Dielectric Analysis. Experimental

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1. Introduction

Dielectric analysis is a measuring technique increasing its use day by day and it has in recent years become one of the most interesting techniques to monitor the evolution of physical and chemical properties during processing and utilization of polymer materials [1]. This is due, in part, to the growing usage of speciality materials in the electrical and electronics industry and to the excellent diagnostic properties possessed by dielectric behaviour. But a major influence to the rise in popularity for these studies is the relative simplicity of much of the apparatus required and the ease with which a very wide range of frequencies can be employed [2].

There are a number of electrical properties that can be readily observed as a function of temperature. The most commonly used techniques follow changes in ac or dc conductivity, capacitance or dielectric properties thermally stimulated discharge currents and the emf developed between dissimilar electrodes in contact with the sample, thermo voltaic detection [3].

This chapter will focus on the dielectric analysis techniques, i.e. ac. Dielectric analysis (DEA or DETA), or dielectometry involve determination of the electrical polarization and conduction properties of a sample subjected to a time-varying electric field. It complements the traditional techniques by allowing the scientist to view molecular motion from a different perspective, that is, through changes in electrical properties. Thus provide both thermal and rheological information. In thermal analysis experiments, the DEA heats and/or cools samples in order to identify thermal transitions. For some measurements, it has extremely high sensitive to changes in physical properties, which makes it possible to detect transitions that are not visible by other techniques. For rheological studies, the DEA is particularly effective because it can monitor the movement of ions in a material. A single dielectric test can identify keys events affecting rheological changes: the time and temperature which correspond to minimum viscosity, the onset of flow, onset of cure, and maximum of rate reaction and completion of cure [4]. While the dielectric analysis does not provide absolute values for viscosity, the shape of dielectric curves usually can be correlated directly to the viscometer profiles of curing resins.

One of the most important advantages of DEA from other techniques is that dielectric information can be obtained almost instantaneously with only minimal disturbance of the process controlled in real time.

We can measure with DEA dielectric properties like permittivity, loss factor and detect the α-transition, secondary transitions (β, γ, etc), rheological phenomena such as viscosity minima, polymerization and cross-linking, segmental mobility, dipolar relaxations and ionic conductivity, vitrification during cure and gelation for thermosetting materials, rate of cure, degree of cure, etc. [4].

2. Experimental Methods

It is a feature of the dielectric technique that measurements can be performed nearly continuously over the frequency range 10^{-4} to $3x10^{10}$ c/s. It exits a particular method for every frequency range. Table 1 summarizes the methods which are employed in particular regions of this large frequency range [2]

Table 1

Frequency Range	Method	Remarks
10^{-4} to 10^{-1} Hz	d.c Transient measurements	Analogous to creep effect
10^{-2} to 10^{2} Hz	Ultra Low frequency Bridge	Precise determination of $\varepsilon' - i\varepsilon''$
10 to 10^{7} Hz	Schering Bridge Transformer Bridge	Precise determination of $\varepsilon' - i\varepsilon''$
10^{5} to 10^{8} Hz	Resonance Circuits	Upper limit of lumped circuit methods
10^{8} to 10^{9} Hz	Coaxial line	Good only for medium and large ε''
	Re-entrant cavity	Good only for low ε'' values
10^{9} to $3x10^{10}$ Hz	H_{01n} cavity resonator	Same as above
	Coaxial lines and waveguides	Good for medium and high ε'' only

These methods may be classified into two general groups: "lumped circuit" and "distributed circuit" method. In the "lumped circuit" range, 10^{-4} to 10^{8} c/s approximately, the experimental technique is designed to measure the equivalent capacitance and resistance at a given frequency. At higher frequencies, the effect of residual inductance in the measuring assembly makes difficult to regard the sample as a resistance-capacitance arrangement. The experimental method for the "distributed circuit" range 10^{8} to $3x10^{10}$ c/s is designed to measure the attenuation factor α and the phase factor β at a given frequency. We shall show below how the experimental quantities, resistance and capacitance, and attenuation and phase factor, are related to the complex dielectric constant ε^{*}.

A large part of the dielectric work on polymers has been confined to the frequency range 10^{2} to 10^{5} c/s. It is however, essential that as large a frequency range as possible should be covered, since dielectric relaxation curves for polymers are broad and very sensitive to a temperature variation.

2.1. Distributed circuits 10^{8} to $3x10^{10}$ c/s

At frequencies above about 10^{8} c/s, it is extremely difficult to make lumped circuit measurements [2], due to the increasing importance of residual inductance. Methods have been developed which avoid this problem, and are based on the concepts of wave propagation through a magnetic waves along rectangular or cylindrical waveguides or coaxial transmission lines (see Figure 1).

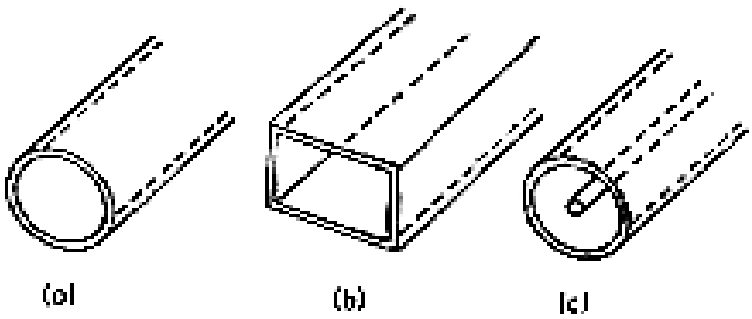

Figure 1.

