INFLUENCE OF WATER ABSORPTION AND TEMPERATURE ON CHARGE TRANSPORT AND ELECTRICAL DEGRADATION IN EPOXY RESINS

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Abstract

The work aims to understand bulk transport mechanisms in epoxy resins and their influence on partial discharge and electrical treeing phenomena.

The charge transport processes in two bisphenol-A epoxy resin systems were studied using dielectric spectroscopy and related to moisture uptake. In both resins, absorbed moisture was implicated in the formation of a bulk quasi-dc (QDC) charge transport mechanism above the glass transition temperature. Complementary investigations of the electrical degradation process in epoxy resins, principally electrical treeing, were also found to be dependent on temperature and moisture absorbed by the samples.

A model for electrical tree growth in flexible epoxy resins has been proposed. The novelty of the model is that it considers a QDC charge transport through the bulk polymer, where proton hopping is suggested as a long range transport mechanism. The time needed for the neutralisation of the space charge accumulated ahead of a growing tree structure by charges involved in the QDC process is suggested as a governing parameter of the tree growth rate. Electrical tree growth is related to changes in the time constant of the QDC process and hence the percolation distance that the protons can travel. At high levels of moisture and/or temperature, multiple percolation paths can be established thus increasing the effective ionic conductivity of the material leading to thermal breakdown when $\tan \delta$ is greater than 1.

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Chapter 1: Aims and context of the current research study

1.1. Introduction

Electrical power systems are designed to fulfil the engineering task of delivering electrical energy to consumers and ensuring reliability of the supply but they also have to meet the economical requirement for reducing cost. According to the projections of the U.S. Energy Information Administration (EIA) the electricity generation and demand will continue to increase worldwide, see Fig.1.1(Report EIA, 2009). The increased load of the power systems adds to their complexity and may require operation at nearly full capacity. Consequently, system reliability becomes more and more significant. Failing to provide reliable supply can cause significant losses to the utility company providing that service.



Fig.1.1: World electricity generation by fuel 2006-2030, derived from Energy Information Administration (2009)

One of the main tasks in ensuring system reliability is preventing equipment breakdown. Breakdown of a particular branch of the power grid can lead to overloading of others and thus can cause a blackout of significant parts of the grid. Therefore, breakdown costs for the utility company are not only direct due to repair of the failed equipment but also indirect due to compensation of the customers for intermittent supply. Recent blackouts in Europe and North America demonstrated that huge economic losses can be incurred as a consequence of power outage. It is argued by Massoud Amin (Amin, 2011) that some \$49 billion per year could be saved in the USA alone by increasing the reliability of the power grid. One of the key components of the future grids will be their ability to identify possible faults automatically, which requires continuous system monitoring and diagnostics.

Other issues related to equipment breakdown are environmental and health and safety. As a result of equipment failure, pollution can occur, e.g. greenhouse gases such as SF_6 can be released to the atmosphere or transformer oil can leak into the soil. The life and health of the personnel working in close proximity to the failed equipment could also be endangered.

The focus of this work is on the electrical breakdown mechanisms that can occur in a solid polymeric insulation. Typical polymers used for electrical insulations include cross-linked polyethylene (in cables), epoxy resins (in transformer bushings), and ethylene propylene rubber (in overhead power line insulators) and additives and fillers may be present in the polymer matrix either to improve some of the physical properties of the insulation or to reduce its cost. In recent years the use of nanofillers in polymers has been intensively investigated (Nelson, 2011).

Different processes can lead to breakdown of the insulation as a result of application of an electric field. The time and electric field scales over which such processes can take place are shown in Fig. 1.2 following (Dissado and Fothergill, 1992). Breakdown mechanisms can be classified as electrical. thermal, electromechanical and partial discharge. Typical degradation mechanisms are electrical and water treeing. The distinction between breakdown and degradation is not clear and depends on the time scales and the conditions under consideration. Breakdown is an experimental phenomenon occurring over short time scales while degradation is an inservice phenomenon taking place over longer time scales with a border region of a day to a month between the two (Dissado and Fothergill, 1992).

Electrical breakdown occurs under high applied electric fields and examples of such mechanisms are Zener breakdown and avalanche breakdown. Zener breakdown is not very likely to occur in polymers since they have wide band gap (>~7 eV) and the required electric fields for Zener breakdown in this case are greater than 10^{10} V/m (Dissado and Fothergill, 1992). Avalanche breakdown takes place at high stresses when charge carriers can acquire sufficient kinetic energy between collisions with the

(polymer) matrix. When they interact with the matrix, they cause impact ionisation and generate more carriers, i.e. avalanche multiplication occurs.



Fig. 1.2: Times and electric fields at which various degradation and breakdown mechanisms take place. From (Dissado and Fothergill, 1992)

Electromechanical breakdown occurs due to the electrostatic attraction of the electrodes which decreases the width of the insulation proportional to the Young's modulus of the insulating material (Dissado and Fothergill, 1992). If the applied voltage is kept constant, the electric field increases due to the decrease in the insulation thickness thereby increasing the attraction ($\propto E^2$) even further. This effect is intensified by the local heating and the softening which is likely to occur as a result. This breakdown mechanism has limited technological significance since polymers in real insulating systems are designed to have sufficient thickness and are rarely used above their softening point.

Thermal breakdown occurs when the conductivity of the material is high and the heat produced by Joule heating cannot be removed fast enough from a unit volume of the insulation. The temperature increases thereby causing further increase in the electrical conductivity and as a result thermal runaway may occur. Partial discharge (PD) is a localised breakdown which causes degradation and which may eventually lead to system breakdown. PDs occur in gas voids within the solid insulation at moderate electric fields.

Under normal operating conditions (low temperature and moderate applied fields) and low electric conductivity of the insulation the most important breakdown mechanism is partial discharge. An electrical ageing scenario was proposed in (Rowe, 2007) that assumes initially defect free insulation, Fig. 1.3. As a result of various stresses, i.e. electrical, thermal, mechanical etc., occurring in the insulation during the in-service operation, a small defect ('void') can be formed at time t₁. The void starts to grow at time t_2 and when it reaches a critical size at time t_3 , PDs appear inside the void. They lead to even faster degradation of the insulation and eventually an electrical tree can be initiated from the void at time t₄. Once initiated the electrical tree will propagate relatively fast, compared to the overall time scale of the ageing process, and when it bridges the distance between the two electrodes, the final breakdown will occur at time $t_5 \ge 30$ years. Electrical trees (Dissado and Fothergill, 1992) can also be initiated from other field enhancing defects such as metal protrusions for example, which can shorten the time to tree initiation and can lead to even faster breakdown of the insulation. However, it is assumed that the most severe defects would be detected during the manufacturer's quality control tests and mainly defect-free equipment will be installed in the power grid, which justifies the 'ageing' scenario described above. Although, the onset of PDs can be used as a precursor for degradation of the insulation, it can take years before the final breakdown of the equipment will occur. From a condition monitoring point of view, it is necessary to know when an electrical tree has been initiated, since the duration of the tree propagation stage will determine the remaining life time of the insulation, typically a few hours or days. Hence, one of the main tasks of the condition monitoring is the correct identification of the processes that occur within the insulation and partial discharge (PD) detection has been proposed as a valuable tool for this purpose.

The material properties of the insulation are likely to have significant impact on the possible breakdown mechanisms. The combination of thermal, mechanical and electrical properties can increase the likelihood that a particular breakdown process can occur. For example, an increase in the electrical conductivity of the polymer can cause thermal runaway. Environmental factors such as ambient temperature and absorbed

moisture are also known to affect some of the material properties of the polymers. The electrical conductivity in polymers is often found to have Arrhenius dependence on temperature (Dissado and Fothergill, 1992). Above the glass transition temperature filled and non-filled epoxy resins have been found to possess high ionic conductivity (Sletbak *et al.*, 1988). In the case of epoxy resins with nanofillers a quasi-dc charge transport was suggested as a possible conduction mechanism at high levels of absorbed moisture (Zou *et al.*, 2008). Therefore, the environmental factors and their impact on the material properties of the polymers and hence on the breakdown mechanisms have to be considered as well.



Fig.1.3: A possible route to electrical ageing involving PDs and electrical treeing (Rowe, 2007)

1.2. Literature Review

1.2.1. Epoxy resins

The purpose of insulators is to provide mechanical support for the conductors and to prevent the flow of electrical current between two electrodes at different potentials, where such a flow is not desirable. Insulating materials, i.e. electrical insulation, should possess the lowest possible electrical conductivity coupled with the maximum resistance to destructive breakdown in high electric fields. Other requirements such as long service life, low cost, ability to withstand high temperatures, and chemical inertness should also be met. Epoxy resins have been selected as a study material, because their practical use as a base resin in electrical insulators, e.g. in transformer bushings and because they allow model defects of different shapes and sizes to be easily fabricated for laboratory scale studies. Also there is a wealth of information about their material properties and the electrical degradation and breakdown processes that occur in epoxy resin based insulation.

Cured epoxy resins are thermoset polymers formed from a reaction of an epoxide resin with a curing agent (hardener). A common epoxy resin used in many applications is Diglycidiyl Ether-Bisphenol-A (DGEBA), which is cured with a polyamine hardener. The pre-polymer DGEBA is synthesised by a base catalyzed step-growth reaction of a dihydroxy compound such as bisphenol-A with an epoxide compound like epiclorohydrinin.

Bisphenol-A [(bis-4-hydroxyphenol)dimethylmethane] is produced by the acidic condensation of phenol and acetone (Carraher, 2007) and the reaction is shown in Fig. 1.4.



Fig. 1.4: Synthesis of bisphenol-A

Epichlorohydrin (chloropropylene oxide) is obtained by dehydrochlorination of 2,3dichloro-1-propanol and hydrin is produced by chlorohydrination of allyl chloride (Carraher, 2007). The process is shown in Fig. 1.5.



Figure 1.6 shows the synthesis of DGEBA. The DGBEA molecular structure is shown in Fig. 1.7 (Petrie, 2006):



Fig. 1.7: DGEBA structure

Figure 1.7 shows that DGEBA is a linear polymer with terminal epoxide groups at both ends and pendant hydroxyl groups occurring at regular intervals along the main polymer chain if n > 1. The various functional groups that comprise the DGEBA

polymer chain influence different properties of the resin (Petrie, 2006). The terminal epoxide groups are highly reactive, followed by the pendant hydroxyl groups along the polymer chain. The epoxide groups take part in the curing process producing additional OH-groups, while the presence of secondary hydroxyl groups along the main chain is a prerequisite for the outstanding adhesion properties of the epoxy resins to many polar surfaces. The aromatic rings that are part of the main polymer chain provide good heat and chemical resistance. Also, good chemical resistance and mechanical flexibility are provided by the aliphatic sequence between ether linkages if the number of repeat groups *n* is greater than zero. The molecular weight of the resin is determined by *n*. The resin is a low-viscosity liquid, if *n* is between 0 and 1, when *n* is greater than 1 the resin is noteworthy to emphasize that commercially available epoxy resins are not necessarily entirely linear or terminated with epoxide groups and some degree of branching exists, if *n* is sufficiently high.

An important feature of the curing process is that cured epoxy resins show low shrinkage, which allows the curing process to take place under vacuum. Hence, the resultant adhesive joints possess a very low degree of internal stress. The curing reaction is exothermic, and the reaction rate is proportional to temperature. Therefore, the temperature at which the reaction occurs has to be monitored in order to avoid excessively high exothermic temperatures that may result in bubble formation, thermal degradation and even potential fire hazards. The exotherm also limits the working life of the resin due to the very fast curing reaction at high temperatures.

The ratio of the resin and hardener determines various properties of the final polymer structure such as toughness, high-temperature strength, and bulk tensile strength. This ratio can also affect the water absorption process in the cured resin (Grave *et al.*, 1998). The diffusion coefficient and equilibrium water uptake have been found to increase with increasing the amine ratio in Grave *et al.* (1998), which can be attributed to the increased number of hydroxyl groups as a result of the curing reaction and increased free volume in the system. Therefore, using the stoichiometric ratio between the epoxy resin and the hardener is essential for stability of the final product and manufacturing of samples with reproducible properties.

The hardening agent often has active primary and secondary amine groups (Stevens, 1986). The pre-polymer molecular weight is increased and the network is formed during the curing reaction. Bridging oxygen in the epoxide group is opened up in a nucleophilic poly-addition reaction, see Fig. 1.8. At first, the primary amine reacts with the epoxide group to give a secondary amine and a hydroxyl group. Then, the secondary amine reacts with another epoxide group to give a tertiary amine and another hydroxyl group (Stevens, 1986). The reaction involving the secondary amines will proceed if they are not too sterically hindered.

 $R_{1}NH_{2} + CH_{2}-CH-R_{2} \xrightarrow{k_{1}} R_{1}NH-CH_{2}-CH-R_{2} \equiv R_{1}'NH$ Primary amine $O \qquad OH \qquad Secondary amine$ $R_{1}'NH + CH_{2}-CH-R_{2}' \xrightarrow{k_{2}} R_{1}'N-CH_{2}-CH-R_{2}'$

Secondary amine

Fig. 1.8: Curing reaction (Stevens, 1986)

Tertiary amine

When the concentration of hydroxyl group increases and becomes significant as a result of the polymerization process, addition etherification is possible (Stevens, 1986). This reaction takes place between OH-groups along the chain and epoxide rings forming ether groups as shown in Fig. 1.9. It does not affect the hydroxyl group concentration but consumes the epoxide groups limiting the cross-linking density and affecting the mechanical properties of the cured resin (Griseri, 2000).

$$\begin{array}{cccc} R_1 & O & & R_1 & OH \\ | & & \swarrow & & & \\ HC-OH & + & CH_2-CH-R_3 & \longrightarrow & HC-O-CH_2-CH-R_3 \\ | & & & & \\ R_2 & & & & R_2 \end{array}$$

Fig. 1.9: Addition etherification (Stevens, 1986)

The curing reaction can be accelerated in the presence of proton donors (Stevens, 1986), such as salicylic acid. It is supposed that in the presence of amine groups, the salicylic acid can react with the amine base producing a mono-anion. Then, the acid group may open the epoxide group ring. This hypothetical reaction would justify the

role of salicylic acid in the system (Griseri, 2000). It is also possible that a fraction of the salicylic acid exists in the hardener as a mixture of mono-anions and di-anions if an additional proton donation can take place as shown in Fig. 1.10. The concentration of both species will depend on the equilibrium conditions.





Mono-anion

Fig. 1.10: Dissociation of salicylic acid in mono-anions and di-anions

A condensation reaction involving salicylic acid and the hydroxyl groups may also take place (see Fig. 1.11), especially later on during the curing process when the hydroxyl group concentration increases:



Fig. 1.11: Condensation reaction involving salicylic acid and hydroxyl groups

Acid anhydrides are also used as curing agents for epoxy resin systems, especially in large casting applications (Petrie, 2006). The most common substances are hexahydrophthalic anhydride (HHPA), phthalic anhydride (PA), nadic methyl anhydride (NMA) and pyromellitic dianhydride (PMDA). An accelerator, such as water, alcohol and imidazoles, is also involved in the curing reaction since the anhydrides do not react readily with the epoxy resins. Further information on anhydride cured epoxy resin systems can be found in Petrie (2006).

In this work only amine cured epoxy resin systems are considered.

1.2.2. Dielectric relaxation in solids

When an ac electric field is applied to a dielectric, polarisation occurs inside the material, which can be expressed by Eq. 1.1 (Jonscher, 1983):

$$P(\omega) = \varepsilon_0 \chi^*(\omega) E(\omega), \qquad (1.1)$$

where $P(\omega)$ is the frequency-dependent polarisation, ε_0 is the permittivity of free space, $\chi^*(\omega)$ is the frequency-dependent susceptibility, and $E(\omega)$ is the applied ac electric field. $P(\omega)$ and $E(\omega)$ are the Fourier transforms of the corresponding time-dependent polarisation and electric field. The frequency-dependent susceptibility is a complex function and it is defined in Eq. 1.2 as the Fourier transform of the response function, f(t).

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) = \int_0^\infty f(t) \exp(-i\omega t) dt$$
(1.2)

The response function, f(t), arises due to the fact that material systems always exhibit a delayed response to an external excitation, unlike for example free space, where the response is instantaneous. The response function is a real function of time, t, and the principle of causality implies that there should be no reaction before action and hence

$$f(t) \equiv 0 \text{ for } t < 0 \tag{1.3}$$

Another important factor that f(t) is assumed to obey is the principle of superposition, which states that the total response of the system, occurring due to a series of delta-function excitations, is a sum of the responses due to the individual excitations (Jonscher, 1983). Here is important to emphasize that the response of the dielectric is assumed to be linear.

The amplitude of polarisation in phase with the applied ac field is given by the real part, $\chi'(\omega)$. The component in quadrature with the applied field is given by the imaginary part, $\chi''(\omega)$, of the complex susceptibility, χ^* . Hence, the real and imaginary components of χ^* can be defined as the cosine and sine transforms of f(t), respectively:

$$\chi'(\omega) = \int_0^\infty f(t) \cos(\omega t) dt$$
(1.4)

$$\chi''(\omega) = \int_0^\infty f(t) \sin(\omega t) dt$$
(1.5)

Another condition is that the above integrals are necessarily finite (Jonscher, 1983). The real and imaginary parts of the complex susceptibility obey the Kramer-Kronig relations as a consequence of the principle of causality and can be expressed:

$$\chi'(\omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{x \chi''(x)}{x^2 - \omega^2} dx$$
(1.6)

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$$\chi''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \frac{\chi'(x)}{x^2 - \omega^2} dx$$
(1.7)

where $\mathcal{P}\int$ denotes a Cauchy Principal Value integral. The Kramer-Kronig relations rely on the Hilbert transform of periodic functions. Thus $\chi'(\omega)$ and $\chi''(\omega)$ are interrelated.

The response function f(t) depends on the structure of the material under investigation and more specifically on the dipole dynamics in the system. Hence, various materials have been found to exhibit a broad range of variation of their time (frequency) dependent susceptibility. Experimental data, presented in the literature, ranges from almost frequency-independent ("flat") responses to low-frequency dispersion (Jonscher, 1996). Attempts have been made to explain the observed variety of dielectric responses under a common theoretical framework. The first theory of dielectric relaxation was proposed by Debye, which regarded relaxation of freelyfloating non-interacting dipoles in a viscous non-polar medium. The Debye model gives an exponential decay of the polarisation (Hill and Dissado, 1985). This situation is rarely encountered in a solid material, where dipoles interact with each other and the resultant relaxation process is non-exponential, i.e. non-Debye. Departures from the Debye response in solids are usually explained in terms of a distribution of relaxation times due to interacting dipoles. Several empirical formulae have been developed to account for the experimentally observed departures from the Debye model, such as Cole-Cole, Cole-Davidson, Williams-Watts and Havriliak-Negami functions (Jonscher, 1983). The common feature amongst them is the power-law dependence on frequency of the complex susceptibility. The Cole-Cole, Cole-Davidson and Williams-Watts functions have one spectral parameter, while the Havriliak-Negami function has two spectral parameters. In general, the use of more free spectral parameters creates more degrees of freedom and hence better fit to experimental data is achieved. These functions have become very popular in the dielectric literature since they can fit quite well particular data sets and often are used for data analysis. However, their main drawback is that most of them do not provide any insight into the physical processes taking place and none can be used to fit all experimental data sets reported in the literature. It has been suggested by Jonscher that all solid polar dielectrics exhibit dipolar relaxation processes that follow fractional power laws in time (or in frequency), with two power-law exponents m and n in the range [0,1] (Jonscher, 1996). He called these power laws "universal" relaxation laws. A summary of some spectral functions used in the dielectric literature and their parameters is given in Table 1.1 after (Das-Gupta and Scarpa, 1999) and (Jonscher, 1983).

| Function | Equation | Parameters | |
|--------------------------------|--|--|-------------------------|
| Debye | $\chi^{\prime\prime}(\omega) \propto \frac{1}{\left[\omega/\omega_p\right]^{-1} + \left[\omega/\omega_p\right]}$ | 0 | 1 |
| Cole-Cole | $\chi^{\prime\prime}(\omega) \propto \frac{1}{\left[\frac{\omega}{\omega_p}\right]^{\alpha-1} + \left[\frac{\omega}{\omega_p}\right]^{\alpha-1}}$ | 0<α<1 | - |
| Cole-Davidson | $\chi^{\prime\prime}(\omega) \propto \frac{1}{\left[\omega/\omega_p\right]^{-1} + \left[\omega/\omega_p\right]^{\beta}}$ | - | 0<β<1 |
| Williams-Watts | $\varepsilon \equiv \frac{\varepsilon^* - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \sum_{n=1}^{\infty} (-1)^{n-1} A_n \exp\left(-\frac{n\beta\pi i}{2}\right)$ | - | 0<β<1 |
| | $A_n - \Lambda$, $\overline{\Gamma(n+1)}$, $\Lambda - \omega t$ | | |
| Havriliak-Negami | $\chi^{\prime\prime}(\omega) \propto \frac{1}{\left[\omega/\omega_p\right]^{\alpha-1} + \left[\omega/\omega_p\right]^{\beta(1-\alpha)}}$ | 0<α<1 | 0<β<1 |
| Dissado-Hill (Dipolar peak) | $\begin{array}{l} \chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1} & \text{for } \omega > \omega_c \\ \chi''(\omega) \propto \chi'(0) - \chi'(\omega) \propto \omega^m & \text{for } \omega < \omega_c \end{array}$ | 0 <m<1< td=""><td>0<n<1< td=""></n<1<></td></m<1<> | 0 <n<1< td=""></n<1<> |
| Dissado-Hill (QDC) | $\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n_1 - 1} \text{ for } \omega \gg \omega_c$ $\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n_2 - 1} \text{ for } \omega \ll \omega_c$ | 0 <n<sub>2<1</n<sub> | 0 <n1<1< td=""></n1<1<> |

Table 1.1. Relaxation models

A physical model that produces the required power law dependence was proposed by Dissado and Hill (1983). According to the Dissado-Hill many-body theory, dielectric relaxation in solids and liquids can be viewed as a result of cooperative connection of the motions of molecular dipoles or ions within and between clusters. In this theory the response function first involves the coupling of relaxation motions within the clusters followed by interactions of the motions in the different clusters comprising the whole ensemble. The corresponding frequency dependent susceptibility is given by Eq. 1.8 (Dissado and Hill, 1983):

$$\chi(\omega/\omega_c) = \frac{\Gamma(1-n)\Gamma(1+m-n)\chi_0}{m\Gamma(m)\Gamma(2-n)} [1+i(\omega/\omega_c)]^{n-1} \\ \times {}_2F_1(1-n,1-m;2-n;[1+i(\omega/\omega_c)]^{-1})$$
(1.8)

where $\Gamma(x)$ denotes the gamma function and $_2F_1(, ; ;)$ is the Gaussian hypergeometric function. In the above expression the susceptibility $\chi(\omega/\omega_c)$ is given as a function of the reduced frequency ω/ω_c , where ω_c is a frequency that is characteristic of the specific relaxation phenomenon (Dissado and Hill, 1983; Jonscher, 1996).

According to Eq. 1.8., a dielectric dispersion (loss peak) occurs when the parameters n and m are in the range, 0 < n < 1, $0 < m \le 1$, with an asymptotic fractional power law frequency behaviour:

$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1} \quad \text{for } \omega > \omega_c$$

$$\chi''(\omega) \propto \chi'(0) - \chi'(\omega) \propto \omega^m \quad \text{for } \omega < \omega_c$$
(1.9)

When the clusters are composed of ions or ionisable entities it has been shown (Dissado and Hill, 1984) that the dielectric response takes a form that can be expressed by Eq. 1.8 with $n = n_1$ and $m = n_2 - 1 < 0$ ($0 < n_1, n_2 < 1$). This form of response was called low frequency dispersion (LFD) by Jonscher (Jonscher, 1996) and quasi-dc (QDC) conduction by Dissado and Hill (Dissado and Hill, 1984). It is characterized by two successive fractional power law responses (sometimes called constant phase angle (CPA) response) converting from one to the other at a characteristic frequency ω_c (see also (Das-Gupta and Scarpa, 1999)):

$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n_1 - 1} \quad \text{for } \omega \gg \omega_c \tag{1.10}$$
$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n_2 - 1} \quad \text{for } \omega \ll \omega_c$$

Such CPA and other fractional power law responses have been related to equivalent circuits with a fractal form (Dissado and Hill, 1989, 1988), i.e. ones exhibiting scaling hierarchy or dilation symmetry (Hill *et al.*, 1991). In the cluster theory the high frequency CPA ($\omega > \omega_c$) arises from the displacement of ions bound to a counter charge to form cluster dipoles (i.e. polarize a cluster). At frequencies below ω_c ions become free from their counter-ion and transfer between clusters giving bigger dipoles. This process differs from that of DC-conduction in that the transferred ions move along structured paths (Nigmatullin *et al.*, 1992) whose probability of existence reduces with the distance transferred i.e. the transport paths behave as percolation systems below the percolation limit such that a connected path does not extend from electrode to electrode (Almond and Bowen, 2004; Feldman *et al.*, 1996). The value of the low frequency power exponent n₂ is governed by the dimension of the structure on which the ions

move and that of the ion-walk on that path (Dissado and Hill, 1989), with the incoherent diffusion value of $n_2 = 0.5$, a lower bound. In many instances a value of n_2 that is very close to zero is found and the response is distinguished from that of a DC-conductivity by the existence of the same frequency dependence in the real susceptibility as in the imaginary component. If charge transport between the clusters does not occur, the theory shows that the theoretical response function (for $n_2 = 0$) reduces to an exact form resulting in a Cole-Davidson (see Jonscher, 1983) dielectric loss peak corresponding to the polarization of non-interacting clusters.

It is noteworthy that the susceptibility function Eq. 1.8 describes an isolated dielectric response function. However in most materials a number of processes are combined to give the total dielectric response. These processes can be classified in two main categories: *bulk processes*, i.e. due to the dielectric material investigated and *interfacial processes*, i.e. due to the contact between the sample and the electrodes or where other inhomogeneities are present. Interfacial phenomena occur when the electrode acts as a barrier in series with the sample and as a result charges accumulate on the interface. They are usually analysed in terms of Maxwell-Wagner-Sillars interfacial polarisation (Blythe and Bloor, 2005), which gives a loss peak with a high frequency region in which:

$$\chi'(\omega) \propto \omega^{-2} \text{ and } \chi''(\omega) \propto \omega^{-1}$$
 (1.11)

Dielectric information can be expressed in several equivalent ways using principal dielectric functions such as complex permittivity ε^* , dielectric modulus M^* , complex capacitance C^* , admittance Y^* , and impedance Z^* (Jonscher, 1999). The relationship between the complex permittivity and susceptibility is given by:

$$\chi^{*}(\omega) \equiv \frac{[\varepsilon^{*}(\omega) - \varepsilon_{\infty}]}{\varepsilon_{0}} = \chi'(\omega) - i\chi''(\omega)$$
(1.12)

where ε_0 is the permittivity of free space and ε_{∞} is the permittivity at very high frequencies. The dielectric modulus is defined as the reciprocal of ε^* :

$$M^* = M'(\omega) + iM''(\omega) = 1/\varepsilon^*(\omega)$$
(1.13)

The impedance of the sample is the ratio of the applied voltage across the sample to the current passing through it:

$$Z^*(\omega) = V(\omega)/I(\omega)$$
(1.14)

The reciprocal of the impedance is called admittance:

$$Y^*(\omega) = I(\omega)/V(\omega) \tag{1.15}$$

In a parallel plane geometry (as the one used in the current study) the complex capacitance can be obtained by:

$$C^*(\omega) = \varepsilon^*(\omega)A/d \tag{1.16}$$

where A/d is a geometrical factor related to a sample of area A and thickness d.

The ratio of the imaginary capacitance (permittivity) and the real capacitance (permittivity) is called loss tangent ($tan\delta$) and it is independent of the geometry:

$$tan\delta = C''(\omega)/C'(\omega) = \varepsilon''(\omega)/\varepsilon'(\omega)$$
(1.17)

As has been mentioned above, the total dielectric response of a real material usually contains information about several processes, which contribute to it. These processes may occur either in parallel or in series. However, it is only possible to interpret the physical response of an individual process; hence it is necessary to split the total response into individual contributions due to the individual processes. One way to do this is by equivalent circuits. Examples of some basic equivalent circuits and their corresponding frequency responses are shown in Table 1.2. More information about this technique can be found in (Jonscher, 1983). The series combination (R-C) of an ideal frequency independent resistor and capacitor is shown in case a) in Table 1.2. This circuit gives a classic Debye response. Case b) illustrates a 'leaky' capacitor. Case c) shows a situation, which physically can be encountered quite often, in which the bulk material is represented by a parallel dc conductance G and capacitance C and in series with it exist a uniform barrier region represented by the blocking capacitance C_s , e.g. polarisation. A more generalised circuit Maxwell-Wagner-Sillars interfacial representing two regions having different properties is shown in case d). In this case, both regions have a parallel capacitance and dc conductance associated with them, however one of them is relatively more conducting and represents the bulk of the sample while the other one is highly capacitive but weakly conducting and represents a barrier region. The last example case e) represents the physical process of diffusion. The equivalent circuit in this case is a distributed R-C line with a parallel conductance to it. The real and imaginary parts of the complex capacitance are equal and both depend on frequency as $\omega^{-1/2}$. At sufficiently low frequencies there is a change in power law dependence of the imaginary capacitance C'' proportional to $1/\omega$ due to the presence of the finite dc conductance G₀.



 Table 1.2. Frequency response of some equivalent circuits (Jonscher, 1983)

1.2.3. PD mechanism in voids

According to IEC 60270:2000 standard (BS EN 60270:2001) a Partial Discharge is: "localized electrical discharge that only partially bridges the insulation between conductors and which may or may not occur adjacent to a conductor". In the context of this work, partial discharges can occur within small <1mm diameter gas filled voids that exist within polymeric insulating materials.

In 1940s Austen and Whitehead (Austen and Whitehead, 1941) proposed a model circuit to represent the void discharge sequence in the insulation under an ac applied voltage. The equivalent circuit of an insulating system containing internal void is shown in Fig. 1.12(a) and the voltages across the void are shown in Fig. 1.12(b). In Fig. 1.12 C_a , C_b and C_c are capacitances of the dielectric without a void, dielectric surrounding the void, and the void, respectively. This model implies that once the ac voltage across the void ($V_{A'B'}$) is greater that the PD inception voltage (V_g – breakdown voltage of the gas in the void) a discharge takes place and as a result the actual voltage across the void drops to the extinction voltage (V_e – voltage across C_b increases by V_g - V_e . Therefore, the number of discharges that will occur in one half-cycle of the applied voltage is determined by the values of the inception and extinction voltages as well as the magnitude of the applied voltage. Thorough investigation of the PD inception and extinction voltages is presented in Hall and Russek (1954).



Fig. 1.12: a) Equivalent circuit. b) Discharge sequence (Kao, 2004)

The model described above approximates quite well the sequence of discharges that occur in a void having metallic (i.e. conducting) surfaces under an ac applied voltage but in order to explain the more complex sequence of PD events in a dielectric bound void (i.e. a void with electrically insulating surfaces), it needs modifications. Mason (1951) has noticed that subsequent PDs are interdependent events due to the deposition of charge on the void's surfaces. He also observed that voids do not discharge homogeneously as in the case of the metallic surfaces, and charge deposition on the void surface is localized. As a result of the localization of PDs, material degradation occurs (Laurent et al., 1981). Consequently, the physical and chemical properties of the void surface are changed (Brunt, 1994). Mayoux (1977) has argued that the most important physical property changed in this process is conductivity of the void surface. This is due to chain scission of the polymer molecules and formation of liquid droplets (especially in the presence of water vapour), which are mixture of simple organic compounds (formic, acetic and carboxylic acids) (Morshuis, 2005). Increased conductivity facilitates the discharge process by modifying the electric field in the void and altering the discharge regime.

Partial discharges can be considered as electron avalanche processes (Kao, 2004; Dissado and Fothergill, 1992). In Fig. 1.13, a graphical representation of an electron avalanche is shown. The availability in the void of a free electron is a necessary condition to initiate the avalanche. This electron will gain kinetic energy under the action of an applied electric field and can collide with a neutral gas molecule. As a result of the collision (if the kinetic energy of the electron is greater than the ionization energy of the gas molecule) a positive ion and two free electrons may be generated. If the applied electric field is high enough and the mean free path between the collisions is large, than these two electrons will also accelerate in the direction of the field and continue the process of impact ionization. The average number of ionizing collisions by one electron per unit length is called Townsend's first ionization coefficient, α (Kao, 2004). However, the probability of ionization by an electron with an energy larger than the ionization energy is not unity. In fact, only a fraction of all collisions with sufficient ionization energy produces ionization, because some inelastic collisions produce only excited atoms or molecules, M^{*} in Fig. 1.13, which lowers the value of α . In some cases, attachments of electrons to gas molecules can occur depending on the type of gas and electron energies, which results in the formation of negative ions, M⁻ in Fig. 1.13,

and also decreases the value of α . Furthermore, electronically excited species can emit photons when they return to the ground state (making optical detection of PD possible). Consequently, these photons can cause photoelectric emission from the polymer surface or photo-ionization of the gas molecules in the void (Dissado and Fothergill, 1992) leading to generation of further free electrons. The condition for discharge continuation is that the local electric field remains higher than the extinction field and the rate of generation of electrons exceeds the rate at which electrons are lost from the avalanche due to attachment to the gas molecules and thus forming excited metastable species or due to attachment to the channel side walls. Water molecules have high electron affinity and they are likely to increase the loss of electrons from the avalanche thus increasing the discharge inception and extinction fields (Mason, 1978). On the other hand, water can be involved in chemical reactions with the polymer surrounding the gas void and thus the physical properties, e.g. surface conductivity, of the void walls can also change. Increased surface conductivity of the void walls is likely to decrease the local electric field below the partial discharge inception and extinction fields.



