Syntheses of 'Hemtex' Simulants of Energetic Materials and Millimetre Wave Characterisation Using the Teraview CW400 Spectrometer: Fundamental Studies for Detection Applications

Hemant J. Desai, Richard Lacey, Daniel O. Acheampong, Anthony Clark, Philip Dixon, Matthew Hogbin, Robert Hudson, Sam Pollock, Usman Waheed, and Hannah Whitmore

11.1 INTRODUCTION

Explosives or energetic materials are hazardous, expensive and difficult to handle safely. Appropriate simulants are desirable in order to overcome these barriers for various purposes. These include training, for both staff and canine or animal olfaction; acceleration of development of novel detection systems to

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H. J. Desai (✉) · R. Lacey · R. Hudson
Defence Science and Technology Laboratory, Salisbury, UK
e-mail: hdesai@dstl.gov.uk; rjlacey@dstl.gov.uk; rjhudson@dstl.gov.uk

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prevent acts of terrorism; and provision of materials for daily calibration/verification of instruments and to aid achievement of regulatory accreditation.

With the advances in active and passive millimetre wave systems for threat detection, there is a need for accurate characterisation of threat materials and simulants with respect to these technologies. A modular process for developing simulants has been created, and formulations have been tested to characterise fundamental properties in the millimetre and submillimetre wave regions.

Characterisation within the frequency range of 25–250 GHz has been conducted using a Teraview CW400 spectrometer. This frequency range covers the majority of active and passive systems, providing data upon which material characterisation can be based.

Many millimetre wave characterisation instruments fail to provide such a large frequency range. Low cost and fast data acquisition make the CW400 an ideal candidate for characterisation work.

Millimetre wave characterisation suffers from the following limitations:

- Low power resolution without cryogenic cooling.
- Complex detection techniques.
- Sample thickness must be large so that uncertainties due to inhomogeneity in target materials are minimised.
- Very little reference data available.

The Teraview CW400 spectrometer was first used to determine the real and imaginary parts of the relative permittivity of reference liquids, to validate the system. Once validated, a characterisation study of a Semtex simulant was undertaken.

11.2 THEORY

Active millimetre wave and submillimetre wave detection technologies are sensitive to the complex dielectric constant (or relative permittivity) of concealed explosives. Simulants designed to match the dielectric

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D. O. Acheampong · A. Clark · P. Dixon · M. Hogbin · S. Pollock
U. Waheed · H. Whitmore
Home Office, London, UK
e-mail: Daniel.Acheampong@dft.gov.uk; Tony.Clark@defra.gov.uk;
philippe@physics.org; matthew.hogbin@homeoffice.gov.uk;
sam.pollock@iconal.com; u.waheed16@imperial.ac.uk;
Hannah_Whitmore@MEEI.HARVARD.EDU

properties (refractive index and absorption coefficient) at the operating frequencies of these systems should be adequate as a simulant for tests. The structure of the material may also be important when the probing wavelength matches the scale of the features in the material (e.g. pelletised explosives or cracks and voids in solid explosives). To match a specific threat material, this could be either a single simulant or a set of simulants, each designed for use in part of the frequency range.

For passive millimetre wave systems, the simulants will need to match some additional physical properties. In addition to dielectric properties, passive millimetre wave imaging is also sensitive to the thermal properties of the explosive, such as the thermal conductivity and specific heat.

The dominant interaction of electromagnetic waves at millimetre wavelengths in most materials is Debye relaxation. Due to frictional forces between dipoles, realignment with an electric field is not instantaneous. This response time is what causes the millimetre wave to be perturbed [1]. The specific interaction with the material by the millimetre waves is governed by the real and imaginary parts of the permittivity (ε_r), which is a complex function expressed as:

$$\varepsilon_r = \varepsilon_r^{'} + i\varepsilon_r^{''}$$

where $\varepsilon_r^{'}$ is the real part of permittivity indicating the polarisation response of a material to the electric field [2] and $\varepsilon_r^{''}$ is the imaginary part of permittivity and measures how dissipative a material is to an electric field.

