Universality in the AC Conductance of Keratinized Tissues

UNIVERSITY OF OSLO

MASTER THESIS BY

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Submitted to Department of Physics

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Abstract

The overall aim of the studies in this thesis is to investigate the universality nature of the conductivity of biological materials and the conduction mechanism using impedance spectroscopy measurement. Universality is a phenomenon which can occur in any condition in the physical world. Different disordered solids shows universality of AC conductivity when the frequency dependent AC conductivity curve normalized (each measured value divided by the DC conductivity and the frequency is normalized with regard to both DC conductivity and temperature).

Impedance spectroscopy is a powerful tools and non-destructive method to characterize materials. Impedance spectroscopy on biological materials is not usually done as a function of temperature. However, the electrical admittance is largely dependent on water content and we wanted to investigate whether biological material show universal conductance behavior when scaled either with regard to ambient relative humidity (RH) or with regard to temperature. Typically human hair, nail and epidermal stratum corneum (skin) are used for this study

Measurement of AC electrical conductance was taken in the frequency range 0.1 Hz to 1 MHz. In different experiments the RH and temperature were changed between each frequency scan and the data analyzed to look for universal behavior.

Furthermore the sorption time constant for the three biological samples were calculated after measuring the sorption isotherm using a DVS instrument.

Contents

List of Figures

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Keywords: Impedance, Conductivity, Universality, Scaling (Normalization), Temperature, Relative Humidity .

Abbreviations:

- *RH*: Relative humidity
- *SC*: Stratum Corneum
- *TEMP*: Temperature.
- *DVS*: Dynamic Vapor Sorption
- *AC, DC*: Alternating Current, Direct Current

Chapter 1

Introduction

1.1 Motivation

Universality and scaling are phenomena which can occur in any condition, type, shape and nature in the physical world. For various reasons in the past few years, the universality and the scaling behavior of the conductivity spectra have received much attention. The theoretical and experimental investigation reported in different scientific literature [1, 2, 3] indicate that different materials such as glasses, amorphous semiconductors, electron conducting polymers etc shows remarkably similar frequency dependence of the AC conductivity. This applies both to electronic and ionic conduction. Typically, the curves showing the conductivity as a function of frequency overlap when the conductivity is normalized (each measured value divided by the DC conductivity) and the frequency is normalized with regard to both DC conductivity and temperature. This phenomenon is commonly called universality.

The present thesis is an experimental investigation of whether biological material show universal conductance behavior when scaled either with regard to ambient relative humidity (RH) or with regard to temperature.

The impedance Spectroscopy technique is a powerful tool and a non-destructive method that can be used to provide information regarding the physical, electrical and chemical properties of materials. Impedance spectroscopy on biological materials is not usually done as a function of temperature. However, the electrical admittance is largely dependent on water content.

AC electrical conductance was measured in the frequency range 0.1 Hz to 1 MHz. In different experiments the RH and temperature were changed between each frequency scan and the data were analyzed to look for universal behavior. Typical biological materials that were used are pieces of human hair, nail and epidermal stratum corneum (skin).

1.2 Goal

The main goal of this thesis is to determine the possible existence of the conductance universality nature in keratinized tissue using electrical impedance spectroscopy measurement and normalization of the measurement result.

A secondary aim beyond the scope of this thesis is the implementation of functions of the result to determine the electrical properties and the conduction mechanisms of keratinized tissue.

1.3 Thesis Structure

The structure of the thesis is as follows:

- **Chapter-1**: Introduces readers to the main aim and motivation of the project. In addition to this it provide the over all stracture of the thesis.
- **Chapter-2**: Provides background information about some of the existing dielectric theory which is related to this project. Furthermore it contains the definition of conductivity and the nature of conductivity in disordered and biological materials and the universality and scaling concepts.
- **Chapter-3**: This chapter provides sample preparation and brief discussion about basic instruments used in the project. Furthermore it provides procedural steps of the measurements of samples electric impedance.
- **Chapter-4**: Provides the dynamic vapor sorption (DVS) measurement results and impedance measurement result of the samples
- **Chapter-5**: provides the data analysis of the sorption time constant of the three samples, plus their impedance and conductivity data analysis including conductance normalized result and discussion.
- **Chapter-6**: Provides the possible conclusion of the results and recommendation for future work

Chapter 2

Background and Literature Review

This chapter focuses on general explanation of the theory of electric conductivity and dielectric nature of biological materials.

2.1 The Dielectric Properties of Keratinized Tissue

Based on their electrical nature materials including biological tissue, can be broadly separated into three categories: conducting, insulating and semiconductors. In conductors, such as metals that are generally good electrical conductors, the electric charges move freely in response to the application of an electric field. As the name indicates semiconductors are material which has electric conductivity between that of conductor and insulator. In semiconductor the current conduction occurs through the movement of free electrons and holes collectively known as charge carriers. Whereas in an insulator (dielectric), the charges are fixed and not free to move. Due to this, dielectrics are materials that are poor conductors of electricity. For more than a century the dielectric response of different materials of solids and liquids has been an active topic of research by different group or department, such as Chemists, Physicists and electrical engineers for various numbers of reasons. Chemists have been trying to obtain information about the molecular structure, interaction and dynamics of the substances under study; Physicists have been looking for the fundamental processes existing in the materials, electrical engineers seeking for improved insulating materials.

Since every material has a unique set of electrical characteristics that are dependent on its dielectric properties, accurate measurements of these properties can provide scientists and engineers with valuable information to properly integrate the material into its intended application for more solid and advanced design parameters. For example, the loss of a cable insulator, the impedance of a substrate, or the frequency of a dielectric resonator can be related to its dielectric properties.

Furthermore the information that is obtained from dielectric properties measurement is also useful in different industrial applications like for improving absorbent, and packaging designs, microwave processing of food, rubber, plastic and ceramics.

Some of the important dielectric properties includes dielectric constant, dielectric loss, loss factor, power factors, AC conductivity , DC conductivity , electrical breakdown strength and other equivalent or similar properties. The term dielectric usually refers to the variation of these properties with frequency, temperature, relative humidity, voltage and composition.