Fig. 1.13: Graphical representation of an electron avalanche in an attaching gas under the action of an applied electric field

The constituents of a discharge are electrons, ions and excited neutral molecules and all could contribute to deterioration of the polymeric insulation (Mayoux, 1976). The impact of the electron avalanche on the polymer causes bond scission, dissociation of low molecular fragments (CO₂, CO, etc.) and negative ions (e.g. H^{-}), and formation of space charge which opposes the applied electric field. Afterwards, the ions and excited species (atoms and molecules) can react with the radicals produced from the electron impact and contribute to the chemical degradation of the polymer. As a result of the

discharge processes, oxidation of the polymer and formation of organic acids are observed (Tanaka, 1986). The simultaneous presence of H_2O , CO_2 and CO is a necessary condition for formation of oxalic acid crystals as discharge by-products on the void surface (Gamez-Garcia, 1987). In Morhuis (1993) the changes observed in the discharge mechanism with time have been attributed to the formation of such acid crystals.

Several PD mechanisms were proposed to occur within the void as the ageing of the dielectric progresses, namely Townsend-like, streamer-like (Devins, 1984; Morshuis, 1993; Morshuis and Kreuger, 1990; Dissado and Fothergill, 1992), and swarming-micro partial discharges (Tanaka, 1986; Dissado and Fothergill, 1992). The latter are also called by some authors pitting (Morshuis, 1993) or glow and pseudo-glow discharges (Bartnikas and Novak, 1992, 1993). Devins (Devins, 1984) was the first to demonstrate that the PD pulse shape, and therefore the PD mechanism is related to the void size and the overvoltage across the gap. For small overvoltages a Townsend-like mechanism occurs while for large ones a streamer-like mechanism is observed and magnitude of the streamer-like discharges is dependent on the void size. Morshuis (1993) named these pulses "Townsend-like" and "streamer-like" PDs due to the similarity between the observed PD pulse shapes to the pulses produced by these 'classical' discharge mechanisms. However, he emphasized that they should not be confused with the streamer theory developed by Meek (Meek and Craggs, 1953) which applies to streamer development between metal electrodes. In a recent review, Bartnikas (2002) stated that despite the differences in the PD pulse shapes, all PD regimes should be regarded as Townsend discharges, i.e. self-sustained avalanche processes. The Townsend 'self sustained' mechanism implies that secondary emission of electrons from the cathode must occur to replenish the avalanche process, while streamer propagation is due to photo-ionisation producing additional free electrons at the head of the electron avalanche. Both types are self-sustained discharges in that the charge formed during ionization does not alter significantly the local electric field. Townsend theory was initially developed for discharges between metal electrodes which remain at fixed electric potentials throughout the discharge process. These mechanisms are therefore only approximations of the processes taking place within voids in polymeric insulation, as charge produced in the void by the partial discharge will collect on the void surface and moderate the local electric field. This space charge contributes to the discharge extinction, which is not the case with metal electrodes, where self-sustained discharges can be maintained. Partial discharges are therefore non-equilibrium transient phenomena where the charge developed by the discharge changes (reduces) the driving electric field and for this reason cannot be considered self-sustaining. The consequence of this is that equilibrium models such as the Townsend mechanism cannot be used to predict PD activity and often numerical simulation techniques have to be employed.

Swarming micro-partial discharges occur when the material degradation has already started and solid by-products have been deposited on the void surface leading to local field enhancement. It has been suggested (Morshuis, 1993) that the formation of organic crystals increases the concentration of the PDs on the crystal tips. They are usually characterized by a small amplitude and large number of discharges per second. Similar effects can occur in electrical treeing when the electrical tree structure becomes electrically conducting and discharges occur only at the growing tree tips (Champion and Dodd, 2001). Some of the problems related to the different discharge mechanisms and their related terminology were addressed by Danikas (1993).

The model of PD process proposed in Fig. 1.12 is a deterministic one. It implies that once the applied voltage is greater that the inception voltage a discharge will take place. However, it was noticed that this is not always the case. Mason (1951) noticed that PDs occur at different inception voltages and he accounted for this phenomena to space charge effects, resulting in interdependence of consecutive events. Space charge deposited on the surface of the void following a discharge will change the local electric field. This space charge induced field is additive to the applied electric field and determines the phase of the applied voltage at which a subsequent discharge takes place. Later, a statistical time lag (Devins, 1984) was introduced as an alternative cause for these fluctuations regarding the inception voltage. The statistical time lag is defined as an essentially random time required for a free electron to appear in the void and to start the avalanche process once the electric field had reached the critical value to cause ionization. Under this assumption, PDs are considered as a stochastic process (Okamoto et al., 2001; Heitz, 1999; Altenburger et al., 2002) governed by the statistical time lag due in part to the quantum mechanical probability for the detachment of an electron under an applied electric field. However, further investigation of the stochastic properties of PDs via conditional distributions (Brunt et al., 1993; Brunt, 1991) confirmed the previous hypothesis that consecutive PDs are interdependent events and this interdependence was called "memory propagation effects". More recent studies on PD events during electrical treeing (Dodd *et al.*, 1995; Dissado *et al.*, 2000) have revealed that PDs show deterministic chaotic behaviour. Deterministic chaos is produced when a non-linear dynamic process containing positive and negative feedback components possessing a time lag between each other, is operated just below the level at which it runs away (Hilborn, 1994). It is called deterministic because there are no stochastic or random features, i.e. it is a mechanism governed solely by analytical equations of motion. Such mechanisms become chaotic when the positive and negative feedback processes can neither come into balance nor dominate over one another. In this case properties determined by the state of the system fluctuate following a never-repeating sequence without ever coming into equilibrium, even though there are no random forces (stochastic features) present.

1.2.4. Partial discharges and electrical treeing

Eventually, the PD activity in the void can cause the initiation of an electrical tree. An electrical tree is the branched growth of narrow tubules within solid insulation (Dissado and Fothergill, 1992) driven by partial discharges which can occur within the tubules and which can lead to the ultimate failure of the insulation. Electrical trees are fractal structures and their shape depends upon the applied voltage, frequency, mechanical stresses and absorbed moisture (Champion and Dodd, 1999; Alghamdi and Dodd, 2007) and morphological factors (Dissado et al., 1997; Kudo, 1998). Their structure can be classified as branch, bush and composite bush-branch, see Fig. 1.14. Electrical trees are often characterised by their fractal dimension (Dissado, 2002) which is a parameter that describes the space filling nature (branch density) of the tree. Branched trees have fractal dimension d_f less than 2 ($d_f < 2$), for bush trees $d_f > 2$ and composite bush-branch trees have fractal dimension approximately equal to 2. The electrical tree breakdown process comprises three distinct stages - initiation (formation of the initial tree), propagation (growth of the electrical tree under an applied electric field) and final breakdown (Dissado, 2002). The breakdown occurs when the electrical tree bridges the electrodes allowing a high destructive current to flow through the insulation. Electrical tree growth is driven by PD activity in the existing tree tubules and it is of primary importance to be able to distinguish between discharges in voids and discharges due to treeing. The latter are considered as much more hazardous for the insulation because treeing can cause failure in a time scale of several minutes to a few hours (Dissado *et al.*, 1997), while voids can discharge for months or even years without severe degradation of the insulation.



Fig. 1.14: Composite images showing different electrical tree structures, a) Branched tree, b) Bush-branch tree and c) Bush tree. Each image shows the image of the tree on a red-on-black background on which a grey-scale image of the light emission due to partial discharges is superimposed. The electrical trees were grown from an embedded pin (shown on the right hand side of each image) which was cast into an epoxy resin.

Two different approaches have evolved during the years to model the electrical treeing phenomena, namely stochastic and deterministic. The major contribution of the stochastic approach is its ability to create fractal structures similar to those experimentally observed. It relies on the random selection of the direction of channel propagation and disregards the physical factors behind this process. On the other hand, development of deterministic numerical models for simulation of PDs during tree growth allows a more detailed study of the factors influencing the tree growth (Dissado et al., 1997; Champion and Dodd, 2001). In these models, partial discharge events are assumed to be localized electron avalanches which occur within the tree channels. The model itself determines the spatial distribution of PDs within the tree structure for a given set of model parameters and electrostatic boundary conditions. In Champion and Dodd (2001) the conductivity of tree walls was introduced as a parameter in the model. Variations of this parameter showed a significant effect on the calculated PD magnitudes. The model results reflect the real world situation where electrically conductive and non-conductive electrical tree structures were observed. Later study (Vaughan and Dodd, 2004) on the chemical composition of electrical trees in polyethylene has demonstrated that increased conductivity in the former case was due to carbonization of the tree walls.

The effect of the space charges produced as a result of the partial discharge activity has been incorporated in a deterministic discharge avalanche model (DAM) and it has been shown the fractal dimension of the tree structures produced depends upon the availability of electrons for back avalanches, the amount of charge produced in each discharge, the fraction of charges that recombine when brought together during a timesegment, and less strongly on the initial value of the minimum distance needed for impact ionisation (Dissado et al., 2000). In addition, other factors such as the recombination of positive and negative charges have been found to be involved in determining the tree structures produced. According to DAM, a reduction of charge recombination and increased electron availability of electrons for back-avalanches gives bush structures, while increasing recombination and reducing electron availability eventually gives straight punctures (Dissado et al., 2000). Also, the amount of space charge available is dependent on the possible bulk charge transport mechanisms inside the dielectric material. A numerical investigation of the effect of DC conductivity on the electrical treeing mechanism using a stochastic model for the tree growth is presented in Noskov et al (1999).

Another important factor affecting the discharge processes during electrical treeing is temperature. Previous research (Champion and Dodd, 2001) has shown that in epoxy resins, conducting trees are formed below the glass transition temperature T_g , whilst non-conducting trees are formed above T_g . These two types of electrical trees exhibit completely different discharge regimes. In conducting trees, discharges have very small magnitudes (<10pC) and usually occur at the growing tree tips, thus it is difficult to detect them by electrical measurement. On the other hand, in non-conducting trees discharges propagate through the tree channels leading to large PD magnitudes (10pC to >1nC).

The fractal dimension of the electrical trees in flexible epoxy resins has been found to increase with increasing amplitude of the applied voltage in Champion and Dodd (1996). For a fixed pin-plane distance of 2mm, trees grown at voltages between 9 and 11kV have a branch type structure (fractal dimension <2). Trees grown at voltages above 13.5 kV have a bush structure (fractal dimension >2), and at 12 kV they form a composite bush-branch type structure (fractal dimension approximately equal to 2). In the electrical trees with a branch structure, PDs occur in two modes. Mode 1 is characterised by bursts in the PD rates during which the tree extent in the pin-plane

direction increases and mode 2 takes place between the bursts when the lateral dimension increases (Champion and Dodd, 1996). In the bush type trees PD dynamics have been found to be much more constant in time with a gradually increasing number of PDs and a lack of bursts in the PD rates.

If the electric conductivity of the resin is high enough thermal runaway may occur. Thermal breakdown is discussed in the next session.

1.2.5. Thermal breakdown

The basic mechanism of thermal breakdown involves heating of at least part of the insulation due to electric power dissipation above a critical temperature which results in a catastrophic failure (Dissado and Fothergill, 1992).

Electrical power is dissipated in an insulator when a voltage is applied across it and temperature increases as a result. The temperature will continue to increase until either thermal runaway takes place or the rate of heating equals the rate of cooling of the insulator, and thus a steady state condition is obtained. The breakdown occurs due to temperature increase either because the insulation is physically changed (such as the breakdown strength is lowered) or the conductivity is increased such that more electrical power is dissipated and hence temperature is further increased leading to a thermal runaway.

The general power balance equation for an elemental volume of the sample is given by Dissado and Fothergill (1992):

$$\frac{dT}{dt} = \frac{1}{C_p D} \left(\sigma E^2 + \kappa \nabla^2 T \right)$$
(1.18)

where C_p is the specific heat capacity of the material at constant pressure, D is the density, σ is the electric conductivity, κ is the thermal conductivity, E is the electric field, T is the temperature and t is the time, C_p , D, σ , and κ are specific material parameters.

If there is a solution of Eq. 1.18 such that $\frac{dT}{dt} = 0$ for temperatures T lower that the critical temperature T_c (T<T_c) a steady-state condition is obtained. However, if T exceeds the critical temperature then thermal breakdown takes place. In this case Eq. 1.18 reduces to:

$$\sigma(T, E)E^2 + \kappa \nabla^2 T = 0 \tag{1.19}$$

In the case of parallel plane geometry and ionic conduction, a numerical procedure for solving Eq. 1.19 is presented in (Hikita and Ieda, 1983). An analytical expression for the maximum thermal voltage (MTV) for ionically-conducting insulators is given in (Dissado and Fothergill, 1992):

$$V_{th} = T_{amb} \left(\frac{8\kappa_0 k_B}{\sigma_0 \phi}\right)^{1/2} exp\left\{\frac{\phi}{2k_B T_{amb}}\right\}$$
(1.20)

The above equation is only an approximation for $\phi \gg 2k_BT$ and it is valid in the case when the runaway starts a few tens of degrees above the ambient temperature T_{amb} and k_B is Boltzmann constant. The MTV as given by Eq. 1.20 is thickness independent. The thermal conductivity is assumed to be temperature independent, i.e. constant, while the electrical conductivity is field independent and with an Arrhenius-type dependence on temperature (Dissado and Fothergill, 1992):

$$\sigma(T) = \sigma_0 exp\left\{-\frac{\phi}{k_B T}\right\}$$
(1.21)

where σ_0 and ϕ are experimentally-determined values which are constant over a given range of temperature.

1.2.6. PD measurement

1.2.6.1. Phase-resolved PD measurements

Nowadays, PD detection and measurement is performed by means of digital PD detectors. Essentially, there are three main categories of PD data patterns obtained under the application of ac electric fields – phase-resolved data, time-resolved data and data without phase or time information (Sahoo *et al.*, 2005). The third category represents variations in discharge pulse magnitudes against the amplitude of the test voltage ($q \sim V$). Time-resolved measurements are implemented when the true shape of the PD pulse is needed for diagnostics of the insulation. Although, this type of data possesses the advantage of relating the pulse shape to the physics of the defect, in general, it is difficult to perform such wide bandwidth measurements "on-site" in real industrial applications due to noise interferences and signal attenuation and distortion when the pulse travels from the site of the defect to the PD detector. Probably, the most commonly used type of data for PD monitoring and insulation diagnostics in the case of ac applied voltages is the phase-resolved data ($\varphi \sim q \sim n$). It represents information in 3D containing the interrelationships of ac voltage phase of PD occurrence φ , discharge

magnitude q, and discharge rate n. A typical PD pattern from an electrical treeing experiment carried out with an alternating voltage of 50Hz applied to the pin electrode is shown in Fig. 1.15. In this figure, voltage phase φ is on the abscissa, discharge magnitude q is on the ordinate, and dot density in each window represents the number of discharges n. Also, note the presence of negative PDs during the positive half-cycle of the applied voltage ($0 < \varphi \le 180^{\circ}$) and presence of positive PDs during the negative half-cycle ($180 < \varphi \le 360^{\circ}$). This has implications for the choice of PD distributions for pattern recognition and will be discussed later on.



Fig. 1.15: Typical PD pattern from an electrical treeing experiment

1.2.6.2. Measurement circuits

In IEC 60270:2000 (BS EN 60270:2001) the requirements for PD measurement systems and several principal circuits are specified. Two most commonly implemented circuits for phase-resolved measurements are shown in Fig. 1.16. These differ only in the position of the load impedance which is used to convert the current pulse in the external circuit following each discharge to a voltage pulse which can be measured using the measurement instrument. The following notations are used in Fig. 1.16: high-voltage supply (U), input impedance of measuring system (Z_{mi}), connecting cable (CC), optical link (OL), test object (C_a), coupling capacitor (C_k), coupling device (CD), measuring instrument (MI), and filter (Z). When a PD occurs within C_a , a redistribution

of charge follows, and image charge is induced on the test object electrodes. This gives rise of a current pulse flowing through C_k and Z_{mi} . The voltage drop occurring on Z_{im} is proportional to the change in image charge (apparent charge) due to the PD event and is measured by the MI. In order to reduce the measurement noise, the coupling capacitor C_k should be discharge free. Usually, the load Z_{im} is RLC type resonant circuit with tuned resonant frequency in the range of several hundred kHz to a few MHz dependent on the required sensitivity. In the case where C_k is connected to CD, an optical link is used to transfer the measured signal to the MI. Often MI is a digital sampling oscilloscope (DSO), which is calibrated by a known charge such that the output reading of the MI is in Coulombs. The filter Z is used to suppress any external noise from the high voltage supply.



Fig. 1.16: a) Coupling device in series with the coupling capacitor (IEC 60270:2000) b) Coupling device in series with the test object (IEC 60270:2000)

1.2.7. PD pattern recognition

During the last few decades PD detection and recognition has found to be an important tool for condition assessment of high voltage equipment, e.g. cables, transformers, generators, as well as a fruitful scientific research area (Stone, 2005; Bartnikas, 2002). An experienced engineer can perform assessment of the insulation observing the phase resolved PD patterns and relating them to a particular defect. The
need for on-line monitoring of the power systems and fast development of computers created the current trend towards computer-aided PD pattern recognition. The application of computer-aided techniques for automating detection and recognition were explored extensively in (Gulski and Kreuger, 1992; Gulski *et al.*, 1990; Gulski, 1991, 1995; Gulski and Krivda, 1993; Strachan *et al.*, 2008; Hozumi *et al.*, 1992).

Pattern recognition is a two-stage process. The first stage is generating a set of features from the measured partial discharge data, which later are used collectively in the second stage - classification (Sahoo et al., 2005). However, the efficiency of the classification algorithm is dependent on the discrimination capabilities of the input features. The technique relies on each input feature containing unique information regarding the type of discharge activity such that the inverse problem of identifying the defect source is reliable. Several algorithms were proposed for PD feature extraction, namely statistical methods (Krivda, 1995; Gulski, 1991; James and Phung, 1995), pulse characteristic tools (Mazroua et al., 1993; Mazroua et al., 1994, 1995), signal processing tools (e.g Wavelet transform, Fourier transform, etc.) (Chang et al., 2005; Hücker T., 1995) and image processing tools (e.g. texture analysis algorithms, fractal features and wavelet-based image decomposition) (Abdul Rahman M.K., 2000; Lalitha and Satish, 2000; Satish L., 1995). The information content obtained by the feature extraction algorithms is then supplied as a vector with each element of the vector representing a unique feature of the partial discharge data to a classification algorithm, which provides as an output the defect type and/or ageing stage. In an attempt to improve the reliability of the classification stage, wavelet decomposition has been applied to distinguish between PD signals and noise (Sagar et al., 2007; Sharkawy et al., 2007). Different classifiers were proposed in the literature including statistical classifiers (Kreuger et al., 1993; Gulski, 1991; Krivda, 1995; Gulski, 1995), pulsesequence analysis (PSA) (Hoof and Patsch, 1995; Patsch and Berton, 2002; Benzerouk et al., 2007), neural networks (Danikas et al., 2003; Gulski and Krivda, 1993; Hozumi et al., 1992; James and Phung, 1995; Mazroua et al., 1993; Mazroua et al., 1994; Chang et al., 2005), fuzzy logics (Montanari et al., 2007; Conti et al., 2004), genetic algorithms (Ziomek et al., 2000), support vector machine (SVM) (Sharkawy et al., 2007) and also various hybrid approaches (Li Y.-M., 2005; Carminati E., 2001). In general, these algorithms proved to be successful in the recognition of single defects. However, most of the research work was based on laboratory specimens with known

defect geometries and controlled test conditions. The applicability of such PD recognition tools for discrimination between PD pulses "in-situ" and "on-line" in real industrial situations is not clear. Another question of significant scientific and practical interest concerns variation of PD patterns with time, i.e. how PDs change with material degradation and ageing. Most of the classification algorithms rely on 'fixed' values of the discriminatory features associated with a particular defect. However, in reality these values change during the degradation of the insulation and it is difficult to define characteristic values for a particular defect.

The reasons why only a few techniques have been adopted for implementation in real industrial application are summarised below:

- Most methods were developed and tested on specimens in controlled laboratory conditions with known defect geometries and suppressed external interference. These conditions are different from the 'real life' situation when these factors are unknown and often the external noise is greater than the measured signal.
- Many pattern recognition techniques (neural networks, fuzzy logics, etc.) are based on the 'black box' approach, i.e. the PD pattern (input feature vector) is mapped to the desired output (defect type and/or ageing stage) by the classification algorithm itself. This requires huge amounts of data to be gathered for all possible defects and/or combination of defects, a task which is quite cumbersome.
- Often the choice for a particular set of discriminatory features is not justified. Usually, the method of 'trial-and-error' is implemented. Therefore, the relationships between the features constituting the input vector are not clear and redundant data is presented to the classification algorithm.

1.3. Object of the present study

Understanding the factors that govern electrical tree growth and the corresponding PD activity is essential for reliable prediction of the remaining life-time of electrical insulation based on PD data. Electrical tree growth in polyethylene under certain operating conditions (room temperature and 40% relative humidity of the environment) has been found to be similar to that in flexible epoxy resins in terms of voltage dependence of the tree growth, growth rate, fractal dimension of the resulting tree

structures, etc. The existing deterministic models (Dodd, 2003; Dissado *et al.*, 2000) of electrical tree growth have been found to be successful in explaining all these general features. However they are not able to explain some of the details. For example, in flexible epoxy resins the observed burst type behaviour in the PD activity while growing branched structures cannot be explained by the current models. A possible reason is that the charge transport through the bulk polymer is rarely considered in such models with the only exception being uniform dc conduction through the polymer (Noskov *et al.*, 1999). However, DC conduction alone cannot explain the experimentally observed behaviour. Usually the existing models consider that the space charge can propagate only a small distance away from the tree tubule tip inside the bulk dielectric (Seralathan *et al.*, 2008; Dissado *et al.*, 2000) or remain trapped in the immediate vicinity of the tree (Dodd, 2003). Therefore the object of the present work is to establish a link between the possible bulk charge transport processes and the electrical degradation mechanism, in particular the influence of bulk charge transport on the partial discharge and electrical treeing processes in flexible epoxy resins.

Both temperature and absorbed moisture are known to affect the electrical properties of epoxy resins and the electrical breakdown mechanisms in these materials. Therefore in order to achieve the goals of the research project it was necessary to carry out a systematic study of the material properties on the selected epoxy resin systems as a function of ambient temperature and absorbed moisture on the one hand and the electrical degradation mechanisms again as a function of temperature and moisture on the other.

This work is structured in the following way. Chemical characterisation of the selected resins and the sample preparation and storage procedures are presented in Chapter 2. In Chapter 3 the water absorption process in the epoxy resins is studied. The influence of absorbed moisture and temperature on the electrical properties of epoxy resins is discussed in Chapter 4. The complementary investigation of the electrical degradation mechanisms as a function of temperature and moisture is presented in Chapter 5. Chapter 6 includes the analysis of the PD data obtained from these experiments. The key aspects of the work are discussed in Chapter 7 and a 'tentative' model for electrical tree growth in flexible epoxy resins is proposed as a result. The main conclusions from the work and some ideas for further investigations on its basis are given in Chapter 8.

Chapter 2: Material description, sample preparation and conditioning

2.1. Introduction

In the present work two epoxy resins have been selected as an insulating material, namely Araldite CY1301 and Araldite CY1311 (Ciba-Geigy, 1982b, a). The Araldite is described by the manufacturers Ciba-Geigy as a bisphenol-A epoxy resin containing a reactive solvent. The two epoxy resin systems are cured with the same hardener HY1300, which is a mixture of formulated aliphatic polyamines. Both epoxy resins are cured with the same stoichiometric ratio of the resin and hardener hence it can be expected that both resins have the same number of functional units. The curing reaction produces the final crosslinked, thermosetting structure with high cohesive strength and adhesion properties. The most important difference between the two systems is that CY1311 is modified with a plasticizer, so that its glass transition temperature is about 0°C and appears in a flexible state at room temperature (~20°C), while CY1301 has glass transition temperature of about 50°C, therefore it is in a glassy state at room temperature. The exact modification of CY1311 was not specified by the manufacturer.

Araldite CY1301 appears as a clear straw-coloured liquid. The epoxide content is in the range 5.0-5.3 mol/kg and chlorine content is 0.3% w/w, which is easily hydrolysable. The viscosity at 25°C is estimated to be between 800 and 1500 mPas and the density is 1.12Mg/m³ at 25°C (Ciba-Geigy, 1982b).

Araldite CY1311 has similar appearance but slightly different physical properties. The viscosity is given as 250-400 mPas at 25°C and the density is 1.10 Mg/m^3 at 25°C (Ciba-Geigy, 1982a). The chlorine content is also lower than in Araldite CY1301 – 0.2% w/w.

The hardener is a clear yellow liquid. The viscosity is in the range 170-210mPas at 25°C and density 1.00 Mg/m³ at 25°C (Ciba-Geigy, 1982b, a).

The details of the chemical composition of the epoxy resin systems and the hardener are not provided by the manufacturer. However, previous study (Griseri, 2000) on CY1301 has revealed the main components comprising the epoxy resin and the hardener and the details of the product synthesis. The base resin is a mixture of Diglycidyl Ether-Bisphenol A (DGEBA) and Iso-Octyl Glycidyl Ether (IOGE). The hardener is a three component system (Griseri, 2000):

- Polyoxypropylene triamine (80% wt)
- Thriethylene Tetra Amine (TETA) (14.3% wt)
- Salicylic Acid (5.7% wt)

The polyoxypropylene triamine and TETA contain the main reactive amine groups, while the salicylic acid is used as an accelerator for the curing reaction.

2.2. GC/MS Analysis of the epoxy resins and the hardener

In order to ascertain a better understanding of the chemical composition of the hardener and the epoxy resins used in this study, a gas chromatography/mass spectrometry analysis (GC/MS) was performed in the Department of Chemistry, University of Leicester. The GC/MS instrumental technique is a combination of a gas chromatograph and a mass spectrometer that can be used to separate, identify and quantify complex mixtures of chemicals (Kemp, 1991). A requirement for the technique to be successful is that the compound to be investigated has to be sufficiently volatile and thermally stable. The samples are analyzed as organic solutions and the investigated material needs to be solvent extracted. In the present case chloroform was used as a solvent for both hardener and epoxy resin.

The sample is vaporized and split by the gas chromatograph in various constituents and these constituents are then analyzed. Each constituent ideally produces a specific spectral peak after a specific period of time that is registered on a chart called the "gas chromatogram". The time elapsed between injection and elution is called the "retention time". The retention time is used to differentiate between the various compounds comprising the sample. The size of the peaks is proportional to the quantity of the corresponding compounds in the sample and the peaks are normalized to the compound possessing the greatest abundance (relative peaks).

The gas chromatogram gives the number of constituents comprising the sample and their relative concentrations but does not specify their chemical composition. Hence, a mass spectrometer (MS) has to be used. In the MS, the sample molecules are bombarded with electrons. In this way, the molecules become electrically charged and they can break into smaller charged fragments. They are then accelerated through a magnetic field. The fragments are deflected by the field according to their mass and charge. Finally, they are collected at the detector, where an ionic current is generated in proportion to their relative abundances. A spectral plot called the "mass spectrum" displays the relative abundance against the ratio mass/charge (the m/z value). The mass spectra of unknown substances are used as fingerprints for their identification by a comparison with known spectra contained in a reference library.

The samples were analysed using a Elmer Perkin AutoSystem XL Gas Chromatograph and Turbo Mass spectrometer (GC/MS). The carrier gas was helium with a 50 ml/min flow rate. The initial temperature of the oven was 45 °C; it was held for 1.5 minutes at this temperature. Then, the temperature was increased to 170°C at a rate of 10°C/min, followed by another increment to 250°C at a rate of 20°C/min. The temperature 250°C was held for 2 minutes in the oven. Hence, the total time of the run was 20 minutes. The eluent from the gas chromatograph was fed through a flame ionization detector to obtain the composition of the sample before it was passed to the mass spectrometer. In the mass spectrometer, the eluent was scanned in the range 100-500 m/z for a total run time of 35 minutes to determine the molecular mass of the sample constituents. The entire procedure is fully automated and the results are presented in the form of a gas chromatogram and corresponding mass spectra.

The gas chromatogram of CY1301 resin is shown in Fig. 2.1. The plot is dominated by one peak occurring at 23.25 min and three significantly smaller peaks. The corresponding mass spectra related to each peak are given in Appendix B. The peak at 23.25 min and the smaller peaks at later times were unambiguously identified as DGEBA with number of repeat units equal to zero. The peak occurring at 14.04 min has been associated with a chlorine containing substance, see Appendix B. This can be explained by the DGEBA synthesis if it took place in abundance of Chlorohydrin intermediate (see Fig. 1.6). In the instruction sheet given by the manufacturer (Ciba-Geigy, 1982b) is reported a value of 0.3% w/w for the chlorine content and part of it may be due to the Chlorohydrin intermediate. Although, IOGE is specified by the Manufacturer as a constituent of Araldite CY1301 epoxy resin (Ciba-Geigy, 1982b), it has not been detected by the mass spectroscopy technique used here.

A similar gas chromatogram was obtained in the case of Araldite CY1311. The dominant peak once again occurred at 23.25 min and was associated with DGEBA. An important difference was the occurrence of a peak at 26.58 min attributed to a siloxane compound. Siloxane oligomers have been reported in (Petrie, 2006) as materials that are

used in epoxy resins as flexibilizers. Organosiloxanes have very low glass transition temperature, good electrical properties, low stress, high flexibility and good thermal and oxidative stabilities. The organic side chains confer hydrophobic properties. It can be concluded that a siloxane-based substance has been used by the manufacturer of the CY1311 epoxy resin to modify the original Araldite CY1301 resin, so that the T_g of the resin is decreased to about 0°C, i.e. as a flexibilizer.

The chemical species comprising the hardener were more difficult to identify but the mass spectroscopy result suggests a composition of the hardener similar to that proposed by Griseri (2000). The peaks occurring at 15.30, 17.93 and 20.12 min can be associated to salicylic acid, triethylene tetra amine (TETA), and polyoxypropylene triamine, respectively due to similarities in the chemical composition as expected from the literature ingredients and the chemical fragments actually recognised by the GC/MS technique.

The complete set of gas chromatograms, mass spectra and fingerprints are given in Appendix B.

The literature survey, manufacturer's data sheets and the results of the GC/MS analysis suggest the main ingredients of the two base resins and the hardener that are shown in Fig. 2.2(a) and Fig. 2.2(b), respectively. The base resin CY1301 contains DGEBA and IOGE. A siloxane compound is used as a flexibilizer in CY1311. The hardener contains TETA, polyoxypropylene triamine and salicylic acid.



Fig. 2.1: Gas chromatograms of Araldite CY1301 (top), Araldite CY1311 (middle), and hardener HY1300 (bottom)





b) Hardener: Triethylene Tetra Amine (TETA), Polyoxypropylene triamine, Salicylic acid

Fig. 2.2: Main ingredients of a) Base resin CY1301; b) Hardener

2.3. Sample preparation

Throughout this work it was necessary to follow a rigorous standard preparation schedule in order to produce fully cured epoxy resin samples with reproducible electrical, chemical and mechanical characteristics. Two types of samples were produced, namely thin film samples used for dielectric spectroscopy and block samples used for electrical degradation experiments. The block samples had size 50mm by 20mm by 5mm (length-height-width). The thin film samples had circular shape with diameter 75mm and thickness 0.7mm or 1.7mm. The samples were manufactured in batches since it was not technologically possible to produce all of them in the same time.

The following sample preparation procedure was followed in both cases:

- The amount of epoxy compound for one mould was calculated from the mould volume and density of epoxy resin (~1g/ml). The required mass of resin (100 parts by weight) and hardener (30 parts by weight), as specified by the manufacturer, were measured in two separate beakers using a balance to an accuracy of 0.1g.
- The epoxy resin and hardener were separately degassed in a vacuum oven for 10 minutes at a temperature 40°C, in order to remove the air bubbles from the solutions.
- Afterwards, the two compounds were mixed together on a hot plate (warmed to maintain temperature of 40°C of the mixture) and stirred thoroughly with a magnetic stirrer for 10 minutes, followed by a second degassing (10 minutes) under vacuum in the oven.
- The moulds were treated with silicone oil release agent to allow easy removal of the samples following cure.
- The mixture was left for two days to cure. Then the individual samples were cut from the mould and identification numbers were inscribed on them.
- The last step was post-curing of the samples in the vacuum oven for one hour at a temperature of 100°C followed by a slow cooling (overnight) to room temperature. This last step ensured that the cure reaction of the resin and hardener has been completed. In order to ensure maximum removal of moisture from the samples, they were kept for 10 days under vacuum in the

oven at room temperature and then they were weighted and stored in humidity controlled containers.

Some of the thin film samples used for dielectric spectroscopy measurements were sputter-coated with gold. The sputter coater used was EMITECH K550X. The coating was made under a stable vacuum of 0.1 mbar with Argon as a process gas. The deposition current was 25 mA and the corresponding deposition rate, as specified by the manufacturer, was 7.5 nm/minute. The gold was sputtered on both sides of the sample. The total time for sputtering on one side of a sample was set to be 8 min and the resultant thickness of the gold layer was estimated to 60 nm. This thickness was sufficient to produce a uniform layer of gold on the sample surface, which was checked by an optical inspection.

A photograph of a sample used in an electrical treeing experiment is shown in Fig. 2.3a. The sample consists of a tungsten pin with a diameter 1mm cast in an epoxy slab. A unique ID number was ascribed on each sample for easy identification. The ID number contains the batch number and the respective sample number in the batch. A gold coated sample used for dielectric measurements is shown in Fig. 2.3b. The gold coating was used to improve the contact between the electrodes and the samples. A mask was used so that three distinct gold regions were obtained with the same shape and surface area as the measurement and guard electrodes used for the dielectric measurements (see Fig. 4.2 and Fig. 4.3). The LV electrode and the guard are coated on one side of the sample and the HV electrode on the other. The role of each electrode is explained in Chapter 4.