2.2. Lumped circuits

In the frequency range 10^{-4} to 10^{8} c/s, it is convenient to regard a polymer sample as being a electrically equivalent to a capacitance C_x with a resistance R_x, at a particular frequency. Both C_x and R_x will in general be frequent dependent. We must now find a relationship between C_x, R_x and the complex dielectric constant ε^*. This will be studied further on.

The lumped circuit techniques to be described are mainly designed to measure C_x and R_x, at a particular frequency. C_x and R_x may be converted to ε' and ε'' values, respectively, knowing C_0. It is also useful for characterizing viscoelastic relaxation [5]. The contribution to the total loss arising from a d.c. conductivity process is given by:

$$\varepsilon_0''(\omega) = \frac{1}{R_x \omega C_0} = \frac{G_0}{\omega C_0} \tag{1}$$

$\varepsilon_0''(\omega)$ can be evaluated in practice by measuring R_0 or $[R_{spec}]$ by a simple direct current method, and using [1] to obtain $\varepsilon_0''(\omega)$ at any desired value of ω.

Some of the different methods arranged according to increasing frequency range are the following: D.C. Transient current method 10^{-4} to 10^{-1} c/s, Ultra-low Frequency Bridge 10^{-2} to 10^{2} c/s, Schering Bridge 10 to 10^{6} c/s, Resonance Circuits 10^{5} TO 10^{8} c/s, Re-entrant cavity 10^{8} TO 10^{9} c/s [2].

2.3. D.C. transient current method 10^{-4} to 10^{-1} c/s

Figure 2 gives a simple circuit to illustrate the method. Switch (S_1, a) is closed, the sample C_x responds to the step voltage V, giving rise to a transient charging current through C_x which is measured by the amplifier circuit. After charging equilibrium has been attained, switch (S_1, b) is closed [opening (S_1,a)], and the transient discharge current is measured.

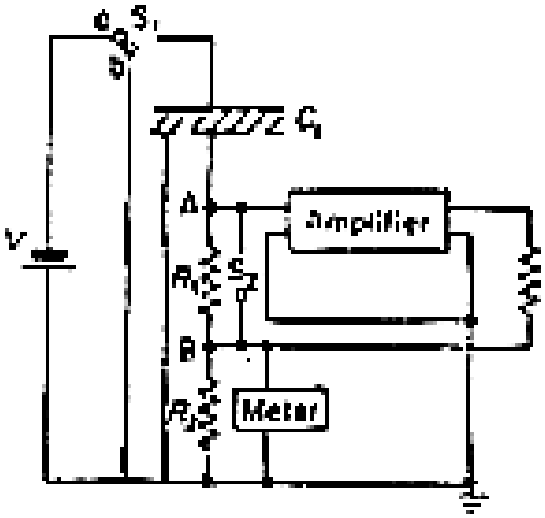

Figure 2. [6]

If the sample consisted of a pure capacitance only, there would be no transient current [2]. Since transients are obtained in practice, the dielectric must considered as having a time-dependent resistance associated with it.

2.4. Ultra –low frequency bridge 10^{-2} to 10^{2} c/s

The main difficulty in the lower region of this frequency range is that the generator cannot be coupled via transformer to the bridge but must be coupled directly. This was achieved in Scheiber´s [7] design, and, also, a Wagner earth was not required to balance the bridge, which is a great time to consumer at low frequencies. The actual bridge works on the Schering bridge principle and using a substitution method very precise ε^{*}_{ω} measurements are possible on polymer compounds. Other bridges used in this region have been reviewed by Scheiber.

The schematic circuit diagram of the Scheiber Bridge is shown in figure 3.

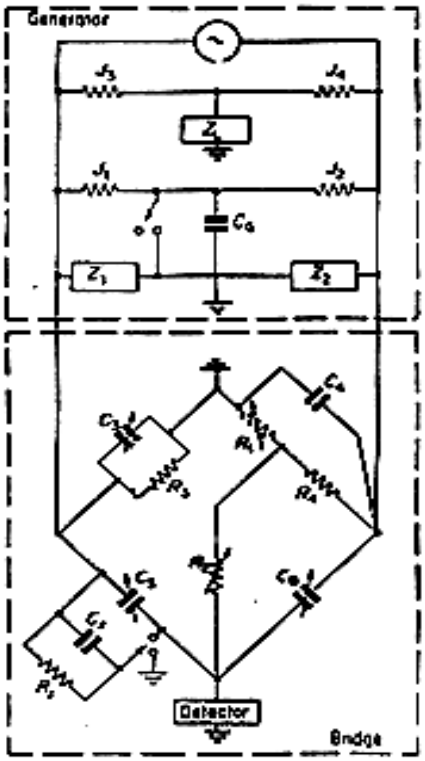

Figure 3.

The generator is directly coupled to the bridge circuit. Z_1, Z_2, and Z_L are stray impedances within the generator, J_1, J_2, J_3, and J_4, are 15 kΩ resistors in the generator. C_G is shorted for bridge measurements. The sample C_x, R_x is measured by balancing the bridge with sample "in" using R_1 and R_2, and C_s. Here R_1 is a 100Ω decade resistor, R_2 = 10^6, 10^7, 10^8, or 10^9 Ω interchangeable calibrated resistors. C_s and C_B are precision three-terminal variable capacitors (10 to 110 μF). C_3 and C_4 are 1000 μμF precision two-terminal capacitors. R_3 and R_4 are matched precision 10^5 Ω resistors.