Living organisms conduct electric currents to some degree because they contain dipoles as well as charges that can move, and also have dielectric properties [4, 5]. For materials that are heterogeneous in structure, charges may become trapped at interfaces. When the atoms or molecules of a dielectric are placed in an external electric field net migration of charge does not occur but the nuclei are pushed with the field resulting in an increased positive charge on one side while the electron clouds are pulled against it resulting in an increased negative charge on the other side. Therefore if we are interested on the electric field produced by this deformed molecules, let us consider it as a two point charges Q and $-Q$ which are separated by a distance d. Two such point charge are known as an electric dipole. When the dielectric has huge array of electric dipole then the dielectric in such state is said to be polarized and this process is known as polarization. The distorted atoms have electric dipole moments of

$$p_i = Q_i d_i \tag{2.1}$$

where Q_i is total charge of i^{th} nuclei and d_i is a distance between the center of negative charge and nucleus.

If there are n dipoles per unit volume of the dielectric, the polarization P is

$$P = \lim_{V \to 0} (\frac{1}{V} \sum_{i=1} p_i) = n\alpha\epsilon_0 E = \chi\epsilon_0 E \tag{2.2}$$

where n is the number of dipoles in dielectric's of volume V, α is the palarizability and $\chi = n\alpha$ is the dielectric susceptibility that depends on the temperature, pressure, and composition of the material.

Susceptance is a macroscopic parameters and is interrelated with a microscopical factor called polarizability $\alpha(\frac{Cm^2}{V})$ then $P = n\epsilon E$.

Polar molecules generally polarize more strongly than non-polar molecules. In non-polar media there is a simple relationship between the polarization and the molecule structure, the Clausius- Mosotti equation [6].

$$\frac{\epsilon_r - 1}{\epsilon_r + 1} = \frac{n\alpha}{3\epsilon_0} \tag{2.3}$$

where ϵ_0 is the relative permittivity (the macroscopic quantity) and $n = \frac{N}{V}$ is the number density.

The validity of the Clausius-Mossotti equation found some limitation. This limitation was noticed when the large difference between the refractive index of visible light and the dielectric constant for for different compound and gasses observed. It can be extended to comprise the contribution from polar molecules. By using Langevin's calculations for the average orientation of permanent magnetic moments in an external field to the electric case and accepting Lorentz's approach for the internal field Debye succeeded in deriving an extension of the Clausius-Mossotti equation which is given as

$$\frac{\epsilon_r - 1}{\epsilon_r + 1} = \frac{4\pi N_A(\alpha^2 + \frac{\mu_0^2}{3KT})}{V_m} \tag{2.4}$$

where V_m is the molar volume and N_A is Avogadro constant, μ_0 permanent dipole moment the kT factor is due to the stastical distribution of polar molecules causing the orientation polarization.

In the Debye equation the dielectric constant depends not only on the molecular polarizability, but also on the permanent moment of the molecules. With the Debye equation the temperature dependence of the dielectric constant could be elucidated to a great extent, especially for low pressure gases, in addition to this the Debye equation offered the possibility of calculating molecular dipole moments from measurements of the dielectric constant [7, 8].

The Debye and Clausius-Mossotti equation are in best agreement with gases but in less agreement with liquids and least with solid. Different authors including Onsager, Van Arkel and Snoek [9, 10] made attempts to explain the deviation of the Debye equation in the case of polar liquids and tried to extend the theory.

Many of these authors assumed that the apparent dipole moment was lowered by association [6, 11].

According to different studies reviewed in [6, 9, 10, 12], the dielectric properties of a biological tissue result from the interaction of an electromagnetic field with its constituents at the cellular and molecular level. The tissue has different response for different regions of the electromagnetic spectrum. In other words the measurement of the dielectric properties of tissue is not only affected and complicated by tissue inhomogeneity, anisotropy, the physiological state of the tissue, and electrode polarization [13]. In addition to this the dielectric properties of tissues are highly frequency and temperature dependent [14]. The dielectric spectrum of tissue consists of three main regions which is known as alpha, beta and gamma dispersion [4, 5, 15].

- *Alpha dispersion*: The alpha dispersion covers in low frequency of hertz to kilohertz range. This is associated with the relaxation of ions tangential to charged membrane surface.
- *Beta dispersion*:The beta dispersion occurs in the intermediate frequency range which extended to 3-4 frequency decades centered in the hundreds of kilo hertz regions, and due to the polarization of the membranes and the macromolecules.
- *Gamma dispersion* : The gamma dispersion occurs in the gigahertz region, this dispersion arises mainly from the relaxation of free water within the tissues

As a dielectric material, biological tissue has the ability to store electromagnetic energy. This is accompanied by the displacement of positive and negative charges under the influence of applied electric field. The mechanism of charge displacement or polarizatation depends on the types of dielectric materials and the frequency of the applied field. There are different kinds of polarization and the total polarizability is given by

$$\alpha = \alpha_e + \alpha_i + \alpha_d \tag{2.5}$$

where α_e is electronic, α_i is ionic, and α_d is dipolar (orientation) polarizabilities.

- *Electronic polarization*: Electronic polarization occurs due to the displacement of the negatively charged electron cloud relative to the positive nucleus of atoms in the external applied electric field. This displacement of charges makes one side of the atoms somewhat positive and the opposite side negative that create a dipole in the atoms.