Fig. 2.3: Epoxy resin samples for: a) electrical treeing experiments; b) dielectric measurements with gold coating

2.4. Conditioning of the cured sample

Cured epoxy resin contains pendent hydroxyl groups on the main polymer chains and can therefore interact with water molecules (McConnell and Pethrick, 2008). As a result, epoxy resins can absorb significant amounts of moisture from the surrounding air leading to an increase in the weight of the samples. All samples were weighed using an analytical balance with a precision of ± 0.1 mg when taken from the vacuum oven; they then were stored in a humidity controlled container in the lab. Constant relative humidity was obtained using saturated salt solutions and deionised water. Lithium chloride (LiCl), magnesium chloride (MgCl₂), potassium carbonate (K₂CO₃), sodium chloride (NaCl) and deionised water, which provide constant relative humidity of 12%, 33%, 43%, 75% and 100%, respectively, over the temperature range 15-30°C, see Fig. 2.4 (OIML, 1996; Greenspan, 1977). The numbers in the parenthesis in Fig. 2.4 are the average values over the entire temperature range. The containers were stored at room temperature ($20\pm3^{\circ}C$). The stability of relative humidity over a range of temperatures was the most important criterion in the selection of the salts, since these salt solutions were also used to maintain the RH in the cell used for the dielectric measurements. The dielectric measurements were carried out at temperatures between 20°C and 70°C. The containers were made from polyethylene which is hydrophobic and therefore acts as a barrier to prevent moisture loss to the environment. The samples were suspended above the saturated salt solutions using a perforated polypropylene sheet as a barrier between the epoxy samples and the solution. The water absorption process is discussed in detail in Chapter 3.



Fig. 2.4: Equilibrium relative humidity values for saturated aqueous salt solutions, data from (OIML, 1996)

2.5. Mass loss measurements

Mass loss measurements were conducted following the post-cure in order to establish if there is any residual moisture present in the samples after the post-cure and to check the stability of the final cured matrix. Six fully cured samples of each resin were placed in a vacuum oven at temperature of 100°C. Weight measurements were performed throughout the experiment to monitor the apparent loss of weight. The samples were periodically taken out of the vacuum oven and measured. The average value of the mass decrement and the corresponding error bars after 1400h in the vacuum oven are shown in Fig. 2.5a and Fig. 2.5b for CY1301 and CY1311 samples, respectively. The CY1301 samples lost 0.137±0.004% within the first 3 days in the vacuum oven, thereafter the samples' mass continued to decrease but at much slower rate as shown in Fig.2.5a. The long term mass loss is likely to be due to oxidation as a result of the prolonged thermal ageing of the samples. Over the same period of time the CY1311 samples have shown a similar trend, i.e. initial decrease of ~0.11% over the first 3 days followed by a continual mass loss after that. Overall, the apparent mass loss

of the CY1311 samples was significantly higher than the value that can be attributed solely to the moisture content (no stable value was obtained during the experiment). Therefore, it was assumed that the siloxane plasticising agent in the flexible resin was decomposing and leaving the sample as a result of the high temperature and vacuum.



Fig. 2.5: Weight measurements of samples kept in a vacuum oven at 100°C a) CY1301; b) CY1311

Figure 2.6 shows a photograph of two samples taken at the end of the mass loss experiment. The sample on the left is a CY1301 sample, while the sample on the right is a CY1311 sample. Both samples show signs of degradation due to the thermal ageing in the vacuum oven. The CY1311 samples have shown much higher degree of degradation, which is illustrated by the change in the colour of the samples. The CY1301 sample has changed its colour from pale yellow (after the post-cure) to dark yellow, while the colour of the CY1311 sample has changed to dark brown (compare with Fig. 2.3). It is likely to be caused either by oxidation or pyrolytic degradation. This is consistent with the hypothesis that the mass loss in CY1311 samples is due not only to the moisture but to flexibilizer as well. Siloxane additive does not take part in the

curing reaction and remains free but highly immobile in the epoxy matrix due to its large molecular weight.



Fig. 2.6: Photograph of a CY1301 sample (left) and a CY1311 sample (right) at the end of the water desorption experiment

2.6. Chapter summary

The GC/MS analysis conducted as a part of this study suggests a chemical composition of the epoxy resins and the hardener as previously reported in the literature and given by the manufacturer in the material data sheet with some additives. The Araldite CY1301 epoxy resin mainly contains DGEBA and probably some Chlorohydrin intermediate, which has not been fully consumed during the DGEBA synthesis reaction. The Araldite CY1311 is a modified version of the CY1301 resin. The CY1311 base resin contains DGEBA with added siloxane flexibilizer, which reduces the glass transition temperature from 50°C to 0°C. The mass spectra suggest that the flexibilizer is most likely a siloxane-based compound. The intensive thermal ageing under vacuum has revealed a significant mass loss only in the case of CY1311 resin, which cannot be explained solely by water desorption process. A possible explanation is that the flexibilizer slowly being removed from the sample under vacuum at high temperatures. Therefore, the flexibilizer contains chemical groups that are nonreactive with the polymer network. The role of the flexibilizer is to reduce the crosslinking density. The two epoxy resin systems are cured with the same hardener HY1300. The GC/MS analysis of a HY1300 sample revealed three main ingredients in an agreement with the literature. The constituents of the hardener are Triethylene Tetra Amine (TETA), Polyoxypropylene triamine and Salicylic acid. The role of the salicylic acid is catalytic. It is used as a proton donor that accelerates the curing reaction. Also, a condensation reaction involving the salicylic acid may take place. This can account for the initial mass loss observed in the epoxy samples after the completion of the postcuring process. The ratio of epoxy resin to hardener was kept constant as prescribed by the manufacturer and the same sample preparation procedure was used throughout this work to ensure that all samples possess identical properties. All samples were conditioned in sealed containers with saturated salt solutions and care was taken to prevent a contact between the epoxy samples and salt solutions. A summary is given in Table 2.1 of the physical properties of the cured epoxy resin systems after a post-cure of 1h at 100°C, all values are taken from the manufacturer's data sheets (Ciba-Geigy, 1982b, a).

| Properties | CY1301 | CY1311 |
|----------------------------------|----------------------------------|------------------------------|
| Mechanical | | |
| Hardness (Shore) at 25°C | D/84/1 | C/60/1 |
| Density | 1.14 Mg/m^3 | 1.12 Mg/m^3 |
| Coefficient of expansion | $65-75 \times 10^{-6}$ linear/°C | $100-150 \times 10^{-6}$ |
| ASTM D 696-70 | | linear/°C |
| Thermal conductivity | 0.21-0.23 W/m°C | 0.19-0.21 W/m°C |
| BS 874 section 4.2.3 (1973) | | |
| Water absorption BS 2782 | 15-25 mg | 80-100 mg |
| 24h at 23°C method 502F (1970) | | |
| Electrical | | |
| Electric strength IEC 243 (1967) | 13-14 MV/m | 12-14 MV/m |
| Step-by-step, 3mm, 20°C | | |
| Permittivity IEC 250 (1969) | 3.7-3.9 | 4.6-5.1 |
| 1 kHz at 20°C | | |
| Loss tangent IEC 250 (1969) | 0.005-0.007 | 0.04-0.08 |
| 1 kHz at 20°C | | |
| Volume resistivity IEC 93 (1958) | 12-14 log ₁₀ ohm m | 9-11 log ₁₀ ohm m |
| Voltmeter-ammeter, 1 min, 20°C | | |

 Table 2.1. Physical properties of cured CY1301 and CY1311 epoxy resin systems

Chapter 3: Water absorption in epoxy resins

Electrical treeing and other electrical degradation processes in various polymers have been found to be dependent on temperature and absorbed moisture (e.g. Dissado and Fothergill, 1992). In the case of epoxy resins, it was suggested that above the glass transition temperature a significant increase in the ionic conductivity occurs that can lead to thermal breakdown at high temperatures and/or high moisture concentration (Sletbak et al., 1988). Also, water absorption has been found to have a profound impact on the electrical treeing (Champion and Dodd, 1999; Alghamdi and Dodd, 2007; Champion and Dodd, 1995b) as the water content determines the fractal dimension and the rate of the tree growth. Absorbed water in epoxy resin based micro- and nano-filled composites has been found to affect their dielectric properties (Hong et al., 2009; Zou et al., 2008) and dielectric measurements have been used to study the water absorption process in epoxy resin systems (Hayward et al., 1997; McConnell and Pethrick, 2008). Therefore, it might be expected that the absorbed moisture will affect the electrical properties of the epoxy resins and consequently the electrical breakdown phenomena. Also, the discharge characteristics of the gas inside the tree channels or voids can be changed due to the presence of water molecules affecting the PD activity. Hence, a thorough study is needed to fully understand the mechanism by which the absorbed water changes the electrical breakdown properties of the epoxy resin. In this chapter, water absorption was studied in two cases - thin films and block samples. It was necessary to consider both cases because the difference in sample geometry would cause differences in the absorption kinetics. The modelling work was carried out to quantify the amounts of 'bound' and 'free' water in the samples prior to testing. The time needed for the diffusion process to reach near equilibrium level was also studied in this way.

3.1. Introduction

According to Carter and Kibler's theory (Carter and Kibler, 1978) water absorption in epoxy resins is anomalous^{*} i.e. non-Fickian. Here, the diffused water molecules are assumed to be in one of two states - 'bound' or 'mobile'. A recent study of water absorption in epoxy adhesives (Popineau *et al.*, 2005) has confirmed Carter and Kibler's hypothesis. Popineau et. al. have used nuclear magnetic resonance (NMR) in their investigation and they have suggested that the 'mobile' water molecules initially diffuse into the polymer matrix through interactions with the polymer chains such as van der Waals interactions, secondary bonding, or polar interactions with polar sites within the polymer. It is assumed that the 'mobile' fraction affects the mechanical properties of the polymer; hence it may cause swelling, plasticisation, and lowering of the elastic modulus and the glass transition temperature T_g of the polymer. The 'bound' water formation starts when all bonding sites along the polymer chains are occupied and water molecules cluster together in the free volume within the epoxy resin matrix (Popineau et al., 2005). The clusters of 'bound' water are large and the water molecules within them are effectively bound with regard to diffusion kinetics, with inner molecules of the cluster weakly interacting with the polymer chains. Therefore, three types of interactions involving the water molecules are important in determining equilibrium concentration in the epoxy matrix: interactions between neighbouring water molecules that produce clusters, interactions between 'mobile' (free) water molecules and the polymer matrix, and interactions between the 'outer' molecules that belong to any particular cluster and the surrounding polymer chains.

3.1.1. Water diffusion in thin films

The non-Fickian diffusion can be described by the following partial differential equations in one dimension (Carter and Kibler, 1978):

$$D\frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t}$$
(3.1)

$$\frac{\partial N}{\partial t} = \gamma n - \beta N , \qquad (3.2)$$

where *D* is diffusion coefficient for mobile H₂O molecules, n – number density of mobile H₂O molecules, N – number density of bound H₂O molecules, γ – probability per unit time that a mobile H₂O molecule becomes bound, β – probability per unit time that a bound H₂O molecule becomes mobile. It is assumed that the 1D diffusion process is an adequate approximation in the case of thin films. This equation differs from the Fick's law by the term $\partial N/\partial t$, which gives the increment of 'bound' water in the sample. If there is to be no 'bound' fraction, i.e. $\partial N/\partial t = 0$, then Eq. 3.1 reduces to the Fick's law:

$$D\frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t}$$
(3.3)

At long times a dynamic equilibrium is achieved between the fractions of bound N_{∞} and mobile n_{∞} water molecules that satisfies the equation $\gamma n_{\infty} = \beta N_{\infty}$. The total water uptake M_{eq} in long-term dynamic equilibrium depends on the temperature and the conditions surrounding the sample, e.g. relative humidity of the environment. Assuming that the diffusion of mobile water is described by simple Fickian diffusion augmented by sources and sinks and the diffusion coefficient *D* of the mobile molecules is not dependent on the concentration, then it may be shown in the case of one dimensional diffusion that (Carter and Kibler, 1978).

$$\frac{N(x,t)}{N_{\infty}+n_{\infty}} = \frac{\gamma}{\beta+\gamma} \left\{ 1 - \frac{4}{\pi} \sum_{l=1}^{odd} (-1)^{\frac{l-1}{2}} \frac{e^{-\beta t}}{l} \cdot \cos\left(\frac{\pi l x}{2d}\right) \right\}$$
(3.4)

$$\frac{n(x,t)}{N_{\infty}+n_{\infty}} = \frac{\beta}{\beta+\gamma} \left\{ 1 - \frac{4}{\pi} \sum_{l=1}^{odd} (-1)^{\frac{l-1}{2}} \frac{e^{-kl^2t}}{l} \cdot \cos\left(\frac{\pi lx}{2d}\right) \right\}$$
(3.5)

Where 2*d* is the sample thickness, $k = \pi^2 D/(2d)^2$, *t* is time and N(x, t) and n(x, t) are number densities of bound and mobile water molecules, respectively, as a function of time and position. Equations 3.4 and 3.5 are convenient approximations which apply when β and γ are small compared with k. Integrating these equations over the sample thickness gives the following expression for the total mass uptake of water M_t (Champion and Dodd, 1995a; Carter and Kibler, 1978):

$$\frac{M_t}{M_{eq}} = 1 - \frac{\beta}{\beta + \gamma} \cdot \frac{8}{\pi^2} \sum_{l=1}^{odd} \frac{e^{-kl^2 t}}{l^2} - \frac{\gamma}{\beta + \gamma} \cdot e^{-\beta t}$$
(3.6)

For short times, t < 0.7/k, Eq. 3.6 can be reduced to:

$$\frac{M_t}{M_{eq}} = \frac{4}{\pi^{3/2}} \frac{\beta}{\beta + \gamma} \sqrt{kt}$$
(3.7)

and for long times where $t \gg 1/k$

$$\frac{M_t}{M_{eq}} = 1 - \frac{\gamma}{\beta + \gamma} \cdot e^{-\beta t}$$
(3.8)

where the diffusion coefficient *D* does not play a role. The rate constants β and γ may be obtained from Eq. 3.8 by re-arranging, taking natural logarithms and plotting $ln\left[\frac{M_{eq}-M_t}{M_{eq}}\right]$ as a function of time *t*. At long times the slope is – β and the extrapolated intercept is $ln\left[\frac{\gamma}{\beta+\gamma}\right]$ assuming that the equilibrium mass M_{eq} is known. The diffusion coefficient *D* can then be obtained from the slope at the origin of the graph of M_t/M_{eq} against \sqrt{t} using Eq. 3.7.

3.1.2. Water diffusion in block samples

Although, the above mentioned procedure can be used to obtain the diffusion parameters from the experimental data, it is valid only for one dimensional case. In reality, the epoxy samples being used are three dimensional; this is particularly important for the block samples used for electrical degradation experiments. Hence, a three dimensional solution should be sought. Having the same assumptions as in the 1D case, it may be shown that for the 3D case (Champion and Dodd, 1995b; Crank, 1975):

$$\frac{N(x,y,z,t)}{n_{\infty}} = \frac{\gamma}{\beta} - \frac{64\gamma}{\beta\pi^3} \sum_{l=1}^{odd} \sum_{m=1}^{odd} \sum_{n=1}^{odd} (-1)^{\frac{l+m+n-3}{2}} \frac{e^{-\beta t}}{lmn} \cos\left(\frac{\pi lx}{2a}\right) \cdot \cos\left(\frac{\pi my}{2b}\right) \cdot \cos\left(\frac{\pi nz}{2c}\right)$$
(3.9)

$$\frac{n(x, y, z, t)}{n_{\infty}} = \frac{\beta}{\beta + \gamma} - \frac{64\gamma}{(\beta + \gamma)\pi^3} \sum_{l=1}^{odd} \sum_{m=1}^{odd} \sum_{n=1}^{odd} \frac{(-1)^{\frac{l+m+n-3}{2}}}{lmn} \cos\left(\frac{\pi lx}{2a}\right) \cdot \cos\left(\frac{\pi my}{2b}\right) \cdot \cos\left(\frac{\pi nz}{2c}\right)$$
$$\cdot \exp\left\{\frac{-tD\pi^2}{4} \left[\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right]\right\} \quad (3.10)$$

where 2a is the length, 2b the thickness, and 2c the height of the sample, D is the diffusion coefficient and t is time. The coordinate system has its origin at the centre of the sample, with x, y and z axes parallel to 2a, 2b, and 2c, respectively see Fig. 3.1. Hence, considerable simplification of Eq. 3.9 and 3.10 is obtained by calculating the water distribution along the z axis from the origin (x = y = z = 0). Using these conditions, and adding the bound and mobile fractions and normalising by the total percentage water absorption M_{eq} at dynamic equilibrium then (Champion and Dodd, 1995b):

$$\frac{N(x, y, z, t)}{N_{\infty} + n_{\infty}} + \frac{n(x, y, z, t)}{N_{\infty} + n_{\infty}} = \frac{M(z, t)}{M_{eq}} =$$
(3.11)

$$=1-\frac{64}{\pi^{3}}\sum_{l=1}^{odd}\frac{(-1)^{\frac{l+m+n-3}{2}}}{l.m.n}\cdot\cos\left(\frac{\pi nz}{2c}\right)\cdot\left\{\frac{\gamma}{\beta+\gamma}\cdot\exp(-\beta t)+\frac{\beta}{\beta+\gamma}\exp\left(\frac{-tD\pi^{2}}{4}\left[\frac{l^{2}}{a^{2}}+\frac{m^{2}}{b^{2}}+\frac{n^{2}}{c^{2}}\right]\right)\right\}$$

Integrating these equations over the sample dimensions gives the following expression for the total mass uptake of water M_t :

$$\frac{M_t}{M_{eq}} = 1 - \frac{\gamma}{\beta + \gamma} e^{-\beta t} - \frac{\beta}{\beta + \gamma} \left(\frac{8}{\pi^2}\right)^3 \sum_{l=1}^{odd} \sum_{m=1}^{odd} \sum_{n=1}^{odd} \frac{1}{(l.m.n)^2} exp\left(\frac{-tD\pi^2}{4} \left[\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2}\right]\right) (3.12)$$



Fig. 3.1: Block sample geometry and coordinate system

3.2. Measurement and characterisation of moisture absorption in cured epoxy resins

3.2.1. Experimental

All samples were produced and stored as described in Chapter 2. Periodically, they were removed from the containers and weighed using the analytical balance to determine the percentage mass increase. The percentage mass increase, M_{t_i} was defined as:

$$M_t = \frac{(M_i - M_0)}{M_0} \times 100, \%$$
(3.13)

where M_i is the measured weight and M_0 is the original weight. The original weight of a sample was considered to be its 'dry' mass, and by original weight of the sample is meant the weight of sample when it was taken from the vacuum oven after the post-cure (Section 2.3). The M_t of representative CY1311 samples for a range of RH values are shown in Fig. 3.2a in the case of thin films and Fig. 3.2b in the case of block samples; note that the time *t* has units of hours on the abscissa. The ordinate is scaled so that the absorption process at low levels of RH is emphasized. As a result the water absorption curves of samples immersed in de-ionised water are not fully shown. The value of M_{eq} in the case of RH100% is ~8%, which is significantly higher than the values obtained at lower humidities. The CY1311 thin film samples have reached near dynamic equilibrium over the period shown in Fig. 3.2a, i.e. 1600h. The period of time required to obtain equilibrium in the case of block samples is ~6000h. The water uptake data of CY1301 resin is shown in Fig. 3.3a and 3.3b. Both types of CY1301 samples have not reached dynamic equilibrium over the investigated period of time. As it can be seen in Fig. 3.3b, the CY1301 epoxy resin block samples require more than 10,000 hours (>1 year) of conditioning to reach equilibrium. It can be concluded that for both resins the uptake M_{eq} at dynamic equilibrium is dependent on the relative humidity of the environment and M_{eq} increases with increasing RH.



Fig. 3.2: Water absorption of CY1311 resin: a) thin film samples, thickness 1.7mm; b) block samples RH 12%(■), 33%(◆), 43%(→), 75%(▲), and 100%(●), time t is in hours



Fig. 3.3: Water absorption of CY1301 resin: a) thin film samples, thickness 1.7mm; b) block samples. RH 12%(■), 33%(◆), 43%(−), 75%(▲), and 100%(●), time **t** is in hours

3.2.2. Calculation of the diffusion parameters

The initial values of the diffusion parameters (β , γ , D, and M_{eq}) were obtained from the slopes of the normalised uptake graphs as explained above (see Eq.3.7 and 3.8). The entire procedure is demonstrated in Fig. 3.4 for a CY1311 block sample conditioned in a container with saturated K₂CO₃, i.e. relative humidity 43%, kept at room temperature (RT). The value of M_{eq} is chosen so that a straight line is obtained at long times in Fig.3.4b. However, these values are correct only for 1D case, while the current example is for a block sample, i.e. 3D diffusion process should be considered. Hence, a programme was written in MATLAB to fit the experimental data (mass uptake) to Eq. 3.12 using the least squares method, where the initial values of the diffusion parameters for the fitting routine were obtained from normalized plots such as ones shown in Fig. 3.4. The Levenberg-Marquardt method was used to fit the data (Press et al., 1992). The block samples were selected as a datum because of their smaller surface area to volume ratio. This allowed more accurate determination of the 'dry' mass of these samples compared to the thin films used for dielectric measurements. The results obtained for Araldite CY1311 epoxy resin are presented in Table 3.1 and the corresponding values for Araldite CY1301 are given in Table 3.2. Both tables contain the initial values determined from the experimental data and the adjusted values from the fitting routine. The fitting algorithm was tested for convergence and the 95% confidence intervals for the nonlinear least squares parameter estimates are also given in Tables 3.1 and 3.2.



Fig. 3.4: Graphs used to obtain the parameters (β , γ , D, and M_{eq}) of anomalous water diffusion from the measurement data obtained for CY1311epoxy resin sample conditioned at RH43%, RT, time **t** in hours

| Graphical method | Units | RH75% | RH43% | RH33% | RH12% |
|--------------------------|--------------------------------|-------------|-------------|-------------|-------------|
| M _{eq} | % | 3.6 | 1.65 | 1 | 0.25 |
| k | h ⁻¹ | 0.295 | 0.383 | 0.316 | 0.050 |
| D | $m^{2}h^{-1}$ | 7.47E-07 | 9.70E-07 | 8.00E-07 | 1.26E-07 |
| β | h ⁻¹ | 1.54E-04 | 1.08E-04 | 1.08E-04 | 1.55E-04 |
| γ | h⁻¹ | 2.24E-03 | 1.56E-03 | 1.56E-03 | 8.33E-04 |
| Least Squares Fitting | Units | RH75% | RH43% | RH33% | RH12% |
| М _{еq} | % | 3.44±0.01 | 1.59±0.01 | 0.95±0.01 | 0.23±0.01 |
| D | m ² h ⁻¹ | 2.5±0.5E-08 | 2.7±0.5E-08 | 2.8±0.9E-08 | 1.3±0.8E-08 |
| β | h⁻¹ | 8.8±0.3E-04 | 9.7±0.3E-04 | 8.9±0.5E-04 | 6.0±1.4E-04 |
| γ | h ⁻¹ | 2.5±0.3E-03 | 2.7±0.3E-03 | 2.7±0.5E-03 | 1.0±0.6E-03 |

Table 3.1: Diffusion parameters of CY1311epoxy resin at different humidity levels

Table 3.2: Diffusion parameters of CY1301epoxy resin at different humidity levels

| Graphical method | Units | RH100% | RH75% | RH43% | RH33% | RH12% |
|--------------------------|--------------------------------|-------------|-------------|-------------|-------------|-------------|
| M _{eq} | % | 2.2 | 1.4 | 0.6 | 0.46 | 0.16 |
| k | h⁻¹ | 0.00197 | 0.00137 | 0.00187 | 0.00184 | 0.00187 |
| D | m ² h ⁻¹ | 4.99E-09 | 3.46E-09 | 2.21E-09 | 4.65E-09 | 4.75E-09 |
| β | h ⁻¹ | 7.62E-05 | 6.21E-05 | 8.13E-05 | 7.25E-05 | 4.24E-05 |
| γ | h ⁻¹ | 8.50E-05 | 7.55E-05 | 7.14E-05 | 8.09E-05 | 1.01E-04 |
| Least Squares Fitting | Units | RH100% | RH75% | RH43% | RH33% | RH12% |
| M _{eq} | % | 1.64±0.05 | 0.96±0.02 | 0.48±0.01 | 0.34±0.01 | 0.08±0.01 |
| D | m ² h ⁻¹ | 1.1±0.4E-08 | 1.0±0.3E-08 | 1.2±0.3E-08 | 9.7±4.2E-09 | 2.7±1.8E-08 |
| β | h⁻¹ | 3.4±0.5E-04 | 3.4±0.4E-04 | 3.6±0.3E-04 | 3.6±0.5E-04 | 2.9±0.9E-04 |
| γ | h⁻¹ | 0.9±0.3E-03 | 1.1±0.3E-03 | 1.1±0.2E-03 | 1.1±0.4E-03 | 0.9±0.4E-03 |

The values of the diffusion parameters given in Table 3.1 and Table 3.2 appear to be consistent with the initial hypothesis of a concentration independent absorption process. Significant deviations from the general trend in the values of the parameters occur only at the lowest values of the relative humidity. This can be explained with the very low value of M_{eq} at RH12% in both cases (CY1311 and CY1301). A difficulty in obtaining completely 'dry' (zero moisture level) samples and in maintaining stable RH over extended periods of time, and the measurement errors associated with the gravimetric measurements contribute to the uncertainty present in the fitted values. The measurement data were acquired over a period of time longer than a year. Occasionally, it was necessary to add de-ionised water in the containers with RH higher than the average humidity of the environment and also it was necessary to add salt in the containers with RH lower than the average humidity of the environment in order to

maintain a stable value of RH inside the containers. However some fluctuations in the RH were inevitable. The container with saturated K_2CO_3 needed least intervention, therefore the data acquired at RH43% is considered to be the most representative and used in the examples below.

The conditions for the validity of Eq.3.4 and 3.5 are satisfied for all RH levels since the characteristic diffusion constant k is at least an order of magnitude higher than the probability rates β and γ when one dimensional diffusion process is considered only. The values of the diffusion coefficient in the case of CY1311 are greater than those obtained for CY1301. The CY1311 samples are in a flexible state at room temperature, hence there are significant segmental motions of the polymer chains which may facilitate the diffusion process of water molecules, while the CY1301 samples are in glassy state, have smaller free volume than CY1311 samples and therefore longer times are need for the water molecules to penetrate inside the sample.

The ratio $\beta/(\beta + \gamma)$ gives the fraction of mobile water molecules and is approximately equal to 0.25 for the two resins and is independent of RH, although the values of γ and β are different in both cases. It has been shown in Chapter 2 that the difference between the two epoxy resins is the presence of a flexibilizer in CY1311 resin. The results of the GC/MS Analysis have suggested that the flexibilizer is a siloxane compound. It is expected that its side chains confer hydrophobic properties (Petrie, 2006). However, it can be concluded that the amount of flexibilizer in the cured CY1311 resin is not sufficient enough to affect the absorption process and the water absorption depends solely on the properties of the polymer matrix.

A MATLAB programme was used to fit Eq.3.12 to the experimental data and therefore to verify the consistency of the anomalous diffusion model with the actual uptake data obtained from the measurements. It was also used to compare the anomalous diffusion model with the Fickian model. An example is shown in Fig. 3.5 in the case of a CY1311 epoxy sample conditioned in environment with RH 43%. It was necessary to adjust the values of diffusion parameters for the Fickian model and a new fitting routine was implemented using Eq. 3.12 with $\gamma = 0$. The value of the diffusion coefficient according to the Fickian model is $D_F = 2.7 \pm 0.5E - 09 \text{ m}^2\text{h}^{-1}$ and the value of total mass at equilibrium is $M_{eq} = 1.59 \pm 0.01\%$. A good agreement was found between the experimental data and the anomalous model calculations based on the fitted values of the parameters given in Table 3.1 and 3.2. Also, the anomalous diffusion model fits the experimental data significantly better than the Fickian model. According to the anomalous model near equilibrium level is reached after 6000h. The result for a similar CY1301 sample is given in Fig. 3.6. The departures from a simple Fickian behaviour appear to be less pronounced in the case of CY1301 resin. In this case, the Fickian diffusion coefficient is $D_F = 7.9 \pm 0.4E - 10 \text{ m}^2\text{h}^{-1}$ and the value of long-term equilibrium mass is $M_{eq} = 0.48 \pm 0.01\%$. The value of the diffusion coefficient is much lower in the case of CY1301 and the equilibrium level is not reached even after 9000h. The insufficient time for the diffusion process to reach equilibrium and the underestimation of the initial value in the fitting routine of M_{eq} may be a reason why the diffusion process appears to be apparently more Fickian than in the case of CY1311.

In order to illustrate the anomalous character of the diffusion process in CY1301 resin, data acquired from a thin film sample with thickness 0.7mm was fitted. The result of the fitting routine is shown in Fig. 3.7 where once again the experimental data is compared with computed data from a Fickian and an anomalous diffusion model. In this case, only one dimensional diffusion is considered through the sample thickness *d*.



Fig. 3.5: Water diffusion in CY1311 epoxy resin, RH 43%, experimental data and model calculations



Fig. 3.6: Water diffusion in CY1301 epoxy resin, RH 43%, experimental data and model calculations



Fig. 3.7: Water absorption in CY1301 thin film sample, RH 75%, experimental data and model calculations

Both Fickian and anomalous model fit well the initial uptake for times less than 200h. However at t > 200 h only the anomalous model is in a good agreement with the experimental data, where the long term increase in moisture content is due to accumulation of bound moisture. Even for this very thin sample the anomalous model predicts a few years before the equilibrium level is reached, while the Fickian model predicts only a few hundred hours. It can be concluded that the Fickian model is not applicable to model the water absorption process in the epoxy resins studied here.

3.3. Modelling water diffusion in block samples

The aim of the modelling was to estimate the water profile in the block samples used for electrical breakdown experiments as a result of the conditioning of the samples in different environments. A MATLAB programme was used to calculate the moisture profiles in the block samples according to Eq. 3.11. An example is shown in Fig.3.8 in the case of a CY1311 sample conditioned in an environment with RH43%. The boundary condition is that the moisture on the surfaces of the sample is in equilibrium with the RH of the environment. The bottom profile gives the initial condition at time t=0 and the top one gives the moisture profile after 1680h (10 weeks). The time was chosen to match the typical waiting time before the treeing or void experiments were carried out, namely 10-12 weeks. The time step between the profiles is 168h (1 week) in Fig. 3.8. The profile line passes through the centre of the sample along its z-axis (height of the sample), in x=0, y=0 plane. The axes orientation and the sample geometry



Fig. 3.8: Moisture profile in CY1311 epoxy resin, RH 43%, after 1680h, time step 168h

are given in Fig. 3.1. The centre of the sample was chosen to be the origin of the Cartesian coordinate system. The small ripples in the profile result from the finite number of terms used for the series expansion. Similar results were obtained for the other experimental conditions but are not shown here for brevity. However, this approach allowed only the total mass uptake to be calculated but not the time evolution of the individual contributions of 'bound' and 'mobile' water. Equations 3.11 and 3.12 are valid only for a uniform block sample, which is another limitation of this model. For example, it is not possible to model a defect (e.g. void) inside the sample using the Eqs. 3.11 and 3.12.

In order to overcome the above stated drawbacks of the modelling based on series approximation of the partial differential equations used to describe the diffusion process, a FEMLAB model was developed based on Eq. 3.1 and Eq. 3.2. FEMLAB is an engineering tool that performs equation-based multiphysics modelling using finite element analysis (FEA). FEMLAB can be used to solve these partial differential equations directly. The advantage of modelling in FEMLAB lies in its greater flexibility and importantly the FEMLAB model does not use the approximation that $k \ll \beta, \gamma$. It allows different geometries and boundary condition to be defined easily. This can be used to model the water diffusion process in different types of samples used in the current study, e.g. thin films and block samples. Also, it can be used to model samples having defects or complex shape.

The profiles of the total moisture uptake were calculated again at the same time step as in the case of the series approximation so that a direct comparison could be made between the two numerical techniques, namely the series approximation and the FEA. The results of the FEA simulation are shown in Fig. 3.9. In this case the simulation time was again 1680h with the time step between the profiles being 168h. These profiles have a slightly more concaved shape than the ones computed previously by the MATLAB programme. As stated above, FEMLAB provides direct solution of the partial differential equations Eq. 3.1 and Eq. 3.2 unlike the series expansion which uses the approximation $k \ll \beta, \gamma$, which explains the difference between the two solutions. The FEMLAB solution is physically more realistic. The fractions of mobile and bound water are given in Fig. 3.10 a) and b), respectively. The water profiles are calculated along the z-axis (sample height) and the time step is 168h as before. The mobile water fraction penetrates the sample quickly, while the bound fraction builds up at a much slower rate and almost uniformly along the sample height. The total water content is calculated as the sum of the two fractions. The ripples in the profiles are due to the finite size of the elements used in the 3D modelling.

In the case of CY1311 the FEA shows that there is a small concentration gradient along the pin-plane distance, i.e. between z=0.008m and z=0.010m. After 10 weeks of conditioning the amount of moisture in this region is at least 80% of M_{eq} and the diffusion of the mobile fraction can be considered complete.



Fig. 3.9: FEA simulation of the total water content in CY1311 epoxy resin, RH 43%, after 1680h, time step 168h



Fig. 3.10: Moisture profiles in CY1311 epoxy resin, RH 43%, after 1680h, time step 168h a) mobile water b) bound water

Another simulation was carried out for the case of a CY1301 sample conditioned at RH43%. Figure 3.11 shows the profiles of total moisture uptake and Fig.3.12a) and b) shows the concentration of mobile and bound water molecules, respectively. The same computational procedure was used as in the previous example of CY1311 resin.

After 10 weeks of conditioning the amount of moisture in the pin-plane region is at least 50% of M_{eq} in the case of CY1301. The amount of absorbed moisture in the resin is less than the previous case due to the smaller diffusion coefficient.



Fig. 3.11: FEA simulation of the total water content in CY1301 epoxy resin, RH 43%, after 1680h, time step 168h



Fig. 3.12: Moisture profiles in CY1311 epoxy resin, RH 43%, after 1680h, time step 168h a) mobile water b) bound water

3.4. Modelling water absorption in thin film samples

The water diffusion process in thin film samples used for dielectric spectroscopy was modelled in a similar way as above. Only samples without sputter coated gold electrodes on them were considered in modelling the absorption process. The aim was to estimate the time required for the samples to reach a dynamic equilibrium with the environment. A photograph of a thin film sample is shown in Fig. 2.3b. Figure 3.13 shows the profiles of the total moisture uptake in the case of a CY1311 sample with thickness 1.6mm conditioned at RH75%. The profile line passes through the centre of the sample along its z-axis (thickness of the sample). The boundary condition again is that the moisture on the surfaces of the sample is in equilibrium with the RH of the environment. In this case the simulation time is 3000h (~4 months) and the time step between the profiles is 300h in Fig. 3.13. The simulation result shows that at least 3000h of conditioning are required for the sample to reach a dynamic equilibrium with the environment.