2.5. Schering bridge 10 to 10^6 c/s

This is the most common method for the measurement of ε^* particularly in polymer work. Various designs differing in detail are used, but the basic principle of one of the most commonly used is illustrated in figure 4. This is a simple capacitance bridge [2].

For a sample in arm A, at balance we have $(Z_A Z_C)_{in} = (Z_B Z_D)_{in}$. Here Z_A is the total impedance for arm A, etc. For sample out, only C_1 and C_4 need be adjusted rebalance the bridge giving $(Z_A Z_C)_{out} = (Z_B Z_D)_{out}$.

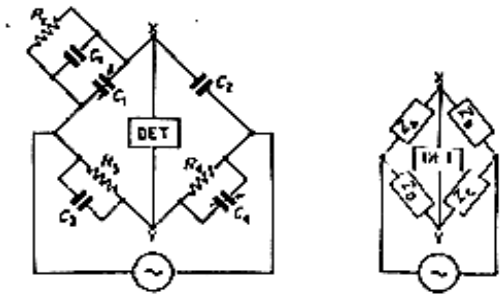

Figure4.

The Schering Bridge is capable of very high accuracy for ε′ and ε′′ and the uncertainty of measurement is often due to the fact that the sample dimensions are not known to the accuracy that C_1 and C_4 changes can be determined.

2.6. Resonance circuits 10^5 to 10^8 c/s

Above about 10^6 c/s the effects of stray impedance (particularly inductance) become increasingly significant. The bridge methods cannot be used above about 10 Mc/s for this reason. Various methods have been devised for this range and we shall confine ourselves to the conductance variation resonance method which is probably the most widely used in polymer studies and also gives very precise results. This is illustrated schematically in figure 5. [8]

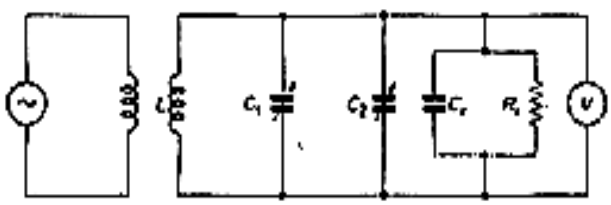

Figure 5.

The resonance circuits is made up of two precision variable capacitors C_1 and C_2 , inductance L, the sample C_x, R_x, and the voltmeter V. The circuit is brought to resonance using a loosely coupled generator circuit of variable frequency. At resonance the half-width δ^{in} of the resonance curve is determined using the micrometer capacitor C_2 (≅ 0-8 μμF). The sample is then withdrawn from the resonance circuit and resonance restored by changing C_1 only.

2.7. Re-entrant cavity 10^8 to 10^9 c/s

For low loss factor (tan $\delta \cong 10^{-4}$) a resonant cavity is appropriate in the frequency range 10^8 to 10^9 c/s. Figure 6 shows Parry´s [9] apparatus in schematic form. The method is an extension of the Hartshorn-Ward [8] method (1936) to higher frequencies.

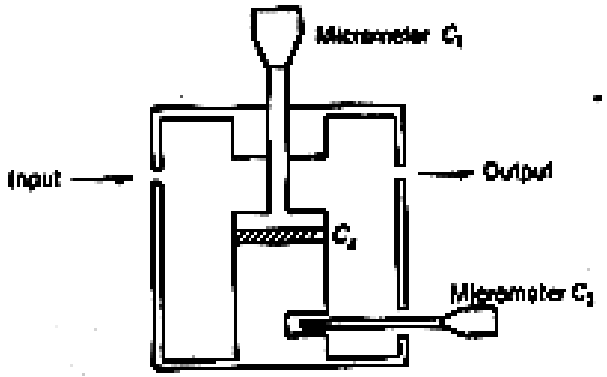

Figure 6.

The sample is placed between the electrodes, and the system is equivalent to a closed coaxial transmission line in which the central conductor in two parts, separated by the sample. The cavity is brought to resonance using frequency as the variable, the resonance being detected using a silicon crystal and loop.

In particular, this chapter will be devoted to describe designed by TA Instruments, that is, the Dielectric Analyzer DEA 2970 that works in the frequency range from 0.003 to 100 kHz, thus belonging to the "lumped circuits".

3. Description

3.1. Hardware

The DEA 2970 dielectric analyzer is an add-on module for any of the TA Instruments Thermal Analyst Systems [10]. It consists of a sensor and ram/furnace assembly (Figure 7), incorporated in a cabinet which contains the supporting electronics. There are four types of sensors (Figure 9) - ceramic parallel plate, ceramic thin film, ceramic single surface, and remote single surface - which are interchangeable and disposable. The system's exceptional versatility permits analysis of bulk or surface properties, using milligram or full-size product samples (e.g., in a laboratory oven, a large part in a moulding press or sheets of prepreg in storage). Sensor disposability not only is a convenience and ease-of use feature, but it makes possible the measurement of hard-to-handle samples.

The ceramic sensors are mounted in the ram/furnace assembly, which provides all the necessary environmental conditions: controlled heating and cooling, atmosphere, and applied force. The ram, driven by a stepper motor, applies a constant force or maintains constant plate spacing, based on information from a force transducer and a linear variable differential transformer (LVDT). This assures desired electrode spacing and optimum surface contact with the sample. Sensor insertion and removal are quick and easy, requiring no tools, fasteners or soldering [10]. All electrical contacts are made automatically.