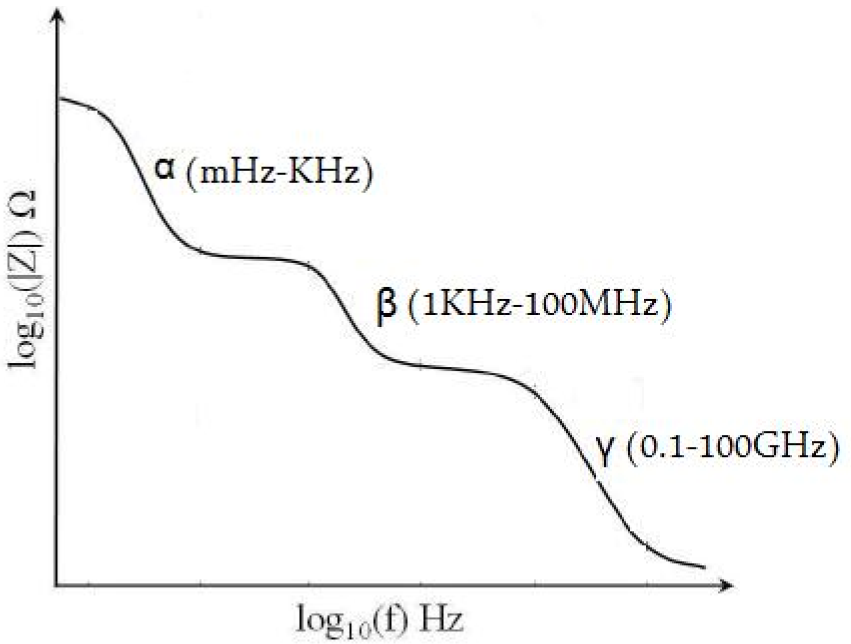

Figure 2.1: The schematic of the dispersion of biological tissues.

- *Ionic polarization*: Ionic polarization occurs in the materials which have ionic character of bonds. It then by definition has internal dipoles which exactly cancel each and other are unable to rotate. The external field then induces net dipoles by slightly displacing the ions from their resting position. A good model materials for this case simple ionic crystal like NaCl.
- *Orientation polarization*: Orientation polarization occurs in the materials which have molecules with their own dipole momentum which can rotate freely. The external fields align these dipoles to some extent and thus induce a polarization of the materials. A good example for this case is water.

The electronic contribution is present in any type of substance, but the presence of the other two terms depends on the material under consideration.

2.1.1 Skin

Many therapeutic and diagnostic techniques rely upon the application of electrical fields or the measurement of electrical properties. or the interaction of the electromagnetic radiation with the target tissue since skin is the interface of the body with environmental agents including electromagnetic fields; the knowledge of its dielectric properties is of importance in the assessment of human exposure and in numerous biomedical applications. There is also interest within the cosmetics industry to use the dielectric properties of skin as an indicator of the efficacy of dermatological and cosmetic treatments [16]. The skin is the largest organ of the body which protects us from microbes and the elements, helps regulate body temperature, and permits the sensations of touch, heat, and cold. Skin is a very interesting tissue because of its highly inhomogeneous structure, which thus leads to inhomogeneous dielectric properties.

Skin has three layers:

- *Epidermis*: the outermost layer of skin, provides a waterproof barrier and creates our skin tone. Its thickness varies in different types of skin. It is the thinnest on the eyelids at 0.005 mm and the thickest on the palms and soles at 1.5 mm [17]. It contains special cells called melanocytes which produce the pigment melanin that gives the skin colour. The epidermis contains different layers, but the one that defines its dielectric properties the most is the outermost layer, the stratum corneum. This layer is composed of dead, flat skin cells that shed about every two weeks.
- *Dermis*:Beneath the epidermis, contains tough connective tissue, hair follicles, and sweat glands.
- *Hypodermis*: The deeper subcutaneous tissue is made of fat, connective tissue, larger blood vessels, and nerves

The stratum corneum is a solid state substance, not necessarily containing liquid water, but with moisture content dependent on the surrounding air humidity. Stratum corneum is not soluble in water, but the surface will be charged and a double layer will be formed in the water side of the interphase. Stratum corneum can absorb large amounts of water (e.g. doubling its weight). Stratum corneum may be considered as a solid state electrolyte, perhaps with few ions free to move and contribute to DC conductance. The stratum corneum contains such organic substances as proteins and lipids, which may be highly charged but bound, and therefore contributing only to AC admittance [6].

Human skin has high impedance to alternating current of low frequency. This impedance is greatly dominated by stratum corneum at a frequency below 10 kHz [18].

The impedance of the skin at low frequency AC is influenced by different factors like the way in which contact is made with the skin surface, electrode size and geometry and skin hydration [19].

After measuring the impedance of the skin and the stratum corneum using a two electrode system and an AC bridge Yamamoto and Yamamoto [20] conclude that the skin Stratum corneum forms a high electric resistance layer, which makes skin one of the most resistive tissues in the human body.

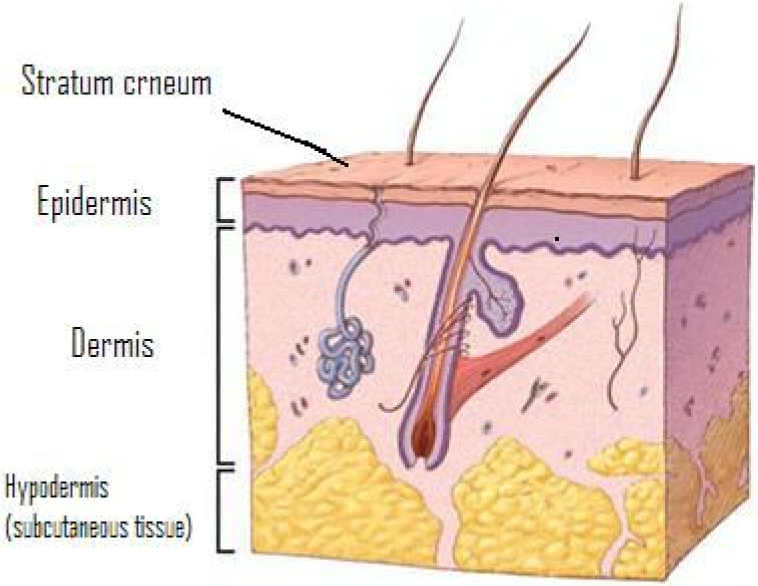

Figure 2.2: Structure of skin (common wikipedia).

The frequency response of the skin is complex and its broad dispersion is composed of several dispersion mechanism due to the inhomogeneous nature of the stratum corneum. It produces both alpha and beta dispersion with different dispersion mechanism.

2.1.2 Hair

Hair is formed by a flexible elastic and strong structural protein known as keratin. This is the same kinds of protein that makes up the nails and the outer layer of the skin stratum corneum.