Broadly, the refractive index ($n \approx \sqrt{\epsilon'}$) determines the reflection coefficient from the material surface(s), and the loss tangent $\left(\tan\delta = \frac{\varepsilon_r^{''}}{\varepsilon_r^{'}}\right)$ determines the degree of attenuation experienced as the wave propagates through the material.

The CW400 spectrometer measures the change in optical path length, and therefore the phase difference through the material which can be used to derive the refractive index and real part of the dielectric constant since ($n \approx \sqrt{\epsilon'}$) as follows:

$$n = 1 + \frac{\varphi c}{2\pi fL}$$

where φ = phase difference measured, f = millimetre wave frequency, L = thickness of dielectric and c = speed of light.

For relatively low loss materials, the loss can be approximated by the Beer-Lambert law and used to derive the following [3]:

$$\varepsilon_r'' = \frac{\alpha\lambda\sqrt{\varepsilon_r'}}{\pi}$$

where α is the exponential loss factor and λ is the wavelength of the incident wave. The exponential loss factor α is calculated from the measured amplitudes of the incident and transmitted waves through the material [4].

11.3 EXPERIMENTAL

11.3.1 *Materials*

Simulant materials were prepared in-house. The ingredients were purchased mostly from Aldrich unless stated otherwise. Basic Yellow 40 (BY40) was purchased from Keystone UK. Their synthesis procedures are reported below. Once the materials were made, they were kept in sealed anti-static bags and the contents handled with nitrile gloves.

11.3.2 *Synthesis Procedure*

The original Hemtex simulants were made to mimic Semtex-1H and consisted of:

• Hexamine (as a replacement for RDX)	200 g
• Pentaerythritol (as a replacement for PETN)	200 g
• Polystyrene-co-butadiene	30 g
• Tributyl citrate	30 g
• n-Dioctyl phthalate	30 g
• N-Phenyl-2-naphthyl amine	5 g
• Sudan IV	5 g

The main principle was to remove energetic moieties and to be as close as possible in terms of material properties and atomic ratios. Hence, the nearest synthesis precursors were considered first as ingredients. Adjustments were then made to alter properties or provide fluorescence for trace application as deemed appropriate. This created a modular method. A table of the ingredients of the 6 Hemtex simulant formulations used here is shown in Table 11.1. The Hemtex009 and Hemtex010 formulations were created to compare any batch-to-batch variation and were more pliable than the other formulations. The Hemtex013, Hemtex014, Hemtex016 and Hemtex025 were chosen to provide different physical properties, especially malleability.

The general procedure to make simulants tested here is as follows.

Hexamine crystals were ground to an approximate grain size of table salt or sugar (as a method to determine particle size distribution was not available) so that a more uniform mix would form. The polymer (polystyrene-co-butadiene) was dissolved at room temperature, using dichloromethane (DCM), approximately 300 cm^3 (Aldrich, used as received) by stirring in a large bunged conical flask. The dissolved polymer was mixed with the remaining ingredients, as shown above, using a commercial heating food mixer (Kenwood Chef). The mixture was stirred thoroughly for 8 hours, in total, and the solvent was gradually evaporated off in a fume cupboard by heating the mixture to 40 °C during and following mixing. A card-ice/acetone cold trap was used to retrieve as much of the solvent as possible before suitable disposal. After the composition was found to be of a similar texture to Semtex, it was then heated to 100 °C, to remove any trapped solvent for a further 1 hour. The final material was pliable like a real plastic explosive. The pliability could be adjusted by using the PEG polymer which made the composition softer and easier to manipulate.

The solutions of 0%, 0.1%, 1% and 10% chlorobenzene in cyclohexane by volume were prepared for a parallel liquids characterisation study. The chemicals were 99.9% pure and were purchased from Aldrich Chemical Co.