The simulation result for a CY1301 sample with thickness 1.6mm conditioned at RH75% is shown in Fig. 3.14. The simulation time is 8000h (~11 months) and the time step between the profiles is 800h. According to Fig. 3.14 at least 8000h of conditioning are required for the sample to reach a dynamic equilibrium with the environment in the case of CY1301 resin.



Fig. 3.13: FEA simulation of the total water content in a CY1311thin film sample, RH 75%, after 3000h, time step 300h



Fig. 3.14: FEA simulation of the total water content in a CY1301thin film sample, RH 75%, after 8000h, time step 800h

3.5. Modelling water desorption in thin films

In order to assess the possibility that the epoxy samples can lose moisture during the dielectric measurements, although the humidity in the cell was controlled via beakers with saturated salt solutions (see the next chapter), a simulation of the water desorption process was carried out. The three electrodes were modelled as non-penetrable boundaries. Because the epoxy samples used for the dielectric measurements had a diameter bigger than the diameter of the guard electrode, a part of the sample was still available for desorption. The size of the guard electrode was subtracted from the overall diameter of the sample in order to simplify the geometry of the model and to reduce the computational time. A diagram of the electrode arrangement is given in Fig. 3.15. A FEMLAB model was developed to model the desorption process. In this case, the initial condition was that the moisture is at dynamic equilibrium in the sample and desorption was allowed only from edge of the sample that was not covered by the top electrode. The values of the diffusion parameters used for the finite element simulation are taken from Table 3.1 (fitted values). The simulated water desorption profiles after 168h are shown in Fig. 3.16, where the extent of the top electrode is specified. The time step

between the profiles is 12h. The period of 168h was chosen for this simulation because it corresponds to the longest duration of the dielectric experiments conducted. It should be noted in Fig. 3.16 that the sample loses moisture only from its periphery and the amount of water between the electrodes remains constant. This is an important outcome regarding the consistency of the dielectric measurements. Also, the value of the total mass decrement was comparable to the one found during the dielectric measurements.



Fig. 3.15: Diagram of the electrode arrangement for the dielectric measurements



Fig. 3.16: Moisture desorption in a CY1311 epoxy resin sample, sandwiched between metal electrodes, RH 43%, after 168 hours

3.6. Chapter summary

Both epoxy resin systems under study CY1311 and CY1301 have shown anomalous (non-Fickian) water absorption. A MATLAB programming was used to fit the experimental data to the theoretical equations for anomalous diffusion and the validity of the model was demonstrated. FEMLAB modelling was used to simulate the water absorption and desorption behaviour in samples with different geometries and conditions. The two numerical methods, namely series approximation and finite element analysis that have been used yielded similar results in good agreement with the experimental data. The modelling allowed the amount of moisture (mobile and bound) to be predicted for any sample geometry, environment and conditioning time. In the case of block samples after 10 weeks of conditioning (typical waiting time before the breakdown experiments) the amount of moisture in the region is at least 80% of Meg in the case CY1311 and 50% of Meq in the case of CY1301. The simulations of water absorption process in thin films suggest that 3000h are required to reach a dynamic equilibrium in the case of CY1311 resin and the CY1301 require 8000h. The water desorption simulation has shown that the amount of moisture inside the sample between the measurement electrodes remains constant during the dielectric spectroscopy experiments.
Chapter 4: Dielectric properties of epoxy resins

In order to understand the relationship between temperature and absorbed moisture on the degradation processes in epoxy resin, it is necessary to first understand the electrical characteristics of the material. In particular the dielectric properties, electrical conduction and dielectric loss due to polarisation need to be clearly understood. To do this it is necessary to take a systematic approach in characterising the temperature and moisture dependence on the dielectric properties. In addition it is necessary to be able to separate bulk phenomena from interfacial processes. The latter may relate to the experimental method employed in the characterisation and not necessarily be involved in the processes leading to electrical degradation of the material. It is also necessary to ensure that the samples used in the characterisation are homogeneous, from the point of view of the temperature and absorbed water concentration, during the measurements otherwise interfacial effects may dominate and make more difficult the interpretation of bulk phenomena. Hence for the case of moisture absorption it is necessary to condition the samples until a uniform concentration exists in the material, i.e. to condition the samples in a known humidity environment for a time greater than, 1/k, (k is the characteristic diffusion constant) to ensure that the mobile fraction of absorbed moisture has reached a uniform concentration. This time is dependent on the sample thickness as well as the diffusion coefficient, D, and can be estimated from the measurements taken in Chapter 3. It is also critical when taking frequency domain measurements of the dielectric properties, particularly at frequencies down to 1 mHz that the temperature of the sample does not change significantly over the period of the measurements as this will lead to errors in the dielectric spectra.

In the current work, the dielectric properties of epoxy resins were studied using frequency-domain measurements and the results obtained are presented in this chapter. The samples were produced and conditioned as described in Chapter 2. The temperature and absorbed moisture dependencies of the dielectric spectra were investigated and the measurement data were analysed in terms of the Dissado-Hill model of the dielectric relaxation. The dielectric spectra have been found to comprise both interfacial features and bulk response. The interpretation of the spectra presented here differs substantially from the previous explanations published in the literature.

The dielectric properties of Araldite CY1301 have been studied using frequencydomain spectroscopy and several processes have been found to contribute to the overall spectrum (Griseri, 2000; Zou, 2007). According to their characteristic frequency these processes can be classified as low-, mid- and high frequency processes. In Griseri, (2000) the low frequency process was attributed to DC conduction, the mid-frequency dispersion was related to the glass transition temperature and recognised as α -relaxation and no particular interpretation was given to the high frequency process. However, no account was provided for the level of absorbed moisture in the samples in her work. Similar interpretations for the low frequency process were proposed in Zou (2007) and Zou *et al.* (2008), where this process was attributed to either DC conduction (at low temperatures and low levels of absorbed moisture) or quasi-dc (QDC) charge transport (at high water content and high temperatures). However, the origin of the midfrequency dispersion has been related to the presence of 'bound' water molecules in the epoxy matrix and again no interpretation was given for the high frequency process (Zou, 2007).

4.1 Introduction

The principle of operation of the Frequency Response Analyzer (FRA) is based on direct vector measurement of the ratio of ac voltage applied across a capacitive sample and the ac current through it at a given frequency, ω , i.e. a measurement of impedance, $Z(\omega)$, (Jonscher, 1996). A schematic diagram of a FRA with a dielectric interface, a reference capacitor and a sample connected to it is shown in Fig. 4.1. The FRA consists of a Generator and two "Correlators". The sinusoidal applied voltage V₁ of a set frequency and amplitude is produced by the Generator. This voltage is applied to a sample, which may be a parallel plane capacitor of a known geometry. Then, the current I_S through the sample is fed to an operational amplifier configured as a current to voltage converter. This eliminates any spurious voltage drops that may occur during the measurement by providing a virtual earth to the sample. The output of the amplifier (V₂ \propto I) is fed to a Correlator, which correlates this signal with the input voltage V₁. Two integrals are calculated in the process of correlations of the two signals (Jonscher, 1996):

$$J_p = \int_0^{2\pi N_c/\omega} I_s(t) \sin(\omega t) dt$$
(4.1)

$$J_q = \int_0^{2\pi N_c/\omega} I_S(t) \cos(\omega t) dt$$
(4.2)

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Fig. 4.1: Schematic diagram of a FRA with a dielectric interface and a variable reference capacitor, adapted from Liu (2010)

where J_p and J_q are the parallel and quadrature integrals, respectively and the integration is performed over N_c cycles. The correlation procedure is based on the following property of integrals of harmonic functions of integer frequencies ω_1 and ω_2 :

$$\int_{0}^{\pi} \sin(\omega_{1}t) \sin(\omega_{2}t) dt = 0$$

$$\int_{0}^{\pi} \cos(\omega_{1}t) \cos(\omega_{2}t) dt = 0 \quad \text{if } \omega_{1} \neq \omega_{2} \quad (4.3)$$

$$\int_{0}^{\pi} \sin(\omega_{1}t) \cos(\omega_{2}t) dt = 0$$

If $\omega_1 = \omega_2$, then the first two integrals have a finite value $\pi/2$, while the third one is always zero.

The current I_S comprises two parts. The first one has a phase shift φ with respect to the frequency ω of the applied voltage V_1 and the second is a random noise component with wide range of frequencies Ω that differs from ω . The total current I_S is given below (Jonscher, 1996):

$$I_{S}(t) = A[\cos\varphi\sin(\omega t) + \sin\varphi\cos(\omega t)] + \text{noise}$$
(4.4)

where A is the amplitude of the signal. Integrating the expression in the square bracket according to Eq. 4.1 and 4.2 gives $A\cos\varphi$ and $A\sin\varphi$, respectively. The tangent of the phase angle φ , is obtained from the ratio of the two integrals, while A² is obtained from the sum of the squares. If the period of integration is sufficiently long compared with

the period of the lowest noise frequency, then the noise component has no significant contribution. The above procedure is known as correlation of the current signal with the applied voltage, which aims to minimize the effect of the noise present in the system. The applied signal V_1 and the sample signal V_2 are measured by two phase sensitive voltmeters and are fed to the two channels of the FRA as shown in Fig. 4.1.

The dielectric interface contains capacitors and resistors, which are consecutively switched to match the frequency-dependent impedance of the sample (Jonscher, 1996). A requirement of the Interface is to have an amplifier characteristic, which is frequency independent over the entire measurement range (typically 10^{-4} - 10^{5} or 10^{7} Hz). The impedance $Z = (i\omega C)^{-1}$ of a low-loss capacitor is inversely proportional to frequency; hence the required range of magnitudes of the resistors in the feedback circuit of the Dielectric Interface should be as many as the number of decades in the frequency range.

A typical frequency sweep starts with the highest frequency in the specified range and continues by decrementing the frequency in equal steps on a logarithmic scale with a given number of points per decade. The FRA measurements are usually automated by means of a personal computer. It is important to automate the data acquisition process since a single cycle can take up to 3 h at the lowest frequency and the integration is usually performed over several cycles. Hence, the entire frequency sweep can take several days for a fixed temperature and even longer if several temperature levels are considered. The lower limit of conductance G that can be measured using this technique is 10^{-13} S, while $tan\delta$ can be measured in the range $10^{-4} < tan\delta < 10^3$ depending on the frequency being measured and the sample capacitance and conductance.

4.2. Experimental

The dielectric measurements were carried out on thin film samples of thickness 0.7 ± 0.1 mm and 1.7 ± 0.1 mm and a diameter of 70 mm. All samples were prepared and stored as described in Chapter 2. A sufficient time was allowed for the water absorption process to reach near saturation level. Hence, all samples were measured at times $t \gg 1/k$, where k is the characteristic diffusion constant, when 1D diffusion process is considered and both mobile and bound water molecules were present into the samples (see Chapter 3). A special cell enclosed in a temperature controlled oven shown in Fig. 4.2 was used for the dielectric measurements, which allowed stable values of

temperature and relative humidity to be maintained and monitored during the experiments (Zou, 2007). The saturated salt solutions used to maintain the humidity in the cell were the same as in the storage containers (see Chapter 2). The only exception was in the case when samples immersed in deionised water (RH 100%) were measured. In this case a beaker with NaCl, instead of deionised water, was used to provide a high level of RH but to avoid possible condensation inside the cell at higher temperatures. The temperature and humidity lags of the system were measured and care was taken to ensure enough time for the sample to reach equilibrium before measuring its impedance. A three-electrode configuration was used for the measurements, shown in Fig. 4.2 and Fig. 4.3. The three electrodes were made from brass and sputter coated with gold to ensure good contact. The HV electrode was connected to the voltage generator side of the dielectric interface and current flow through the material measured using the LV electrode, connected to the I input of the dielectric interface. The guard electrode was used to eliminate the influence of surface currents, which may obscure the bulk response of the material. The weight of the guard electrode was used to load a compression spring and provide mechanical force to the LV measurement electrode to ensure good contact with the epoxy sample. In this way, the volumetric expansion of the epoxy sample, which occurs when samples are heated to higher temperatures, was accommodated. The values of the temperature and relative humidity during the experiments were monitored by a temperature and humidity probe Digitron 2020R placed in the cell via a gland located in the side wall of the sealed chamber.



Fig. 4.2: The electrode system for dielectric spectroscopy



Fig. 4.3: A photograph of the measurement cell

Connections from the measurement electrodes and the dielectric analyser were made using coaxial bulkhead connectors (see Fig. 4.3) ensuring that stray capacitive currents are diverted to earth and not measured by the dielectric analyser. The complex impedance of the samples was measured as a function of frequency using a Solartron 1255HF frequency response analyser (FRA) and a Solartron 1296 dielectric interface. In this technique, the amplitude and phase of the electric current flowing in the sample due to an applied AC electric field between two parallel plate electrodes is measured (Jonscher, 1983). For consistency, the same magnitude of applied electric field was used for the samples having different thicknesses. The magnitude of the applied voltage was therefore scaled with the sample thickness. Two voltage levels were used 1.5V rms and 0.6V rms for samples with thicknesses 1.7 mm and 0.8 mm, respectively. For all samples the dielectric response was measured over the frequency range 3.7×10^{-4} to 1.0×10^5 Hz. The data were acquired over two cycles of integration and 7 data points per decade were taken. In order to control the measurement temperature, the measurement chamber was placed in a Genlab oven with a Eurotherm 2204 temperature controller to minimise temperature fluctuations during the measurements. The temperature was kept within $\pm 1^{\circ}C$ of the target level by the controller during the measurement. The dielectric properties of CY1311 samples were measured over the temperature range 20 to 60°C and the corresponding temperature range was 20 to 80°C for CY1301 samples. In this way the CY1301 samples were measured both below and above their glass transition temperature, while the CY1311 samples were tested to at least 20°C above it.

4.3. Results

Some results from the dielectric spectroscopy measurements on CY1301 and CY1311 epoxy resin obtained during the current research project are presented in Dodd et al. (2010a, 2010b).

4.3.1. Dielectric response of Araldite CY1301

The dielectric response of a 'dry' (as defined in Section 3.2.1) CY1301 sample at different temperatures is shown in Fig. 4.4. Similar type of responses have been observed in (Zou, 2007; Griseri, 2000) for the same epoxy resin. The dielectric response at 20°C and 40°C, well below the glass transition temperature, T_g, is almost frequency independent or 'flat' (as defined by Jonscher, 1996) when plotted against frequency on a log-log plot. The real part of the permittivity, ε ', is constant over the measured frequency range and the imaginary component, ε '', is dominated by instrumental noise at frequencies below 100Hz. At higher frequencies, the imaginary component increases above the noise level but remains temperature independent indicating an instrumental response. At a temperature of 60C, at 10C above the glass transition temperature, the real component, ε ', begins to increase at low frequencies <0.001Hz and the imaginary component becomes greater than the instrumental noise. At a temperature of 80°C, 30°C above the glass transition temperature for this resin, two separate dielectric processes become prominent; a low frequency response where the slope of the real part of permittivity becomes close to -1, and a mid frequency dispersion where a increment in the real part of the permittivity is observed as well as a corresponding peak in the imaginary part of the permittivity. The dielectric spectra above and below the glass transition temperature is fundamentally different with dielectric relaxation processes only occurring in this frequency range when the epoxy resin is above its glass transition temperature. Although this may be suggestive that additional segmental motion of the polymeric molecular chains may be responsible for the observed relaxations, absorbed moisture is also implicated as described below for samples measured at 80C.



Fig. 4.4: Real (solid markers) and imaginary (open markers) parts of the relative permittivity of epoxy resin CY1301 at temperatures $20^{\circ}C(\blacksquare)$, $40^{\circ}C(\diamondsuit)$, $60^{\circ}C(\blacktriangle)$ and $80^{\circ}C(\boxdot)$, sample thickness 1.7mm, dry sample

A master plot of the humidity dependence of the dielectric spectra at 80°C is shown in Fig.4.5 of four samples conditioned in containers with saturated salt solutions of LiCl, MgCl₂, and NaCl and de-ionised water (as described in Section 2.4) having relative percentages of absorbed moisture 0.21%, 0.46%, 1.28% and 2.55%, respectively. The master plot is a normalization technique, which consists in shifting the spectra along the horizontal and/or vertical axes, so that they are made to coincide with each other and a single response curve is obtained (Jonscher, 1983). In Fig. 4.5, the values of the absorbed moisture in each sample and the corresponding frequency shifts are given below the spectra. The spectra are normalized with respect to the highest humidity data. The four spectra coincide over the entire frequency range producing a single 'master' curve that covers over 10 decades of frequency. The real and the imaginary part of the permittivity appear almost parallel at the very low and the very high end of the frequency range. This behaviour can be described by Eq. 1.10 and characterises QDC charge transport. The divergence from parallel real and imaginary parts can be explained by the presence of DC conduction in the sample which has an effect only on the imaginary component of the permittivity. The DC conduction process makes the slope of ε '' equal to -1. The process in the mid frequency range characterised by a dispersion in the real part and an associated loss peak in the imaginary can be described by Eq. 1.9.



Fig. 4.5: Master plot of the humidity dependence of CY1301 samples, temperature 80° C, thickness 1.7mm

4.3.2. Dielectric response of Araldite CY1311

The dielectric response of a 'dry' CY1311 sample at different temperatures is shown in Fig. 4.6. The glass transition temperature of this particular resin is 0°C; hence all spectra are obtained above this temperature. These spectra closely resemble Fig. 4.5, i.e. the response of CY1301 at 30°C above its T_g , but shift with frequency with increasing temperature. Due to the lower glass transition temperature of CY1311 epoxy resin, it was also possible to obtain master plots for both temperature and humidity dependence on the dielectric response. A master plot of the dielectric spectra obtained at different temperatures from a sample conditioned in environment with RH30% is shown in Fig. 4.7. The locus of the translation point is given below the master curve and the spectra are normalised with respect to the data obtained at the highest temperature. The master curve again comprises two processes: a QDC and a midfrequency dispersion. As a consequence of the lower glass transition temperature of CY1311, it was possible to take measurements at much higher relative temperatures (from the glass transition temperature) and the low frequency dependence of the QDC process is better revealed than the case of CY1301.



Fig. 4.6: Real (filled) and imaginary (open markers) parts of the relative permittivity of epoxy resin CY1311 at $20^{\circ}C(\clubsuit)$, $40^{\circ}C(\clubsuit)$, and $60^{\circ}C(\clubsuit)$, sample thickness 1.7mm, dry sample



Fig. 4.7: Master plot of the temperature dependence of CY1311 sample, absorbed moisture 0.6%, thickness 1.7mm

The humidity dependence on the dielectric spectra of four samples, conditioned in environments with RH 15%, 30%, 75% and 100% and the corresponding mass uptakes prior to the dielectric measurements were 0.21%, 0.72%, 3.0%, and 7.2%, respectively. The locus of the translation point is given below the master curve and the spectra are normalized with respect to the highest humidity data. In this case, the high frequency

ends of spectra appear to coincide, however there are significant differences in the mid and low frequency regions. The increment of ε ' associated with the mid-frequency dispersion appears to have varying amplitude from sample to sample. In the low frequency region, the real and imaginary parts of the permittivity do not run parallel to each other as expected from a QDC response. In this region, the slope of ε '' is equal to -1, while ε ' has a slope greater than -1, which varies from sample to sample. The increment in ε ' associated with this additional dispersion is of an order of magnitude greater than that expected from the underlying QDC. Such large increments in the real part of the measured permittivity can be obtained when the polarisation phenomenon occurs over a small thickness of the sample, as described by Eq. 1.16, as the area of the sample remains constant. Hence, the spectra in Fig. 4.8 suggest that another dispersion process takes place at low frequencies in samples with higher water content, consistent with Maxwell-Wagner interfacial polarisation as described by Eq. 1.11. This new dispersion process occurs at lower frequencies than the mid-frequency dispersion previously described. The overall features of the process imply a Maxwell-Wagner interfacial polarization related to the increased water content in the samples.



Fig. 4.8: Master plot of the humidity dependence of CY1311 samples, temperature 30°C, thickness 1.7mm

4.3.3. Comparison between the dielectric responses of CY1311 and CY1301 resins

Figure 4.9 shows a comparison between the dielectric properties of CY1311 and CY1301 at the same temperature (~30°C) above their respective glass transition temperatures. The CY1311 sample was conditioned in an environment with RH15% and the level of absorbed moisture in the sample was 0.2%, while the CY1301 sample was conditioned at RH33% and the corresponding mass uptake was 0.4%. Although the moisture content was slightly different, Fig. 4.9 demonstrates that the dielectric behaviour of epoxy resins at the same temperature above their glass transition temperature and with similar moisture contents give rise to dielectric behaviour which is effectively equivalent. Given that CY1301 and CY1311 have different chemical constituents (see Chapter 2) and therefore a different cured molecular structure, the dielectric measurements show that the electrical properties are governed only by humidity and the relative temperature above its glass transition temperature. The chemical constituents just determine the glass transition temperature of the final cured resin.



Fig. 4.9: Real (solid) and imaginary (open markers) of the relative permittivity of epoxy resin CY1301, 80°C (■) and CY1311, 30°C (●), thickness 1.7mm.

4.4. Equivalent circuit model

The dielectric measurements above T_g were analysed in terms of the following equivalent circuit given in the inset to Fig. 4.10 (Dodd et al., 2010b). All processes are considered to be independent and additive towards the total response in a parallel circuit configuration. Hence such a circuit model was initially chosen to fit the dielectric data. The circuit represents four processes in parallel: a QDC, a mid-frequency dispersion (D), a dc conductance (G) and a frequency independent capacitance (C_{∞}). The fit to the experimental data was found to be good and an example is shown in Fig. 4.10, where the experimental data points are shown with markers and the overall fitted response is plotted with thickened lines.

The response is dominated by two processes, namely quasi-dc (QDC) conduction, characterised by parallel real and imaginary parts in a log-log plot at the very low and very high frequencies measured, and a mid-frequency dielectric dispersion (D). The dispersion (D) is superimposed on the QDC response in the mid-frequency range. QDC and D are circuit components that obey the Dissado-Hill model for dielectric relaxation. Each of them is fully described by four parameters: characteristic frequency, amplitude, and two power law exponents characterising the frequency dependence below and above the characteristic frequency of the particular process, in accordance with Eq. 1.8. The dc conductance (G) is important only at low frequencies. It affects only the imaginary part of the complex capacitance and leads to a small difference in the power law exponents for the real and imaginary components of the capacitance (and hence permittivity) in the lowest frequency range measured. The contribution of C_{∞} is significant at the highest frequencies measured as an additive term to the real part of the complex capacitance.

Each Dissado-Hill process is characterised by four independent parameters: two power law exponents, a characteristic frequency and a magnitude. Hence, the total number of free parameters to fit the data was ten (four for each Dissado-Hill component, one for the dc conductance and one for the frequency independent capacitance, respectively) according to the equivalent circuit shown in Fig. 4.10. Fitting the experimental data to an equivalent circuit at different temperatures and levels of absorbed moisture allowed the individual contribution of each process and their temperature and humidity dependence to be obtained. A non-linear least squares algorithm was used as a fit routine. The results of the fitting program are presented in Appendix C.



Fig. 4.10: The equivalent circuit representing dielectric data obtained (inset) and the individual contributions of each process in a log-log plot, experimental data points: real capacitance (◊) and imaginary capacitance (○); fitted data in thickened lines

4.4.1. Temperature and humidity dependence of the dielectric response above the glass transition temperature

The characteristic parameters of the processes comprising the dielectric spectra have been obtained by fitting the experimental data to the equivalent circuit shown in Fig. 4.10. This allowed the temperature and humidity dependence of the characteristic frequency and amplitudes of the dispersive circuit elements to be obtained together with the magnitude of the DC conductivity (Dodd et al., 2010a; Dodd et al., 2010b). Arrhenius plots of the characteristic frequency (as described in section 1.2.2 and defined in Eq. 1.18) of the QDC process at different levels of absorbed moisture are shown in Fig. 4.11a and the corresponding plots of the magnitude of the DC conductance are presented in Fig 4.11b. The values of the activation energy W of the process can be calculated using the following expression (Jonscher, 1983):

$$W = 0.198/\Delta, eV \tag{4.5}$$

where Δ is the change per one decade of the frequency shift and the abscissa is expressed in terms of $10^3/T$, K^{-1} .

The values of the activation energy for the QDC process are in the range 1.0-1.2eV and have not been found to have any distinguishable dependence upon the amount of absorbed moisture. At high moisture uptakes, the values of the activation energy for the



Fig. 4.11: Temperature and humidity dependence of: a) characteristic frequency of QDC process b) DC conductance. Water uptake $0.20\%(\blacksquare)$, $0.72\%(\diamondsuit)$, $3.0\%(\bigstar)$ and $7.2\%(\textcircled)$, CY1311 resin, sample thickness 1.7mm

DC conductance are similar to those found for the QDC process and are in the range of 1.0-1.1eV, while at lower moisture contents they are in the range 1.3-1.4eV.

The departure from Arrhenius behaviour observed at very high moisture content (>3%) and high temperature in Fig.4.11b is probably due to a poor fit between the experimental data and the circuit model in this case. The result of the fitting programme for a sample conditioned in de-ionised water (mass uptake 7.2%) is shown in Fig. 4.12 The equivalent circuit shown in Fig. 4.10 was not able to reproduce the real part of the relative permittivity successfully, even though the imaginary part was fitted reasonably well. A line with slope -1 is drawn in Fig.4.12 as a reference. The slope of the real part of the permittivity of the measurement data is bigger than -1, while the imaginary components is parallel to the reference line. This suggests an additional relaxation process, which has not been included in the equivalent circuit appears to be the reason for the poor fit. This process occurs at low frequencies and only in samples with high moisture content, see Fig. 4.8. The increment of the real part of permittivity associated with it is several orders of magnitude suggesting a dispersive interfacial polarization (Jonscher, 1983) as its origin.



4.12: The dielectric response of a CY 1311 sample (mass uptake 7.2%), thickness 1.7 mm and the fitted data according to the equivalent circuit shown in Fig.4.10, real (◊) and imaginary (○) capacitance; fitted data in thickened lines.

The real and imaginary part of the dielectric susceptibility are Kramers-Kronig related (Lovell, 1974). As was stated earlier Kramers-Kronig relations are consequence of the causality principle and they are special case of Hilbert transform. Since the Hilbert transform of a constant is zero, an attempt was made to determine the magnitude of the dc conductance using the Kramers-Kronig transformation of the real part of the capacitance. This should give the imaginary capacitance but excluding the dc conductance component. Subtracting this from the measured imaginary capacitance should in theory give a residual equal to the dc conductance component. However it was found that a significant truncation error occurs in the transformation of the real part of the capacitance when the QDC low frequency power law approaches 1.0 even though the QDC process itself is KK compatible. The analysis of the truncation error suggested that the response has to be extrapolated many orders of magnitude (more than 10 decades) in frequency towards zero and outside the range of the experimental data observed. Although, the computational procedure of such extrapolation was feasible, its credibility was not clear and further attempts to calculate the magnitude of the dc conductance on the basis of the Kramers-Kronig transform were abandoned. As a result the magnitude of the dc conductance was obtained solely on the basis of the equivalent circuit model.

The moisture dependence of the dc conductance and characteristic frequency of the QDC process in CY1301 at temperature 80°C is shown in Fig. 4.13. The dc conductance shows an exponential dependence on the absorbed moisture and a power law relationship has been found to be a better fit for the characteristic frequency of the QDC process (Dodd et al, 2010b). From the data presented in Fig. 4.13, the following empirical relations can be suggested in the case of Araldite CY1301:

$$\sigma_{dc} = A_1 \exp\left(2.8x\right) \tag{4.6}$$

$$f_{ODC} = A_2 x^{3.9} \tag{4.7}$$

where A_1 , and A_2 are proportionality constants and x(%) is the level absorbed moisture in the sample. Given the dependence of the magnitude of both processes upon the moisture uptake, it is likely that the charge transport in both QDC and DC conduction is due to charges moving with the absorbed water system within the epoxy resins. The DC conduction is likely to occur as a result of charge transport on percolation clusters that cross the epoxy resin sample, whereas the QDC behaviour corresponds to transport on sub-percolation clusters (i.e. ones that are not connected across the sample). Therefore, it is likely that the same charge carriers are involved in the 'true' DC conduction and the QDC response, with the different responses arising because of the connectivity or otherwise of the transport system. The high activation energies involved taken together with the absence of charge transport in the glassy material indicates that the charge transport requires the aid of large scale segmental polymer motions in order to transfer the charge carriers. This implies that it is dynamical percolation that is involved (Kozlovich et al., 1998; Schönhals and Donth, 1984) with the segmental motions moving chains that carry absorbed water molecules to positions where the charge carrier can be transferred from chain to chain.

An example of charge transport mechanism dependent on water content in polymers is proton transfer in Nafion fuel cell membranes (Moilanen et al., 2008). It has been found that water dynamics slows significantly as the hydration of Nafion membrane decreases and that the proton-transfer kinetics is strongly correlated to the dynamics of water. The dependence of proton-transfer in Nafion on the hydration level is similar to what has been found in the current study regarding ω_c of the QDC process. This may suggest that proton transfer along hydrogen bonded water clusters is a possible charge transport mechanism in the case of epoxy resins as well. A further discussion on the charge carriers and the transport mechanism involved is presented in Chapter 7.





4.4.2. Bulk and interfacial processes

The analysis so far implied that QDC is a bulk charge transport process. In order to verify that and to ascertain the origin of the mid-frequency dispersion D, the dependence of the measured capacitance upon sample thickness was investigated. A bulk response would have a permittivity that is a property of the material and for parallel plate geometry would give a capacitance that is inversely proportional to the sample thickness, as in Eq. 4.8, with $\varepsilon_0\varepsilon_r$ constant for given conditions of temperature and absorbed moisture.

$$\varepsilon_0 \varepsilon_r = \frac{d}{A} \times C_{meas} \tag{4.8}$$

where *A* is the electrode area and C_{meas} is the measured capacitance. Since an interface capacitance has a value that is not dependent upon the sample thickness, use of Eq. 4.8 gives an apparent value for $\varepsilon_0\varepsilon_r$ that increases with sample thickness *d*. Samples with two different thicknesses were therefore measured under the same conditions, so as to identify bulk and interfacial features of the response. The results for the real part of the relative permittivity of two samples with thicknesses 0.8 and 1.7mm measured at 30°C are shown in Fig. 4.14. The samples were conditioned in a container with relative humidity 30% and the respective relative mass uptakes were 0.7%. The dispersion (D) shows a pronounced thickness dependence, which can be seen in the different magnitudes of the dielectric increment for the two samples. Therefore, it can be

concluded that the dispersion (D) is an interfacial feature. On the other hand, the two spectra coincide at the very low and high frequencies, showing that the QDC process is a bulk, i.e. material, property. A similar dielectric response (QDC and superimposed mid-frequency dispersion) was observed in the case of hydrated biopolymers (Shablakh *et al.*, 1984), where the mid-frequency dispersion has been found to be electrode dependent and hence interfacial while the QDC process has been identified as a bulk response.



Fig. 4.14: Real components of the relative permittivity of CY1311 epoxy resin samples at 30°C, sample thickness 0.8 (Δ) and 1.7mm (\Diamond), 0.7% mass uptake

An investigation of the electrode-sample contact was carried out by sandwiching a sample between two glass plates. This sample had been conditioned in a container with a high relative humidity (75%), which facilitated the adhesion between the epoxy sample and the glass plates. Photographs reveal three types of contact between the epoxy sample and the glass plates, namely no contact, single-sided, and double-sided contact (see Fig.4 15). The different types of contact can be distinguished by the colour of the reflected light in Fig. 4.15 due to the differences in the corresponding refractive indices of the materials in contact can be thought as a combination of R-C elements with both the QDC and DC conduction combining to charge the capacitance of the regions of poor contact. This would explain the introduction of an interfacial dispersion process (D) into the spectra. Electrodes of sputtered gold would eliminate these regions of poor contact and hence remove the dispersion D.



Fig. 4.15: Contact zones between an epoxy resin sample and two glass plates

In order to investigate further the possible interfacial nature of the dispersion (D), one of the CY1311 samples (thickness 1.7mm) was sputter coated with gold (see Section 2.3). The dielectric spectra obtained at 60°C before and after the sputtering are presented in Fig. 4.16. The initial dispersion (D) of dielectric increment of e' of one decade was replaced by a new dispersion (D1) having much higher dielectric increment of 3 orders of magnitude but occurring at lower frequency. The shape of this new relaxation process closely resembles Maxwell-Wagner-Sillars (MWS) interfacial polarization, with the frequency exponent q of $\varepsilon' \propto \omega^{-q}$ being greater than 1, see (Jonscher, 1983) Similar results were obtained with a CY1301 sample above the glass



Fig. 4.16: Real (solid) and imaginary (open markers) of the relative permittivity of an epoxy resin sample CY1311, at 60°C, before the sputter coating (●) and after the sputter coating (■), thickness 1.7mm, mass uptake 0.72%.

transition temperature, which are not shown here for brevity. It is suggested the sputtered gold electrodes had created a nearly homogeneous layer and thus eliminated the dispersion process (D), with the new dispersion (D1) attributed to a blocking effect of the gold to any ions that might be present in the bulk of the epoxy resin. The temperature master plot of the dielectric response of a CY1311 gold coated sample is shown in Fig. 4.17. All individual spectra conform to a single master curve over more than 10 decades of frequency. The increment in the real part is associated with the dispersion process D1 as stated above. At frequencies below the characteristic frequency of the D1 dispersion process, evidence for a diffusion process is found in the real part of the permittivity. The slope of the real part has a slope of approximately -0.5 as expected for a diffusion process; see Table 1.2, case (e). The imaginary part of the permittivity has a slope of -1 indicating a parallel conductance term.