Similar to stratum corneum, hair is composed of dead cells which are cemented together by keratins. The major differences are, for example, that lipids represent about 10 percent of the mass of the stratum corneum, but only 2% of the mass of hair. Each strand of hair consists of three layers.

- *Medulla*: The innermost layer which is only present in large thick hairs.
- *Cortex*: The middle layer which provides strength and both the color and the texture of hair.
- *Cuticle*: The outermost layer of hair. The cuticle is thin and colorless and serves as a protector of the cortex.

The hair grows from the papilla and with the exception of that point of generation is made up of dead, cornfield cells. It consists of a shaft that project above the skin, and a root that is embedded in the skin. The hair root is enclosed within a hair follicle. At the base of the hair follicle is the dermal papilla. The dermal papilla is feed by the bloodstream which carries nourishment to produce new hair. The dermal papilla is a structure very important to hair growth because it contains receptors for male hormones and androgens. Androgens regulate hair growth. The electrical conduction mechanisms are most probably similar in these materials and hair is therefore to some extent a proper model of pure stratum corneum.

2.1.3 Nail

Nail is formed by a flexible elastic and strong structural protein known as keratin. This is the same kinds of protein that makes up the hair and the outer layer of the skin. But it is harder than stratum corneum which is due to the hard alpha karatin in the nail as opposed to the more soft beta karatin in the stratum corneum [6].

The fingernail acts as a protective plate and enhances sensation of the fingertip. The protection function of the fingernail is commonly known, but the sensation function is equally important. The fingertip has many nerve endings allowing us to receive volumes of information about objects we touch. The nail acts as a counter force to the fingertip providing even more sensory input when an object is touched.

Despite the natural position and its readily availability which makes it easy to perform electrical measurements on, the electrical admittance of human nail has not been extensively investigated. The electrical admittance of keratinized tissue is typically logarithmically dependent on water content or ambient RH, and the electrical properties of nail resemble those of stratum corneum and hair [17, 21].

2.2 Conductivity

The conductivity of the materials is usually thought of as the property which depends up on the ease with which electric charges can be transferred through the materials by the application of electric fields. Of course electrical conductivity is properties of a material that measure the ability of the material accommodates the movement of electric charges. It is the ratio of the current density to the electric field strength. Its SI unit is Siemens per meter.

$$j = \sigma E \tag{2.6}$$

which is in the form of Ohm's law.

According to Kittel [22] the magnitude of electrical conductivity is determined by

$$\sigma = \frac{n\tau e^2}{m} \tag{2.7}$$

where m is mass of electron, e is the electron charge.

1. The density of charge carriers per unit volume (n).
2. The charge carriers (the charge carriers will be electron, hole or ions) (e).
3. The average drift velocity of the carriers per unit electric field and the relaxation time τ.

Furthermore the nature of the chemical bonding plays a virtual role in determining the types of conductivity whether ionic or electronic [23], and this completely independently of any particular physical process, whether by "free" carriers as in metals and crystalline semiconductors or by hopping transport polaronic (polaron is a quasiparticle which used in condensed matter physics to understand the interaction between electrons and atoms in a solid material) etc.

The electrical conductivity can be measured in two forms as DC and AC conductivity (σ_{dc} and σ_{ac}) respectively).

The DC conductivity provides only a quantitative measure of the materials, assuming that there is single dynamic response characterizing the ionic conductor. Thus, DC conductivity provides less information of the entire dynamic behavior of the sample. Whereas, AC conductivity can shed considerable light on the microscopic nature of the ionic conducting process in the material.[24]

Ac conductivity is the electrical conductivity in the presence of alternating current field. Unlike dc conductivity this conductivity depends upon the frequency of the AC field.

If there is an electric field E, the electrons acquire a drift velocity V_d then the equation of motion of the conduction electron is given by

$$m(\frac{\mathrm{d}V_d}{\mathrm{d}t} + \frac{V_d}{\tau}) = (-e)E \tag{2.8}$$

where the second term proportional to the drift velocity represents the frictional force which plays a role in resisting the accelerated motion of the electron. when the steady state reached the $\frac{\mathrm{d}V_d}{\mathrm{d}t} = 0$ as a result the above equation solved as

$$V_d = \frac{(-e)\tau E}{m} \tag{2.9}$$

The current density is given by

$$j = (-Ne)V_d \tag{2.10}$$

thus the current density can be rewrite as

$$j = \frac{(Ne^2\tau)E}{m} \tag{2.11}$$

where (Ne) is the charge per unit volume. With in light of equation 2.9 to 2.11 leads to the expression of DC conductivity as

$$\sigma_d c = \frac{N_e^2\tau}{m_e} \tag{2.12}$$

Having this the expression AC conductivity is given as

$$\sigma = \frac{\sigma_0}{1 - i\omega\tau} \tag{2.13}$$

When we rationalize the above equation we will get

$$\sigma = \frac{\sigma_0}{1+\omega^2\tau^2} + \frac{i\omega\omega_0\tau}{1+\omega^2\tau^2} \tag{2.14}$$

Hence conductivity is a complex quantity which can be rewritten as

$$\sigma = \sigma' + i\sigma'' \tag{2.15}$$

where σ' is the real part which is given by

$$\sigma' = \frac{\sigma_0}{1 + \omega^2\tau^2} \tag{2.16}$$

And σ'' the imaginary part which is given by

$$\sigma'' = +\frac{i\sigma_0\omega\tau}{1 + \omega^2\tau^2} \tag{2.17}$$

The fact is that the imaginary conductivity represents the ease of displacement of electric charge in a dielectric while its real part (i.e. the AC conductivity) is the quantity to which the rate of heat development in the materials is proportional. For aqueous biological materials, the conductivity arises mainly from the mobility of hydrated ions and other processes.

2.2.1 Temperature and frequency dependence of conductivity

In crystalline solids crystal structure plays a key to the various electronic conduction phenomenon's in both metals and semiconductors. But, of course, not all the solids are crystalline and not all the conductors are electronic.A metal has large weakly temperature-dependent DC conductivity, a nonmetal has a much smaller DC conductivity which, however, increases strongly with increasing temperature [22]. Only for disordered nonmetals is AC conduction different from dc observed far below phonon (crystal lattice vibration) frequencies. Any feasible electronic application of disordered material implies that the material can conduct an electric current via some kind of charge-transport mechanism. In disordered solids such as polymers and glass the conduction of mobile charges includes electron, hole and polaron hopping.