11.3.3 Characterisation

The Teraview CW400 spectrometer produces coherent continuous waves sweeping from 10 GHz to 1.8 THz. Such a large frequency sweep is uncommon and made possible due to the unique method of controlling frequency using a temperature differential between two lasers (Fig. 11.1).

Two class 3B DFB lasers with wavelength of ~850 nm are frequency-offset using Peltier heaters that incrementally change the central wavelength. The laser beams at ω_1 and ω_2 are coupled together to produce a beat frequency ω_{THz} which is split to both the emitting and receiving modules [6]

Table 11.1 Compositions of 6 Hemtex explosive simulant formulations characterised using the Teraview CW400 spectrometer

Unique identifier code	*Nominal weights*	*RDX replacement*	*PETN replacement*	*Plasticiser*	*Plasticiser*	*Polymer*	*Polymer*	*Stabiliser (nitro ester)*	*Solvent*	*Other chemical*
Hemtex009	~2 kg	Hexamine	Pentaerythritol	Di-n-octyl phthalate	Tributyl citrate	Polystyrene co butadiene	Poly (ethylene glycol) (PEG)	*N*-Phenyl-2-naphthylamine	DCM	
Hemtex010	~2 kg	Hexamine	Pentaerythritol	Di-n-octyl phthalate	Tributyl citrate	Polystyrene co butadiene	Poly (ethylene glycol) (PEG)	*N*-Phenyl-2-naphthylamine	DCM	
Hemtex013	~500 g	Hexamine	Erythritol	Di-n-octyl phthalate	Tributyl citrate	Polystyrene-co-butadiene	–	*N*-Phenyl-2-naphthylamine	DCM	
Hemtex014	~500 g	Cynamic acid	Pentaerythritol	Di-n-octyl phthalate	Tributyl citrate	Polystyrene co butadiene	–	*N*-Phenyl-2-naphthylamine	DCM	
Hemtex016	~500 g	Phosphonitrillic chloride	Pentaerythritol	Di-n-octyl phthalate	Tributyl citrate	Polystyrene-co-butadiene	–	*N*-Phenyl-2-naphthylamine	DCM	
Hemtex025	~500 g	Urea 200 g	Pentaerythritol 100 g	Di-n-octyl phthalate 30 g	Tributyl citrate 30 g	Polystyrene-co-butadiene 30 g	–	*N*-Phenyl-2-naphthylamine 5 g	DCM	Basic yellow 40 100 g

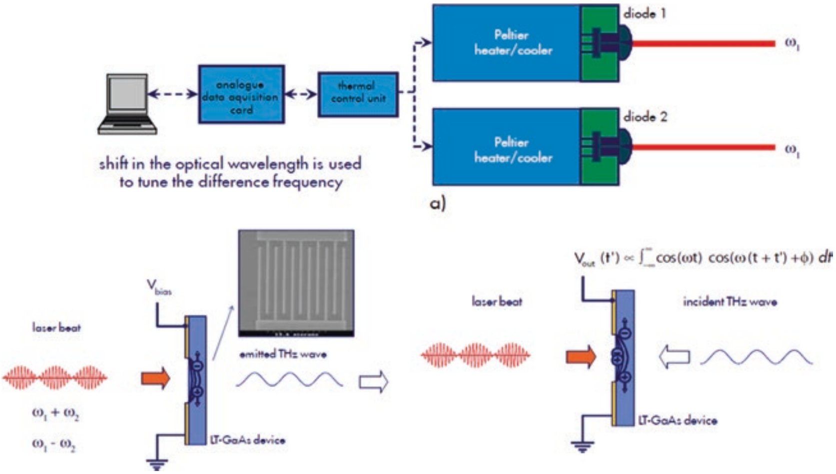

Fig. 11.1 Schematic diagram of how the lasers are offset and how the CW wave is produced and detected [5]

$$\omega_{\mathrm{THz}} = \omega_1 - \omega_2$$

where ω = angular frequency.

