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SIMULTANEOUS NON-INVASIVE MICROWAVE DIELECTRIC SPECTROSCOPY AND DYNAMIC MECHANICAL ANALYSIS FOR STUDYING DRYING PROCESSES

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Abstract

The aim of this paper is to describe how a dynamic mechanical analyser can be used together with the microwave coaxial line technique. This coupling enables the simultaneous recording of changes in the mechanical properties and moisture content of materials as a function of time or temperature at a selected frequency. The sample is placed either directly under the probe or clamped in the sample holder of the dynamic mechanical analyser. Sample positioning and heating is accurately controlled by the mechanical analyser and its temperature controller. Samples can be subjected to a constant static force, a frequency or both. A micro probe, recently designed for measurements on semi-rigid and rigid surfaces [1], and connected to a network analyser was used to monitor the moisture content of the samples.

Keywords: complex heterogeneous materials, dynamic mechanical analyser, microwave dielectric spectroscopy

1. The coaxial line technique

1.1 Introduction

The open-ended coaxial line with the network analyser measuring system is a relatively new technique. It was originally proposed by Tanabe and Joines in 1976 [2] and its first use was to measure the electrical properties (complex permittivity and conductivity) of solutions and various tissues. This work was presented in 1980 [3]. The test sample in this case was homogeneous and semi-infinite.

Recently, the performance of the measuring system and a 3.6 mm outside diameter (OD) probe was investigated, both theoretically and experimentally, for polar liquids over the frequency range 0.13–20 GHz [4]. This microwave frequency region has the advantage that measurements are fast and can follow the changes in sample properties in real time.

1.2 Theory

An electromagnetic signal source (network analyser) connected to an open-ended coaxial line causes fringing electromagnetic fields to emerge from the open end of the probe. If the end of the probe is surrounded by a sample then the signal

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is significantly affected. This process depends critically upon the dielectric properties of the material through which the fields pass and if it is polar, non-polar, and whether small polar molecules are involved. In the microwave region only the response from small polar molecules such as water, methanol are observed. The reflection characteristics at the interface are measured by the network analyser. The permittivity of the terminating sample is related to the reflection coefficient by matching the fields at the boundary of the probe and the sample [1]. The background work including the solution to the resulting complex equation and a full study of the admittance models has been described elsewhere [4]. This is the basis of the technique for measuring the dielectric properties of materials using the open-ended coaxial line technique.

The coaxial line technique measures the relative complex permittivity of samples: $\varepsilon^* = \varepsilon' - j\varepsilon''$, (where j is the square root of –1). The real part (ε') is the permittivity and the imaginary part (ε'') gives the loss or power absorption of the dielectric. The permittivity ε' is highly correlated with moisture content. The value of water (small polar molecule) [approx. 80.1 (20°C)] exceeds greatly the values for dry or non-polar materials [values lie between 2 and 5] [5]. The behaviour of ε' (real part) is more regular than that of the loss factor with respect to changes in the moisture content and frequency of the applied fields [5]. For this reason permittivity ε' values are measured in this work as a function of temperature or time.

1.3 Equipment

The equipment consists of a system controller connected to a HP8720C network analyser which generates a swept signal in the range of 50 MHz to 20 GHz. The microwave region is sensitive to the presence of small polar molecules, in particular water molecules (Fig. 1) which rotate in an applied a.c electric field at a frequency of 17 GHz at 20°C. Measurements (either single frequency time/temperature scans

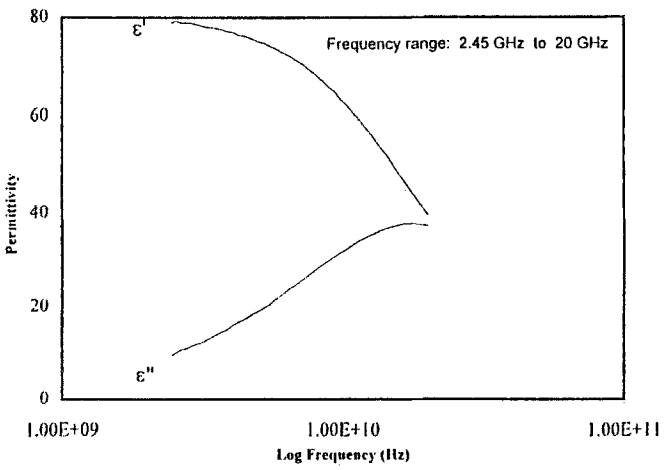

Fig. 1 Dielectric measurement of water at 20°C. Data collected over working range of analyser (2.45 GHz to 20 GHz)

or multi-frequency isothermal scans) were made using two probes and these will be referred to as: small probe, OD=0.86 mm, and the standard probe, OD=3.6 mm. The small probe was enclosed in a stainless steel protective sheath to prevent damage to the probe.