Here we can try to the discuss some of the charge carrier mechanisms in disordered materials. In the ordered crystalline semiconductors transport properties are based on band theory with defined electronic energy structure consisting of energy bands and energy gaps. But here in disordered materials transport properties are determined by the presence of localized electron states [25] and the electronic energy spectrum of disordered materials can be treated as quasi-continuous. The energy levels related to the spatially localized states usually fill the energy spectrum continuously [26]. Localized states can either play the role of traps terminating charge carrier transport via extended states or they can be used by charge carriers in the so-called hopping transport mode, in which the carriers move via direct tunneling between the localized states.In disordered materials there exists some energy level that separates the extended states from the localized ones. This energy level is called the mobility edge.

Since the density of states (DOS) defined as the concentration of states per unit energy, per unit volume usually decreases when the energy moves away from the mobility edges towards the center of the mobility gap, the energy regions of localized states in the vicinity of the mobility edges are called band tails. Furthermore the temperature dependence of the electrical conductivity indicates the fundamental transport mechanisms of charge in disordered materials. Only at high enough temperature the electrical conductivity of disordered materials dominated by the electron transport via delocalized states above the mobility edge, because at delocalized states an essential fraction of charge carriers fill these states. With decreasing temperature, the concentration of such electrons decreases exponentially and consequently their contribution to electrical conductivity diminishes.

Under such circumstances, tunneling transitions of electrons between localized states in the band tails dominate charge transport in disordered semiconductors. This transport regime is called hopping conduction [7, 27] since an incoherent sequence of tunneling transitions of charge carriers resembles a series of their hops between randomly distributed sites. Each site in this picture provides a spatially localized electron state with some energy E.

According to numerous experimental studies disordered solids shows a similar behavior in regard to their frequency and temperature dependent conductivity. A typical frequency dependence of the conductivity spectrum shows three distinguished region

1. Low frequency dispersion.
2. An intermidate frequency plateau.
3. In extended dispersion at high frequency

At low frequencies, one observes a constant conductivity while at higher frequencies the conductivity becomes strongly frequency dependent. In disordered materials, hopping frequency and trapping phenomena are expected to have major influences on the electrical properties. The generality of this behavior for many widely different classes of materials was pointed out by Jonscher and his co-workers [28].

The AC conductivity of most disordered semiconductors depends on frequency according to a power law. This power law has been observed in numerous materials at different temperatures in a wide frequency range [1, 2, 28]. And is expressed in the form of

$$\sigma(\omega) = \sigma_d c + A\omega^s \tag{2.18}$$

where ,σ is the conductivity , ω is angular frequency and the pre factor A and the frequency exponent (the power law exponent) s are both weakly dependent on temperature and it is generally found that $0 \leq s \leq 1$, tending to the limiting value of unity at low temperatures. The first term σ_0 is the low frequency (or D.C.) conductivity and found to be thermally activated with Arrhenius exponential law equation (Arrhenius equation is a formula used to describe thermally-induced processes/reactions such as temperature variation of diffusion coefficients, population of crystal vacancies, creep rates).

$$\sigma_{dc} = \sigma_o \exp[-(\frac{E_A}{kT})^\beta] \tag{2.19}$$

where the pre-exponential factor σ_{dc} depends on the underlying system and the power exponent β depends on the material and also sometimes on the temperature range in which the conductivity is studied; E_A is the activation energy and k is the Boltzmann constant It has been observed this type of behavior in many other materials including polar polymers and ionic conductors.

A vast collection of experimental study and modeling indicates that there are several kinds of charge transport or charge carrier mechanisms which are usually characterized by carrier drift mobility and its dependence on the applied electric field, temperature, frequency and other relevant parameters [7, 25] .

These frequency and temperature dependent conduction mechanisms are in common in disordered solids. As mentioned above in the high frequency region, the conductivity increase with frequency. The frequency dependence of the conductivity or so called universal dynamic response(UDR) of ionic conductivity is related by a simple expression given by Jonscher's Powar Law [2] shown in the above equation.

According to different scholars [1, 3] the power-law description is slightly inaccurate, because the exponent must generally increase somewhat with frequency in order to fit with experimental data. A more general approach is to consider the scaling formalism associated with the time-temperature superposition (TTS) principle [3].

2.2.2 Dielectric relaxation phenomena in complex materials

According to Yuri Feldman [29] complex material is a very broad and general class of materials, which include associated liquids, polymers, biomolecules, colloids, porous materials, composites ferroelectrics and liquid crystals. The valuable information about the structure of the material and its dielectric behavior for fundamental studies as well as for technological applications can be obtained through observing the dynamic response under time-varying electric field. To measure the dynamic response [8], we can use either the time domain approach or the frequency-domain approach. These two approaches are equally powerful methods for studying dielectric phenomena. In fact the two approaches are Fourier transforms of one another [28]. In the time-domain approach, we measure the time dependent polarization immediately after the application of a step-function electric field, or measure the decay of the polarization from an initial steady state value to zero after the sudden removal of an initial polarizing field. This decay is generally referred to as dielectric relaxation. One of the most attractive aspects in the dielectric response of compex materials is the dielectric relaxation phenomenon, which can show the direct connection that often exists between the dipolar species and the charge carriers in the materials. Different researchers produced various model of permittivity for different materials and most of these produced models typically fit the complex dielectric permittivity data according to a relaxation theoretical model. The complex permittivity ϵ of a medium as a function of the field's frequency ω can be expressed as [28].

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \tag{2.20}$$

where ω is the angular frequency, ϵ' is the real component, which is in phase with the applied electric field, ϵ'' is the imaginary component, which is in quadrature with the applied field. Both the real and imaginary componets of the complex dielectric permittivity are related each other by the Kramers-Krong relation as shown below.

$$\epsilon'(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon''(\omega')}{\omega' - \omega} d\omega' \tag{2.21}$$

and

$$\epsilon''(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\epsilon'(\omega')}{\omega' - \omega} d\omega' \tag{2.22}$$

where P denotes the Cauchy principal value. So the real and imaginary parts of such a function are not independent, and the full function can be reconstructed if one of its parts is given.