Fig. 4.17: Master plot of the temperature dependence of gold coated CY1311 sample, absorbed moisture 0.72%, thickness 1.7mm

The original parallel equivalent circuit was therefore modified to incorporate the interfacial effects of poor contact in the case of the uncoated samples and interfacial polarisation in the case of the gold coated samples. These two cases are illustrated schematically in Fig. 4.18. The modified equivalent circuit is shown in the inset to Fig. 4.19. Instead of the dispersion Dissado-Hill element describing the mid-frequency dispersion, D, a series network of a QDC component representing the bulk material and having the same parameters as the parallel connected QDC but in series with a series

blocking capacitance, Cs, representing the air-gap in the case of imperfect contact or the interface region in the case of the gold coated samples. The same parameters were used to describe the QDC process in both branches of the equivalent circuit. In the case of the gold coated samples it is necessary to set the amplitude of the parallel connected QDC component to zero as the interface region will extend across the entire area of the sample. The aim of this analysis was to see if the equivalent circuit would have sufficient degrees of freedom to encompass the range of dielectric data observed and therefore support the interpretation of the interfacial phenomena described above.

In the case of gold coated samples C_s represents the blocking capacitance as a result of a formation of electrical double layer. The charges (most likely ions) that take part in the QDC transport are not able to cross the gold layer and therefore accumulate at the gold interface, where they form a double layer and give rise to Maxwell-Wagner-Sillars (MWS) interfacial polarization D1. The diffusion process can be related either to formation of a diffuse double layer (Lewis, 2004) further away from the electrode or due to charge transport across the interface, which is facilitated by the field intensification in this region.



Fig. 4.18: Sample-electrode interface zone: a) uncoated sample; b) gold-coated sample (not in scale)

The modified equivalent circuit was used to model the experimental data in both cases. The result for an uncoated sample is shown in Fig. 4.19 where a typical experimental data set was chosen. The modified circuit was able to reproduce the overall shape of the dielectric response using a lower number of free parameters. It



Fig. 4.19: The modified equivalent circuit representing the dielectric data (inset); Real (filled) and imaginary (open markers), real (solid line) and imaginary (dashed line) fitted data in the case of uncoated sample

required only 7 free parameters, 4 for the QDC process as before and one for each of the processes C_{inf} , C_s and G. The values of the parameters, describing the QDC, C_{inf} and G were taken from the original equivalent circuit with some adjustment. Another example is shown in Fig. 4.20 in the case of gold-coated sample. In order to model these experimental data only the magnitude of the QDC process and C_s were adjusted from the previous example of an uncoated sample, the values of the remaining parameters were kept the same. The amplitude of the QDC process in the branch parallel to C_{inf} and G was set to zero, hence the charges involved in the QDC process are charging the interfacial blocking capacitance C_s created by the gold layer, which is in series with the bulk QDC. The only discrepancy between the model and the experimental data occurs in the low frequency range, where the experimental data suggest that a possible diffusion process takes place, however such process has not been modelled in the equivalent circuit.

In conclusion, the modified equivalent circuit possesses the necessary degrees of freedom to reproduce the experimental data reasonably well and it is believed that it models accurately the physical processes that give rise to the dielectric spectra observed in this study.



Fig. 4.20: The modified equivalent circuit representing the dielectric data (inset); Real (filled) and imaginary (open markers), real (solid line) and imaginary (dashed line) fitted data in the case of gold coated sample

4.5. Chapter summary

In this chapter the dielectric response of epoxy resins was investigated as a function of temperature and humidity. Above the glass transition temperature both resins studied here have shown similar dielectric response, although CY1311 is a chemically modified version of CY1301 with added plasticizer. The controlling parameters were found to be dependent on the temperature above the Tg of the epoxy resin and the amount of absorbed moisture with the chemical constituents of the epoxy resin controlling the glass transition temperature. Both bulk and interfacial features have been identified to contribute to the total response. The dispersion process in the mid-frequency region has been shown to be due to the imperfect contact between the sample and the electrodes. The evidence suggest that the mid-frequency dispersion (D) is an interfacial feature and should not be confused with a material property such as an α -relaxation (the rubber phase material response). The bulk processes comprised a QDC process, a dcconduction and frequency independent capacitance. The bulk dc conductivity and the characteristic frequency of the QDC in CY1311 epoxy resin were found to have similar activation energies in the range 1.0-1.4eV and hence a common origin for the charge carriers involved. In the CY1301 resin, at temperature above the glass transition

temperature the dc conductance was found to be exponentially dependent upon water content with the characteristic frequency of the QDC exhibiting a power-law dependence upon water content. The identification of a QDC process indicate that the dominant bulk charge transport conforms to a cluster transport model in which charges, possibly ions, are displaced within clusters at high frequency and between clusters at low frequency with the lower frequency power law. The implications of absorbed moisture and temperature on the electrical degradation mechanisms will be explored in the next chapter.

Chapter 5: Electrical degradation in epoxy resins

5.1. Introduction

So far in this work, the water absorption process and its influence on the electrical properties of epoxy resins have been presented and the importance of using reproducible samples with a known chemical composition has been emphasized. In this chapter, the effects of temperature and humidity on the electrical degradation processes in the epoxy resins are investigated. The electrical degradation experiments were carried out in the same temperature and moisture ranges as in the dielectric measurements. In this way, a relationship between the observed degradation mechanism and the dielectric properties of the epoxy resin can be established.

Also a set of experiments were carried out at different levels of applied voltage. In this case the samples were conditioned in an environment with a fixed relative humidity and they were tested electrically at room temperature. The objective was to establish the tree growth characteristics as a function of the applied voltage and to compare the results with these published in the literature thus establishing consistency with previous work.

Supplementary experiments were carried out to study the possible effects of moisture and temperature on PD activity in voids. The objective is to separate the effect of moisture on the dielectric properties of the polymer matrix from the effect it may have on the electron avalanche mechanism and hence on the partial discharge process as a whole. Therefore the hypothesis to be tested is that moisture affects the electron avalanche process. This can be achieved by varying both temperature and moisture content in the void. The hypothesis to be tested is that temperature and moisture affect the partial discharge process in the same way, which implies that the dielectric properties of the resin surrounding the void have a dominant role rather than the changes in the avalanches process. This is the case because temperature and moisture affect the dielectric properties of the host resin in the same way (see Chapter 4), while the electron avalanche process has complex dependence on both temperature and moisture and moisture. In the context of this work, PDs in voids are discharges that have been characterised in small size (~1mm) gas filled voids adjacent to a metal electrode.

5.2. Experimental plan

In order to study the effects of absorbed moisture and temperature on the degradation processes in epoxy resins the following experimental plan was developed given in Table 5.1. The temperature range and humidity ranges are chosen to match the conditions under which the dielectric properties of the epoxy resins were studied, (see Chpater 4). Samples were stored under five different relative humidity environments so that a broad range of absorbed moisture in the samples can be obtained (see Chapter 3). Tests at six different temperatures were performed to study the effect of temperature on electrical degradation. According to this plan samples of both resins; CY1301 and CY1311 were prepared and two different experiments were to be conducted, namely treeing experiments and PDs in voids, hence four different types of samples were needed. Four designations are used in Table 5.1 to denote the different types of samples. Codes 'G' and 'GV' denote "glassy" CY1301 samples used for electrical treeing and PD in voids, respectively. Codes 'F' and 'FV' denote "flexible" CY1311 samples used for electrical treeing and PD in voids, respectively. All electrical treeing samples are to be tested at applied voltage 13.5 kV rms (for consistency with previous published data on these resins) and all PD in voids tests are to be carried out at voltage 7.5 kV rms (to reduce the possibility of tree initiation from the void). Each code in Table 5.1 represents an individual sample that has to be stored and tested at the specified conditions. The total number of samples stored in a particular environment is given below the table. Also sub-totals for each type of samples stored at that environment are given. On the right are given the total number of samples of each type to be produced. In total 105 samples had to be produced and tested according to the experimental plan given in Table 5.1.

In most cases it is envisaged that two identical samples are to be tested at each particular condition, i.e. level of absorbed moisture and temperature. The exceptions are CY1311 stored at RH44% and RH100% and CY1301 samples (test at 40°C), all intended for treeing experiments. In the literature the electrical tree growth in samples conditioned at RH44% is well documented. Therefore, the CY1311 treeing samples stored at this environment are to be tested mainly for consistency with the published data. The reason to have fewer samples stored at RH100% is that it was expected that the electrical conductivity of the samples would be very high in this case and that an 'instantaneous' breakdown would occur. The CY1301 treeing samples are primarily

intended to study the electrical tree growth below and above T_g and to be able to compare the results with the literature (Champion *et al.*, 2000). Hence the tests at 40°C are somewhat auxiliary and only one sample per environment is envisaged.

| | Relative humidity | | | | | | |
|--------|-------------------|---------------|-------------|---------------|----------------|--|--|
| Temp. | 15% | 30% | 44% | 75% | 100% | | |
| | GGFFFV | G G F F FV FV | G G F FV FV | G G F F FV FV | G G F FV FV GV | | |
| 20C | FV GV GV | GV GV | GV GV | GV GV | GV | | |
| | | F F FV FV GV | | | | | |
| 30C | FF | GV | F | FF | F | | |
| | | F F G FV FV | | | | | |
| 40C | FFG | GV GV | FG | FFG | FG | | |
| | | F F FV FV GV | | | | | |
| 50C | FF | GV | F | FF | F | | |
| | | F F FV FV GV | | | | | |
| 60C | FF | GV | F | FF | F | | |
| | | G G FV FV GV | | | | | |
| 70C | GG | GV | GG | GG | GG | | |
| | G=5 | G=5 | G=5 | G=5 | G=5 | | |
| | F=10 | F=10 | F=5 | F=10 | F=5 | | |
| | FV=2 | FV=12 | FV=2 | FV=2 | FV=2 | | |
| | GV=2 | GV=12 | GV=2 | GV=2 | GV=2 | | |
| Total: | 19 | 39 | 14 | 19 | 14 | | |

| Table : | 5.1. | Experin | nental | plan |
|---------|------|---------|--------|------|
|---------|------|---------|--------|------|

Applied voltage:

• Electrical treeing: V=13.5 kV rms @ 50Hz

• PDs in voids: V=7.5 kV rms @ 50Hz

G - glassy CY1301, treeing

F- flexible CY1311, treeing

FV - CY1311, void sample

GV - CY1301, void sample

5.3. Experimental details

5.3.1. Experimental apparatus

A schematic diagram of the existing electrical treeing test rig within the University of Leicester HV laboratory is shown in Fig. 5.1 and has previously been described (Champion *et al.*, 1996). A Faraday cage was used to locate the HV circuit, the sample under test and the PD detector in order to exclude external noise from the sensitive detection electronics thereby ensuring all discharges that are detected were from the sample. All electrical connections into the cage are through low pass filters and PD signals are coupled out of the cage optically. The main components located within the Faraday cage are; a 20kV 50Hz step-up transformer, a test cell containing the sample and a RLC load circuit coupled to the HV conductor via an oil filled discharge free capacitor. A photograph of the Faraday cage and the respective components in it is shown in Fig. 5.2.



Fig. 5.1: Diagram of the experimental set-up for PD experiments



Fig. 5.2: Photograph of the Faraday cage used for PD experiments

The test cell was made out of glass to facilitate the optical detection of the light emission as a result of the PDs and a glass lens was used to focus the emitted light onto the CCD camera sensor, which was mounted over a hole cut into the side of the cage. A LED mounted internally but switched externally, was used for providing backillumination of the samples when required to capture an image of the growing tree structure and also facilitated aligning the sample and focusing the CCD camera lens. By acquiring two consecutive images, one without back illumination to produce an image of the light emission, it was possible to superimpose these images to produce a composite image of the light emission within the tree structure. The sample was clamped into the cell such that the base of the sample (the surface opposite the pin-tip) was pressed against the metal base of the cell. The pin electrode is connected to the HV whilst the metal base of the cell was connected to earth potential. The sample cell was filled with silicone oil to prevent electrical discharges occurring along the surfaces of the sample. Temperature control of the cell was achieved using two cartridge heaters and a temperature sensor embedded in the cell's plane electrode (metal base) and a temperature controller located external to the Faraday cage.

The CCD camera was used to record the low levels of light emitted as a result of PD events occurring within the tree structure and to record the tree structure using back illumination. The CCD camera was a Peltier cooled device (temp ~ -70° C) so that to reduce dark noise build-up on the chip and hence allow long exposure times if the light emitted is weak. The CCD chip had a wide spectral response from the near IR to the near UV and a high quantum efficiency of 66% at a wavelength of 550nm. The CCD camera was controlled by a personal computer (IBM PC in Fig.5.2) via a high speed serial link which enabled images to be stored to hard disk for later analysis.

The load circuit was of a conventional type consisting of a damped resonant RLC circuit of resonant frequency 200 kHz and was used to convert the short duration ~10ns PD current pulses into voltage pulses. An optical fibre link was used to transfer the PD voltage pulses from the detector to the DSO and also prevented both electrical interference signals entering the Faraday cage and as a guard against possible damage to the oscilloscope in a case of sample breakdown. Another PC was used to control the data acquisition process from the DSO and to store the PD data to hard disk. In order to provide a phase reference of the high ac voltage applied to the sample, the DSO

simultaneously recorded the ac voltage from a low voltage (LV) transformer. A Variac autotransformer was used to control the voltage applied to the HV transformer primary and hence the HV applied to the sample over the range 0 to 20kV rms.

The HV supply was calibrated by monitoring the secondary coil of the HV transformer using a 1000:1 HV probe to a DVM. The voltages were recorded as a function of the variac dial reading.

The PD detector and measurement system were calibrated using a test capacitor of 10 pF and a square wave generator of 10V amplitude to provide an injecting charge of 100 pC. The calibration capacitor was connected to the RLC load circuit and the voltage of the pulse registered by the storage oscilloscope was measured. For the system described above the calibration constant was 200 pC per volt. The noise level of the PD detection system was ± 1.5 pC. The HV transformer has been found to be discharge free below 17 kV rms.

At high temperatures it was necessary for the cell to be thermally insulated with an expanded polystyrene lagging to minimise heat loss and to ensure that constant temperature was maintained in the cell during the tests. Small apertures were cut into the lagging to allow light from the LED to enter the cell and light from PD to leave the cell and detected using the CCD camera.

5.3.2. Samples for tree growth and PD in Voids

All samples were prepared and stored as described in Chapter 2. Tungsten carbide pins having a shank diameter of 1 mm and pin-tip radius of 3 μ m were cast in the epoxy slabs (see Fig. 2.3).The samples used for electrical treeing experiments had pin-plane geometry with distance between the pin and the plane 2±0.5 mm. They were tested electrically 10-12 weeks after their manufacturing.

In some of the samples with an embedded pin, the pin was partially extracted by approximately 1mm to form a void. Void samples were made from both resins CY1311 and CY1301. The pin extraction took place immediately after the post-cure of the samples. A hydraulic machine was used to extract the pins in the case of CY1301 samples at room temperature. However, in the case of CY1311 it was necessary first to freeze (at temperatures below $T_g\sim0^\circ$ C) the samples and then the pin extraction was done manually while the resin was still in its glassy state. The extraction procedure was not perfect and caused de-bonding of the pin from the epoxy matrix and some damage to the resin near to the pin-tip. Following partial extraction and to prevent

subsequent movement of the pin, a two-part rapid cure epoxy adhesive was used to bond the pin to the top of the sample. In this way, the void formed in the sample, as a result of the pin extraction, was also sealed from the environment. The void samples were then immediately placed in the controlled humidity containers following the conditioning procedure described in Chapter 2. A schematic diagram of the void geometry is shown in Fig. 5.3. The length of the voids (lv) measured from the pin tip to the bottom of void was 1 ± 0.3 mm.



Fig. 5.3: Void geometry

5.3.3. Constant temperature tests function of applied voltage magnitude

Only CY1311 samples were used in all electrical treeing experiments. Electrical tests were carried out to study the voltage dependence of the tree growth at the following voltage levels: 9, 10, 11, 12, 13.5 and 15 kV rms. All the samples were conditioned at RH43% only and the electrical tests were carried out at room temperature of approximately 17°C. Throughout each experiment, phase resolved partial discharge activity recorded by the storage oscilloscope was saved to disk for subsequent analysis. For each partial discharge data set, the PD data acquisition time was 1s and data acquisition was repeated every 10 seconds. Hence each partial discharge over a time period of one second. Concurrently with the acquisition of partial discharge data, images of the emitted light due to the partial discharges and back illuminated images of the RLC load circuit when large breakdown currents flow, the electrical tree experiments were terminated when the trees had grown approximately two-thirds of the pin-plane distance.

5.3.4. Tree growth at constant voltage magnitude and variable temperature and moisture

An applied voltage was 13.5kV rms for all tests. The treeing experiments were performed using the same protocol as above, but all samples were subjected to an applied voltage of 13.5kV rms. Experiments were conducted over the temperature range 20-70°C and over a range of absorbed moisture in accordance with Table 5.1. Since the glass transition temperature of the resin is 0°C, all treeing experiments were performed above T_g of the resin.

5.3.5. Measurements of PDs in Voids

The test voltage in this case was 7.5 kV rms in order to minimise the possibility of electrical tree initiation even after prolonged periods of PD activity. The experimental conditions were selected so that the RH dependence on PD activity over the range 15-100% and the temperature dependence on PD activity over the range 20-70°C could be studied.

5.4. Results

5.4.1. Constant temperature

Typical sets of back illuminated photographs obtained using the CCD camera of trees grown at different applied voltages are shown in Fig. 5.4. The photographs on the left in Fig. 5.4 show the images of the pins before the start of the experiments. A reference scale and the level of the applied voltage are given for each of these images. In all photographs the image of the pin tip is on the right and the bottom electrode is on the left. taken approximately half way through the tree growth are shown in the middle column and images of the final tree structures taken after the experiments have been terminated are shown in the right hand column. The dark spots in the images are due to contaminants in the test cell, not actual defects inside the samples. In each case, the fractal dimension of the tree (determined by visual inspection) does not appear to change significantly during the propagation stage.

The fractal dimension of the electrical trees in flexible epoxy resins has been found to increase with increasing amplitude of the applied voltage. For a fixed pin-plane distance of 2 ± 0.5 mm, trees grown at voltages between 9 and 11kV had a branch type structure (d_f <2). Trees grown at voltages above 13.5 kV had a bush structure (fractal dimension >2), and at 12 kV they had formed a composite bush-branch type structure (fractal dimension approximately equal to 2).



Fig. 5.4: Photographs during the electrical tree growth, CY1311 resin

The electrical tree experiments conducted in this work have confirmed previous observations that the tree growth and the corresponding PD activity in flexible epoxy resins is dependent on the applied voltage (Champion and Dodd, 1996).

Superimposed images of the back-illuminated tree structure and the light emission due to the partial discharge activity were created illustrating the spatial extent of the corresponding PDs. An example is shown in Fig. 5.5, where two images with different levels of contrast are shown. The highest intensity light comes from within the bush structure near the pin tip and only a few discharges propagate along braches in the periphery of the tree. Concurrently with the optical detection of the tree structure, phase-resolved PD data were acquired, i.e. the apparent charge magnitude and the corresponding phase of occurrence with respect to the applied voltage. The spatial extent of the PDs and their corresponding magnitudes (see Table 5.2) suggest that the structures were non-conducting (Champion and Dodd, 2001).

The tree growth time, defined as the time required by the electrical tree to cross 2/3 of the pin/plane distance, is shown in Fig. 5.6 as a function of applied voltage magnitude. A similar relation in the case of Araldite CY1311 between the applied voltage and the time to breakdown has been found in Champion *et al.* (1994).



Fig. 5.5: The pictures show the image of the tree on a red-on-black background on which a grey-scale image of the light emission due to partial discharges is superimposed.



Fig. 5.6: The tree growth time as a function of the applied voltage, CY1311 resin

The PD amplitudes measured during the tree growth were in the range between 10pC and 10nC depending on the length of the electrical tree channels. Two parameters were calculated to characterise the PD activity during the entire tree growth, namely the average number of discharges per second (s⁻¹) and the average discharge magnitudes. These average values were calculated over all one second data acquisition intervals acquired for a given tree. The values obtained at different levels of the applied voltage are summarised in Table 5.2. In the first column for each parameter in Table 5.2 the values represent individual experiments, and the sign "/" is used as a delimiter when more than one experiment was carried out at the same level of the applied voltage. In the second column for each parameter is given the group average plus/minus one standard deviation calculated over all experiments carried out at this level of the applied voltage. In general, there are no significant differences in the PD rates between the different data sets. However, the average magnitudes tend to increase with increasing fractal dimension of the tree structure (see Fig. 5.4).
Table 5.2. Values of the PD characteristics at different voltage levels, samples conditioned in RH 44%, tested at RT

| Applied voltage, kV rms | Average number of discharges per second, s ⁻¹ | | Average discharge magnitud pC | |
|-------------------------------|--|----------|----------------------------------|--------|
| 9 | 1000/832/919/888 | 910±70 | 182/103/135/100 | 130±38 |
| 10 | 1270/1130/771 | 1057±257 | 165/122/109 | 132±29 |
| 11 | 835/895/960 | 897±63 | 178/160/107 | 148±37 |
| 12 | 1084/715 | 900±261 | 240/184 | 212±40 |
| 13.5 | 725/602 | 664±87 | 165/194 | 180±21 |
| 15 | 779/676/1020 | 825±177 | 416/427/334 | 392±51 |

The values in Table 5.2 show significant variation when the values from different experiments carried out at the same voltage level are compared. There are a few reasons that can explain the observed variability. First, the tree growth is a dynamic process and the corresponding PD activity changes with time both in term of PD magnitudes and PD rates as the tree propagation progresses. Hence, ascribing a single characteristic value to a particular tree structure or experimental condition is not entirely feasible. However later in this chapter it will be shown that this type of analysis can be used to discriminate between electrical treeing and runaway breakdown. In this set of experiments the only controlled parameter was the applied voltage but the results are likely to suggest that other factors known to affect the electrical tree growth such as temperature and humidity (Densley, 1979; Champion and Dodd, 1999) should be considered and controlled in order to obtain reproducible electrical trees and corresponding PD patterns (Champion and Dodd, 1996). The effect of temperature and absorbed moisture on the electrical tree growth in flexible epoxy resins is presented in the next section.

A thorough analysis of the PD data obtained from the electrical treeing experiments is presented in Chapter 6.

5.4.2. Variable temperature and moisture

The effect of absorbed moisture on the electrical treeing process is illustrated in Fig.5.7, where the images of four trees grown in samples with moisture levels of 0.1%, 1.0%, 2.4%, and 6.9% are shown in a) to d), respectively. The images shown in Fig. 5.7 and Fig. 5.8 were taken after the end of the corresponding experiment and represent the final tree structures obtained. The fractal dimension of the electrical trees decreased with increasing the level of absorbed moisture. In the samples with higher level of moisture the degradation mechanism has changed from electrical treeing to thermal breakdown. A similar picture was observed when the effect of the temperature was considered. Images of four electrical trees grown at different temperatures are shown in Fig. 5.8. The respective samples were conditioned in a sealed container with RH 30% and had acquired about 0.6% mass increment prior to the treeing experiments. The fractal dimension of the trees shown in Fig. 5.8 decreased with increasing temperature. At temperatures above 50°C thermal runaway was observed.



Fig. 5.7: Electrical degradation and breakdown at different levels of absorbed moisture, temperature 20°C, applied voltage 13.5kV rms, pin-plane distance 2mm:
a) moisture level of 0.1%, b) 1.0%, c) 2.4%, d) thermal breakdown at 6.9%, CY1311 resin

In general, increasing temperature and/or moisture led to faster tree growth and lower fractal dimension of the corresponding electrical trees. Although the overall mechanism of electrical treeing did not change (PD driven phenomenon), the details of PD dynamics have been found to change significantly with increased temperature and moisture content. At even higher values of temperature and moisture, it was possible to identify a set of values for which the degradation mechanism (electrical treeing) changed to breakdown (thermal runaway). The electrical tree growth times and the conditions at which breakdown took place are given in Table 5.3. Once again, the experiments were terminated before the trees were able to bridge the pin and the plane electrodes. This was done mainly to preserve the tree shapes and also to protect the RLC load circuit from possible damage. However in some cases the sample breakdown occurred very fast (in less than 10s) after the voltage application and no tree images were recorded in this period of time. These cases are designated in Table 5.3 by the letter 'B' and thermal breakdown is assumed to be a likely breakdown mechanism.



Fig. 5.8: Electrical degradation and breakdown at different levels of temperature, absorbed moisture 0.6%, applied voltage 13.5kV rms, pin-plane distance 2mm; a) temperature 20°C, b) 30°C, c) 40°C, d) combination of treeing and thermal breakdown at 50°C, CY1311 resin

| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
|-----------------|-------|-------|------|------|------|------|
| RH15 (0.1%) | 51min | 17min | 40s | 4min | 2min | 30s |
| RH30 (0.6%) | 7min | 3min | 3min | 10s | В | В |
| RH44 (1.0%) | 7min | 1min | 45s | В | В | В |
| RH75 (2.4%) | 30s | В | В | В | В | В |
| RH100 (6.9%) | В | В | В | В | В | В |

Table 5.3. Tree growth time

B – breakdown (the sample broke down in less than 10s)

Using the same approach as above, in Table 5.4 and 5.5 are given the number of discharges per second and the average discharge magnitudes, respectively, during the entire tree growth. In the cases where breakdown had occurred, no PD data were collected. At low temperature and low moisture conditions the average values of both discharge rates and magnitudes are similar to the values given in Table 5.1 and can be considered as typical values characterising the PD activity during the electrical treeing growth. However, the average PD magnitudes decrease at high values of temperature and/or humidity, while the corresponding number of PDs per second increases significantly. Under the same conditions, the corresponding tree growth times are very short and indicate a runaway process (Dissado *et al.*, 1997). Hence, the PD rates can be used to differentiate between the two regimes, electrical treeing and runaway.

| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
|-------------|-------|------|-------|------|-------|-------|
| RH15 | | | | | | |
| (0.1%) | 691 | 1164 | 1821 | 2715 | 11670 | 16850 |
| RH30 | | | | | | |
| (0.6%) | 1010 | 1928 | 3496 | | | |
| RH44 | | | | | | |
| (1.0%) | 1085 | 3291 | 18094 | | | |
| RH75 | | | | | | |
| (2.4%) | 14258 | | | | | |
| RH100 | | | | | | |
| (6.9%) | | | | | | |

Table 5.4: Average number of discharges per second [s⁻¹] during the entire tree growth

| 8 | | | | | | |
|--------|------|------|------|------|------|------|
| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
| RH15 | | | | | | |
| (0.1%) | 252 | 236 | 226 | 218 | 81 | 5 |
| RH30 | | | | | | |
| (0.6%) | 241 | 182 | 232 | | | |
| RH44 | | | | | | |
| (1.0%) | 336 | 153 | 68 | | | |
| RH75 | | | | | | |
| (2.4%) | 98 | | | | | |
| RH100 | | | | | | |
| (6.9%) | | | | | | |

 Table 5.5. Average discharge magnitude [pC] during the entire tree growth

5.4.3. Partial discharges in voids

In Fig. 5.9a is shown an image of a gas-filled void in a CY1301 sample and in Fig.5.9b is shown the corresponding light emission as a result of the PD activity. A superimposed image of the void shape on a red-on-black background and a grey-scale image of the light emission due to partial discharges is shown in Fig. 5.10. It can be seen from Fig. 5.10 that the light intensity is highest near the pin tip. In the case of flexible epoxy resin samples it was crucial that the polymer matrix was disrupted as least as possible during the pin extraction procedure in order to sustain PDs for prolonged periods of time without initiating an electrical tree. Two images of a CY1311 sample with multiple cracks around the void, which were formed during the pin extraction procedure, are shown in Fig.5.11 a) and b). These images were taken before and after the electrical test. Multiple electrical trees were initiated when HV was supplied to the pin electrode, although the voltage was kept at 7.5 kV rms during the test. In general, tree inception was favoured in all flexible epoxy samples with cracks or crazes in the vicinity of the void.





Fig. 5.9: PDs in a gas-filled void, CY1301 sample: a) void shape; b) light emission from the void discharges



Fig. 5.10: The picture shows the image of the void shape on a red-on-black background on which a grey-scale image of the light emission due to partial discharges is superimposed. The light intensity is highest near the pin tip



Fig. 5.11: Images of a gas-filled void, in CY1311 sample: on the left before the electrical test, on the right two electrical trees have been initiated during the test

The PD data obtained at varying temperatures and moisture levels are summarised in Table 5.6 and Table 5.7, respectively. The CY1311 samples broke down at elevated temperatures and/or moisture content, which is indicated in both tables. For the same set of experimental conditions, the average number of PDs per second in voids in CY1311 resin is greater than the corresponding value for the CY1301 samples, while the average discharge magnitudes show opposite trend, i.e. PD magnitudes are greater in the case of CY1301 samples. This can be ascribed to the higher electrical conductivity of the CY1311 samples compared to CY1301 resin. The space charge deposited by the PDs can effectively be removed due to the conductivity of the bulk material thus allowing more discharges to take place per half-cycle of the applied voltage (see Chapter 7). The temperature dependence in the case of CY1311 also supports this hypothesis, since increasing temperature leads to increased bulk conductivity, assuming Arrhenius dependence of temperature on conductivity (see Chapter 4).

Since temperature and moisture appear to have similar effect on the PD activity in gas voids, the dominant role in the observed changes in the PD activity has to be attributed to changes in the material properties of the polymer surrounding the gas void.

The results of the detailed PD data analysis are presented in Chapter 6.

Table 5.6. Temperature dependence of PD activity in voids, samples stored in an environment with RH30%

| | CY1311 mass uptake 0.7% | | | CY1301 mass uptake 0.2% | | | |
|------|-------------------------|-----------------|------------|-------------------------|-----------------|------------|--|
| | Void | Average | Average | Void | Average | Average | |
| т∘с | size, | number of | discharge | size, | number of | discharge | |
| г, с | mm | discharges | magnitude, | mm | discharges | magnitude, | |
| | | per second, | рC | | per second, | рC | |
| | | s ⁻¹ | | | s ⁻¹ | | |
| 20 | 0.9 | 2771 | 42 | 1.2 | 1172 | 75 | |
| 30 | 1.0 | 2183 | 63 | 1.2 | 1233 | 100 | |
| 40 | 0.7 | 3174 | 49 | 1.2 | 1350 | 79 | |
| 50 | 0.6 | 8409 | 35 | 0.8 | 1309 | 142 | |
| 60 | 0.5 | breakdown | breakdown | 0.9 | 900 | 227 | |
| 70 | - | breakdown | breakdown | 1.0 | 1748 | 155 | |

| Fable 5.7. Moisture dependence of P |) activity in voids, temperatur | e 20°C |
|--|--|--------|
|--|--|--------|

| Absorbed | | | | |
|----------------|---|-----------|---------------------------------------|--|
| moisture, % | Void Average number of size, mm discharges per second, s ⁻¹ | | Average discharge magnitude, pC | |
| 0.1 | 0.8 | 2608 | 31 | |
| 0.6 | 0.9 | 2771 | 42 | |
| 1.1 | 0.8 | 3104 | 42 | |
| 2.5 | 1.0 | 3761 | 70 | |
| 6.7 | 0.8 | breakdown | breakdown | |

| Absorbed | CY1301 | | | | |
|-----------|----------|-------------------|-------------------|--|--|
| moisture, | Void | Average number of | Average discharge | | |
| % | size, mm | discharges per | magnitude, | | |
| | | second, | рС | | |
| | | s ⁻¹ | | | |
| 0.05 | 1.0 | 1563 | 72 | | |
| 0.2 | 1.2 | 1172 | 75 | | |
| 0.3 | 0.8 | 1500 | 45 | | |
| 0.6 | 0.8 | 2019 | 70 | | |
| 1.0 | 1.2 | 1212 | 27 | | |

5.4. Chapter summary

Both temperature and absorbed moisture affect the electrical tree growth in flexible epoxy resins. Increasing temperature and/or moisture leads to faster tree growth and lower fractal dimension of the corresponding electrical trees, see Fig. 5.12. It was possible to identify a set of values of temperature and moisture for which the degradation mechanism (electrical treeing) changes to breakdown due to increased conductivity of the samples. Although the overall mechanism of electrical treeing does not change (PD driven phenomenon), the details of PD dynamics change significantly with increased temperature and moisture. It has been found that temperature and moisture have similar effects on the PD process. The results suggest that the moisture absorbed in the samples affects their material properties rather than the electron avalanche process.

Electrical treeing



Fig. 5.12: Transition from electrical treeing to thermal breakdown in flexible epoxy resins

Chapter 6: PD data analysis

The PD data obtained from the electrical treeing and discharge in voids experiments, described in Chapter 5, were analysed using a standard statistical technique (Gulski, 1991) and Pulse Sequence Analysis (PSA) (Hoof and Patsch, 1995).

The space charge formed within the insulation as a result of a partial discharge creates a local electric field that opposes the formation of further electron avalanches. Therefore PDs in voids and in electrical trees are self-extinguishing events. The life-time of this space charge will be determined by the electrical properties of the void wall or the surface conductivity of the tree channels. Space charge will also be transported into the base resin away from the electrical tree due to transport of charge within the material. Hence the electrical conduction and dielectric characteristics of the material are likely to govern the lifetime of this space charges. In this chapter the characteristics of the partial discharges will be studied using a number of conventional statistical tools and time sequence analysis tools in order to determine the influence of the material properties on the partial discharge activity and therefore on electrical treeing degradation.

