intrinsic permittivity behaviour for each constituent of the PF based upon, e.g. the HN expression, take into account of the dilution of ferrite particles by the EM theory, e.g. Bruggeman equation, and then fitting them to the data by least-squares schemes. However, such an interpretation is arbitrary if there is no clear prescription for the proper choice of the intrinsic permittivity of various constituents of the PFs. In addition, there is little doubt that the fit parameters would be greatly affected by the manner of fitting the data considering the polydispersity of the ferrite particles and the relatively small range of frequencies explored.

The starting point of an investigation into the dielectric properties of any tension-strained material is to determine its equation of state in terms of stress, strain, and effective permittivity (or conductivity). While some work has been performed on the quantitative dc conductivity response of polymers under tensile stress [4, 7], the corresponding ac microwave response has not yet received the amount of attention it deserves. Very recently, Brosseau and Talbot [7] suggested that the GMNM functional form $(\lambda - 1/\lambda^2)$ may be applicable to a variety of soft materials for calculating the tensile stress dependence of ε and μ providing that the elasticity network in the material occurs in a manner that is topologically similar to the elasticity network of a conventional rubber. We here assess the wider applicability of the model by comparing predictions (solid and dashed lines in Fig. 5.) to experimental measurements of the electromagnetic parameters of a set of PFs.

In Figure 5, we present the plots of

$$\Delta\varepsilon' = \frac{\varepsilon'(\lambda=1)-\varepsilon'(\lambda>1)}{\varepsilon'(\lambda=1)} \quad \text{and} \quad \Delta\varepsilon'' = \frac{\varepsilon''(\lambda=1)-\varepsilon''(\lambda>1)}{\varepsilon''(\lambda=1)}$$

for PF samples at 500 MHz in function of the extension ratio λ. Here it can be observed that the experimental trend is in excellent agreement with the GMNM functional form constrained to pass through the origin.

It is worth considering in some detail the processes leading to the emergence of an interpretation of the experimental data such as those represented in Figs. 3 and 6. We are dealing with a complicated problem, in which the dominant feature is its stochastic and interactive nature. This means that no simple model involving non-interacting entities pursuing deterministic trajectories, such as orientations of dipoles, can adequately represent the true situation. The complexity may be structural in origin (ferrite grain boundaries, defects), or it may be rooted in complex electromagnetic and mechanical interactions (many different exchange couplings, perhaps competing).

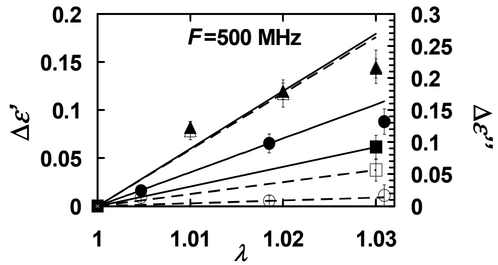

Fig. 5. Dependences of $\Delta\varepsilon'$ and $\Delta\varepsilon''$ for PF samples on the extension ratio λ; $F = 500$ MHz at room temperature; circles squares and triangles correspond to PF1, PF2 and PF3, respectively. Open (filled) symbols correspond to B (A). The best-fit solid curves (constrained to pass through the origin) to the functional form ($\lambda - 1/\lambda^2$) are also shown

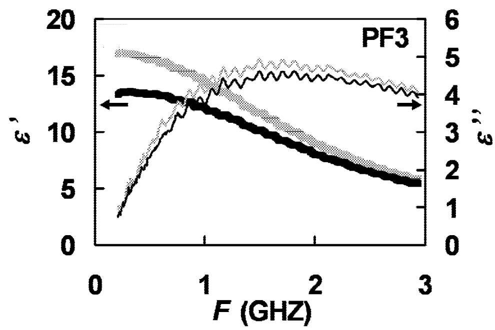

Fig. 6. Real and imaginary parts of the effective permittivities for a magnetized and demagnetized PF3 sample at room temperature. The thick (thin) solid lines represent the real (imaginary) parts of the permittivity. Magnetized (demagnetized) sample corresponds to the black (grey) curve

The above discussion has been made on a phenomenological basis irrespective of any particular mechanisms of relaxation. The generally accepted mechanisms for these features are discussed now. Two possible types of polarizing species, i.e. dipoles and MW, may contribute to the microwave behaviour. At frequencies high enough, the polarization responses of the two corresponding types can be empirically described by the same fractional power law. Thus, it is quite difficult to discriminate between the two contributions. We also observe that the permittivity spectra do not provide a full description of the dielectric relaxation spectra since we considered limited sets of data in the GHz range of frequency.