The first dielectric relaxation model was produced by Peter Debye in 1929, which consider ideal non interacting dipoles to an alternating external electric field. On his model, Debye proposes the following expression for complex dielectric permittivity [28].

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau} \tag{2.23}$$

where ϵ_{∞} is the permittivity at the high frequency limit, ϵ_5 is the static, low frequency permittivity, and τ is the characteristic relaxation time of the medium. Peter Debye referred the dielectric relaxation to the time required for dipolar molecules (ones whose charges are unevenly distributed) to orient themselves in an alternating electric field. But the Debye model does not sufficiently describe the dielectric relaxation of disordered materials such as glass-forming liquids, amorphous polymers, and so on. The above Equation adequately describes the low-frequency behavior of the observed complex permittivity of many simple polar liquids. However the experimental result in polar dielectric materials have shown that correction to the simple model is necessary. The Cole-Cole model introduces the first correction which is used to describe dielectric relaxation in polymers. This correction was made by considering a distribution function for the relaxation time [30]

It is given by the equation

$$\epsilon\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (i\omega\tau)^{1-\alpha}} \tag{2.24}$$

The exponent parameter α , which takes a value between 0 and 1, allows to describe different spectral shapes. When $\alpha = 0$, the Cole-Cole model reduces to the Debye model. When $\alpha > 0$, the relaxation is stretched, i.e. it extends over a wider range on a logarithmic scale than the Debye relaxation. Another group produced a corrected model known as the Havriliak-Negami relaxation model which is an empirical modification of the Debye relaxation model, accounting for the asymmetry and broadness of the dielectric dispersion curve. The model was first used to describe the dielectric relaxation of some polymers, by adding two exponential parameters to the Debye equation as shown below.

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon^s - \epsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^\beta} \tag{2.25}$$

where the exponents α and β describe the asymmetry and broadness of the corresponding spectra.

When the symmetry parameter β is equal to 1 the Havriliak-Negami equations reduced to the Cole-Cole equation. Another special case of Havriliak-Negami relaxation ($\beta < 1$, $\alpha = 0$) is known as Cole-Davidson relaxation [30, 29].

2.2.3 Conductivity of biomaterials

The body can be considered as a composite volume conductor comprising a number of spatially distributed tissues with differing electrical properties [31]. Conductivity is one of the basic and important properties characterizing the electrical properties of biological materials. The conductivity σ is the proportionality factor between the electric current density and the electric field, and is a measure of the ease with which 'delocalised' charge carriers can move through the material under the influence of the field. Unlike metallic conductors, electrical conduction within biological tissues is due to ions. In the presence of an electric field, the conductivity arises mainly from the movement of mobile hydrated ions within the aqueous biological medium [32]. This ion mobility is also temperature dependent.

Tissue is a very inhomogeneous material; conductivity, relative permittivity and other electrical properties vary widely between different biological tissues and these parameters also vary with the frequency of the applied field. For instant according to Schwan [33] and Grimnes [5] the dielectric permittivity of biological tissues typically decreases with increasing frequency in three major steps (i.e. dispersions) which are designated the α ,β and γ dispersions,

The α dispersion (10 Hz to a few kHz) is generally considered to be associated with the relaxation of ions tangential to charged membrane surfaces, while the beta dispersion (1 kHz to several MHz) [34], associated with the polarization of cellular membranes and protein and other organic macromolecules (and probably bound water). The γ dispersion (>10 GHz) arises mainly from the relaxation of free water within the tissues.

2.2.4 Effect of water in electrical properties of keratinized tissue

Water is one of most important environmental factors that can affect and modify the physical and chemical properties of hairs, skin and nails [35, 36]. As we know skin plays an important role as interface between the internal body and the external environment and it controls the exchange between the inside and outside environments. Body hair contributes to tempreture homeostastis and protects the skin from ultraviolet irradiation. Nail is also used for search for food for some animals [35]. Of course water is not found only in the external environment of the body, but it is also the basic constituent of the different body tissue and is often crucial to maintain their functional characteristics.

Keratins are a family of proteins which are made up of amino acids, karatins contain amino acid cystin which have many side-chain endings that helps to form a strong covalent bond with water molecules. Furthermore the physical properties of the keratin tissue, such as flexibility and permeability are dependant on the dehydration. Electrical conductivity is sensitive to any change in chemical composition, structure of study material and also permits to state whether the observed changes are permanent or temporary. Different researcher observed the decrease in stratum corneum impedance to increase in water content. In the independent investigation of the relationship of dielectric constant and water content of stratum corneum observed that an increment of dielectric constant accompanied by increase of hydration [37]. The relationship between the resistivity and water content measurement can provide information about stratum corneum hydration characteristics [38].

Increase of water content in keratin tissue has been found to increase, in general, molecular mobility. Similar to an increase in temperature. Particularly, the water content-dependent electrical conductivity has been found to reflect ionic mobilities in the water-swollen keratin tissues.

2.3 Scaling and universality

There are many examples and evidence from the literature that the electrical properties of a large number of materials, such as glasses, amorphous semiconductors, electron conducting polymers etc, shows evidently similar frequency dependent AC conductivity curves [1, 39]. In most of these solids, the AC conductivity follows the Arrhenius equations with universally similar AC conductivity. The shapes of the curves are so analogous that it is impossible to distinguish between the ionic and electronic conductivity [26]. Typically, the curves showing the conductivity as a function of frequency fall on a single master curve (overlap) when the AC conductivity spectra of different temperatures are normalized (each measured value divided by the DC conductivity) and the frequency is normalized with regard to both DC conductivity and temperature. This phenomenon is commonly called universality.