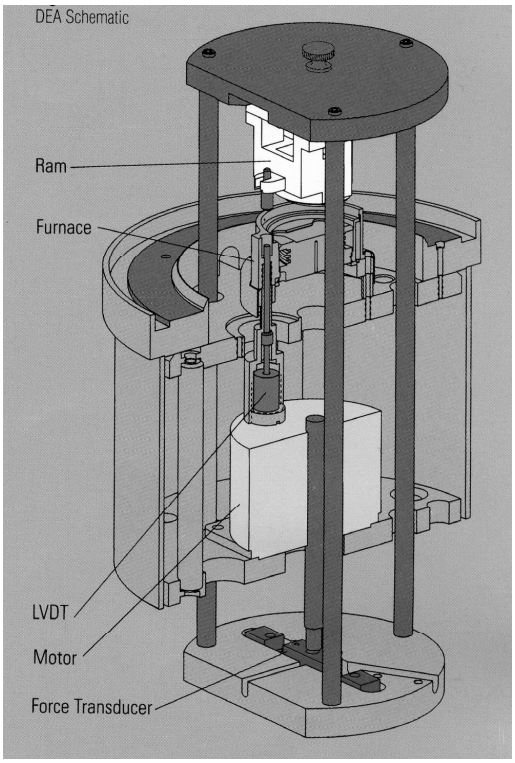

Figure 7.

The remote single-surface sensor* consists of a flexible ribbon cable with a microdielectrometer sensor at one end and a connector at the other. The sensor end is designed to be embedded in a sample; the connector end is for attachment to the instrument.

The module cabinet contains the electronic circuits and software for experiment control and data handling, a keyboard/display for local control of operation, and a GPIB interface for communication with the controller.

The controller is an essential component of the complete DEA system. It is used to program experiments, analyze results, and customize reports. A plotter is required for preparation of hard copy reports.

We will see in detail all this components and how it manages

3.2. Electronics

The heart of the DEA system is its electronic circuitry and software. They implement the theory of the technique and give life to the hardware, making the system effective, practical, accurate, and fast. Results are produced almost instantaneously.

One key to the effectiveness of the DEA 2970 is its measurement technique, which avoids the limitations inherent in instruments based on a Wheatstone bridge. This makes possible accurate measurements at low frequencies as well as high frequencies, and contributes to the instrument's operating speed.

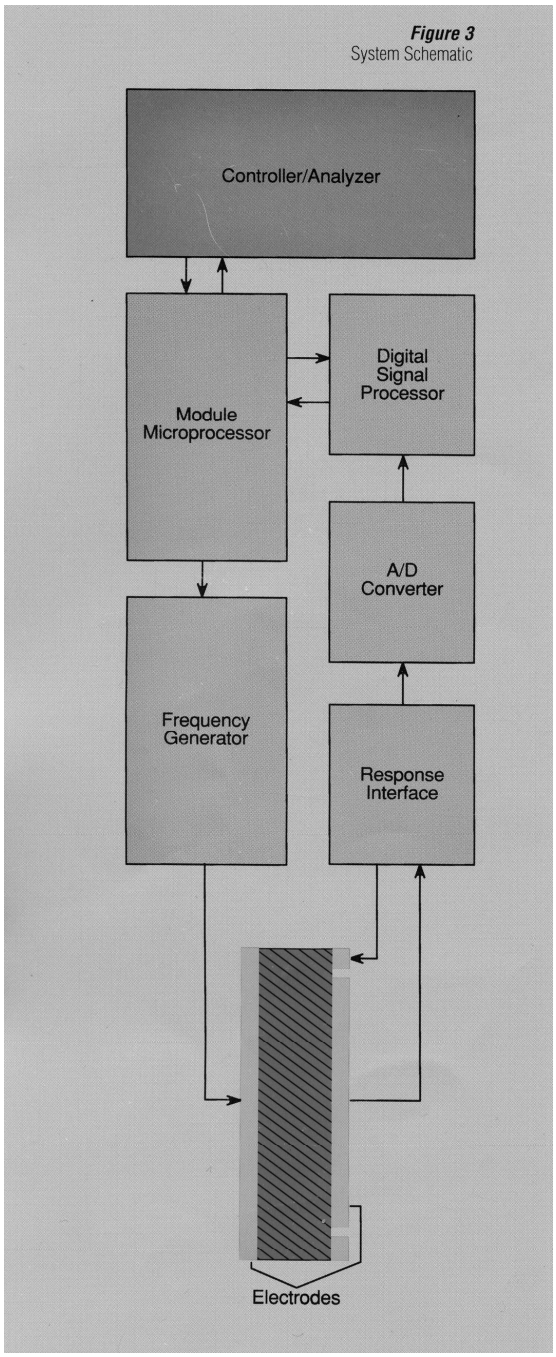
Figure 3
System Schematic
Controller/Analyzer
Module Microprocessor
Digital Signal Processor
A/D Converter
Frequency Generator
Response Interface
Electrodes

Figure 8.

Precision and accuracy are further assured by complete factory calibration of the measurement electronics.

Design of the electronic system is depicted in Figure 3. Components of the system and their functions are:

Controller/Analyzer: This is the operator's primary interface with the instrument. It is used to program experiments and analyze results. The DEA module can be operated from all of the TA Instruments Thermal Analyst Controllers.

Module Microprocessor: A microprocessor/computer is the heart of the module's operating electronics.

Located in the DEA module, it controls all instrument functions, including operation of the experiment, mathematical manipulation of data, and communication with the controller [10].

Frequency Generator: The frequency generator synthesizes a specific, high-purity sine-wave signal to establish an electrical field and excite the sample. The computer memory stores a 32K-point sine-wave generation table. Each point is a 16-bit number, which gives a signal resolution of 1 part in 64,000.