The THz beatnote incident on the LT-GaAs substrate causes scintillation to occur. By use of a bias voltage connected to a bow-tie antenna, an electric field between the two plate-ends creates a dipole effect [7]. This causes continuous terahertz waves to be emitted.

Detection is made possible by using homodyne detection. The optical probe beam and the incoming wave interact with the semiconductor substrate connected to the antenna. The system uses a lock in detection scheme based on modulation of the emitter bias voltage which allows for the current to be converted into a measurable signal. A fibre stretcher delay line is used to vary the relative phase of the emitter pump and receiver probe beams, enabling vector measurements of the THz signal.

The current setup of the system includes PMMA lenses that collimate the output from the system and then focus it onto the detector after it passes through the sample. The simulation below shows the effect the lenses have on the wavefronts emitted from the receiver module. Wavefronts with minimal curvature ensures minimal change in amplitude when passing through the dielectric. Furthermore, lenses ensure a

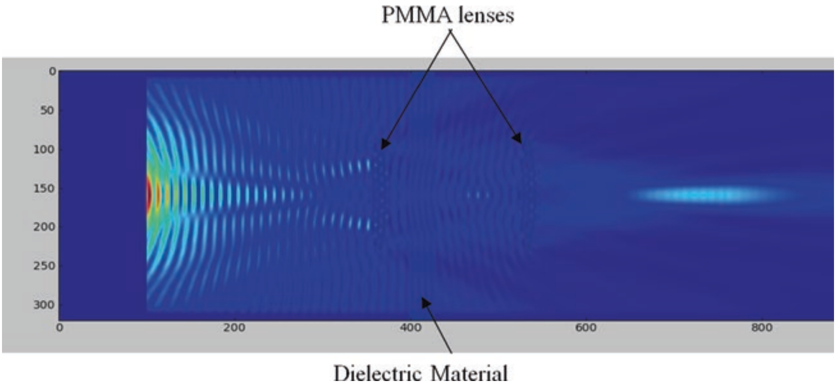

Fig. 11.2 Diffraction pattern of the continuous wave at 30 GHz, as it passes through the PMMA lenses, and the dielectric material

predictable diffraction pattern (Fraunhofer diffraction) observed in the receiver plane with and without a dielectric. In comparison, without lenses the variation of power received on the detector creates significantly greater variability within results (Fig. 11.2).

11.4 Results and Discussion

11.4.1 *Liquid Characterisation Results*

The objective of the experiment was to validate the CW400 with materials already characterised as reference materials. Reference data [8] was obtained from BCR Project 43 organised by National Physical Laboratories (NPL).

A PTFE sample holder was used to contain the liquid during characterisation. This material is strong and robust, resistant to chemicals and low loss, so the effect on the measured results should be negligible (Fig. 11.3).

Comparing reference data to measured data for low and medium loss materials (Figs. 11.4 and 11.5), we estimate a 1% error in ε_r' and 20% in ε_r'' in the low loss materials and an improved accuracy as the concentration of chlorobenzene, and hence the loss, is increased. For high loss materials, measurements for ε_r' and ε_r'' were accurate to 0.5% and 2%, respectively, when compared to NPL reference data [8]. We are therefore confident in our subsequent results.