The characteristics of PD are intimately related to the electrical treeing degradation process as material degradation is caused by energy dissipated in the discharge activity. The characteristics of the PD from electrical treeing differs from other PD phenomena such as surface discharges or corona discharges and many workers have proposed that measurement of the statistical parameters of the amplitude and phase distribution of PD activity can be used as a basis for identification of the defect type and thus has importance for condition monitoring of HV electrical equipment. Statistical features such as mean, standard deviation, skewness and kurtosis, have been widely used and reflect the perceived wisdom that the PD events appear at random within the distribution and hence the PD activity is essentially a stochastic process. An alternative view is that the PD events are influenced by the previous history of events due to the formation of space charge in the material surrounding the tree structure or a void. Time sequence analysis of the correlations that exist between consecutive discharges has been proposed as a possible method for extracting information regarding the type of defect producing PD (Hoof and Patsch, 1995). The underlying assumption here is that the influence of one discharge on a subsequent discharge should last at least a time of the order of the period of the ac cycle. Previous work (Dodd et al., 1995) on tree growth in CY1311 epoxy resin has demonstrated that the partial discharge activity and hence the tree growth conforms to a deterministic mechanism in which the process is in a state of deterministic chaos. In addition, the partial discharge activity in this resin (Champion and Dodd, 1996) was found to exhibit regular bursts of behaviour in which the numbers of partial discharges per half cycle increase significantly leading to rapid tree growth. These regular bursts of PD activity were found to be reproducible in samples tested under identical conditions and the number and duration of the bursts determined by the magnitude of the applied ac voltage; again pointing to an underlying deterministic mechanism controlling the pd dynamical behaviour. As yet no mechanism has been proposed to explain the burst behaviour which has cyclic behaviour lasting several minutes and hence much longer than the one cycle of the ac voltage. Such mechanisms should also be sensitive to the experimental conditions of applied voltage and pin-plane distance and should have dynamical features lasting much longer than one ac cycle. Hence it would be expected that many parameters that can be determined from the partial discharge activity during tree growth should reflect these dynamical features.

6.1. Introduction

6.1.1. Statistical analysis of PD data and pattern recognition

The measured PD data can be presented as phase resolved data if an ac voltage is applied (Sahoo *et al.*, 2005). An example of PD data acquired over time interval of 1s from an electrical treeing experiment and the reference ac voltage cycle are shown in Fig. 6.1, where each individual PD event is denoted by a dot. It is a commonly used practice to represent such data as φ -q-n pattern, since it contains information about the phase of occurrence (φ), magnitude (q) and number (n) of PD events with respect to the applied ac voltage cycle. Since the PDs show an apparent scatter in terms of phases of occurrence and magnitudes they are often regarded as stochastic processes and standard statistical techniques are applied to analyse the data (Brunt, 1991). However in such a representation of PD data, any causal relationship between successive PD events is effectively lost as the PD events over many cycles are usually superimposed and the actual sequence of events can no longer be determined.



Fig 6.1: A typical φ -q-n pattern from an electrical treeing experiment

Several statistical distributions have been proposed in the literature to characterise phase-resolved PD patterns and a set of statistical parameters has been employed to describe quantitatively these distributions. By dividing the power cycle of the test voltage into a number of phase windows the following distributions can be obtained (Krivda, 1995; Gulski, 1991; Okamoto and Tanaka, 1986):

- Maximum pulse height distribution $H_{qmax}(\phi)$ represents the maximum discharge magnitude in each window as a function of the phase angle ϕ .
- Mean pulse height distribution $H_{qn}(\phi)$ the average discharge magnitude in each phase window as a function of ϕ
- Pulse count distribution $H_n(\phi)$ the number of discharges in each window as a function of ϕ
- Total charge distribution $H_{qs}(\phi)$ total charge in each window as a function of ϕ
- Pulse magnitude distribution H_n(q) the number of discharges as a function of discharge magnitude q



Fig. 6.2: The $H_{qn}(\phi)$ distribution profile change measured at different times, PD due to tree growth in a CIGRE Method I electrode system (Okamoto and Tanaka, 1986)

Usually, the above mentioned distributions are separately defined for the positive and negative half-cycles of the applied voltage. This is done under the assumption that voltage half-cycles and PD pulse polarities coincide but often this is not true and PDs of opposite polarity to that of the applied voltage appear before the zero crossing of the voltage, see Fig. 6.2. Therefore, an alternative way to define these distributions is to use the pulse polarity rather than the half-cycles of the applied voltage (Stone, 2005). Also, in Fig. 6.2 it can be seen that PD statistics (in this case mean pulse height distribution) exhibit significant temporal variations. These temporal variations reflect the changes in the local conditions in the tree channel and on the channel surface, i.e. change in the gas composition and electrical conductivity of the channel surface, where the discharges take place and respectively the physical processes that occur within the insulation and they are the main obstacle to reliable PD-based diagnostics.

The information contained in the discharge distributions should be quantified in order to obtain knowledge about the degradation mode and to be able to use it in a pattern recognition classifier. This is achieved by characterisation of the PD distribution shapes by various statistical parameters. These statistical parameters (also called "statistical operators") often constitute elements of an input feature vector, which is used for discrimination between various defects. The most commonly used parameters are (Sahoo *et al.*, 2005):

Mean:
$$\mu = \frac{\sum_{i=1}^{N} x_i f(x_i)}{\sum_{i=1}^{N} f(x_i)}$$
 (6.1)

Variance:
$$\sigma^2 = \frac{\sum_{i=1}^{N} (x_i - \mu)^2 f(x_i)}{\sum_{i=1}^{N} f(x_i)}$$
 (6.2)

Skewness:
$$Sk = \frac{\sum_{i=1}^{N} (x_i - \mu)^3 f(x_i)}{\sigma^3 \sum_{i=1}^{N} f(x_i)}$$
 (6.3)

Kurtosis:
$$Ku = \frac{\sum_{i=1}^{N} (x_i - \mu)^4 f(x_i)}{\sigma^4 \sum_{i=1}^{N} f(x_i)}$$
 (6.4)

Where N is the number of phase windows in a half-cycle, x_i is the recorded value and $f(x_i)$ is the weight of the i-th window. The mean is a measure of the central tendency of the data. The variance is a measure of the dispersion of the data around the mean. The skewness (Sk) is a measure of the asymmetry of the distribution. For symmetric distributions skewness is equal to zero, Sk = 0. Skewness is positive if the distribution is asymmetric to the left, Sk > 0, and negative when the distribution is asymmetric to the right, Sk < 0. Kurtosis is a measure of the sharpness of the distribution. For a normal distribution, the kurtosis value is greater than 3, and if the distribution is flatter than the normal distribution the kurtosis value is less than 3. Sometimes instead of kurtosis, kurtosis excess is used, which refers to what extent the value of kurtosis for a particular distribution is bigger or smaller than that for the normal distribution. Therefore for sharper distributions kurtosis excess is positive, Ku > 0, and for flatter distribution kurtosis excess is negative, Ku < 0.

Some additional parameters have also been proposed to assess the differences/similarities between the PD distributions of the positive and negative half-

cycles of the applied voltage, or alternatively the positive and negative polarity pulse distributions (Gulski and Krivda, 1993). Such parameters are the cross-correlation factor, the discharge asymmetry, the modified asymmetry and others (Sahoo *et al.*, 2005).

6.1.2. Pulse Sequence Analysis

An alternative approach for PD data analysis is to regard the PD events not as stochastic processes but as a time series where a strong causal relationship exists between consecutive events (Hoof and Patsch, 1995). The basic assumption here is that the electric charges that are deposited by previous discharges remain in the vicinity of the discharge site and modify the local electric field. In this way, the ignition conditions for the occurrence of a subsequent discharge are affected and as a result the PDs should not be treated as independent random events. A change in the conditions inside a void due to electric charges deposited by a previous discharge was reported as early as Mason (1951).

The basic principle of Pulse Sequence Analysis (PSA) is illustrated in Fig. 6.3, where a sequence of PDs is shown for simplicity with one discharge occurring at each half-cycle of the applied voltage. In order to account for the correlation between the consecutive PD pulses, a series of voltage (Δu_1 , Δu_2 , Δu_3 , ... Δu_i) and time differences (Δt_1 , Δt_2 , Δt_3 , ... Δt_i) between successive PD events are determined where u_n is the value of the applied voltage at the time t_i of the inception of the i-th PD. Alternative parameters that can be used for PSA are charge differences (Δq_1 , Δq_2 , Δq_3 , ... Δq_i) and phase differences ($\Delta \varphi_1$, $\Delta \varphi_2$, $\Delta \varphi_3$, ... $\Delta \varphi_i$) between the consecutive discharges, where q_i is the measured amplitude of the i-th PD pulse and φ_i is the corresponding phase angle of the ac applied voltage. The analysis proceeds with plotting the consecutive differences Δu_i versus the preceding ones Δu_{i-1} . An example is shown in Fig. 6.4 for three different defects: a) corona, b) electrode-bounded cavity and c) electrical tree, the data from (Patsch and Berton, 2002). The scatter plots shown in Fig. 6.4 are quite different from one another and hence can be used for defect classification and PD based diagnostics of electrical insulation systems.

Further developments in the PSA method have suggested a differential ratio $\Delta u/\Delta t$ to be used for analysis of PD data acquired especially from solid insulation (Patsch and

Berton, 2002). In this way, a different scatter plot is obtained. The clusters of data points appear to be better separated and less scattered in the case of $\Delta u/\Delta t$ plot compared to the case when Δu is used only. An example is shown in Fig. 6.5 in the case of an electrical tree in polyethylene.



Fig. 6.3: Basic principle of PSA method



Fig. 6.4: Scatter plots of measured discharge sequences for different types of defects (a) corona, (b) electrode-bounded cavity, and (c) electrical treeing. The arrows indicate the sequence of data points. From (Patsch and Berton, 2002)



Fig. 6.5: PSA of PD pulses during tree initiation in polyethylene on the basis of scatter plots of U (in kV) and $\Delta U/\Delta t$ (in kV ms⁻¹): (a) the last 200 pulses before and (b) the first 200 pulses after an electrical has been initiated. From (Patsch and Berton, 2002)

6.2. Analysis of PD data derived from Room Temperature treeing experiments

6.2.1. Statistical analysis of PD activity

In order to assess the relationships between the various statistical and physical parameters characterising the PD activity during electrical tree growth, the pulse magnitude distributions $H_n(\mathbf{q})$ and the pulse count distribution $H_n(\boldsymbol{\varphi})$ were considered when analysing the phase resolved PD data. These distributions can be defined for the positive and negative polarity discharges. In the case of $H_n(\mathbf{q})$, the total distribution of both positive and negative PD magnitudes was also considered.

For each distribution four statistical moments were calculated: mean, standard deviation, skewness and kurtosis. In addition, two physical parameters were also calculated, the power dissipated by the partial discharge activity and the number of partial discharge events in each one second data record. The power dissipated (P) in the sample as a result of the partial discharges is calculated by the following expression:

$$P = \frac{1}{\Delta t} \sum_{i=1}^{N} V_i q_i = \sum_{i=1}^{N} V_i q_i$$
(6.5)

In the above equation the acquisition time, Δt , for the data set is one second, V_i is the instantaneous voltage at which the i'th PD event occurs with a magnitude, q_i , and N is the total number of PD events in the one second time interval. In the case of the number of discharges, the total number and the number of positive and negative amplitude discharges were considered.

The time variations of the statistical parameters characterising $H_n(\mathbf{q})$ and the physical parameters are illustrated for a typical sample in Fig. 6.6 and the

corresponding plots for $H_n(\boldsymbol{\varphi})$ are shown in Fig. 6.7, in the case of an electrical tree grown at 10 kV rms and moisture content 1.1%. The time for the tree growth in arbitrary units is shown on the abscissas and the corresponding statistical or physical parameters are on the ordinates. The actual time for the entire tree growth was 28 min, so the unit of time shown on the abscissa corresponds to approximately 20 seconds.



Fig. 6.6: Variations of mean charge[C], standard deviation [C], skewness, kurtosis of H_n(**q**), dissipated power and number of discharges as function of time, CY1311 sample, 10kV rms, moisture content 1.1%, Red dashed line – positive PD, Blue dotted line – negative PD, Green solid line - total number/power

The mean values of the positive and negative PD amplitudes were found to increase in absolute values during the tree propagation. Large PD amplitudes therefore relate to the length of the tree and hence the spatial distance in which the PDs can propagate in the tree structure. From the plot of the power dissipated in the sample as a function of time, burst type behaviour can be identified and also it can be seen in the corresponding plot that the number of PDs increases significantly during the bursts. In general, it is difficult to relate the statistical parameters characterising the H_n(q) distribution directly to the observed burst type behaviour. However, it is important to highlight that the mean and standard deviation increase with the time of propagation, i.e. PD magnitudes become bigger as the tree channels grow in length. If $H_n(\phi)$ distributions are considered it can be seen in Fig. 6.7 that the average phase of occurrences shifts during the burst periods to lower values, i.e. from 235 degrees to 220 degrees for the negative discharges and from 60 degrees to 45 degrees for the positive discharges and hence the burst can be easily identified from the corresponding plot as a function of time.



Fig. 6.7: Variations of mean phase angle[degrees], standard deviation [degrees], skewness and kurtosis of $H_n(\varphi)$ as a function of time, CY1311 sample, 10kV rms, moisture content 1.1%, Red dashed line – statistics of positive PDs, Blue dotted line – negative PDs; same sample as in Fig. 6.6.

The average phase of discharges occurrence fluctuates between two levels for the positive and negative discharges, respectively, as it is shown in Fig. 6.7. The first level is related to the periods between the bursts of the tree growth. The second level at which discharges occur is during the bursts, when the average phase shifts to lower values. The phase shifts in the mean discharge angle shown in Fig. 6.7 to lower angles suggest that the influence of space charge on the discharge activity becomes greater during bursts in the PD activity. In particular the build-up of space charge in the tree and surrounding resin during one half cycle enhances the local electric field during the next half cycle promoting discharges to occur at lower phase angles. This effect is less obvious during the times between bursts in the PD activity.

Although the discharge characteristics between the positive and negative discharges appear similar from the analysis above, it is expected that the net charge accumulating within the sample during tree growth should be close to zero. To check for asymmetry between the negative and positive discharges, the accumulated positive and accumulated negative PD amplitudes were calculated for each data set throughout the tree growth experiment. Typical data from the same electrical tree experiment as described above are plotted against time in Fig. 6.8. Early on in the tree growth, for the first two bursts in the PD activity, the accumulated positive and negative charge is essentially the same. However, during the two later bursts, the positive charge becomes greater than the negative charge accumulating within the sample during tree growth and an example is shown in figure 6.9. Early on in the tree growth the total accumulated charge remains close to zero. However, during the third and subsequent bursts significant build-up of positive charge occurs within the material.



Fig. 6.8: Total positive (*) and negative (+) charge as a function of time – sample 10 kV rms



Fig. 6.9: Build-up of charge into the tree structure as a function of time – sample tested at 10 kV rms

6.2.2. Correlations between the statistical and physical features of PD activity

In order to establish if correlations exist between the various statistical parameters and physical parameters derived from PD amplitude data a correlation analysis was performed. For each combination of two parameters, the parameters were plotted against each other on a scatter plot and the resultant correlation coefficient calculated. The statistical parameters were split into three groups, derived from the positive discharges, the negative discharges and all the discharges (both positive and negative). In the case of the positive and negative discharges, good correlations were found to exist between the mean and standard deviation, the skewness and kurtosis and between the average power per discharge and standard deviation. An example is shown in Fig. 6.10 as a scatter plot of standard deviation and average power. The regression line is also shown in the figure. In this case the PD data were obtained from an electrical tree grown at applied voltage 9 kV rms.

These correlations were found to be preserved under different experimental conditions as shown in Table 6.1 for the positive discharges and in Table 6.2 for the negative discharges. Poor correlations were found in the case of mean and skewness and standard deviation and between skewness and average power per discharge. Further details can be found in (Dodd *et al.*, 2008).



Fig. 6.10: A typical plot of average power vs. standard deviation $H_n(q)$ during the growth of an electrical tree

| Table 6.1. | Correlation | coefficients | between | different | parameters | of positive | PD |
|------------|-------------|--------------|---------|-----------|------------|-------------|----|
| magnitude | s | | | | | | |

| Material | Applied voltage (kV rms) | Correlation coefficient between mean and standard deviation | Correlation coefficient between skewness and kurtosis | Correlation coefficient between average power and standard deviation |
|----------|--------------------------------|---|---|--|
| CY1311 | 9 | 0.932 | 0.851 | 0.919 |
| CY1311 | 10 | 0.954 | 0.843 | 0.945 |
| CY1311 | 11 | 0.956 | 0.948 | 0.964 |
| CY1311 | 12 | 0.963 | 0.890 | 0.949 |
| CY1311 | 13.5 | 0.967 | 0.870 | 0.981 |
| CY1311 | 15 | 0.980 | 0.910 | 0.986 |

 Table 6.2. Correlation coefficients between different parameters of negative PD magnitudes

| Material | Applied voltage (kV rms) | Correlation coefficient between mean and standard deviation | Correlation coefficient between skewness and kurtosis | Correlation coefficient between average power and standard deviation |
|----------|--------------------------------|---|---|--|
| CY1311 | 9 | 0.924 | 0.726 | 0.909 |
| CY1311 | 10 | 0.916 | 0.737 | 0.922 |
| CY1311 | 11 | 0.916 | 0.925 | 0.964 |
| CY1311 | 12 | 0.950 | 0.889 | 0.978 |
| CY1311 | 13.5 | 0.988 | 0.906 | 0.986 |
| CY1311 | 15 | 0.988 | 0.967 | 0.985 |

A good correlation between the standard deviation and the average power was found also in the case of the total distribution of both positive and negative discharges. However in this case, the mean and the skewness values were always near zero as the combined distribution of both positive and negative discharges is essentially symmetrical, which resulted in poor correlations when these parameters were involved as shown in Table 6.3.

| Material | Applied voltage (kV rms) | Correlation coefficient between mean and standard deviation | Correlation coefficient between skewness and kurtosis | Correlation coefficient between average power and standard deviation |
|----------|--------------------------------|---|---|--|
| CY1311 | 9 | -0.450 | 0.027 | 0.989 |
| CY1311 | 10 | -0.553 | -0.312 | 0.994 |
| CY1311 | 11 | -0.743 | -0.117 | 0.996 |
| CY1311 | 12 | -0.077 | -0.421 | 0.979 |
| CY1311 | 13.5 | -0.579 | -0.369 | 0.998 |
| CY1311 | 15 | -0.433 | 0.143 | 0.996 |

 Table 6.3. Correlation coefficients between different parameters of both positive and negative PD magnitudes

The average power was calculated by dividing the total power by the number of discharges in the 1s interval. The results also demonstrate strong correlation between a physical parameter such as average power and a statistical parameter such as standard deviation of $H_n(\mathbf{q})$. Therefore it provides a link between the physical processes which give rise to the PD activity in a particular defect and the statistical features of the measured PD data and could offer an interesting diagnostic tool relating the physical state of the degradation process to the statistical characteristics of the PD data. In particular the relation between the average dissipated power (P_{av}) and the tree length or volume may enable tree growth rates to be determined and lifetime predictions to be made from the statistical nature of the PD data alone.

The correlation between the average power and the standard deviation of PD magnitudes was further investigated. The ratio of the dissipated power and the number of discharge per second gives the average power per discharge, P_{av} :

$$P_{av} = P/N = \frac{1}{N} \sum_{i=1}^{N} V_i q_i$$
(6.6)

It was stated above that the average power is correlated to the standard deviation σ_q of H_n(**q**).

$$P_{av} \propto \sigma_q$$
 (6.7)

If a coefficient of proportionality A is introduced, then Eq. 6.7 can re-written as:

$$P_{av} = A_P \sigma_q \tag{6.8}$$

Where the standard deviation is calculated by:

$$\sigma_q = \sqrt{\frac{\sum (q_i - \bar{q})^2}{N}} = \sqrt{\frac{\sum q_i^2}{N} - (\bar{q})^2}$$
(6.9)

Next the total distribution of PD amplitudes is considered (combined distribution of positive and negative PDs), which is a symmetrical distribution around zero, so the mean charge is approximately equal to zero, $\bar{q} \approx 0$. Therefore, we can neglect the second term in the nominator in Eq. 6.9, which reduces the expression for the standard deviation to:

$$\sigma_q \approx \sqrt{\frac{\sum q_i^2}{N}} \tag{6.10}$$

Substituting (6.6) and (6.10) into (6.8) and rearranging the two sides, the following expression can be obtained relating V_i , q_i and N:

$$\frac{\sum V_i q_i}{\sqrt{N \sum q_i^2}} \approx const$$
(6.11)

The above expression was found to be valid for the whole set of experimental conditions. The scatter plots of the average power as a function of the standard deviation of the discharge magnitudes for 32 electrical treeing experiments are shown in Fig. 6.11. These experiments were conducted at different levels of the applied voltage, temperature of the environment and level of absorbed moisture in the samples. All plots show a good correlation between the two parameters and a linear regression model such as Eq. 6.8 can be used to represent this relationship. The fitted values of the gradient A_P at different levels of the applied voltage are given in Table 6.4. The values in Table 6.4 are given with 95% confidence limits. The gradient A_P of the regression line appears to be voltage dependent and increases with increasing the rms value of the applied voltage. It is noteworthy that A_P does not depend on the fractal dimension of the resultant tree structure. This is illustrated in Fig. 6.12 where the data were obtained from electrical trees grown at 13.5 kV rms at different levels of absorbed moisture and/or temperature. The data shown in Fig. 6.12 are taken from Fig. 6.11. Although, the fractal dimension

of these tree structures varies between 1 and 2 (see Chapter 5), the data scatter is significantly less than the scatter due to the voltage dependence shown in Fig. 6.11.

| Applied voltage, | Gradient A _P , | | |
|------------------|---------------------------|--|--|
| kV rms | W/pC | | |
| 9 | 8310±1367 | | |
| 10 | 9171±628 | | |
| 11 | 10144±1958 | | |
| 12 | 9882±2374 | | |
| 13.5 | 11959±1757 | | |
| 15 | 14174±1792 | | |

Table 6.4. Voltage dependence of the gradient A_P



Fig. 6.11: Plots of average power vs. standard deviation of $H_n(q)$, 32 samples, the rms values of the applied voltage are given in the legend



Fig. 6.12: Plots of average power vs. standard deviation of $H_n(q)$, 8 samples, applied voltage 13.5 kV rms, values of the temperature and moisture are given in the legend

6.2.3. Fitting two-parameter distributions to PD measurement data

An attempt was made to fit the sample data to a particular theoretical distribution. A histogram of typical sample data for 1s acquisition period is shown on Fig. 6.13. This histogram represents the distribution of the absolute value of the PD magnitudes. It should be noted that the distribution is skewed. Therefore, the theoretical distribution also should be skewed. A good candidate is Weibull distribution, which is often used to describe PD data (Cacciari *et al.*, 1995). Other theoretical distributions that have similar features are Gamma and Log-normal distributions. These distributions possess proportionalities between their moments as will be discussed below, which are also found to be inherent for the sample PD data statistics. An example is given for Gamma distribution but similar mathematical expressions can be derived for the other two distributions as well.



Fig. 6.13: Histogram of typical PD data from electrical treeing

The cumulative density function (cdf), the probability density function (pdf) and the statistical moments of Gamma distribution are calculated by (Patel et al., 1976):

$$F(x|a,b) = \frac{1}{b^{a}\Gamma(a)} \int_{0}^{x} t^{a-1} e^{-\frac{t}{b}} dt, \qquad (6.12)$$

where F(x|a,b) is cdf of Gamma distribution, a - shape parameter, b - scale parameter

$$f(x|a,b) = \frac{1}{b^{a}\Gamma(a)} x^{a-1} e^{-\left(\frac{x}{b}\right)}$$
(6.13)

where f(x|a,b) is pdf of Gamma distribution

$$\mu = a.b \tag{6.14}$$

$$\sigma = b\sqrt{a} \tag{6.15}$$

$$Sk = \frac{2}{\sqrt{a}} \tag{6.16}$$

$$Ku = \frac{6}{a} + 3 \tag{6.17}$$

From equations 6.14 to 6.17 it is clear that mean and standard deviation and linearly dependent quantities as they contain both parameters a and b and that skewness and kurtosis are linearly dependent as they contain just the parameter, a. Hence only two parameters are linearly independent; either mean or standard deviation and skewness or

kurtosis. The same conclusions are found when considering the log-normal distribution and the Weibull distribution however the mathematical analysis is more complex. It can therefore be concluded, given the correlations found between the four statistical moments derived from experimental PD magnitude distributions, that the PD amplitude distributions conform to a two-parameter skewed distribution.

The result of the distribution fitting procedure for the three distributions is shown on Fig. 6.14 for a typical PD data set.



Fig. 6.14: PD data and fitted Weibull, Gamma and Log-normal distribution

All three distributions provide a reasonable approximation to the experimental data. In order to assess which distribution best fits the data, the following 'goodness-of-fit' test statistic has been developed:

$$G_{fit} = \left(\frac{\sum_{i}^{N} |e_{i} - o_{i}|}{|e_{i_{U}} - e_{i_{L}}|}\right) \cdot \frac{1}{N}, \qquad (6.18)$$

where G is the 'goodness-of-fit', e_i is the expected value of the statistical moment of the theoretical distribution, o_i is the observed value of the statistical moment of the sample data, e_{i_U} is the upper value of the confidence interval for the corresponding statistical moment, e_{i_L} is the lower value of the confidence interval for the corresponding statistical statistical moment, N is the number of acquisition periods taken during the growth of each electrical tree. This 'goodness of fit' test statistic was calculated for the mean,

standard deviation, skewness and kurtosis for each tree (see Table 6.5). The general trend in the 'goodness-of-fit' was that the statistical moments of the theoretical distribution became less able to fit the experimental data as the statistical moment was increased. That is, in general, better fits were obtained for the mean and standard deviation than those obtained for the skewness or the kurtosis. This is possibly due to the limited number of PDs in each data set which led to an increase in statistical noise for the higher statistical moments. Overall, the 'Goodness-of-fit' test statistic suggested that Weibull distribution is the best fit to the experimental data. However, it can be argued that the differences in the values of the test statistic for the three distributions were not very large and possibly any two-parameter skewed distribution can fit the experimental PD data reasonably well.

| Applied voltage rms values [kV] | Statistical moments | G | | |
|------------------------------------|---------------------|-------|------------|---------|
| | | Gamma | Log-normal | Weibull |
| 9 | Mean | ≈ 0 | 0.05 | 0.05 |
| | Standard Deviation | 0.14 | 0.33 | 0.13 |
| | Skewness | 1.60 | 2.72 | 1.25 |
| | Kurtosis | 2.71 | 1.96 | 1.12 |
| 10 | Mean | ≈0 | 0.08 | 0.04 |
| | Standard Deviation | 0.10 | 0.45 | 0.09 |
| | Skewness | 2.63 | 3.10 | 1.14 |
| | Kurtosis | 3.43 | 3.92 | 2.27 |
| 11 | Mean | ≈0 | 0.11 | 0.04 |
| | Standard Deviation | 0.27 | 0.46 | 0.22 |
| | Skewness | 2.63 | 2.78 | 1.21 |
| | Kurtosis | 2.70 | 1.70 | 1.60 |
| 12 | Mean | ≈ 0 | 0.05 | 0.04 |
| | Standard Deviation | 0.17 | 0.30 | 0.16 |
| | Skewness | 1.74 | 2.11 | 1.61 |
| | Kurtosis | 2.19 | 2.76 | 2.08 |
| 13.5 | Mean | ≈0 | 0.04 | 0.04 |
| | Standard Deviation | 0.10 | 0.34 | 0.13 |
| | Skewness | 1.33 | 2.36 | 0.36 |
| | Kurtosis | 2.68 | 0.66 | 0.78 |
| 15 | Mean | ≈0 | 0.08 | 0.05 |
| | Standard Deviation | 0.33 | 0.32 | 0.29 |
| | Skewness | 2.82 | 2.12 | 2.25 |
| | Kurtosis | 2.84 | 3.35 | 2.18 |

 Table 6.5. 'Goodness-Of-Fit' estimates for Gamma, Weibull and Log-normal distribution

Although some of the statistical features can be correlated to the physical parameters characterising the electrical tree growth, it is necessary to acquire a long data record so that the actual degradation mode can be ascertained. In some cases (high level of moisture and/or high temperature) the tree growth rate was too fast to allow enough time for extended data acquisition. Hence, PSA was used in an attempt to envisage a characteristic parameter that can successfully discriminate between the different modes of degradation from a single data set and provide a better insight into the physical processes that take place.

6.3. Pulse sequence analysis of PD activity

6.3.1. Relationship between φ-q-n and PSA plots

The differential ratio $\Delta U/\Delta t$ was chosen as a characteristic parameter for the PSA analysis of the PD data. A typical PSA plot is shown in Fig. 6.15a in the case of burst type behaviour and in Fig. 6.15b between the bursts. In both cases 6 clusters can be identified, which are labelled arbitrary with numerals 1 to 6. The main differences are in the cluster orientation and scatter. Clusters 1 and 4 are comprised of more data points than the others and are oriented approximately along the 45° line shown in the plots. In Fig. 6.15a clusters 3 and 6 are aligned parallel to the horizontal axis, while in Fig. 6.15b they are more scattered. In both plots cluster 2 and 5 appear equally distant from the 45° line. The same number of clusters with the same orientation can be found in Fig. 6.5, which represents PD data from electrical tree growth in polyethylene. The similarity of the plots obtained from electrical trees in different materials and their consistency from one data set to another suggests that the $\Delta U/\Delta t$ return maps such as ones shown in Fig. 6.15 represent the basic dynamics of the PD activity as a result of electrical treeing.



Fig. 6.15: A PSA of PD pulses in CY1311 epoxy resin on the basis of return map of $\Delta U/\Delta t$ (in Vs⁻¹) during: a) burst; b) between the bursts

The origin of the clusters was investigated and a relationship has been found between the cluster numbers, their orientation and the phase of PD occurrence with respect to the applied ac voltage. Clusters 1 and 4 are related to the time (phase) differences between the consecutive discharges that comprise the negative or positive polarity PD distributions respectively, while clusters 2, 3, 5 and 6 occur as a result of the transition between the two distributions. The trajectory, which the consecutive differential ratios $\Delta U_n/\Delta t_n$ describe, is also illustrated in Fig. 6.15 (see Fig. 6.5 for a comparison in the case of polyethylene). In Fig. 6.16, the φ -q-n plot of the data used to produce Fig. 6.15b is shown. If the first discharge occurs during the positive half cycle of the applied voltage, the consecutive discharges take place in a region (indicated by the red line in Fig. 6.16) where the applied voltage increases almost linearly and $\Delta U_n/\Delta t_n$ is positive, since Δt_n is always greater than zero. Hence, the consecutive ratios $\Delta U_n/\Delta t_n$ belong to Cluster 1 until the last discharge on the positive half-cycle takes place. The next discharge will take place either at the negative half-cycle or if a sufficiently large amount of space charge is deposited by the last positive discharge then the following negative discharge can take place even before the polarity reversal of the applied voltage, i.e. (φ <180°) (see Fig. 6.16). The ratio $\Delta U_n/\Delta t_n$ becomes less than zero. Then the pair $\Delta U_n/\Delta t_n < 0$, $\Delta U_{n-1}/\Delta t_{n-1} > 0$ forms Cluster 2. The following discharges occur at the negative half-cycle of the applied voltage and the ratio $\Delta U_n/\Delta_n$ remains negative until the last negative discharge. Since Δt_{n-1} (between the last positive and the first negative discharge) is always much greater than Δt_n , the ratio $\Delta U_{n-1}/\Delta t_{n-1}$ is always smaller than $\Delta U_n/\Delta t_n$ and Cluster 3 is formed in this way. The following succession of negative discharges gives rise to Cluster 4. By analogy, the formation of Clusters 5 and 6 can be explained with the transition from negative to positive PDs.



Fig. 6.16: The φ -q-n plot of the PD data used to generate Fig. 6.15b

At high levels of absorbed moisture and/or temperature a quite distinctive $\Delta U/\Delta t$ pattern has been obtained, which resembles more a runaway regime rather than an electrical tree growth (Dissado *et al.*, 1997). An example of such plot is shown in Fig. 6.17 for a sample tested at 20°C, moisture content 2.42%. In this case, the breakdown of the sample occurred in less than 30 sec. The PD record for 1s acquisition contained a very high number of PDs, more than 10000 (see Table 5.4) with a relatively small magnitude (average magnitude 100 pC, see Table 5.5). The PDs occurred in phase with the applied voltage as shown in the inset to Fig. 6.17. Hence, the resultant PSA plot is remarkably different from the plots in Fig. 6.15 characterising the electrical tree growth. Using the above notations, Clusters 1 and 4 appear aligned and in parallel with the 45° line, the remaining clusters are significantly smaller and with less scatter than before. It can be concluded that the scatter plots of the ratio $\Delta U/\Delta t$ are able to discriminate between the different regimes (electrical tree and runaway) and modes (burst and between the bursts) that can occur in an epoxy resin based insulation.



Fig. 6.17: A PSA of PD pulses in CY1311 epoxy resin on the basis of scatter plots of $\Delta U/\Delta t$ (in Vs⁻¹), runaway

6.3.2. PSA of PDs from voids

The PD activity in voids was analysed in terms of φ -q-n patterns and PSA analysis in a similar way as in the case of electrical treeing. The temperature and moisture dependences of the PD patterns acquired from voids in CY1311 and CY1301 epoxy resin are illustrated in Fig. 6.18 and Fig. 6.19, respectively. The CY1311 samples were tested above T_g only, while the CY1301 samples were tested below and up to 20°C above T_g of the resin. In Fig. 6.18 and Fig. 6.19 the φ -q-n plots are shown on the left and the corresponding PSA plots on the right. The data were acquired after 10 min of discharge activity and the acquisition period was 1s. Since the discharge activity and the corresponding PD patterns remained stable throughout the experiments, the patterns shown in Fig. 6.18 and Fig. 6.19 can be considered as representative for the PD process in recessed voids in epoxy resins under the specified conditions.

In the case of CY1311 epoxy resin samples, there is an asymmetry between the positive and negative PD distributions shown in Fig. 6.18 with the number of the negative PDs being considerably higher than those of positive PDs. At low temperatures and moisture (see Fig. 6.18a), the phase angle at which the negative PDs start to occur is less than 180°. Some of the positive PDs also take place during the negative half-cycle of the applied voltage, i.e. in the phase window between 330° and 360°, while the remaining positive discharge show significant scatter across the positive half-cycle of the applied voltage, i.e. the phase window between 0° and 180°. This is reflected also in the PSA plot where Cluster 4 (using the designations in Fig. 6.15) associated with the negative PD distribution is easy to distinguish, while the Cluster 1 associated with the positive PDs shows a significant scatter. Increasing temperature and/or moisture result in phase shifts in both positive and negative pulse count distributions. At the highest level of temperature and moisture the negative PDs occur in phase with the applied voltage, i.e. between 180° and 360°. The positive PDs occur in a narrow phase window in the first quadrant of the applied voltage, i.e. between 0° and 90°. The corresponding changes in the PSA plot associated with the increased levels of moisture and temperature are a decrease in the scatter of the clusters and their alignment in a similar way as in the case of PD data obtained from electrical treeing.