1.4 Applications

In general, dielectric measurements, particularly with coaxial sensors, have been widely used in food-processing [6] and medical fields [7–10]. However, the small probe (OD 0.86 mm) has only been used recently with the specific application to paintings [1]. It was considered that the probe would have the spatial resolution to distinguish between adjoining regions of differing pigmentation and differing media, and that it would be possible to monitor moisture uptake in different regions of a painting. Measurements were made on semi-rigid and solid surfaces [1]. The small size, as mentioned above, limits depth of sample penetration and negates to some extent the lack of homogeneity of the sample which is required by the mathematical model. It also means that small samples can be measured and that monitoring can be performed in localised regions of the sample.

2. Dynamic mechanical thermal analysis

A Rheometric Scientific DMTA Mk3 instrument was used to provide a measure of the viscoelastic properties and changes in displacement under a tensile or compressive force. Measurement of these parameters can be made over a temperature range and isothermally.

3. Combined technique

3.1 Amendments to DMTA

In order to accommodate the probe, modifications were made to the DMTA measuring head. The furnace lid was removed, which involved overriding its normal automatic operation. It was then necessary to manually close the furnace. In order that the probe could pass through the furnace lid the optical window assembly was removed and replaced by two 3 mm thickness aluminium plates in which 10 mm holes had been drilled to accommodate the probe. In order to maintain it in a vertical position, over the DMTA head, a clamping system with vertical and horizontal adjustment was constructed to hold the probe. Figure 2 shows the experimental set-up for the combined system.

3.2 Coaxial line (measuring system)

The probe was connected to the network analyser by means of a flexible 3.5 mm test port cable fitted with "K" connectors at both ends. The flexibility of this cable enabled the probe to be correctly positioned relative to the DMTA measuring head. A probe suitable for the type of sample and experiment to be performed was chosen

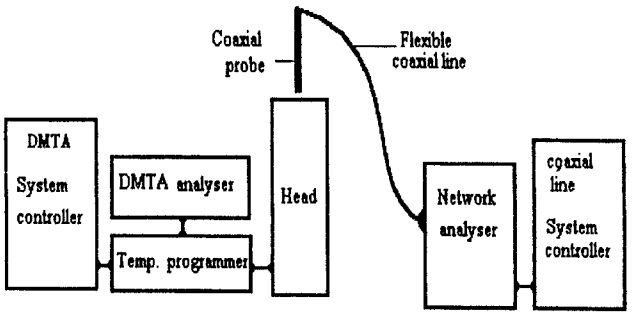

Fig. 2 Schematic representation of the simultaneous system

and calibrated. Calibration consisted of an open and short circuit measurement of the probe, followed by a known standard. In this case distilled water was the standard and a piece of Indium was used to provide a short circuit. The system was tested with samples of egg white and egg yolk to which water had been added.

3.3 System operation

The DMTA system controller was used to control the temperature, and the network analyser software allowed data to be collected in coincidence with the DMTA software.

In these measurements use was made both of the compression and tensile modes of measurement. In the case of the compression mode (Fig. 3) the standard probe of diameter 3.6 mm was used. The measuring head, however, could accommodate a sample up to 20 mm. The sample was placed on the bottom circular metallic plate

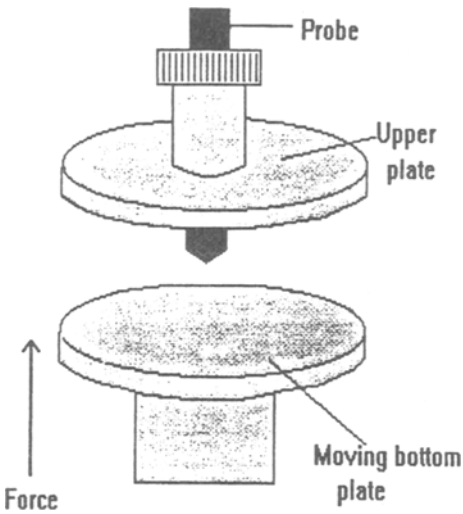

Fig. 3 Compression mode, showing adjustable upper plate, allowing different depths of penetration for the probe