In the absence of free charge carriers in disordered semiconductors, AC conductivity $(\sigma(\omega)$ is different from DC conductivity (σ_{dc}) , and σ_{dc} increases as a function of temperature, For many ion conducting disordered semiconductor materials, the hopping movements of the ions exclusively determine the AC conductivity $\sigma(\omega)$. On the other hand the quantum mechanical tunneling gives rise to electronic conduction in disorder solids, even though the AC conductivity curves of these two different mechanisms look similar. The ionic conductivity of disordered semiconductor at low frequency, $\sigma(\omega)$ is usually independent of frequency and it is called as σ_{dc}. Above a characteristic frequency, $\sigma(\omega)$ increases with frequency.

From the analysis of the frequency and temperature dependent ionic conductivities of amorphous materials, such as inorganic glasses, at frequency below a few MHz, It is possible for almost all disordered solids to scale AC data at different temperatures into one single curve, the so-called master curve. The existence of a master curve is sometimes referred to as the time-temperature superposition principle (TTSP). This means that frequency dependent conductivities measured at different temperatures display identical shapes.

The scaling behavior in AC conductivity was first proposed by Taylor [26] for ion conducting glasses by plotting the dielectric loss against scaled frequency. The frequency axis was later modified by Isard using the product of frequency and dc resistivity. They found similar features for the conductivity master curves for different glasses. The scaling law of AC conductivity follows the expression.

$$\frac{\sigma(\omega)}{\sigma_{dc}} = F(\frac{\omega}{\omega_s}) \tag{2.26}$$

where F is a temperature independent function and ω_s is temperature dependent scaling parameter. This frequency scaling parameter has been approached differently by various researchers [40]. When Sidebottom (1997) observed the conductivity master curve for alkali oxide glasses, polymers and doped crystals and concluded he approached the frequency scaling parameter ω_s as hopping frequency ω_p for a given sample at different temperatures and different samples at an arbitrary temperature[41, 42]. Then recently Summerfield [43] approached the scaling frequency as $\sigma_{dc}T$ and $\frac{\sigma_{dc}T}{x}$ or $\frac{\sigma_{dc}T}{n_c}$ respectively. For a given composition at different temperatures and different composition at an arbitrary temperature, where x is mole fraction of mobile ions, and n_c is carrier concentration. They apply this method to sodium borate glasses [40] of different compositions. However, the superposition of the master curves show deviation with different compositions when it is scaled by $\sigma_{dc}T$. This deviation in the master curve is accounted by scaling the frequency axis by $\frac{\sigma_{dc}T}{x}$, but after checking for different sodium germanate glasses, Sidebottom [44] concluded that the master curves for different compositions are not exact for this modification, there are small differences in shape between the master curves. He endorsed the differences in shape of master curves, to the changes in the ion hopping length with changing alkali oxide content of the glasses along with the cation number density. Then he proposed a new scaling approach which uses the scaling frequency parameters as $\frac{\sigma_{dc}}{\epsilon_0 \triangle \epsilon}$ in Sidebottom scaling for a given sample at different temperatures and different samples at an arbitrary temperature. Later on in 2000, Schroder and Dyre [1] proved that the temperature dependent conductivity spectra of a given glass can be superimposed onto a master curve upon application of Sidebottom scaling approach, if the shape of these spectra does not depend on temperature.

2.3.1 Cause of Universality

As mentioned above scaling and universality are important concepts that arise in many circumstances in our physical world. Universality is the observation that there are properties for a large class of systems that are independent of the dynamical details of the system. The system first appears to behave differently for differing materials, but when appropriately scaled, display an underlying common behavior among all materials. In these instances, scaling and universality serve to reduce the process to simpler parts so that a deeper understanding might be achieved [45]. But so many models and postulates has been produced and studied for the last half century to understand and know what the cause of this AC universality. In 2000 Jeppe C. Dyre and Thomas B. Schroder[1] mentioned that Ac universality is not associated with exact power laws. Despite this there is a connection to critical phenomena, because AC universality is caused by the underlying percolation, and percolation is a critical phenomenon.

Percolation theory is a general mathematical theory of connectivity and transport in geometrically complex systems. It was developed to mathematically deal with disordered media, in which the disorder is defined by a random variation in the degree of connectivity [**?**].

According to Brian Berkowitz and Robert P. Ewing [46], the connectivity of the system elements are used to determine many properties of a macroscopic system. The properties of a system which emerge at the onset of macroscopic connectivity within it are known as percolation properties. At percolation the system contains sufficient fraction of entities which connect locally to lead global connection. This global connection is a continuous string of locally connected entities which is unbounded in size except as may result from limitations of a finite-sized system.

To illustrate the concept of connectivity [46, 47] consider a cubic lattice in two dimensions and suppose p is a parameter that defines the average degree of connectivity between each nearest-neighbor link in some arbitrary system. When p is low few links are marked and connected clusters of marked links are small. When p increases the average cluster size also increases. But at a particular value of p an infinite cluster first appears. This value of p is known as the percolation threshold (p_c) and is the fundamental characteristic of percolation theory When p< p_c it is not possible to follow the lines from one end to the other, so there is no infinite connected cluster of marked links (lines). But when p>p_c it is possible to follow lines across from one side other.

When p = 0, all neighbors are totally isolated from every other. When p = 1, neighbors are connected to some maximum number of neighbors. At this point, the system is connected from one side to the other, since there are paths that go completely across the system as shown in the figure 2.3 .

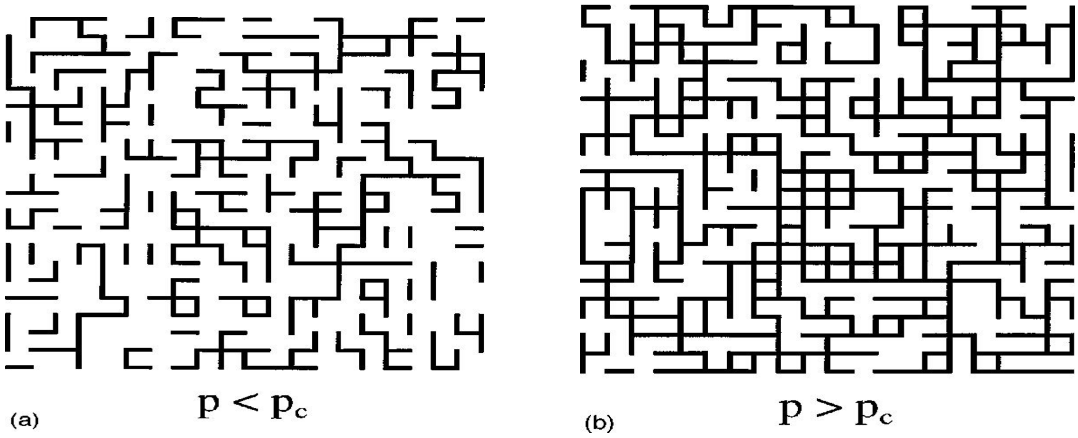

Figure 2.3: Percolation in two dimensions (On an underlying square lattice each nearest-neighbor link is marked black with probability p. (a) shows the case when p <p_c, (b) shows the case when p >p_c. ([1])).