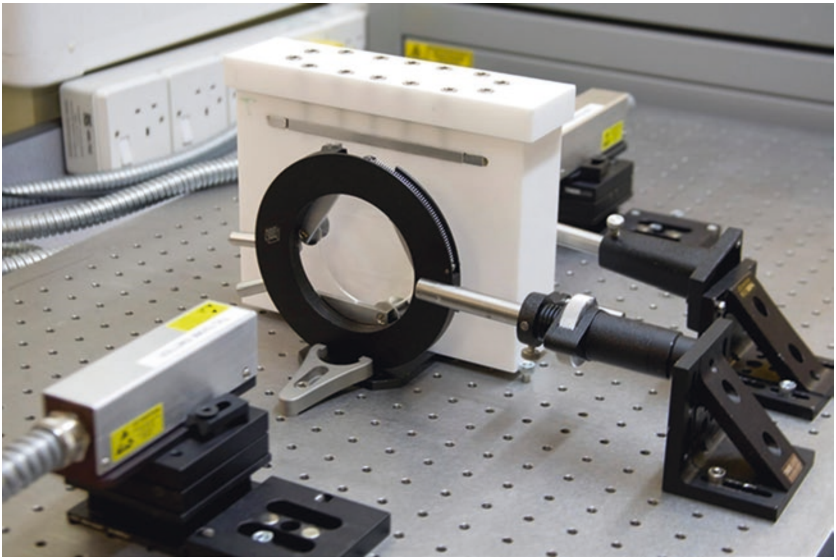

Fig. 11.3 Current arrangement of the CW400 system. Liquid is placed inside the solid PTFE block, which is hollow inside, and designed to work similarly to a cuvette. The emitter is to the left of the image and the receiver to the right. Both modules are placed at the focal length of the lenses ~14 cm

11.4.2 Simulant Characterisation Results

This experiment characterised six different formulations of Hemtex. These materials were characterised by placing them between two polyethylene slabs separated by spacers. The slabs were compressed to keep the sample under constant and equal pressure. This ensures faces are perpendicular to the optical bench and surface defects are minimised. Using spacers also ensures the thickness of the material is known accurately when under compression.

Figures 11.6 and 11.7 shows measurements made with the CW400 on the different batches of the simulant material detailed above.

Age, malleability and concentration of plasticiser are all variables that may affect millimetre wave measurements, and so it is necessary to repeat and vary these types of experiments.

The simulants were compared with Semtex as the threat material which varies from ~1.6 to 1.75 in refractive index according to the literature [9, 10] possibly due to batch-to-batch variation. The Hemtex simulants