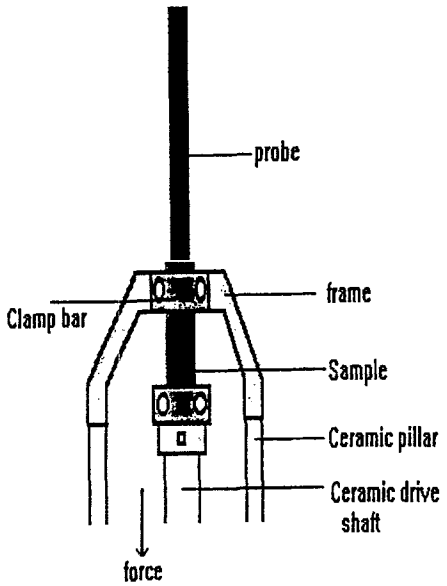

Fig. 4 Tensile mode, allows mechanical testing while probe sits on sample protruding from clamps

and the sample was subjected to a compressive force. The presence of the metallic plate below the sample assisted in optimising the reflection of the microwave radiation along the coaxial line. In the case of the tensile mode – (Fig. 4), an arrangement which is most suited for the thin films and fibres, the sample was clamped as shown and measured with either no force or a known applied force.

4. Experimental procedure

4.1 Coaxial line measurements for liquids

Each sample was placed into a small glass sample bottle. The bottle was raised until the end of the probe was 10 mm below the surface of the liquid. Permittivity (ε') data were then collected over the frequency range 2.45 GHz to 20 GHz.

4.2 Combined technique measurements

A) Leather

The following leather samples [11] were chosen for this study: (a) unaged tanned leather (goat), (b) artificially aged tanned leather (goat). Leather samples (1 mm thick, 5×5 mm square) were soaked overnight in water. Each sample was removed from the water and any excess moisture was wiped away. To prevent any sample from adhering to the compression disc, a DSC aluminium crucible (8 mm diameter, 1.5 mm depth) was used. The compression plate was then raised, using the DMTA stepper motor mechanism, until the sample was in contact with the probe.

Isotherms at 30°C and thermal scans to 100°C at 2°C min^{-1} were performed on the wet leather samples in this mode under a compressive force of 0.2 N. Drying times and displacement were measured as a function of temperature.

B) Paper

Samples of untreated and deacidified groundwood paper [12] were tested. They were placed in the tensile frame, and the sample was allowed to protrude from the top so that the probe could contact the sample. The materials were soaked for 12 h in water and the excess moisture removed before mounting. Tests were performed isothermally under a constant tensile force. The small probe was used for these tests. A modification was made to the tensile clamp so that the probe could contact the sample under a preselected static force (Fig. 5). This allowed the probe to measure the samples directly under tension. Experiments at differing static tensile force levels (0.03 N and 0.1 N) were performed.

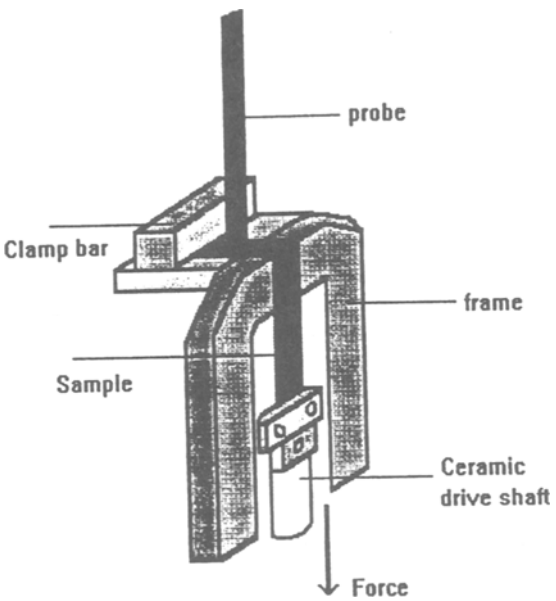

Fig. 5 Simultaneous dielectric and mechanical measurements made under tension

C) Food

The dough and cheese samples were placed directly onto the compression disc, which was attached directly to the drive shaft. Using this technique soft samples could be quickly mounted directly into the measuring head. Due to the softness of the food samples the standard probe was chosen because of the larger surface area of the end of the probe. A long isothermal drying tests was carried out on the cheese sample and a thermal dynamic mechanical test was performed on the dough sample to 110°C at 2°C min^{-1}.