Electrodes: The input frequency signal at a specified voltage is applied to the sample through the input electrode. The output electrode receives the response current from the sample.

Response Interface: An electronic interface reads the measured response current generated by the sample, amplifies the signal, and sends it to the A/D converter. It also feeds the signal back to the guard ring on the response electrode (and to the cable shielding) to assure voltage equilibrium with the electrode, and thus prevent current leakage.

A/D Converter: The A/D converter transforms the amplified analog signal to a digital format.

Digital Signal Processor (DSP): Signals from the ND converter and information about the input voltage are used by the DSP to determine the in-phase and out-of-phase current.

The processed phase and gain signals are then sent back to the *Module Microprocessor,* where they are combined with sample-thickness measurement signals from the LVDT to calculate permittivity (□′) and loss factor (□′′).

The entire process - from frequency generation to final calculations - takes place almost instantaneously, making meaningful results available in real-time. They can be read on the controller screen or the module display.

4. Principle of Operation

A complete dielectric analysis system requires the DEA 2970 module*, a Thermal Analyst controller/analyzer and a plotter for preparation of hard copy reports [11].

4.1. Programmer/Controller/Analyzer

The controller/analyzer is used for programming an experiment, performing other operator-programmable control functions, and analyzing data. With it, the operator establishes all conditions and parameters for an experiment, such as method, temperature program, sample spacing, and force. These instructions are transmitted to

the module's operating software, which is resident in a microprocessor located in the electronics base of the DEA module. The microprocessor also contains programming for mathematical calculations, data manipulation, and calibration factors.

During an experiment, the module's keyboard/display unit can be used as a local control centre for controlling the position of the ram, starting or stopping the experiment, or displaying current status.

4.2. Ram/Furnace Assembly

The furnace (Figures 8 and 10) contains a mica-clad Inconel heater attached to a silver block and surrounded by a channel for liquid-nitrogen cooling to sub-ambient temperatures. The computer controls heating or cooling rate and liquid nitrogen flow. A recess at the bottom of the furnace seats the bottom parallel-plate sensor or ceramic single-surface sensor. A metal drip pan is used as a furnace liner to prevent contamination and assure easy cleanup.

The rams are plug-in, modular devices. Two different rams are offered, one for use with the parallel-plate sensor and thin film sensor (Figure 8), the other for the single-surface sensor (Figure 10). Both contain spring-loaded probes to make electrical contact with the sensors positioned on the surface of the furnace cavity. The parallel-plate ram also seats and provides electrical contacts for the top parallel-plate sensor. A cylindrical plunger connected to an LVDT measures sample thickness during the experiment. The ram assembly is secured to atop plate, which in turn is attached to three metal posts connected to the ram motor, located under the furnace. Ram operation is controlled by the operating software, and uses inputs from the force transducer and LVDT to monitor applied force and sample thickness. The operator can program for limits based on minimum plate spacing and/or maximum force. By monitoring these variables, it is possible to obtain accurate test data on a sample even after it has undergone dramatic changes in physical form, such as melting or curing. Ram covers are provided to protect rams from contamination by samples and to help make cleanup easy.

4.3. Electrodes/Sensors

In a dielectric analysis experiment, a sample is placed in contact with electrodes and subjected to an applied sinusoidal voltage. Sample response is measured as a function of time, temperature, and frequency. The electrode assemblies serve two purposes: transmitting the applied voltage to the sample, and sensing the response signals.

The different geometries of the sensors make possible the measurement of bulk or surface properties for a wide variety of solid, paste, and liquid materials.

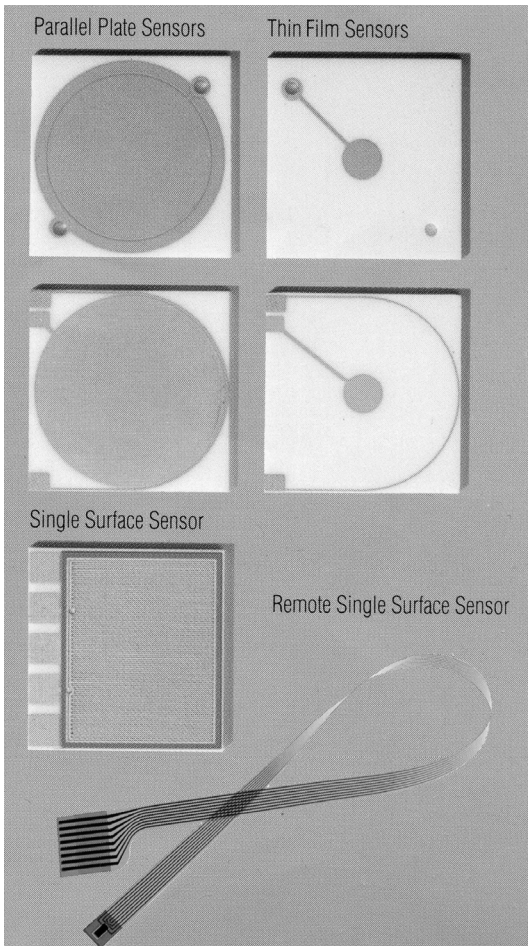

Figure 9.

The two electrode geometries commonly found in dielectric analysis are the parallel plate capacitor and the interdigitated (or comb) electrode. But this equipment has four types of electrode/sensors: Ceramic Parallel Plate, Ceramic Thin Film, Ceramic Single Surface and Remote Single Surface. The interchangeable DEA sensors are the key to the DEA system; they provide precise measurement in bench top analysis of bulk sample properties and sample surface properties [11]. Figure 9 shows the four types of sensors.