In the case of CY1301 samples, the φ -q-n and PSA plots given in Fig. 6.19 show little temperature and humidity dependence. In this case, the positive and negative PD distributions appear more symmetric to each other and the phase windows in which the discharges occur remain constant over the temperature and humidity ranges studied here. The corresponding PSA plots resemble those obtained in the case of electrical treeing due to the fact that the discharges occur in similar phase windows in both cases.



Fig. 6.18: PD activity in CY1311 samples with a void, on the left φ -q-n plot and on the right PSA plot: a) moisture 0.1%, 20°C; b) moisture 0.6%, 20°C; c) moisture 2.5%, 20°C; d) moisture 0.6%, 50°C; after 10 min of discharge activity, data acquisition time 1s



Fig. 6.19: PD activity in CY1301 samples with a void, on the left $\boldsymbol{\varphi}$ -q-n plot and on the right PSA plot: a) moisture 0.05%, 20°C; b) moisture 0.2%, 30°C; c) moisture 0.6%, 20°C; d) moisture 0.2%, 70°C; after 10 min of discharge activity, data acquisition time
6.4. Chapter summary

In this chapter the PD data from electrical treeing experiments and PDs in voids have been analysed. In the case of electrical trees, it has been found that both positive and negative PD magnitude and PD pulse count distributions are skewed. As a consequence a number of correlations exist between the statistical moments characterising these distributions. The statistical moments (mean, standard deviation, skewness and kurtosis) have been found to be non-stationary and to change their values in the course of the tree growth. A correlation was also obtained between the standard deviation of the total distribution and the average power per discharge, which gives a quantitative relation between the instantaneous voltage, discharge magnitude and number of discharges. This relation was found to be valid for the whole set of applied voltages and environmental conditions and therefore holds for both bush-type and branch type trees. It can be used as an indicator that provides information about the electrical tree growth process. Also it can be concluded, given the correlations found between the four statistical moments derived from experimental PD magnitude distributions, that the PD amplitude distributions conform to a two-parameter skewed distribution.

The PSA was used as an alternative approach for analysis of PD data. A relationship between the φ -q-n and PSA plots has been demonstrated. The PSA method was used to differentiate between the different degradation modes (electrical treeing and runaway) and arguably, the PSA plots present a better visualization technique for a PD-based diagnostics of the electrical insulation. An advantage of the PSA representation is the fact that information about the PD magnitudes is not required in the data analysis, while the information about the degradation mode is preserved.

Temperature and absorbed moisture have been found to affect the PD activity in voids in a similar way, therefore the observed changes in the PD dynamics are likely to be related to changes in the material properties of the host resin rather than the electron avalanche process.

Chapter 7: Discussion

So far in this work, a chemical characterisation of the epoxy resin systems has been presented in Chapter 2. The chemical constituents of CY1311 and CY1301 epoxy resins and HY1300 hardener have been identified using GCMS. The resins are typical DGEBA type pre-polymer and CY1311 contains also a silicone additive to reduce the glass transition temperature from 50°C (for the fully cured CY1301) to 0°C (for the fully cured CY1311). The hardener is a polyamine with added accelerator salicylic acid. The water absorption process in both epoxy resins has been studied and conforms to an anomalous and therefore non-Fickian diffusion. These results are consistent with absorbed moisture existing in two different states within the epoxy matrix; a mobile fraction interacting with the polymer network and a bound fraction due to nucleation of water molecules probably occupying regions of high free volume. The results of the dielectric study of the electrical properties of epoxy resin as a function of absorbed moisture and temperature were presented in Chapter 4. Below the glass transition temperature, the epoxy resin has a flat spectrum with no identifiable relaxations. However above the glass transition temperature in the two epoxy resin systems, the two dominant charge transport process were identified; QDC transport and DC conduction. Their dependence on temperature and amount of absorbed moisture has been studied. The results suggest inter- and intra-cluster ionic transport facilitated by large-scale segmental motion of the polymer network in the case of the QDC process and in the case of DC conduction the formation of a percolation pathways through the resin network. Both these processes scale in the same way with temperature and absorbed moisture. The effect of temperature and absorbed moisture on PD within voids and electrical tree growth was investigated in chapters 5 and 6. Both moisture and temperature were found to affect the PD behaviour in a similar way. Hence the PD characteristics are fundamentally determined by the electrical charge transport properties of the epoxy resin and moisture has little impact on the electrical properties of the discharging gas within the void or electrical tree.

In this chapter a relationship is established between the QDC charge transport and the electrical degradation processes. A 'tentative' model for electrical tree growth in flexible epoxy resins is proposed and thermal breakdown is suggested as likely breakdown mechanism at higher temperature and/or moisture levels due to the increased ionic conductivity of the resin.

7.1. Origin of Charge Carriers involved in the QDC process

An important question that has not been answered yet is about the nature of the charge carriers involved in the QDC process. Frequently, QDC is associated with ion transfer between neighbouring clusters, although it can also have electronic nature (Jonscher, 1996; Dissado and Hill, 1984). The dielectric spectra of hydrated biopolymers (Shablakh et al., 1984; Suherman et al., 2002; Suherman and Smith, 2003) have been found to be similar to the epoxy resin spectra presented in Chapter 4.In all these cases a QDC charge transport was identified as a bulk charge transport process and a dispersion process superimposed in the spectra was identified to be due to electrode-sample interface. Proton transfer was suggested as a possible long-range charge transport mechanism in these QDC dominated system and some and evidence from the isotope dependence of the observed QDC process has been presented in Suherman et al. (2002) supporting this hypothesis. The chemical composition of the epoxy resin systems has the potential for proton transfer. The curing of an epoxy resin occurs as a result of a reaction between a hardener such as diamine and the terminal epoxide groups. This reaction can be accelerated in a presence of proton donors such as salicylic acid. Salicylic acid has been reported in literature to be present in the hardener and its role was ascribed to facilitate the polymerisation reaction (Griseri, 2000). The GC/MS analysis presented in Chapter 2 also seems to support the presence of salicylic acid.

As described in Chapter 2 the role of the salicylic acid in the epoxy system is complicated. It may react in the presence of amine groups giving a mono-anion and the acid group thus formed may open the epoxide group ring. There is a possibility that some salicylic acid exists in the hardener as mono-anions or as di-anions assuming that additional proton donation may occur (see Fig. 1.10). The concentration of both species will depend on the equilibrium conditions. Also, during the cure reaction a condensation reaction involving salicylic acid and hydroxyl groups may occur (Griseri, 2000), when the concentration of hydroxyl groups is increased due to opening of the epoxide ring. This reaction can account for the presence of initial moisture after the epoxy samples have been post-cured as reported in Section 2.5. Thus the presence of

salicylic acid may be a necessary prerequisite for proton donation and consequently proton transfer along hydrogen bonded water clusters, which gives rise to the observed QDC behaviour. Figure 7.1 shows dissociation of a salicylic acid molecule in the presence of water. The consequent proton transfer can be understood in terms of "structural diffusion" (Marx, 2006). It is a topological defect that migrates through the hydrogen-bonded system rather than actual mass diffusion of either protons H^+ or H_3O^+ protonic complexes. The process requires simultaneous breaking and making of covalent bonds in interchange with making and breaking of the associated hydrogen bonded network. In this way the proton can be shifted along the cluster as shown in Fig. 7.1.





Fig.7.1: Proton donation and transport in epoxy resins. (Top) Dissociation of salicylic acid in the presence of water. (Bottom) Proton transfer along a cluster of hydrogen bonded water molecules from (Marx, 2006)

The inter-cluster charge transfer is facilitated by the uptake of moisture, as it can be seen in Fig. 4.5 and Fig. 4.8. It is possible that cluster(s) can form a complete percolation path through the polymer at very low water content (below the detection sensitivity of the measurement technique used) or such clusters exist even without any water in the sample i.e. from the salicylic acid reactions. The QDC behaviour, which appears in the samples measured here, would therefore relate to isolated clusters that do not participate in a percolation path through the sample. The DC conductance can be related to the establishment of multiple percolation paths through the entire polymer network.

An anomalous diffusion model was presented in Chapter 3 for the water absorption in the epoxy systems with the water molecules being in bound and mobile states. A recent study on water diffusion in epoxy systems using deuterium NMR analysis (Popineau et al., 2005) has suggested that the mobile water is constituted of H₂O molecules interacting with the polymer network while the bound water occurs as a result of formation of water clusters. Therefore, the formation of water clusters appears to be correlated with the observed QDC behaviour. However, the lack of detectable charge transport below $T_{\rm g}$ and the high activation energy indicates that significant segmental motions of the polymer network that are only possible above Tg have to occur for the inter-cluster motions to take place, i.e. the percolation is a dynamic process. Hence, the inter-cluster charge transport occurs along filamentary paths through the bulk of the material that are limited in length. Such charge displacements would give rise to variations of the local electric field and could be of importance for electrical degradation in epoxy resins (Flandin et al., 2005). They would also occur during an electrical treeing experiment where local field fluctuations are important in determining the tree shape (Dissado, 2002), and could be of importance in explaining the effect of moisture on tree shape in epoxy resins (Champion and Dodd, 1999).

7.2. Effect of bulk charge transport on the electrical degradation and breakdown in epoxy resins

Typical values of the characteristic frequency ω_c of the QDC process are given in Table 7.1 at different levels of absorbed moisture and temperature. These values were obtained from the dielectric data by a least squares fitting procedure to the equivalent circuit presented in Fig. 4.10. The values in red in Table 7.1 indicate that an 'instantaneous' breakdown of the sample was observed under the same conditions (see Table 5.3). When ω_c is greater than the frequency of the applied voltage, the charge transport between clusters is allowed and this leads to formation of superclusters (extended percolation paths). Hence the cluster polarisation will occur at longer distances. The charge deposited at the tips of the electrical tree as a result of the PD activity can be effectively removed by this mechanism leading to reduced space charge within the tree structure. Thus the negative feedback of the space charge electric field is reduced or eliminated resulting in higher PD rates (see Table 5.4) giving rise to faster growing trees (see Table 5.3). Reduced space charge surrounding the tree will lead to less field enhancement during the next half cycle and hence trees are likely to grow with lower fractal dimension."

| <u> </u> | | | | | | |
|-----------------|------------------|------------------|-----------------|-----------------|-----------------|--------|
| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
| RH15 | 1.2E-2± | 1.9E0± | 9.0E0± | 2.8E1± | 8.7E1± | 2.2E2± |
| (0.1%) | 2.6E-3 | 1.3E-1 | 2.9E-1 | 8.3E-1 | 2.8E0 | 5.5E0 |
| RH30 (0.7%) | 2.0E0± 1.4E-1 | 1.5E1± 6.0E-1 | 8.0E1± 1.5E0 | 3.6E2± 1.0E1 | 7.3E2± 2.7E1 | - |
| RH75 (2.4%) | 4.9E2± 2.1E1 | 1.9E3± 1.7E2 | 5.8E3± 3.5E2 | 2.3E4± 1.7E3 | 6.6E4± 5.8E3 | - |
| RH100 (7.2%) | 8.5E3± 9.1E2 | 3.6E4± 6.8E3 | 1.5E5± 2.8E4 | 3.3E5± 7.6E4 | 6.6E5± 1.5E5 | - |

Table 7.1. Characteristic frequency [Hz] of the QDC charge transport process as a function of temperature and humidity, CY1311

It is noteworthy that the corresponding values of ω_c , at which breakdown has occurred, are much higher than the frequency of the applied voltage (50Hz). Therefore the critical factor for the transition from electrical degradation to breakdown is the length of the percolation path. It has been suggested in the literature that in epoxy resins an increase in the ionic conductivity at temperatures above T_g and at high moisture levels may lead to thermal breakdown even at moderate electric fields (Sletbak *et al.*, 1988). The values of the DC conductance given in Table 7.2 were calculated using the equivalent circuit model proposed in Fig. 4.9 from the dielectric data presented in Chapter 4. Again the red font indicates conditions under which an instantaneous breakdown was observed. The uncertainty increases under high temperature and moisture conditions due to possible contributions from (interfacial) processes that have not been modelled using the proposed equivalent circuit. The transition from electrical treeing to thermal breakdown occurs when the value of the DC conductance is greater than 10nS.

| numury, CI 1011 | | | | | | |
|-----------------|--------|--------|--------|--------|--------|--------|
| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
| RH15 | 6.6E0± | 3.0E1± | 1.8E2± | 8.7E2± | 2.8E3± | 3.6E3± |
| (0.1%) | 2E-1 | 2.0E0 | 7.0E0 | 2.6E1 | 9.5E1 | 1.4E2 |
| RH30 | 4.0E1± | 1.8E2± | 1.5E3± | 9.4E3± | 3.3E4± | |
| (0.7%) | 2E0 | 1.2E1 | 4.2E1 | 3.5E2 | 1.2E3 | - |
| RH75 | 1.8E3± | 2.3E4± | 1.0E5± | 1.1E5± | 3.9E5± | |
| (2.4%) | 9.2E1 | 6.4E3 | 4.4E3 | 7.1E4 | 2.1E5 | - |
| RH100 | 4.4E4± | 2.1E5± | 1.2E6± | 6.5E6± | 8.0± | |
| (7.2%) | 2.1E3 | 7.3E4 | 1.1E6 | 3.4E6 | 6.0E6 | - |

Table 7.2. DC conductance [pS] as a function of temperature andhumidity, CY1311

The corresponding fitted values for $\tan \delta$ at 50 Hz are given in Table 7.3. The transition to thermal breakdown occurs when the effective conductivity of the resin exceeds a critical value which is dependent on temperature and absorbed moisture such that $\tan \delta > 1$.

| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
|--------------|------|-------|-------|-------|-------|------|
| RH15 (0.1%) | 0.07 | 0.09 | 0.10 | 0.16 | 0.29 | 0.43 |
| RH30 (0.7%) | 0.09 | 0.11 | 0.25 | 0.81 | 2.00 | - |
| RH75 (2.4%) | 0.68 | 2.65 | 7.09 | 12.09 | 18.90 | - |
| RH100 (7.2%) | 6.62 | 15.63 | 27.69 | 45.08 | 41.84 | - |

Table 7.3. Tan δ @50Hz as a function of temperature and absorbed moisture

7.3. Effect of bulk charge transport on the PD process

As a consequence of proton transfer along water clusters, the electrical charges deposited by the discharge can be neutralised and replaced with ionic charges of the same sign further away from the tree structure and reducing the space charge field that opposes the applied electric field. Thus the local conditions for the inception of the next discharge will occur after a reduced delay; with the delay controlled by the bulk ionic conductivity. The higher the bulk conductivity or higher the characteristic frequency of the QDC process the greater number of PD events in each half cycle.

Fig. 7.2 shows a simplified equivalent circuit model that was used to study the effect of bulk charge transport on the gas discharges. The circuit represents a void in

series with the bulk of the material. The void is represented as a spark gap in parallel with G_V , where G_V is the surface conductance of the void. A capacitor C_B in parallel with a conductance G_B represents the bulk capacitance and conductance of the epoxy resin, respectively. This model can be used for simulation of the PD activity either in the case of an electrode-bound void or as an approximation to an electrical tree, if the entire tree structure is assumed to discharge simultaneously. The electric field for PD inception, Eon, and extinction, Eoff, were separately defined for each half-cycle of the applied voltage stress, E_{AC} , as free parameters. The values of E_{on} and E_{off} were chosen to match typical experimental PD data for electrical treeing and must have similar values for both polarities as the PD discharge patterns are essentially symmetric(see Chapter 6).. The value of value of G_V was set to zero to model electrical tree channels that are non-conducting and the value of C_B was chosen to be 2.2nF. The peak value of the 50Hz sinusoidal applied stress was 19.6 kV/mm, and the values for Eon and Eoff were 11.6 kV/mm and 10.9 kV/mm for the positive polarity and 11.3 kV/mm and 10.7 kV/mm for the negative polarity respectively. A study of the PD inception and extinction voltages and stresses in voids in different insulating materials can be found in Hall and Russek (1954).



Fig. 7.2: Equivalent circuit for PD simulation

Fig. 7.3 shows on the left the phase-resolved plots and on the right the PSA return maps obtained from two calculations over 50 cycles of the applied voltage at two different values of the conductance G_B , namely $G_B = 5.10^{-11}$ S and $G_B = 5.10^{-6}$ S. The values of G_B were chosen to simulate the increase in DC conductance with increasing temperature and/or moisture (see Table 7.2). In the phase-resolved plots, the PD pulses

are indicated by the green lines, the voltage across the spark gap is given in black, the voltage across the insulation (capacitor C_B) in red and the applied sinusoidal voltage in blue. The simulations resemble closely the experimental data. In the case of a lower conductivity of the bulk resin (Fig.7.3a) the PDs occur in the first (Q1) and third (Q3) quadrants of the applied voltage. The differential ratio dU/dt was used to analyse the simulated data and to obtain the PSA plots in the same way as the experimental data presented in Chapter 6. The PSA return map shown in Fig. 7.3a consists of six clusters, which have similar appearance and alignment as in the case of burst type behaviour during an electrical tree growth. It was not possible to model the experimentally observed fluctuations in the PD activity, which on the PSA map appear as scatter in the six clusters, that occurs between the bursts in the PD activity using the simple equivalent circuit in Fig. 7.2. Between the bursts the tree fractal dimension has been found to increase, which implies multiple discharge sites and less correlation between the individual PD events.



Fig. 7.3: PD simulation over 50 cycles of the applied voltage, phase resolved data (left), PSA plot(right); a) $G_B = 5.10^{-11} \text{ S}$; b) $G_B = 5.10^{-6} \text{ S}$

An increased bulk conductivity of the resin leads to an increase in the number of PDs per cycle and a shift in the phase window over which the PDs occur (see Fig.7.3b). Hence, they take place in phase with the applied voltage and even after the positive and negative voltage peaks, i.e. the negative discharges occur in Q1 and Q2, and the positive discharges in Q3 and Q4, respectively in Fig 7.3b. This is reflected in the corresponding PSA return map, where the clusters associated with positive and negative PD distributions extend along the 45° line. Similar return maps were observed in the cases of runaway electrical tree growth.

In the case of a runaway tree growth, the effective bulk conductivity of the resin is very high and it can be considered nearly homogeneous throughout the bulk resin. The circuit element G_B is a reasonable approximation in this case and it is able to explain the transition in the PD activity from typical electrical tree growth to runaway growth due to the high effective bulk conductivity. Under low temperature and moisture conditions, however, the effective bulk conductivity of the resin is low and a QDC charge transport should be considered rather than DC conduction. The QDC charge transport and the underlying cluster model are usually understood in terms of fractal circuits (Dissado and Hill, 1989; Dissado, 1990; Hill *et al.*, 1991). The equivalent circuit in Fig. 7.2 does not account for the fractal geometry of the electrical tree structure and the build-up of local space charges. Therefore, it does not provide a sufficient complexity to mimic the fluctuations seen experimentally. The influence of the QDC process on the electrical tree ing is discussed in the next section.

7.4. A 'tentative' model for electrical tree growth in flexible epoxy resins

Figure 7.4 shows a 'tentative' model for electrical tree growth in flexible epoxy resins in the presence of QDC charge transport. The electrical tree inception stage (Dissado, 2002) is not considered here. The model requires that a gas tubule has been formed within the resin adjacent to the needle electrode and discharges may occur in the tubule. A model for electrical tree initiation in epoxy resins can be found in (Wu and Dissado, 2005).

In Table 7.4 are summarised the parameters that are likely to have an impact on the electrical tree growth in flexible epoxy resins according to the model proposed here.

| Parameter | Description | Symbol |
|-------------------------------|--|--------------|
| Cluster correlation length | Max. distance at which charges can be separated | ξς |
| | within a cluster | |
| Cluster polarisation time | Time needed to separate the positive and negative | $	au_{ m c}$ |
| | charge at distance l_c within a cluster, $l_c < \xi_c$ | |
| Percolation distance | Mean intracluster distance that can be travelled by | lp |
| | a proton | |
| Critical frequency of the QDC | Critical frequency below which the intracluster | ω |
| process | charge transport is allowed | |
| Recombination time constant | Time needed for proton – shallow trapped | $	au_{ m e}$ |
| (protons-electrons) | electrons recombination process | |
| Recombination time constant | Time needed for proton - negative ion | $	au_{i}$ |
| (protons-negative ions) | recombination process | |

 Table 7.4. Parameters affecting the electrical tree growth in flexible epoxy resins

Polarised clusters of positive (protons) and negative ions, which are required for the QDC process to occur, should be present in the epoxy matrix due to the applied electric field. The dielectric data presented in Chapter 4 suggests that cluster polarisation occurs at frequencies from ω_c to greater than 100 kHz, therefore the cluster polarisation time τ_c is very short, i.e. cluster polarisation can be considered to occur in phase with the applied voltage without a time lag. The negative ions involved in the QDC have much bigger size than the protons and hence they can be considered immobile, and hence the intracluster charge transport mechanism is due to proton hopping.

In Fig. 7.4a is assumed that a partial discharge has just occurred and deposited electrons near the tree tip. These electrons are likely to become trapped. The chemical composition of the epoxy resin systems has the potential for both shallow and deep traps. Possible sources for deep traps in the polymer matrix can be the benzene rings due to their high electron affinity. The electron affinity of the phenoxyl group (part of the DGBEA molecule) is 2.253eV (CRC Handbook of Chemistry and Physics, 2008). The electrons in such deep traps will effectively ionise the molecular moieties thus creating immobile negative ions. The presence of space charge in the polymer matrix will contribute to fluctuations in the local electric field.



Fig. 7.4: A 'tentative' model of electrical tree growth in flexible epoxy resins

The separation between the trapped electrons and the protons from the polarised clusters is likely to be shorter that the cluster polarisation length ξ_c and Fig. 7.4b shows that recombination between some of the trapped electrons and the protons may occur on a time scale τ_e shorter than the half-period of the applied voltage, leaving negative ions near the tree tubule end as a consequence. When the polarity of the applied sinusoidal voltage reverses (see Fig. 7.4c) the total electric field across the tree tubule will be enhanced due to the presence of the negative space charge. Thus the electrons remaining in the shallow traps can be released giving rise to PDs in the gas tubule. However, there still will be some negative charge in the polymer matrix due to the negative ions. After the next polarity reversal the local field created by these negative ions will oppose the applied field, thus preventing further discharges in the existing tubule. New tubules will be formed in the places where the local electric fields allow electron avalanches to take place and damage the polymer (Dodd, 2003). As a result the fractal dimension of the electrical tree will increase.

The negative charge in the bulk resin will create local dc bias field and further proton hopping from the bulk can be expected to take place as indicated in Fig. 7.4d at times longer than ω_c^{-1} . In this way the negative ions in the immediate vicinity of the original tree tubule will be neutralised with a time constant τ_i . The recombination time constant τ_i , hence, depends on the internal structure of the infinite cluster, i.e. the backbone of the percolating system (Stauffer and Aharony, 1994). Negative ions will still be present in the polymer but this time they will be further away from the tip of the original tree tubule on a distance l_p depending on the proton hopping path as shown in Fig. 7.4e. Spreading of the space charge in the bulk resin will allow further electron avalanches to take place in the initial tree tubule. As a result of the PD activity the electrical tree will grow in the pin-plane direction as indicated by the dashed line in Fig. 7.4f. The further tree growth will proceed by repeating the sequence of steps from a) to f).

It is important to emphasize that in practice the sequence of steps from a) to f) will take place over more than just two cycles of the applied voltage shown in Fig. 7.4. According to the proposed model the life-time of the negative charge (ions and deep trapped electrons) in the vicinity of the tree tips governs the growth rate in the pin-plane direction. Proton hopping is the likely mechanism for the observed QDC charge transport. A possible source of protons is hydrolysis of salicylic acid present in the hardener. The likely percolation paths are through the hydrogen bonded water clusters within the bulk resin. The amine groups part of the hardener's chain have high proton affinity (CRC Handbook of Chemistry and Physics, 2008) and are also likely proton hopping sites. This may explain why QDC is observed even at very low moisture concentrations. Increasing the level of temperature and/or moisture tends to facilitate the QDC charge transport process. Hence, the influence of the absorbed moisture and temperature on the electrical degradation mechanisms can be understood in terms of their influence on the bulk charge transport. The experimental results presented in Chapter 5 also support this hypothesis. The possible impact of charges (positive and negative ions) in the gas tubules due to the PD activity is not considered here. It is likely that they will be neutralised from consecutive discharges after the voltage polarity reversal and so their effect can be neglected on the time scales considered here.

The model in Fig. 7.4 requires that during the electrical tree growth a significant amount of charge is stored in the bulk resin in the vicinity of the tree structure. As a result a net charge imbalance will occur between the PDs taking place during the positive and negative polarity of the applied voltage, respectively. Experimental evidence for build-up of charge during the tree growth is shown in Fig. 6.9.

At low temperature and moisture conditions, $\boldsymbol{\omega}_{c}$ is much smaller than the frequency of the applied voltage $\boldsymbol{\omega}$ and hence the time constant τ_{i} is very long, which causes electrical trees with high fractal dimensions to be formed, i.e. bush trees. Increasing $\boldsymbol{\omega}_{c}$ decreases the value of τ_{i} thus the tree growth in pin-plane direction is facilitated and as a result electrical trees with low fractal dimension are formed, i.e. branch trees. If $\boldsymbol{\omega}_{c} >> \boldsymbol{\omega}$, the cluster polarisation extends over the entire percolation path between the pin and the plane and a thermal breakdown will occur.

The relative contributions to $\tan \delta$ of the DC conductance and the QDC process are given in Table 7.5. It can be seen from Table 7.5 that QDC has a higher contribution under all experimental conditions suggesting that proton hopping is the dominant charge transport mechanism through the bulk resin. The levels of the activation energy presented in Chapter 4 also support the hypothesis that charge transport mechanism has ionic nature.

| | 20°C | 30°C | 40°C | 50°C | 60°C | 70°C |
|--------|--------------|--------------|--------------|-------------|-------------|-----------|
| RH15 | | | | | | |
| (0.1%) | 0.0004/0.069 | 0.002/0.084 | 0.0096/0.091 | 0.04/0.11 | 0.13/0.16 | 0.16/0.27 |
| RH30 | | | | | | |
| (0.7%) | 0.002/0.084 | 0.009/0.0995 | 0.07/0.18 | 0.35/0.43 | 1.29/0.71 | - |
| RH75 | | | | | | |
| (2.4%) | 0.067/0.62 | 0.70/1.95 | 2.43/4.66 | 1.42/10.67 | 3.13/15.77 | - |
| RH100 | | | | | | |
| (7.2%) | 0.95/5.68 | 2.64/12.99 | 6.00/21.69 | 18.35/26.73 | 12.73/29.10 | - |

Table 7.5. Contributions to $Tan\delta@50Hz$ due to DC conduction (left) and due to QDC (right)

7.5. Calculation of critical parameters for thermal breakdown

In order to test the hypothesis that thermal breakdown occurs when the effective electrical conductivity of the resin is high, steady-state thermal breakdown was considered in two cases, namely homogeneous applied electric field and divergent field, i.e. in the case of parallel plane and pin-plane geometry, respectively. In the case of parallel plane geometry the analytical expression Eq. 1.20 was used to calculate the maximum thermal voltage (MTV) that can be sustained. A finite element model was used to solve Eq. 1.19 numerically in FEMLAB in the case of a pin-plane geometry and to obtain the critical temperature T_c above which breakdown takes place. Since Eq. 1.19 and Eq. 1.20 are derived for dc fields only, the peak value of the ac applied voltage $V_0 = \sqrt{2} * V_{rms}$ was used as a reasonable approximation in all calculation. Since the electrical degradation experiments presented in Chapter 5 were conducted at 13.5kV rms, a value $V_0 = 19kV$ was used in the calculations for steady-state thermal breakdown.

7.5.1. Parallel plane geometry

Eq. 1.20 provides easy to compute analytical solution for the MTV. The dielectric data presented in Chapter 4 could be used to calculate the parameters ϕ and σ_0 as shown in Fig. 7.5. The parameters ϕ and σ_0 were obtained at four levels of absorbed moisture from the fitted expressions given in Fig. 7.5. The thermal conductivity κ_0 of the resin is assumed to be constant, i.e. temperature and moisture independent and its value is taken from the data provided by the manufacturer of the resin (Ciba-Geigy, 1982). The value for $\kappa_0 = 0.2 \text{ Wm}^{-1}\text{K}^{-1}$ was used in all calculations. The Boltzmann constant is $k_B = 1.38066 \times 10^{-23}$, J. K⁻¹.



Fig. 7.5: Arrhenius plots of DC conductance at various levels of absorbed moisture $0.20\%(\blacksquare), 0.72\%(\diamondsuit), 3.0\%(\bigstar)$ and $7.2\%(\bigcirc)$

The calculated values for ϕ and σ_0 at each concentration of absorbed moisture are given in Table 7.6 and the MTV is calculated for two ambient temperatures. The values of the ambient temperature were chosen to match the experimental conditions at which transition from electrical treeing to thermal breakdown was observed (see Table 5.3). Thus the calculated value for MTV can be compared to the applied voltage V₀. Thermal runaway will occur if V₀ is greater than the MTV, otherwise electrical treeing will be observed. A very good agreement is found between the predicted and the actual experimental values. The only exception is at absorbed moisture 3.0% since thermal breakdown was observed to take place at 30°C (303K) in the experiment, while the calculated value for MTV suggests that ambient temperature higher than that is required. However, there is a significant deviation exactly at this level from the general trend in the fitted values of the dc conductivity given in Fig. 7.5. It appears that this particular value is underestimated, which may account for the observed discrepancy.

| Absorbed moisture, % | Para | meters | T _{amb} , K | MTV, kV | Vo | Predicted | Observed |
|----------------------------|------------|---------|----------------------|---------|----|-----------|-----------|
| 0.2 | σ_0 | 2E+11 | 353.15 | 16 | | Breakdown | Breakdown |
| | φ | 2.1E-19 | 343.15 | 30 | | Treeing | Treeing |
| 0.7 | σ_0 | 6E+14 | 333.15 | 15 | | Breakdown | Breakdown |
| | φ | 2.3E-19 | 323.15 | 34 | 10 | Treeing | Treeing |
| 3.0 | σ_0 | 6E+9 | 303.15 | 30 | 19 | Treeing | Breakdown |
| | φ | 1.7E-19 | 293.15 | 57 | | Treeing | Treeing |
| 7.2 | σ_0 | 7E+12 | 293.15 | 14 | | Breakdown | Breakdown |
| | φ | 1.9E-19 | 283.15 | 28 | | Treeing | Treeing |

Table 7.6. Calculated values for MTV in the case of steady-state thermal breakdown

7.5.2. Pin- plane geometry

The above calculations were in the case of a homogeneous electric field. In order to investigate the effect of divergent fields a finite element model was set up in FEMLAB to solve numerically Eq. 1.19. The model solves simultaneously the coupled partial differential equations from heat transfer and dc conductive media modules in FEMLAB. The dc conductivity of the epoxy resin was modelled once again using the Arrhenius relationship Eq. 1.21. The same values of the parameters ϕ and σ_0 were used as in the previous section (see Table 7.6). A two-dimension model with axial symmetry was chosen for the task. It was necessary to generalise the pin geometry and to reduce the size of the modelled domain in order to ensure convergence. The model geometry and the corresponding boundary conditions are shown in Fig. 7.6. The pin electrode is at constant potential V₀ and the plane electrode is ground. Both electrodes and the electrical insulation boundaries are at fixed ambient temperature T_{amb}. The axis of symmetry is also shown in Fig. 7.6. The pin-plane distance is 2mm. The initial conditions were T_0 equal to the ambient temperature, i.e. the sample is in thermal equilibrium with the environment before the voltage application and V_0 is the potential of the pin electrode. The critical temperature T_c can be identified from the simulation results as the maximal temperature at which a convergent solution can be obtained. An example of a steady-state solution of Eq. 1.19 at the critical temperature is shown in Fig.7.7. The colour scale gives the temperature (in K), while the contours represent the equipotential lines. The simulation result shows that a hot spot is formed underneath the pin electrode at T_c.



Fig. 7.6: The geometry of 2D axial symmetry model, domain size 3x3.5mm, 8432 mesh elements



Fig. 7.7: Simulation result for $T_c=331$ K in the case of absorbed moisture 0.7%, $V_0=19$ kV, steady-state solution

The model also allowed a time-dependent solution to be obtained. However, in this case $\frac{dT}{dt} \neq 0$ in Eq. 1.18 and it was necessary to find values for the specific heat capacity C_p and density D. The manufacturer of the resin provides a value for the density of the cured CY1311 resin, D=1.12 Mg/m³ (Ciba-Geigy, 1982). The value for $C_p=1.52 \text{ Jg}^{-1}\text{K}^{-1}$ for cured epoxy resin was selected from the Tables of Physical & Chemical Constants (2005). The result of the transient solution for the pin-plane midpoint is shown in Fig. 7.8. It shows the time variation of the temperature at this point. When the ambient temperature is below the critical temperature, a steady state solution is obtained and the overall increase in the temperature is just few degrees K. When the critical temperature is approached a longer period of time is needed to reach a steady-state value. A thermal runaway occurs once the ambient temperature exceeds the critical value. The greater the value of T_{amb} above T_c, the faster is the runaway process. The results of the transient analysis are summarized in Table 7.7 where T_c is given as a function of the level of absorbed moisture in the sample. The value of RH is given in the parenthesis as a reference. The same results are obtained as in the case of homogeneous electric field. In general, they agree well with the experimental observation and the only exception is in the case of moisture level 3.0%, where slightly higher temperature value is predicted (compare Table 7.7 with Table 5.3).