5. Results

5.1 Coaxial line

Figure 6A shows the dielectric behaviour for water, egg white, egg yolk and a 50/50 mixture of egg yolk with water. The result for the 50/50 mixture of egg yolk with water indicates that it lies between that of the pure egg yolk and the pure water. This is as expected if water remains in the free state. A simple ratio of the measured permittivity value against that for water, at a selected frequency (in this case 2.45 GHz), at a given temperature, will give an estimate of the free water content for the material (section 1.2).

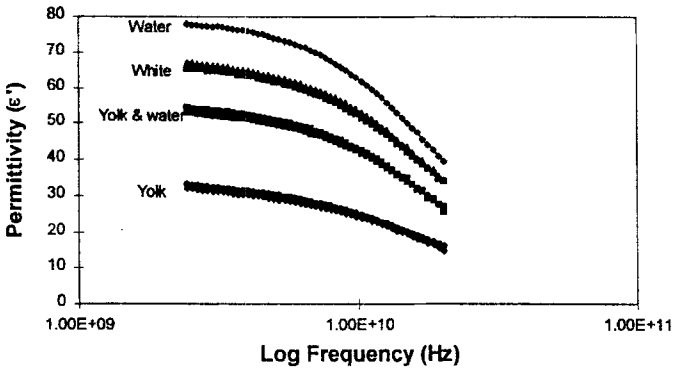

Fig. 6A Dielectric behaviour of water, egg white, egg yolk and a 50/50 mixture of egg yolk with water

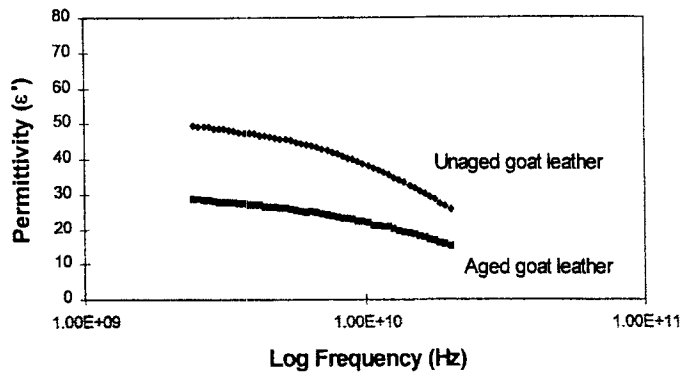

Fig. 6B Dielectric behaviour of unaged and aged goat leather after soaking in water for 24 h

A) Leather

Figure 6B clearly shows a major difference between the unaged and aged goat leather samples. The unaged sample has a higher initial moisture content, after soaking, than the aged sample. Unaged/aged leather samples have similar curves mechanically and dielectrically (Fig. 7). Mechanically, the unaged goat leather Fig. 7

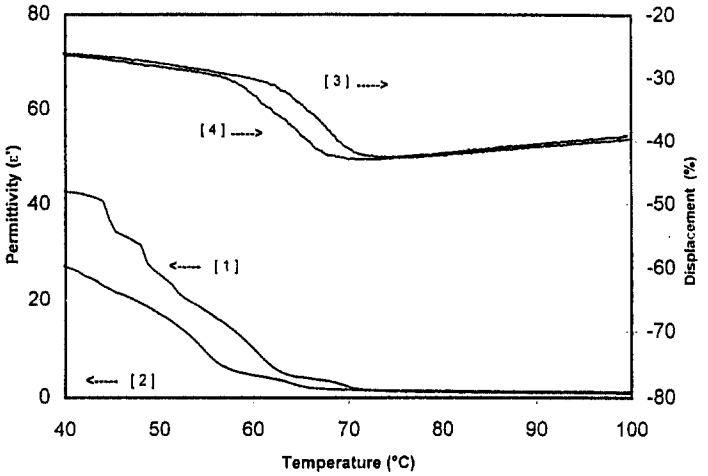

Fig. 7 Thermal scan of unaged and aged goat leather after soaking in water for 24 h. Permittivity (ε′) for [1] unaged and [2] aged goat leather. Displacement (%) for [3] unaged and [4] aged goat leather

[4] requires a higher temperature to dry than the aged Fig. 7 [3]. The drying times for the unaged Fig. 7 [1] are longer than for the aged Fig. 7 [2].