Each of them measures in a different mode, as we detail next.

4.3.1. Parallel plate

The parallel plate sensor is used to evaluate bulk dielectric properties in a material, and to track molecular relaxations [10].

Simples to be measured with this sensor must be 2.5 mm in width and 2.5 mm in length. Maximum and minimum spacing are 0.75 mm and 0.125 respectively. It will be seen further on the type of simples that can be measured by this sensor.

As it was mentioned previously the measurements are performed in volume, as the applied electric field crosses the whole sample and because of this the measurement is not surface one. This sensor is shown in Figure 10.

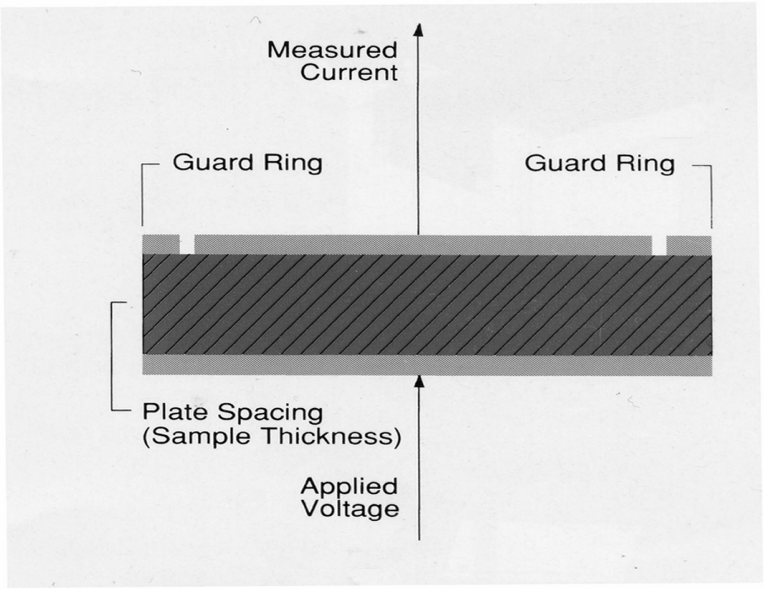

Figure 10.

As it can be seen, the voltage is applied in the bottom, and crosses the simple being the output electric current measured by the upper sensor where is converted to an output voltage that is amplified. A platinum resistance temperature detector (RTD) surrounds he perimeter of the gold electrode and measures the temperature of the sample. The temperature is controlled directly by the RTD. A guard ring around the perimeter of the upper electrode corrects for electric field fringing and for stray capacitance at the edge of the plates. Signal circuits are connected through pads on the lower sensor, which contact spring probes attached to the ram.

When parallel plates are used, these are calibrated by making a capacitance measurement in a dry nitrogen atmosphere [10]. The simple is placed between the two sensor plates alter making this capacitance measurement. The stepper-motor then drives the sensors together to a pre-selected plate spacing or force setting. The plate spacing (sample thickness) recorded at the start of the method is used throughout the experiment in the calculation of ε' and ε''.

4.3.2. Ceramic Single Surface

The ceramic single surface sensor, based on a coplanar interdigitated-comb electrode design, is used for surface property evaluations and curing experiments, and is

ideal for liquid samples. The assembly is composed of a ceramic substrate, metal ground plate, and high temperature insulating layer, electrode arrays, platinum resistance temperature detector (RTD), and electrical contact pads. The temperature is controlled directly by the RTD. The sensor is placed at the bottom of the oven and the sample positioned on its top surface. Ram pressure assures intimate sample/electrode contact. Spring probes attached to the ram make contact with pads on the sensor, completing the signal circuits (see Figure 11).

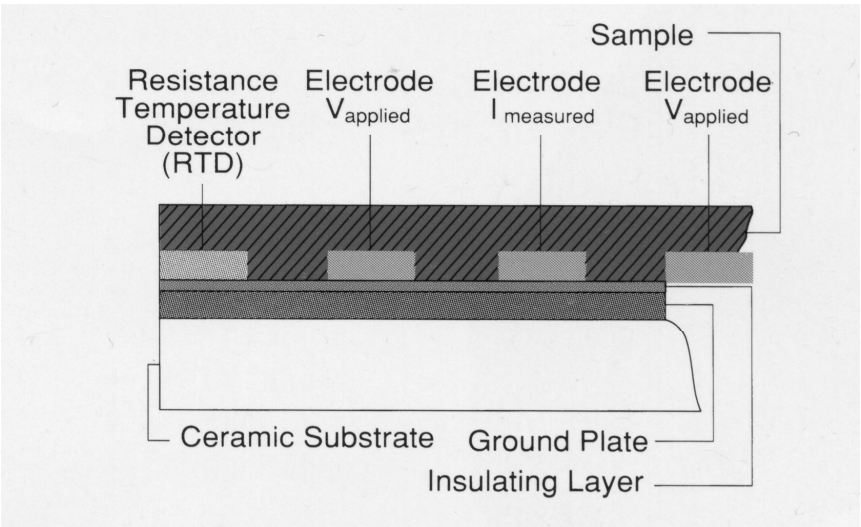

Figure 11.

When operating the DEA in the ceramic single surface mode, the sensor is calibrated by making a capacitance measurement in a dry nitrogen atmosphere. The sample is loaded onto the sensor after making this capacitance measurement. The stepper-motor then drives the ram toward the sensor to a pre-selected thickness or force setting. ε′ and ε′′ are calculated from the current and phase data using a calibration table stored in the instrument memory.