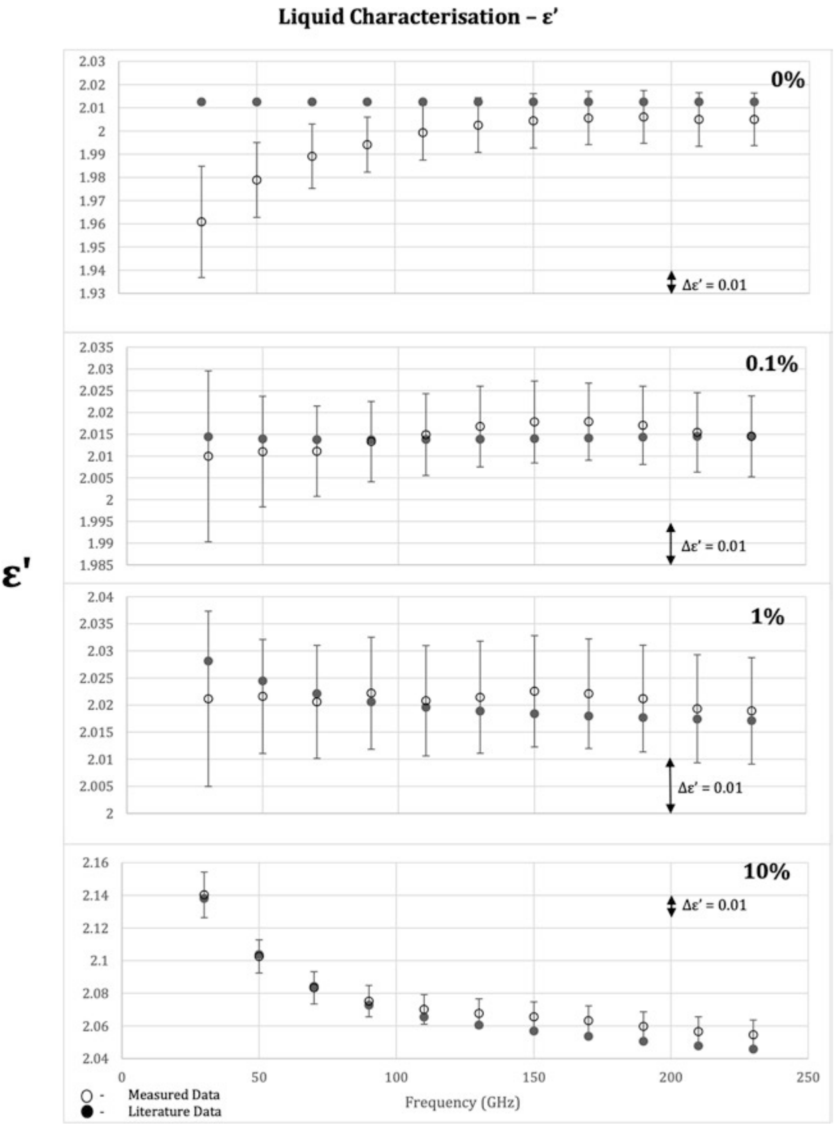

Fig. 11.4 Comparison of measured data against NPL reference data [8] for different concentrations of chlorobenzene in cyclohexane. Graph compares ε_r' against frequency for 0%, 0.1%, 1% and 10% chlorobenzene in cyclohexane, respectively. Literature data [8] for ε_r' accurate to ±0.2% [8]. Error bars [1] for measured data represent standard error with 95% confidence. Note the data points represent the raw data; the connecting lines are for indication purposes