B) Paper

Figure 8 clearly shows that initial values of moisture content of the samples are different. The reference paper sample Fig. 8 [1] has a higher moisture content than

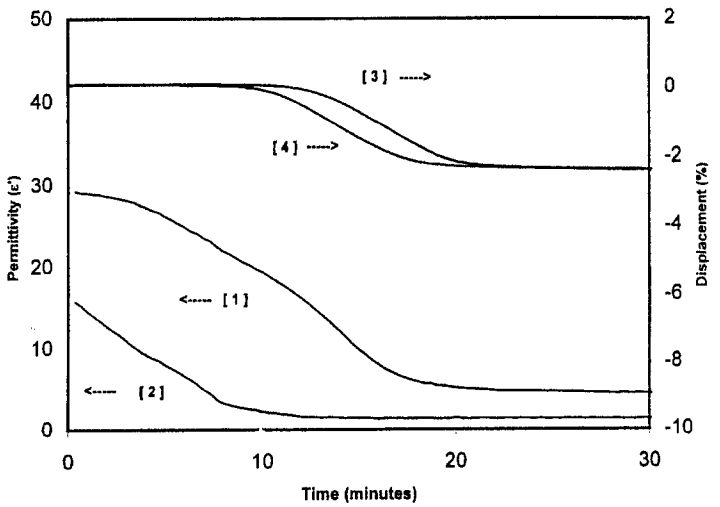

Fig. 8 Isothermal (30°C) drying spectra of groundwood paper after soaking in water for 24 h. Permittivity (ε′) for [1] reference (untreated) and [2] Battelle treated. Displacement (%) for [3] reference (untreated) and [4] Battelle treated

the deacidified paper Fig. 8 [2]. The drying of the samples isothermally at 30°C shows distinctly differing drying profiles. The dielectric curves of the treated samples Fig. 8 [2] show a rapid loss of moisture and after approximately 10 minutes the majority of the water is lost. However, the reference samples Fig. 8 [1] show a more gradual loss of moisture and it takes approximately twice as long as the treated samples Fig. 8 [2] before the majority of moisture is lost. The deacidification treatment [12] which is non-aqueous based clearly affects the rate at which moisture is lost. The mechanical data Fig. 8 [3] and Fig. 8 [4] show the same general trend as the dielectric. The effect of increasing the static force on the sample is shown (Fig. 9). It is clear that it decreases the time for drying the paper.

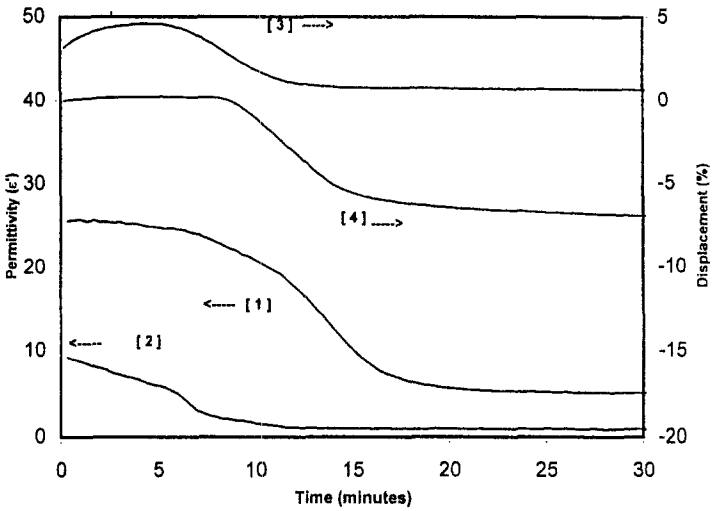

Fig. 9 Isothermal (30°C) drying spectra of groundwood paper after soaking in water for 24 h, under tension, measured with two different forces 0.03 N and 0.1 N. Permittivity (ε′) for [1] 0.03 N and [2] 0.1 N. Displacement (%) for [3] 0.03 N and [4] 0.1 N