4. Conclusions

The work reported in this paper represents the most comprehensive experimental study to date of the frequency dependence of the electromagnetic parameters of tension-strained PFs. The general results collected and the trends observed have been discussed. Specific findings of the developments presented here are listed below.

We have studied a set of three commercially available PF samples with different magnetic characteristics as a result of different materials and different processing parameters. As described above, the tensile strain generated in the PFs causes significant changes of the electromagnetic parameters in the microwave range of frequencies. This is a direct manifestation of the elasticity network structure of the PFs. Another perspective on the electromagnetomechanical coupling comes from considering the GMNM model to account for the interconnected network of chains and ferrite grains which spans the entire structure. A complete description of this coupling would require involving a broad range of time and length scales, which is beyond the scope of this study. Nevertheless, as illustrated in Fig. 4, the quantitative agreement between modelling and experiment at low stress levels shows the GMNM model as viable physics to be included in studies of electromagnetomechanical coupling in PFs. This peculiar property of the response of PFs to uniaxial stress may have important implications in the design of magnetoactive smart composite materials with optimized electromagnetic properties.

The series of experiments reported here suggests that, for a given PF, deviations of ε from the archetypal dipolar Debye relaxation model occur in the range of frequencies explored. These features are tentatively associated with MW interfacial polarization. We emphasize again that accounting for the effective dielectric behaviour of these composite materials, without characterizing the intrinsic electromagnetic parameters of the individual constituents and the internal morphology, remains speculative. However, an interesting consequence of the data presented above is that the phenomenological scaling ansatz (GMNM) is also consistent with the experimentally observed permittivity change under elongation, indicating that the variations of permittivity and permeability are clearly mutually dependent. Designing magnetic materials, where parameters such as the type of ferrites or the composition can be finely tuned, allow a high degree of customization of magnetically soft materials.

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Appendix. Relaxational modelling of homogeneous dielectric materials

Extensive investigations have been focused on this issue and we have referenced only the papers that are the most relevant to the work carried out here. Several theoretical approaches have been developed to describe the relaxation modelling in dielectrics [16].

The simplest model has been eventually described by Debye [17]. In the Debye formulation of dielectric relaxation, the complex permittivity is written as

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \left(\varepsilon_s - \varepsilon_\infty\right)\frac{1}{1+i\omega\tau} \tag{A1}$$

where ε_s and ε_∞ denote the static ($\omega = 0$) permittivity and the limiting permittivity at high frequencies ($\omega\tau \to \infty$) which depends on atomic and electronic polarizability, respectively. For the case of a single characteristic relaxation time τ, the points (ε', ε'') lie on a semicircle with the centre on the ε' axis and intersecting this axis at $\varepsilon' = \varepsilon_s$ and $\varepsilon' = \varepsilon_\infty$.

This approach is intuitively attractive since the one exponential modelling in the time domain, i.e. Eq. (A1) in the frequency domain gives an adequate description of the behaviour of the orientation polarization for many condensed matter systems. Despite the intuitively attractive features of this formulation, there are practical problems in implementing Eq. (A1) due to difficulties inherent to the complexity of the material, e.g. distribution of relaxation times.

For a continuous distribution of relaxation times, one can substitute the $1/(1 + i\omega\tau)$ into Eq. (A1) by $\int_0^\infty \frac{g(\tau)d\tau}{1+i\omega\tau}$, where it is assumed that the weighting function is normalized such that $\int_0^\infty g(\tau)\,\mathrm{d}\tau = 1$. An alternative method, described by the Havriliak–Negami (HN) expression, has been put forward [18]

$$\varepsilon = \varepsilon_\infty + \left(\varepsilon_s - \varepsilon_\infty\right)\frac{1}{\left(1+\left(i\omega\tau\right)^\alpha\right)^\beta} \tag{A2}$$

where it is assumed that the non-negative quantities α and β gauge the symmetric and asymmetric broadening of the dielectric loss spectrum, respectively. This expression reduces also to Eq. (A1) for $\alpha = \beta = 1$.

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