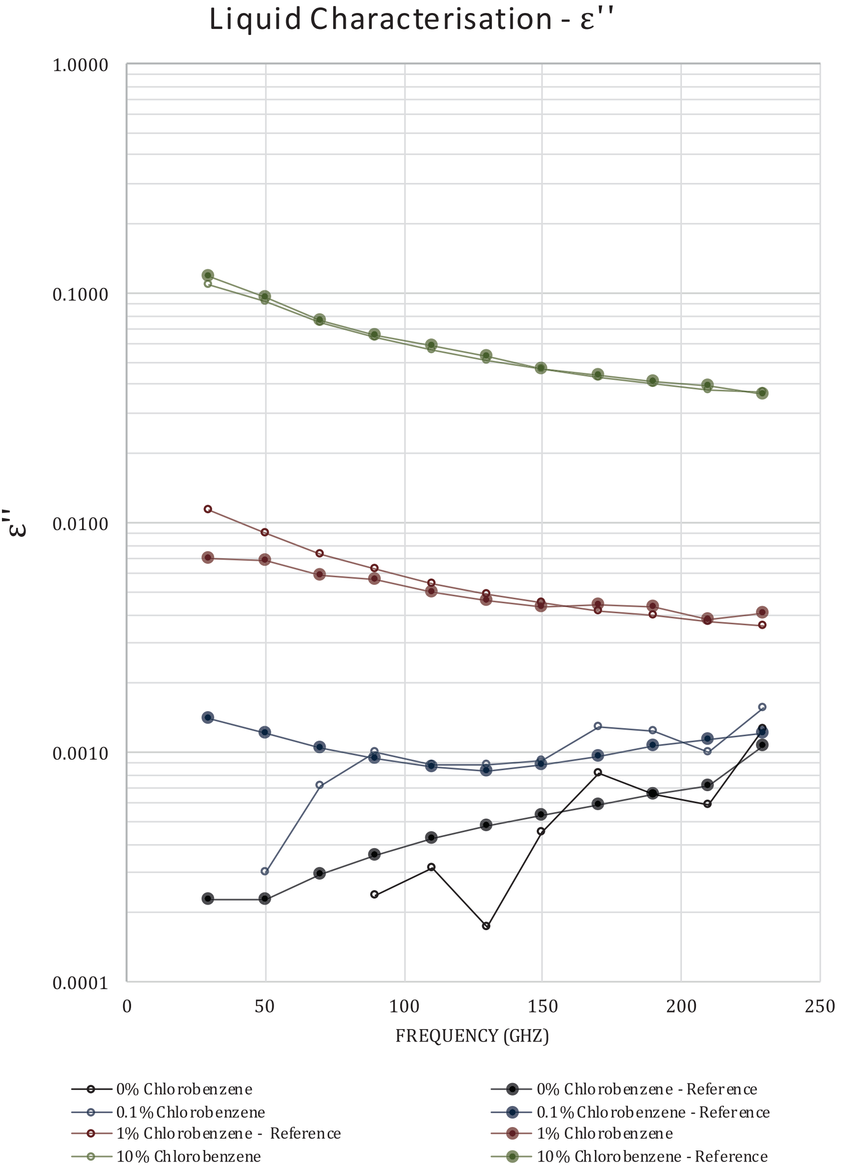

Fig. 11.5 Comparison of measured data against NPL reference data [8] for different concentrations of chlorobenzene in cyclohexane. Graph compares ε_r'' against frequency for 0%, 0.1%, 1% and 10% chlorobenzene in cyclohexane, respectively. Literature data [8] for ε_r'' accurate to ±1% [8]. Error bars [1] for measured data represent standard error with 95% confidence. Note the data points represent the raw data; the connecting lines are for indication purposes

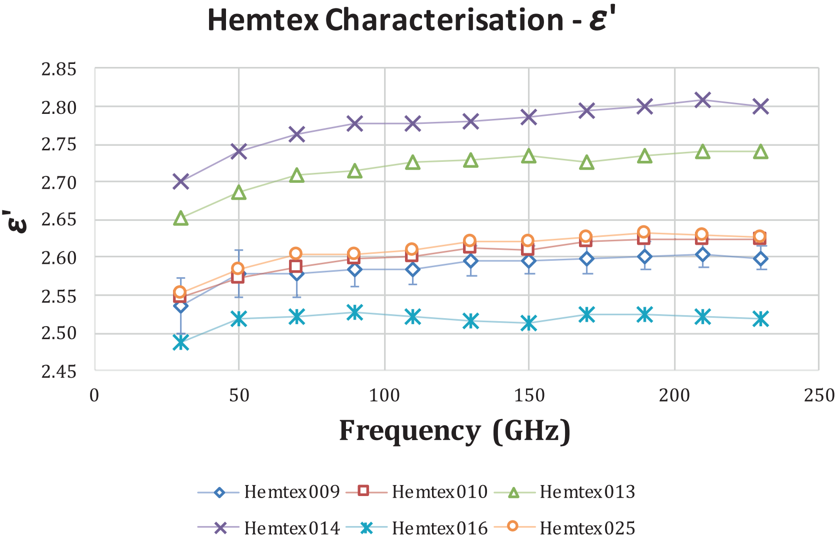

Fig. 11.6 Real permittivity against frequency for six simulant materials. Note the data points represent the raw data and the connecting lines are for indication purposes. For clarity, error bars are only shown for Hemtex009. As stated in the results discussion, the average error across the measured spectrum for ε_r' is ~1%

reported in this work have refractive indexes ranging from 1.58 to 1.68, across the frequency range of 30–230 GHz, which is within the limits of real Semtex implying that Hemtex materials are viable simulants.

On average across the spectrum taken, measured data for ε_r' and ε_r'' had a standard error with 95% confidence of ~1% and ~50%, respectively. The high error in loss measurements particularly varied at lower frequencies, likely due to scattering from voids. The error in ε_r'' for measurements taken between 150 and 230 GHz improves to 35% when excluding batch Hemtex014 which introduced significant uncertainty in loss measurements likely due to void sizes and batch variation.