C) Food

As the sample of dough is heated it begins to soften but the permittivity shows a small increase which maybe due to the water interacting with the polysaccharide matrix [13]. However, at approximately 80°C the sample begins to rapidly lose moisture and there is a corresponding drop in permittivity and a rise in log storage modulus (Fig. 10).

Figure 11 show the drying of cheese. At first moisture forms on the outside of the sample and there is a corresponding increase in permittivity. After approximately 5 h this moisture begins to evaporate and the permittivity begins to fall. The displacement trace shows the expected rapid penetration into the surface of the cheese at the start but as the cheese begins to dry and the surface become hard then the degree of penetration decreases.

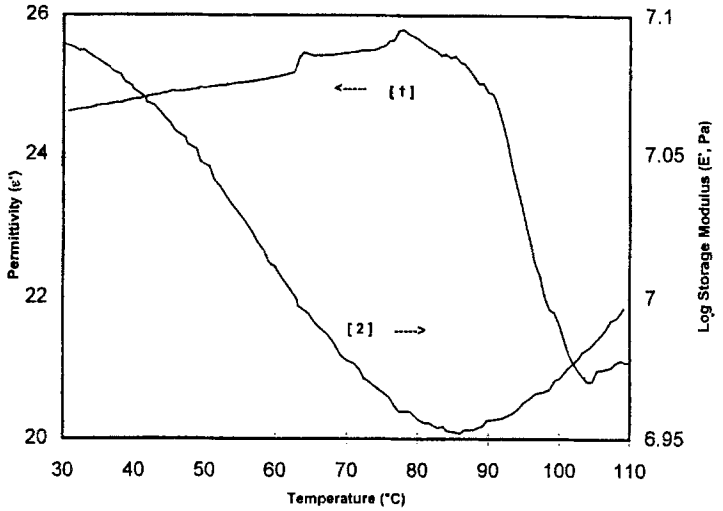

Fig. 10 Thermal scan of dough. Permittivity (ε′) for [1] and Log Storage Modulus E' (Pa) for [2]

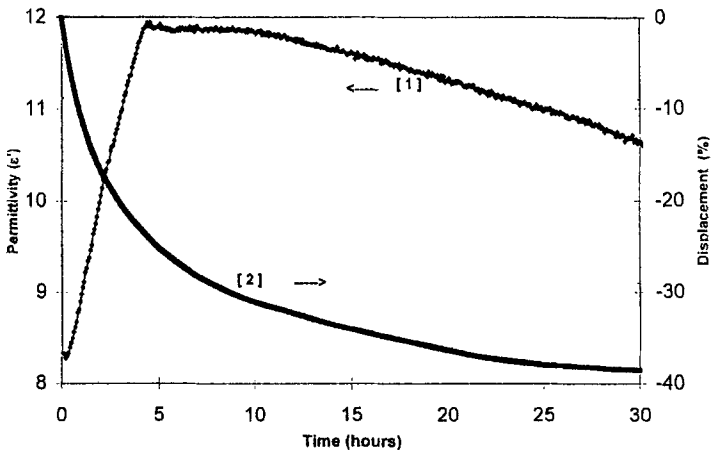

Fig. 11 Isothermal (30°C) spectra for cheese. Permittivity (ε′) for [1] and displacement (%) for [2]

Conclusions

The simultaneous dynamic mechanical and coaxial line technique has been shown to provide a procedure which not only monitors the change in mechanical properties but also through the permittivity values provides a direct measure of changes in moisture content of the samples. As referred to in an earlier section [1.4], the demand for monitoring moisture content is high. In this paper emphasis

has been given to the instrumentation and what the combined technique is able to measure. A detailed account of conservation and environmental related measurements including leather, paper and canvas samples will be reported elsewhere.

Plans are in hand to make further software and instrumental developments and to provide a means of scanning the surface of a material, thereby mapping moisture distribution whilst the mechanical properties are also being monitored.

* * *

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