4.3.3. Sputter-coated sensor

Sputter-coated measurements are used to evaluate bulk dielectric properties in a thin film material. A metallic electrode is sputter coated, under vacuum, directly onto the sample surface to improve sample/measurement electrode contact. The lower electrode, positioned on the surface on the furnace, is a contact pad that sets up the electrical field and makes contact with the electrode surface sputtered onto the sample. A platinum resistance temperature detector (RTD) surrounds the perimeter of the gold electrode and measures the temperature of the sample. The temperature is controlled directly by the RTD.

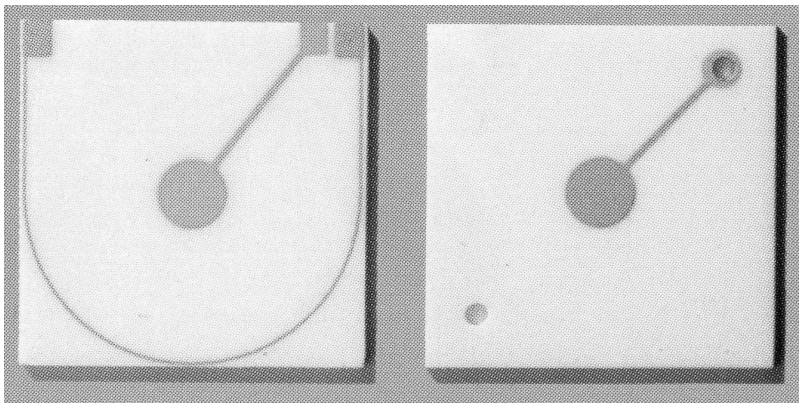

Figure 12.

The upper electrode, attached to the face of the ram, also acts as a contact pad to make contact with the electrode surface sputtered on the sample. It measures the generated current, which is then converted to an output voltage and amplified. Signal circuits are connected through the pads on the lower sensor, which contact spring probes attached to the ram. The plate spacing (sample thickness) is measured when the ram closes. This can be changed before the experiment is started, and is used throughout the experiment is started, and is used throughout the experiment in the calculation of ε′ and ε′′.

4.3.4. Remote Single Surface Sensor

The remote single surface sensor is used for surface property evaluations and curing experiments. In addition, because of the flexible design and ribbon-cable leads, it can be embedded in a sample of any size for product development. Applications include monitoring dielectric properties of a polymer during moulding, or while exposed to adverse environments such as solvents or ultraviolet light. It is also possible to embed the sensor in full-sized prototype products during development for a long-term test of end-use performance or stability and heat history during storage. In this mode, the sample is returned periodically to the instrument for evaluation.

The coplanar interdigitated-comb design of the electrodes is similar to that of the ceramic single surface sensor, but the sensing area is considerably smaller. It uses coplanar, interdigitated-comb electrodes with the electrode array vapour-deposited on a silicon substrate, supported by a carrier of polyamide film and connected to conductors in the ribbon cable.

The connector end of the ribbon cable is plugged into an interface box, which is connected to the front of the instrument. The flexibility of the cable and small sensor size, together with the use of a signal amplifier in the integrated circuit adjacent to the sensor array, allows the sensor to monitor a sample up to 10 feet away from the instrument.

Sample temperature is measured by a thermal diode adjacent to the sensing array. ε′ and ε′′ are calculated from the current and phase data using a calibration table stored in the instrument memory [11].

Dielectric measurements are very sensitive to moisture. We have to keep all the sensors in a desiccator.

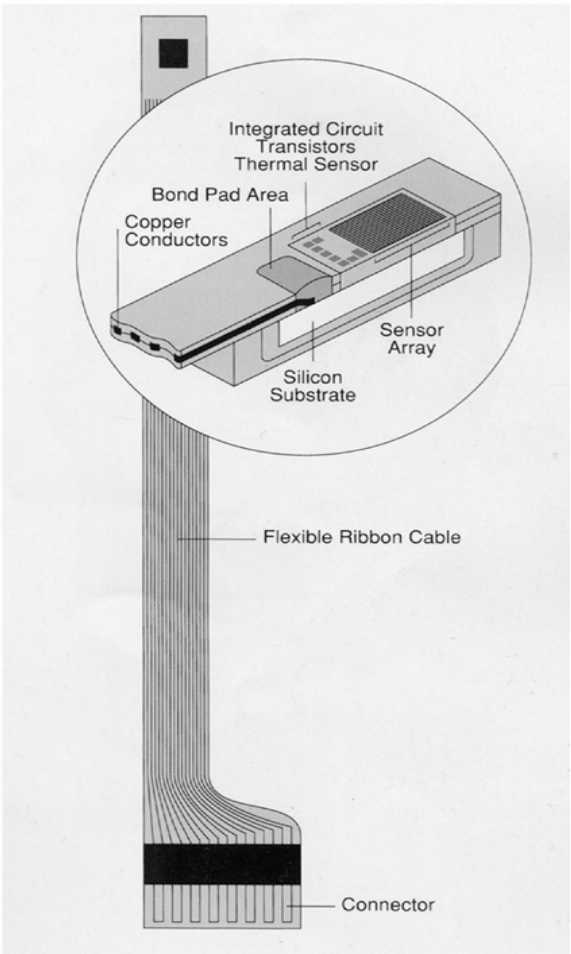

Figure 13.