11.5 CONCLUSIONS

The main conclusion of this work is that the Hemtex class of modular simulants reflect fundamental properties of explosives that millimetre wave and submillimetre wave technologies are sensitive to.

We characterised known liquids to test the Teraview CW400 system. We showed that at the frequency range of 30–230 GHz, for higher loss

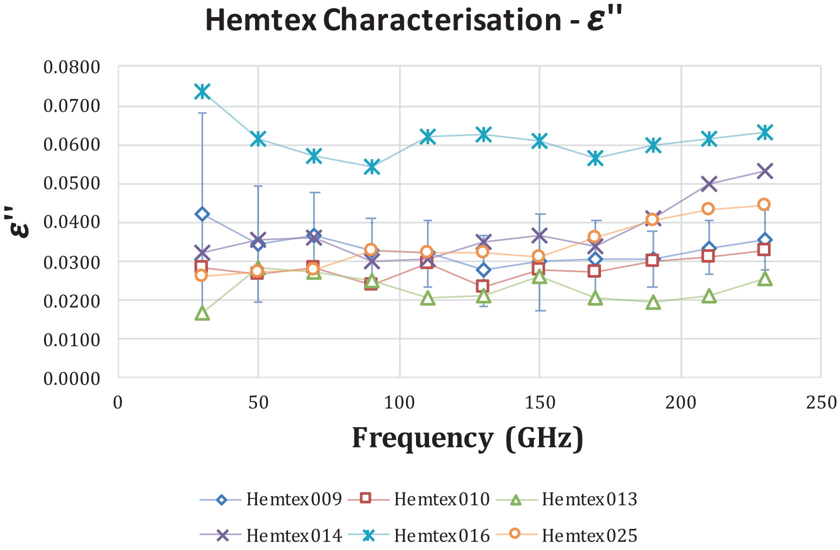

Fig. 11.7 Imaginary permittivity against frequency for six simulant materials. Note the data points represent the raw data and the connecting lines are for indication purposes. For clarity, error bars are only shown for Hemtex009. As stated in the results discussion, the average error across the measured spectrum for ε_r'' is ~50%

materials, the results are well within the acceptable range for characterisation, given that threat simulant materials vary between batches produced. These reference material measurements give confidence in the accuracy of the complex permittivity measurements we have recorded for simulants.

At the lower end of the spectrum ~30 GHz and for low loss materials is still a significant error of 20% in ε_r''. This is due to the system limitation in the characterisation of loss for non-absorbing materials, due to the transmission setup used and diffraction effects having a prominent effect on results.

Simulant characterisation provides good evidence of the variability in the refractive index that we would expect between different batches of energetic materials. Absorption of Hemtex samples posed more problems as grain size and quality of material have a visible effect at the millimetre wavelengths. Ideally, particle size distributions of the grains should be determined and related to absorption. Nevertheless, these characterisation results show that a modular approach potentially enables design of appropriate explosives simulants.

The value of appropriate simulants for millimetre wave and submillimetre wave threat detection technologies is significant. Simulants are safer to handle than real explosives in trials, especially where Person-Borne Improvised Explosives Devices (PBIED) are to be detected. Moreover, they are easier to store and cheaper than real explosives, which allows development times for new instruments to be reduced. It must, however, be noted that any detection instruments should be checked with real materials before submission for regulatory accreditation and certainly before deployment in real situations. If these checks have been conducted, then Hemtex simulants should also be viable for daily or routine verification/calibration of approved millimetre wave detection systems.

The work reported has to be applied to millimetre and submillimetre wave detection systems seeking to find illicit materials hidden, especially on people, at non-contact distances ranging ideally from metres to tens of metres. To accelerate research and development of such systems, often referred to as 'stand-off' detection, in a safer and cost-effective manner instead of using real materials with attendant hazard is an aspiration. Future work could include further characterisation of chlorobenzene in cyclohexane to understand the uncertainties with the CW400. A solid reference material of low, medium and high loss will also need to be selected to test the true capability of this system.

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