Fig. 7.8: Time variation of the temperature at the pin-plane midpoint, $T_c=331$ K, absorbed moisture 0.7%, $V_0=19$ kV, transient solution

| Table 7.7. Critical temperatures | for thermal breakdown at different level | ls of |
|----------------------------------|--|-------|
| absorbed moisture | | |

| Absorbed moisture | Critical temperature |
|-------------------|----------------------------|
| 0.2% (RH15) | $T_c = 80^{\circ}C$ (353K) |
| 0.7% (RH30) | $T_c = 58^{\circ}C$ (331K) |
| 3.0% (RH75) | $T_c=39^{\circ}C$ (312K) |
| 7.0% (RH100) | $T_c=17^{\circ}C$ (290K) |

7.6. Chapter summary

In this chapter the impact of temperature and moisture on the bulk charge transport mechanisms have been related to the electrical degradation and breakdown mechanisms. As a result a 'tentative' model for electrical tree growth in flexible epoxy resins has been proposed. The novelty of the proposed model is that it considers a QDC charge transport through the bulk polymer, where proton hopping has been suggested as long range transport mechanism. A recombination time constant, i.e. time needed for neutralisation of the space charge in the vicinity of the tree structure by charges involved in the QDC process, is suggested as a governing parameter of the tree growth rate. The impact of temperature and absorbed moisture on the electrical tree growth is hence related to changes in the characteristic frequency of the QDC process, i.e. the time constant of the process and the percolation distance that the protons can travel. At high levels of moisture and/or temperature multiple percolation paths can be established thus increasing the effective ionic conductivity of the material leading to thermal breakdown when tan $\boldsymbol{\delta}$ is greater than 1.

Chapter 8: Conclusions and Further Work

The aim of this work was to study the factors that influence the electrical degradation in epoxy resins caused by partial discharges and to investigate the corresponding variations in partial discharge activity. The work has been carried out to improve the current understanding of the processes of electrical degradation and breakdown that take place within epoxy resin based insulation and also from a practical point of view to identify a set of characteristic features that can be used for condition monitoring and diagnostics of HV insulation systems.

The following conclusions summarize the advances in knowledge and understanding as a result of this work:

- 1. The dielectric spectroscopy study of epoxy resins as a function of temperature and absorbed moisture has revealed 4 processes above the glass transition temperature T_g , namely:
 - a. DC conduction
 - b. QDC
 - c. Interfacial polarisation
 - d. Frequency independent capacitance
- 2. The two charge transport mechanisms, namely quasi-dc (QDC) and DC conduction, have been identified as bulk conduction mechanisms in epoxy resins in a flexible state, i.e. above T_g , and at low frequencies. It has been found that QDC conduction is the dominating dielectric response. Both processes are thermally activated and also dependent on the moisture absorbed in the resin.
- 3. It was proposed that the observed QDC behaviour might be due to proton hopping within and between clusters at frequencies lower than the critical frequency of the process. Protons originate from the dissociation of water molecules in the presence of acid groups, e.g. salicylic acid. The QDC characteristic frequency scales with increasing temperature and absorbed moisture.
- 4. The QDC interpretation supports previous work using gravimetric measurements and NMR which concluded that moisture within the polymer matrix exists in two phases free mobile water and bound water in clusters.

- 5. Interfacial polarisation responses have been identified with an imperfect contact between the sample and measurement electrodes or due to blocking effect of the electrodes. Such relaxation responses have previously been attributed to bulk response mechanisms in the literature, e.g. α -relaxation, on a range of dispersive materials exhibiting QDC.
- 6. It has been demonstrated that the electrical properties of bulk resin affect the degradation mechanisms, i.e. electrical treeing and thermal runaway. It has been confirmed that temperature and moisture absorbed in the samples affect electrical tree growth in a similar way. The growth time and the fractal dimension of the trees have been found to decrease with both increasing temperature and moisture concentration. The above observations were explained as due to the effective removal of the charge deposited at the tips of the electrical tree as a result of the PD activity by cluster polarisation that occurs at longer distances, producing a route for carrier transport in the quasi-dc form and thermal heating of the material.
- 7. Both QDC and DC conduction contribute to the effective conductivity of the resin at the power frequency. Levels of temperature and moisture concentration were identified at which the degradation mechanism (electrical treeing) changes to thermal breakdown. The transition to thermal breakdown has been explained as due to the formation of percolation paths that extend over the entire distance between the pin and the plane such that the loss tangent exceeds unity, $tan\delta > 1$.
- 8. Several correlations have been found to exist between the physical parameters characterising the PD activity during electrical treeing and the statistical moments characterising the corresponding φ -q-n distributions. Also, correlations have been found to exist between the statistical moments characterising the φ -q-n distributions, e.g. between the mean and the standard deviation, and between the skewness and the kurtosis. The PD amplitudes during treeing have been found to conform to a two-parameter skewed distribution and the above correlation can be explained by the known dependence between the statistical parameters describing two-parameter probability distributions, such as Weibull, Gamma or Lognormal distribution used for statistical analysis of the PD data.

- 9. The details of PD dynamics during the electrical tree growth have been found to change significantly with temperature and absorbed moisture. The average PD magnitudes have been found to decrease with increases in both temperature and humidity, while the corresponding number of PDs per second to increase. This is considered to be a further consequence of the space charge decay with increasing inter-cluster charge transport.
- 10. The analysis of PDs acquired during the electrical tree growth revealed asymmetry between the φ -q-n distributions of positive and negative discharges indicating a build-up of net charge in the tree structure during the tree propagation. This net charge builds up a DC space charge field enhancing discharges on one half-cycle and accounting for the long term fluctuations in the PD activity, i.e. bursts in the PD activity, which have been shown in the past to be related to the applied AC voltage and resultant tree fractal dimension. Both temperature and absorbed moisture are likely to influence the build-up of net charge and to alter the tree growth dynamics.
- 11. The Pulse Sequence Analysis (PSA) of PD data was able to discriminate between discharges in voids, electrical trees and runaway breakdown. It has also been shown that the PSA patterns are related to the bulk charge transport in the resin. Hence PSA points the way for a possible tool to infer the state of the insulating material and useful for condition monitoring and assessment.

On the basis of the current study, further work may include:

1. In the current study, QDC was identified as the dominant dielectric response in epoxy resins above T_g . It is of considerable interest to investigate the parameters of the underlying cluster network, e.g. mean cluster size, fractal dimension, correlation length etc., which can further improve our understanding of polymeric materials. The nature of the charge carriers involved in the QDC process is another issue worthwhile further investigation. The idea proposed here that proton hopping is a possible charge transport mechanism has to be verified. An isotope dependence of the QDC process has been previously reported in the literature related to hydrated biopolymers and requires further investigation in the case of epoxy resins. Hence, a set of experiments can be

devised using deuterium oxide to ascertain the origin of the charge carriers involved in the QDC process. Further investigation of the nature of the charge carriers involved in the DC conduction mechanism, i.e. electrons or protons

- Molecular spectroscopy can be used to investigate in further detail the fractions of bound and mobile water and the structure of the hydrogen bonded system. A further study can include also dielectric spectroscopy of "contained" water clusters.
- 3. QDC conduction has been found in nano-filled epoxy resins. The effect of nanofillers on the cluster network has to be studied in further detail. The questions about the interaction of the nanofiller, the water molecules and the base resin also have to be answered.
- 4. The results of the current study suggest that care must be taken where epoxy resin based insulation is used for HVDC applications. The effective bulk conductivity of the resin under DC conditions is expected to be very high if the ambient temperature exceeds T_g due to possible long-range QDC charge transport. Therefore, an investigation involving real industrial HVDC equipment will be beneficial in determining the practical applicability of epoxy resin based insulation for HVDC.
- 5. Embedding the material properties in the existing deterministic models of electrical breakdown can significantly improve their accuracy. This may lead to better prediction capabilities for the models in terms of insulation lifetime for example. Such models can also facilitate tailoring of new insulation materials with superior dielectric properties.
- 6. The results obtained from the analysis of PD data in this study can be used in condition monitoring and diagnostics of real industrial equipment. An important aspect is the application of PD based monitoring of industrial equipment in a noisy environment, especially in the cases where PDs with low magnitude can be expected, e.g. conducting electrical trees.
- 7. The approach based on the current study towards better understanding of the electrical degradation mechanism and the related variations in the PD activity can be used to study new insulation materials, e.g. nanofilled materials, so that reliable condition monitoring and diagnostics for the future HV electrical equipment will be achievable.

Appendix A: List of publications

- 1. Chalashkanov, N., et al., Pulse Sequence Analysis on PD data from electrical trees in flexible epoxy resins, accepted for publication in Proc. CEIDP 2011, October 16-19, 2011 Cancun, Mexico
- 2. Chalashkanov, N. M., S. J. Dodd, et al., On the Relationship between Bulk Charge Transport and Electrical Breakdown Mechanisms in Epoxy Resins, in Proc. Nord-IS, 2011, 13-15 June, Tampere, Finland
- Dodd, S. J., N. M. Chalashkanov, et al., Influence of Absorbed Moisture on the Dielectric Properties of Epoxy Resins, 2010 CEIDP. West Lafayette, Indiana, USA, 10.1109/CEIDP.2010.5723953
- 4. S.J. Dodd, N.M. Chalashkanov, J.C. Fothergill, Partial Discharge Patterns in Conducting and Non-Conducting Electrical Trees, in Proc. 10th IEEE International Conference on Solid Dielectrics 2010, 4th-9th July, Potsdam, Germany, 10.1109/ICSD.2010.5568217
- S.J. Dodd, N.M. Chalashkanov, J.C. Fothergill, L.A. Dissado, Influence of the Temperature on the Dielectric Properties of Epoxy Resins, in Proc. 10th IEEE International Conference on Solid Dielectrics 2010, 4th-9th July, Potsdam, Germany, 10.1109/ICSD.2010.5567945
- Chalashkanov, N., et al., PD Pattern Recognition Using ANFIS, in Proc. IEEE -CEIDP 2008, October 26-29, Quebec city, Canada, pp. 417 – 420, 10.1109/CEIDP.2008.4772865
- Dodd, S.J., N. Chalashkanov, and J.C. Fothergill, Statistical Analysis of Partial Discharges from Electrical Trees Grown in a Flexible Epoxy Resin, in Proc. IEEE - CEIDP 2008, October 26-29. Quebec city, Canada, pp. 666 – 669, 10.1109/CEIDP.2008.4772838

Appendix B: Results from GC/MS Analysis

B1. Araldite CY1301



Fig. B1.1: Gas chromatograms of Araldite CY1301



Fig. B1.2: Mass spectra associated with the peaks in Fig. B1.1



Fig. B1.3: Fingerprint associated with the peak at 14.04 min in Fig. B1.1



Fig. B1.4: Fingerprint associated with the peak at 23.25 min in Fig. B1.1



Fig. B1.5: Fingerprint associated with the peak at 24.34 min in Fig. B1.1

B2. Araldite CY1311



Fig. B2.1: Gas chromatograms of Araldite CY1311



Fig. B2.2: Mass spectra associated with the peaks in Fig. B2.1



Fig. B2.3: Fingerprint associated with the peak at 22.02 min in Fig. B2.1



Fig. B2.4: Fingerprint associated with the peak at 22.02 min in Fig. B2.1


Fig. B2.5: Fingerprint associated with the peak at 23.56 min in Fig. B2.1



Fig. B2.6: Fingerprint associated with the peak at 26.58 min in Fig. B2.1



Fig. B2.7: Fingerprint associated with the peak at 26.63 min in Fig. B2.1

B3. Hardener HY1300



Fig. B3.1: Gas chromatograms of Hardener HY1300



Fig. B3.2: Mass spectra associated with the peaks in Fig. B3.1



Fig. B3.3: Mass spectra associated with the peaks in Fig. B3.1



Fig. B3.4: Fingerprint associated with the peak at 15.30 min in Fig. B3.1



Fig. B3.5: Fingerprint associated with the peak at 17.93 min in Fig. B3.1



Fig. B3.6: Fingerprint associated with the peak at 17.93 min in Fig. B3.1



Fig. B3.7: Fingerprint associated with the peak at 18.61 min in Fig. B3.1



Fig. B3.8: Fingerprint associated with the peak at 18.61 min in Fig. B3.1



Fig. B3.9: Fingerprint associated with the peak at 20.12 min in Fig. B3.1



Fig. B3.10: Fingerprint associated with the peak at 20.76 min in Fig. B3.1



Fig. B3.11: Fingerprint associated with the peak at 23.75 min in Fig. B3.1

Appendix C. Fitted dielectric data

C1. Araldite CY1301

| T=80°C | da01003, 1 | 1.7mm | da0106, | 1.7mm | | |
|---|--|--|---|---|--|---|
| | | | Fitted | Fitted | | |
| Parameter | Fitted value | Limits | value | Limits | value | Limits |
| Cs1/pF | 7.550E+02 | n/a | 7.525E+02 | n/a | | |
| m1 | 5.958E-01 | n/a | 4.668E-01 | n/a | | |
| n1 | 2.091E-01 | n/a | 2.363E-01 | n/a | | |
| fp1/Hz | 1.705E-02 | 9.3E-04 | 2.533E-02 | 1.4E-03 | | |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | | |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | | |
| Cs2/pF | 1.449E+02 | n/a | 1.471E+02 | n/a | | |
| m2 | -9.852E-01 | n/a | -9.875E-01 | n/a | | |
| n2 | 9.645E-01 | n/a | 9.687E-01 | n/a | | |
| fp2/Hz | 7.899E-03 | 5.9E-03 | 1.731E-02 | 1.4E-02 | | |
| Cin2/pF | 7.465E+00 | n/a | 6.165E+00 | n/a | | |
| g2/pS | 1.282E+01 | 8.1E-01 | 1.889E+01 | 1.1E+00 | | |
| | RMSE = | 3.82E-02 | RMSE = | 3.61E-02 | | |
| | RMSEr = | 1.88E-02 | RMSEr = | 2.11E-02 | | |
| RH12% | RMSEi = | 5.06E-02 | RMSEi = | 4.65E-02 | | |
| T=80°C | da0101, 1 | .7mm | da0107, | da0107, 1.7mm | | 0.8mm |
| _ | | | Fitted | | Fitted | |
| Parameter | Fitted value | Limits | value | Limits | value | Limits |
| Cs1/pF | 6.703E+02 | n/a | 5.706E+02 | n/a | 1 057F+03 | n/a |
| m1 | | | | in/u | 1.0372.03 | |
| | 5.024E-01 | n/a | 6.774E-01 | n/a | 9.124E-01 | n/a |
| n1 | 5.024E-01 1.861E-01 | n/a n/a | 6.774E-01 2.380E-01 | n/a n/a | 9.124E-01 2.416E-01 | n/a n/a |
| n1 fp1/Hz | 5.024E-01 1.861E-01 1.370E-01 | n/a n/a 5.3E-03 | 6.774E-01 2.380E-01 9.700E-02 | n/a n/a 3.4E-03 | 9.124E-01 2.416E-01 7.410E-02 | n/a n/a 2.5E-03 |
| n1 fp1/Hz Cin/pF | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 | n/a n/a 5.3E-03 n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 | n/a n/a 3.4E-03 n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 | n/a n/a 2.5E-03 n/a |
| n1 fp1/Hz Cin/pF g1/pS | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.000E-01 | n/a n/a 5.3E-03 n/a n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 | n/a n/a 3.4E-03 n/a n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 | n/a n/a 2.5E-03 n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 | n/a n/a 5.3E-03 n/a n/a n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 | n/a n/a 3.4E-03 n/a n/a n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 | n/a n/a 2.5E-03 n/a n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.000E-01 1.538E+02 | n/a n/a 5.3E-03 n/a n/a n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 | n/a n/a 3.4E-03 n/a n/a n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- | n/a n/a 2.5E-03 n/a n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 | n/a n/a 5.3E-03 n/a n/a n/a n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 | n/a n/a 3.4E-03 n/a n/a n/a n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 | n/a n/a 2.5E-03 n/a n/a n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 | n/a n/a 5.3E-03 n/a n/a n/a n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 fp2/Hz | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 1.870E+00 | n/a n/a 5.3E-03 n/a n/a n/a n/a 6.5E-01 | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 1.544E+00 | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a 5.1E-01 | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 2.627E+00 | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a n/a 6.4E-01 |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 fp2/Hz Cin2/pF | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 1.870E+00 4.391E+00 | n/a n/a 5.3E-03 n/a n/a n/a n/a 6.5E-01 n/a | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 1.544E+00 4.723E+00 | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a 5.1E-01 n/a | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 2.627E+00 3.073E+00 | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a n/a n/a n/a n/a n/a |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 fp2/Hz Cin2/pF g2/pS | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 1.870E+00 4.391E+00 3.647E+01 | n/a n/a 5.3E-03 n/a n/a n/a n/a 6.5E-01 n/a 6.2E+00 | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 1.544E+00 4.723E+00 3.685E+01 | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a 5.1E-01 n/a 4.4E+00 | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 2.627E+00 3.073E+00 3.167E+01 | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a 6.4E-01 n/a 9.9E+00 |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 fp2/Hz Cin2/pF g2/pS | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 1.870E+00 4.391E+00 3.647E+01 RMSE = | n/a n/a 5.3E-03 n/a n/a n/a n/a 6.5E-01 n/a 6.2E+00 2.68E-02 | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 1.544E+00 4.723E+00 3.685E+01 RMSE = | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a 5.1E-01 n/a 4.4E+00 2.39E-02 | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 2.627E+00 3.073E+00 3.167E+01 RMSE = | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a 6.4E-01 n/a 9.9E+00 2.39E-02 |
| n1 fp1/Hz Cin/pF g1/pS Cs2/pF m2 n2 fp2/Hz Cin2/pF g2/pS | 5.024E-01 1.861E-01 1.370E-01 1.000E-01 1.538E+02 -9.861E-01 9.651E-01 1.870E+00 4.391E+00 3.647E+01 RMSE = RMSE = RMSEr = | n/a n/a 5.3E-03 n/a n/a n/a n/a 6.5E-01 n/a 6.2E+00 2.68E-02 1.41E-02 | 6.774E-01 2.380E-01 9.700E-02 1.000E-01 1.000E-01 1.270E+02 -9.841E-01 9.665E-01 1.544E+00 4.723E+00 3.685E+01 RMSE = RMSE = RMSEr = | n/a n/a 3.4E-03 n/a n/a n/a n/a n/a 5.1E-01 n/a 4.4E+00 2.39E-02 1.31E-02 | 9.124E-01 2.416E-01 7.410E-02 1.000E-01 1.000E-01 2.506E+02 -9.840E- 01 9.700E-01 2.627E+00 3.073E+00 3.167E+01 RMSE = RMSE = RMSE = | n/a n/a 2.5E-03 n/a n/a n/a n/a n/a 6.4E-01 n/a 9.9E+00 2.39E-02 1.45E-02 |

| T=80°C | da0102, 1 | L.7mm | da0108, | 1.7mm | da0104, 0. | 8mm |
|-----------|--------------|----------|------------|----------|--------------|--------------|
| | | | Fitted | | | |
| Parameter | Fitted value | Limits | value | Limits | Fitted value | Limits |
| Cs1/pF | 6.363E+02 | n/a | 5.670E+02 | 1.3E+01 | 7.673E+02 | n/a |
| m1 | 8.911E-01 | n/a | 8.804E-01 | n/a | 9.650E-01 | n/a |
| n1 | 1.897E-01 | n/a | 1.849E-01 | n/a | 2.748E-01 | n/a |
| fp1/Hz | 1.530E+00 | 4.4E-02 | 1.451E+00 | 5.2E-02 | 1.758E+00 | 5.1E-02 |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| Cs2/pF | 1.752E+02 | n/a | 1.823E+02 | n/a | 3.010E+02 | n/a |
| m2 | -9.845E-01 | n/a | -9.847E-01 | n/a | -9.833E-01 | n/a |
| n2 | 9.580E-01 | n/a | 9.562E-01 | n/a | 9.634E-01 | n/a |
| fp2/Hz | 9.877E+01 | 3.7E+00 | 3.319E+01 | 1.4E+00 | 4.836E+01 | 1.7E+00 |
| Cin2/pF | 3.998E+00 | n/a | 4.500E+00 | n/a | 4.099E+00 | n/a |
| g2/pS | 3.487E+01 | 4.8E+01 | 8.149E+02 | 2.5E+01 | 1.477E+03 | 5.3E+01 |
| | | | | | | 1.74E- |
| | RMSE = | 2.01E-02 | RMSE = | 1.59E-02 | RMSE = | 02 |
| | | | | | 51.465 | 1.49E- |
| | RMSEr = | 1.61E-02 | RMSEr = | 1.16E-02 | RIVISEr = | 02 1 0CF |
| RH75% | RMSFi = | 2.34F-02 | RMSFi = | 1.93F-02 | RMSFi = | 1.96E- 02 |
| T=80°C | w0101.1 | .7mm | w0102. | 1.7mm | | |
| | | | Fitted | | Fitted | |
| Parameter | Fitted value | Limits | value | Limits | value | Limits |
| Cs1/pF | 6.607E+02 | n/a | 6.073E+02 | 1.1E+01 | | |
| m1 | 5.824E-01 | n/a | 6.828E-01 | n/a | | |
| n1 | 1.540E-01 | n/a | 1.526E-01 | n/a | | |
| fp1/Hz | 1.579E+00 | 3.4E-02 | 2.276E+00 | 6.2E-02 | | |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | | |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | | |
| Cs2/pF | 1.543E+02 | n/a | 1.593E+02 | n/a | | |
| m2 | -9.808E-01 | n/a | -9.811E-01 | n/a | | |
| n2 | 9.562E-01 | n/a | 9.545E-01 | n/a | | |
| fp2/Hz | 4.425E+01 | 1.4E+00 | 6.182E+01 | 1.6E+00 | | |
| Cin2/pF | 4.081E+00 | n/a | 3.736E+00 | n/a | | |
| g2/pS | 1.347E+02 | 1.9E+01 | 3.802E+02 | 2.3E+01 | | |
| | RMSE = | 1.51E-02 | RMSE = | 1.22E-02 | | |
| | RMSEr = | 9.45E-03 | RMSEr = | 8.22E-03 | | |
| RH100% | RMSEi = | 1.91E-02 | RMSEi = | 1.51E-02 | | |

C2. Araldite CY1311

| Sample 1110 - | 20°C | | 20°C 30°C | | 40°C | | 50° | 50°C | | 60°C | | 70°C | |
|------------------|------------|--------|------------|---------|------------|---------|-----------|---------|------------|---------|--------------|---------|--|
| 1.7mm | | | | | | | | | | | | | |
| | Fitted | | Fitted | | Fitted | | Fitted | | Fitted | | | | |
| Parameter | value | Limits | value | Limits | value | Limits | value | Limits | value | Limits | Fitted value | Limits | |
| Cs1/pF | 4.053E+02 | n/a | 3.949E+02 | n/a | 4.731E+02 | n/a | 5.490E+02 | n/a | 5.621E+02 | n/a | 4.539E+02 | n/a | |
| m1 | 7.858E-01 | n/a | 1.000E+00 | n/a | 1.000E+00 | n/a | 1.000E+00 | n/a | 9.950E-01 | n/a | 7.790E-01 | n/a | |
| n1 | 2.063E-01 | n/a | 1.166E-01 | n/a | 6.352E-02 | n/a | 1.000E-14 | n/a | 1.000E-14 | n/a | 1.000E-08 | n/a | |
| | | 1.3E- | | | | | | | | | | | |
| fp1/Hz | 3.334E-03 | 04 | 3.700E-02 | 1.1E-03 | 2.479E-01 | 5.8E-03 | 1.193E+00 | 2.8E-02 | 4.424E+00 | 1.3E-01 | 2.609E+01 | 7.0E-01 | |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | |
| Cs2/pF | 1.403E+02 | n/a | 1.331E+02 | n/a | 1.431E+02 | n/a | 1.596E+02 | n/a | 1.708E+02 | n/a | 1.583E+02 | n/a | |
| | | | | | | | -9.649E- | | | | | | |
| m2 | -9.684E-01 | n/a | -9.628E-01 | n/a | -9.626E-01 | n/a | 01 | n/a | -9.708E-01 | n/a | -9.705E-01 | n/a | |
| n2 | 9.437E-01 | n/a | 9.411E-01 | n/a | 9.422E-01 | n/a | 9.393E-01 | n/a | 9.419E-01 | n/a | 9.448E-01 | n/a | |
| | | 2.6E- | | | | | | | | | | | |
| fp2/Hz | 1.272E-02 | 03 | 1.905E+00 | 1.3E-01 | 9.021E+00 | 2.9E-01 | 2.816E+01 | 8.3E-01 | 8.732E+01 | 2.8E+00 | 2.217E+02 | 5.5E+00 | |
| Cin2/pF | 9.386E+00 | n/a | 5.607E+00 | n/a | 4.662E+00 | n/a | 4.279E+00 | n/a | 4.695E+00 | n/a | 4.815E+00 | n/a | |
| | | 2.2E- | | | | | | | | | | | |
| g2/pS | 6.621E+00 | 01 | 3.019E+01 | 2.4E+00 | 1.833E+02 | 7.0E+00 | 8.675E+02 | 2.6E+01 | 2.855E+03 | 9.5E+01 | 3.598E+03 | 1.4E+02 | |
| | | 1.84E- | | 1.63E- | | 1.38E- | | 1.60E- | | 2.03E- | | 1.83E- | |
| | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | |
| | | 1.00E- | | 1.30E- | | 1.20E- | | 1.65E- | | 1.90E- | | 1.88E- | |
| | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | |
| | | 2.40E- | | 1.91E- | | 1.53E- | | 1.54E- | | 2.15E- | | 1.78E- | |
| RH12% | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | |

| Sample 1109 - | 20°0 | 2 | 30°C | | 40°0 | 2 | 50° | с | 60°(| 2 |
|------------------|------------|---------|------------|---------|------------|---------|-----------|---------|------------|---------|
| 1.7mm | | | | | | | | | | |
| | Fitted | | Fitted | | Fitted | | Fitted | | Fitted | |
| Parameter | value | Limits | value | Limits | value | Limits | value | Limits | value | Limits |
| Cs1/pF | 6.131E+02 | n/a | 7.872E+02 | n/a | 6.397E+02 | n/a | 6.454E+02 | n/a | 6.702E+02 | n/a |
| m1 | 1.000E+00 | n/a | 1.000E+00 | n/a | 1.000E+00 | n/a | 1.000E+00 | n/a | 1.000E+00 | n/a |
| n1 | 1.593E-01 | n/a | 1.379E-01 | n/a | 3.095E-02 | n/a | 2.739E-02 | n/a | 1.000E-14 | n/a |
| fp1/Hz | 2.277E-02 | 6.4E-04 | 1.161E-01 | 3.6E-03 | 8.833E-01 | 2.0E-02 | 2.854E+00 | 1.3E-01 | 9.838E+00 | 5.7E-01 |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| Cs2/pF | 1.076E+02 | n/a | 1.170E+02 | n/a | 1.351E+02 | n/a | 1.400E+02 | n/a | 1.426E+02 | n/a |
| | | | | | | | -9.524E- | | | |
| m2 | -9.448E-01 | n/a | -9.482E-01 | n/a | -9.487E-01 | n/a | 01 | n/a | -9.571E-01 | n/a |
| n2 | 9.437E-01 | n/a | 9.408E-01 | n/a | 9.331E-01 | n/a | 9.351E-01 | n/a | 9.393E-01 | n/a |
| fp2/Hz | 2.001E+00 | 1.4E-01 | 1.466E+01 | 6.0E-01 | 8.004E+01 | 1.5E+00 | 3.563E+02 | 1.0E+01 | 7.317E+02 | 2.7E+01 |
| Cin2/pF | 3.914E+00 | n/a | 4.283E+00 | n/a | 3.783E+00 | n/a | 3.431E+00 | n/a | 3.456E+00 | n/a |
| g2/pS | 4.027E+01 | 2.3E+00 | 1.805E+02 | 1.2E+01 | 1.507E+03 | 4.2E+01 | 9.414E+03 | 3.5E+02 | 3.269E+04 | 1.2E+03 |
| | | 1.56E- | | 1.81E- | | 1.22E- | | 2.29E- | | 3.15E- |
| | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 | RMSE = | 02 |
| | | 1.12E- | | 1.76E- | | 1.57E- | | 2.90E- | | 4.17E- |
| | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 | RMSEr = | 02 |
| | | 1.90E- | | 1.86E- | | 7.07E- | | 1.45E- | | 1.58E- |
| RH33% | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 03 | RMSEi = | 02 | RMSEi = | 02 |

| Sample 1104 - | 20°C | | 30°C | | 40°C | | 50°C | | 60°C | |
|------------------|------------|---------|------------|---------|------------|---------|-----------|---------|------------|---------|
| 1./mm | Fitted | | Fittad | | Fittod | | Fittod | | Eittad | |
| Parameter | value | Limits | value | Limits | value | Limits | value | Limits | value | Limits |
| Cs1/pF | 6.225E+02 | n/a | 4.125E+02 | n/a | 4.619E+02 | 1.1E+02 | 4.879E+02 | n/a | 5.878E+02 | n/a |
| m1 | 9.006E-01 | n/a | 1.000E+00 | n/a | 9.919E-01 | 4.3E+01 | 1.000E+00 | n/a | 1.000E+00 | n/a |
| n1 | 1.888E-01 | n/a | 8.401E-02 | n/a | 3.962E-02 | 3.2E+01 | 1.000E-14 | n/a | 1.000E-14 | n/a |
| fp1/Hz | 4.428E+00 | 3.0E-01 | 3.643E+01 | 6.9E+00 | 1.245E+02 | 1.0E+03 | 3.530E+02 | 6.3E+01 | 7.882E+02 | 1.6E+02 |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| Cs2/pF | 1.562E+02 | n/a | 2.075E+02 | n/a | 2.238E+02 | n/a | 2.494E+02 | n/a | 2.365E+02 | n/a |
| | | | | | | | -9.666E- | | | |
| m2 | -9.546E-01 | n/a | -9.628E-01 | n/a | -9.638E-01 | n/a | 01 | n/a | -9.708E-01 | n/a |
| n2 | 9.275E-01 | n/a | 9.189E-01 | n/a | 9.091E-01 | n/a | 9.052E-01 | n/a | 9.163E-01 | n/a |
| fp2/Hz | 4.942E+02 | 2.1E+01 | 1.872E+03 | 1.7E+02 | 5.823E+03 | n/a | 2.331E+04 | 1.7E+03 | 6.605E+04 | 5.8E+03 |
| Cin2/pF | 2.313E+00 | n/a | 2.355E+00 | n/a | 7.829E+00 | n/a | 4.468E+00 | n/a | 7.071E+00 | n/a |
| g2/pS | 1.719E+03 | 5.2E+02 | 2.292E+04 | 6.4E+03 | 1.086E+05 | n/a | 1.127E+05 | 7.1E+04 | 3.877E+05 | 2.1E+05 |
| | | 3.43E- | | 8.66E- | | 1.09E- | | 8.49E- | | 1.05E- |
| | RMSE = | 02 | RMSE = | 02 | RMSE = | 01 | RMSE = | 02 | RMSE = | 01 |
| | | 3.86E- | | 1.21E- | | 1.53E- | | 1.19E- | | 1.48E- |
| | RMSEr = | 02 | RMSEr = | 01 | RMSEr = | 01 | RMSEr = | 01 | RMSEr = | 01 |
| | | 2.94E- | | 1.59E- | | 1.36E- | | 1.64E- | | 1.83E- |
| RH75% | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 |

| Sample | 20°0 | | 30°C | | 40°0 | | 50% | r | 60% | - |
|-----------|------------|---------|------------|---------|------------|---------|-----------|---------|------------|---------|
| 1.7mm | 20 0 | | 50 C | | 70 C | | 50 0 | | 00 C | |
| | Fitted | | Fitted | | Fitted | | Fitted | | Fitted | |
| Parameter | value | Limits | value | Limits | value | Limits | value | Limits | value | Limits |
| Cs1/pF | 3.819E+02 | 1.8E-01 | 3.847E+02 | n/a | 1.963E+02 | n/a | 1.960E+02 | n/a | 1.960E+02 | n/a |
| m1 | 9.884E-01 | n/a | 9.874E-01 | 3.2E-01 | 8.475E-01 | n/a | 8.470E-01 | n/a | 6.101E-01 | n/a |
| n1 | 1.000E-08 | n/a | 1.000E-14 | n/a | 1.000E-14 | n/a | 1.000E-14 | n/a | 1.000E-14 | n/a |
| fp1/Hz | 3.482E+02 | n/a | 1.052E+03 | n/a | 3.130E+03 | 2.9E+03 | 2.486E+03 | 3.8E+03 | 4.845E+03 | 8.7E+03 |
| Cin/pF | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| g1/pS | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a | 1.000E-01 | n/a |
| Cs2/pF | 2.712E+02 | n/a | 2.564E+02 | n/a | 2.941E+02 | n/a | 2.940E+02 | n/a | 2.940E+02 | n/a |
| | | | | | | | -9.792E- | | | |
| m2 | -9.758E-01 | n/a | -9.733E-01 | 3.0E-03 | -9.771E-01 | n/a | 01 | n/a | -9.797E-01 | n/a |
| n2 | 9.266E-01 | n/a | 9.340E-01 | 1.8E-02 | 9.207E-01 | n/a | 9.210E-01 | n/a | 9.210E-01 | n/a |
| fp2/Hz | 8.550E+03 | n/a | 3.629E+04 | n/a | 1.475E+05 | 2.8E+04 | 3.334E+05 | 7.6E+04 | 6.631E+05 | 1.5E+05 |
| Cin2/pF | 1.659E+01 | n/a | 4.500E+00 | n/a | 3.210E+01 | n/a | 3.210E+01 | n/a | 3.210E+01 | n/a |
| g2/pS | 4.396E+04 | n/a | 2.098E+05 | n/a | 1.248E+06 | 1.1E+06 | 6.460E+06 | 3.4E+06 | 7.950E+06 | 6.0E+06 |
| | | | | 1.68E- | | 2.38E- | | 2.93E- | | 3.00E- |
| | RMSE = | 0.1082 | RMSE = | 01 | RMSE = | 01 | RMSE = | 01 | RMSE = | 01 |
| | | | | 2.34E- | | 3.36E- | | 4.14E- | | 4.23E- |
| | RMSEr = | 0.14274 | RMSEr = | 01 | RMSEr = | 01 | RMSEr = | 01 | RMSEr = | 01 |
| | | 5.51E- | | 4.23E- | | 2.24E- | | 2.13E- | | 2.56E- |
| RH100% | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 | RMSEi = | 02 |

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