Looking at the components of the measuring system, and the functions they develop, we can get an idea of the parameters to control and modify. These parameters are:

- Type of sensor: to determine which sensor to use for a particular experiment, we will need to consider two factors: the simple to be analysed and the experimental conditions. Table 2 records broadly the different types of measurements and the sensor to be used in every case.

Table 2

SENSOR	TYPE OF MEASUREMENT
Parallel Plate	This sensor is used to evaluate volumetric (or bulk) dielectric properties
Sputter Coated	To be used to evaluate dielectric properties in thin films of material.
Ceramic Single Surface	This sensor is used to evaluate surface properties and cure experiments. Also it is used for liquid samples.
Remote Single Surface	This sensor is a flexible integrated circuit sensor to be used during the cure of a material.

- For the type of material must be taken in account for a correct choice of the sensor to be used. Table 3 provides some examples.

Table 3 [11]

SAMPLE	EXPERIMENTAL CONDITIONS	SENSOR
Thermoset		
Liquid or paste	Analysis during cure is controlled thermal history	Ceramic single surface
Liquid or paste	Analysis in prototype mold or external oven	Remote single surface
Cured film	Post-cure analysis	Parallel plate
Thermoplastic		
Film	Temperature/frequency analysis	Parallel plate
Thin film		Sputter coated
Liquid paint	Analysis during drying or curing controlled thermal history	Ceramic single surface
	Stability during storage and shipment	Remote single surface
Organic liquid		
Low molecular weight	Ambient temperature measurements	Ceramic single surface or Parallel plate
Low molecular weight (oil)	Temperature/frequency transition analysis	Ceramic single surface
	Maturation/thickening analysis	Remote single surface
Sheet molding compound	Cure analysis in a controlled thermal history	Ceramic single surface
	Cure analysis in prototype development mold	Remote single surface
Elastomer		
Cured film	Temperature/frequency transition analysis	Parallel plate
Unvolcanized	Analysis during cure	Parallel plate or Ceramic single surface

- The maximum stress must also be selected. It must be taken into account that the application of an adequate stress ensures a good contact between sensor and sample. The stress range in DEA 2970 goes from 0 to 500 N. It is recommended to apply 300 N for rigid and semi-rigid films, and 500 N for pulverizations. However, the stress to be applied depends also on the type of sensor used. Also it must be considered possible changes of the physical state during measurement (i.e., to go through the melting point, curing of the sample, or ionic pulverized samples) because in these cases the stress to be applied should be lower.

  One other parameter to account for is the minimum spacing (mm) between upper and the lower sensors. This limit must be imposed to prevent liquid or soft samples leakage out of the sensor area during the experiment. These parameters can stop ram motion during the experiment. Because of this the stress applied to a sample must be lower than the maximum stress selected if the gap between the ram and the lower sensor is similar or less than the specified value for the minimum spacing. In other words, the gap must be greater than the specified minimum spacing when the measured stress is higher than the maximum stress selected. For example to analyze rigid or semi-rigid samples at room temperatures, it is recommended a minimum spacing 100 times greater than the sample thickness measured at room temperature. To analyze soft or elastic sample at room temperature, minimum spacing should be 90 % of the sample width at room temperature. The spacing for a soft sample paste must be verified after the material solidifies at lower temperatures, thus to compensate for thermal contraction of the sample. To study epoxy resins and liquid samples using the single surface sensor, minimum spacing should be 2.5 mm.

- To design an experiment it is advisable to control some others parameters such as: purge gas, purge flow, temperature range, frequency, time length of the experiment, etc.

5. How to run a DEA experiment?

In the first place, we have to check the correct performance of the measurement equipment. To keep the dielectric analyzer working to the highest level of performance possible, it is important calibrate it properly. Electronic calibration is done to calibrate the DEA analog board. This type of calibration must be periodically controlled, mainly when laboratory conditions substantially change (temperature, humidity, etc).

In the second place, the type of simples to be analyzed should be considered together with the experiment conditions. By doing so, we can select the type of sensor, minimum and maximum spacing, stress to be applied, possible use of liquid nitrogen (if we work at sub-ambient temperature), purgue gas, or the possible use or more than one.

This group constitutes the so called experimental parameters, that is, the parameters that the equipment needs for a correct performance.

Next step is the design of the operating method or experiment. To operate the DEA 2970 system in experiments at temperature changing at a constant rate, frequencies must be chosen in advance. In this particular measuring system, 28 different values can be chosen, thus estimating the scanning time very useful for the choice of the heating rate.

Once selected the frequency table, the operating method can be designed amongst a great number of options that depend on the results we are looking for.

Once at this point, the type of experiment to analyze must be very clear. They can be sorted into:

- Curing simple experiments
- Solid or cured sample experiments.

In each case, there are two kinas of experiments:

- Isothermal curing experiments, i.e. to keep the simples during a given time at constant temperature as a function of time.
- Dynamic curing, where the sample is subjected to a constant heating (or cooling) rate, or step heating rate, etc.

Isochrone experiments can also be carried out (In which the temperature is modified at constant frequencies) or isothermal experiments carried out doing a frequency scanning at a given temperature.

These are the most common type of experiments that supply important information about the studied system. There are a lot of different modes to be used. Among these: Jump, Equilibrate, Initial temperature, Ramp, Isothermal, Step, Increment, Repeat, Data storage (on/of), Frequency sweep, etc.

Once selected all these steps, the experiment can be started. First step is the calibration of the sensor (without sample and previously subjected to a gas purge) in which temperature data and sensor geometry are recorded. Once verified temperature and geometry, the sample is placed and purge to minimize the non desired humidity is set up.

In this moment the measuring operation can start.

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