Different scholar [1, 48] use resistor-capacitor circuits network for analysis of materials electrical behavior with frequency and temperature.

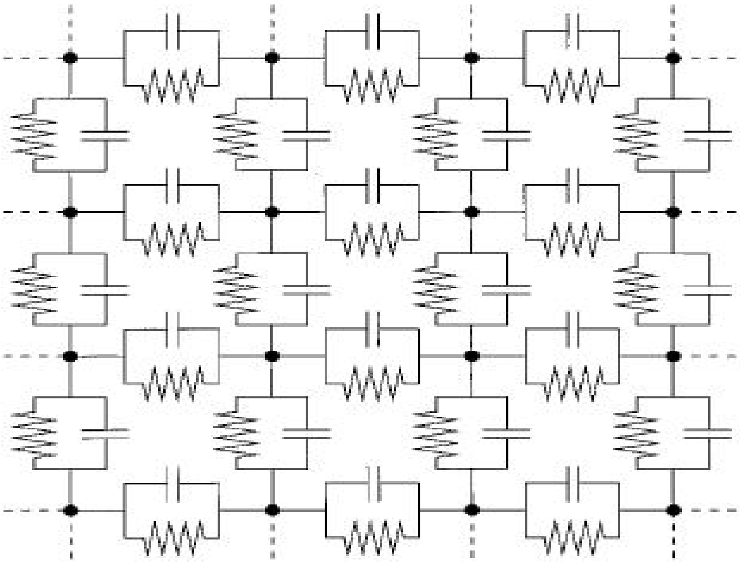

Figure 2.4: Resistor-capacitor circuit network. ([1]).

This network circuit consists of an infinite number of resistors and capacitors combined in parallel to each other as shown in the figure 2.4. The network is made from random resistance which have very different values. But all capacitors are equal which are proportional to the bound charge dielectric constant. The admittance of one of the arbitrary resistor capacitor combined in parallel circuit of this network is given as

$$Y = G + iB \tag{2.27}$$

where G is the real part of the admittance (conductance) and B is the imaginary part of admittance (susceptance)

In the absence of frequency or very low frequency (DC limit) the capacitor has no role and due to this the network can be described as a resistor network. The resistor conductivity is independent of the frequency. Therefore at low frequencies the conductivity of the resistors is large compared to the capacitors.

In this case when the circuit is subjected to a potential difference applied to two opposing faces the DC current pass through the resistors is possible only when the fraction of resistors exceeds p_c . When percolation is reached the admittance of the set of random resistors is dominated by the largest resistors in the pass of the current in the network.

As the frequency increases the AC conductivity (susceptance) of the capacitors begin to increase and at specific frequency ω_m the susceptibility of the capacitor become equal to that of the conductivity of the resistors [1, 48].

That means at frequency ω_m the conductivity of an arbitrary square pieces of conductors (parallel combined resistor and capacitor) in the network can be given as [49]

$$G_c = \frac{1}{R_c} = \frac{\sigma_{dc}\xi^2}{\xi} = \sigma_{dc}\xi = \omega_m C \tag{2.28}$$

Where ξ is the length of the square conducting piece in the network, C is the capacitor.

Dividing all side by C then the critical frequency can be expressed as

$$\omega_m = \frac{G_c}{C} = \frac{1}{R_c C} = \frac{\sigma_{dc}\xi}{C} \tag{2.29}$$

Different sources [50, 51, 52] indicate that the capacitor of a material is inversely proportional to temperature.

$$C \propto \frac{1}{T} \tag{2.30}$$

using equation 2.29 and 2.30 the critical frequency can be defined as

$$\omega_m \propto \frac{\sigma_{dc}\xi}{(\frac{1}{T})} \tag{2.31}$$

Thus

$$(\frac{\omega_m}{\sigma_{dc}T}) \propto \xi \tag{2.32}$$

For the given materials the length ξ is not totally constant but displays very small variation with temperature [51] therefore the right hand side is approximately constant.

As the frequency increases further beyond this point the susceptibility of the capacitor becomes higher and higher. At high frequencies the ac conductivity of capacitors is much larger than the resistors and the resistors can be regarded as open circuits.

Moreover, the capacitance of the materials is also affected by the relative humidity. This effect depends on the types of capacitor, types of dielectric materials used and the air gap between the two plates of the capacitor. Different materials have different ability to absorb water molecules which follow-on change in dielectric constant and therefore capacitance is proportional to the percentage relative humidity of the surrounding atmosphere [49].

That means

$$C \propto \%RH \tag{2.33}$$

Thus, the critical frequency ω_m which the conductivity of resistor and capacitor became equal can be given as

$$\omega_m \propto \frac{\sigma_{dc}\xi}{(\%RH)} \tag{2.34}$$

By rearranging this equation it can be rewritten as

$$(\frac{\omega_m \%RH}{\sigma_{dc}}) \propto \xi \tag{2.35}$$

For the given materials the length ξ is constant. It is independent of relative humidity therefore the right hand side is approximately constant. Therefore changes in the ambient humidity affect the measured capacitance with change in dielectric constant.

Chapter 3

Instrumentation And Measurement Procedure

3.1 Sample Preparation

The samples used for this work were hair, skin and nail. The stratum corneum sample was taken from the heel of a healthy volunteer using an instrument known as aesculup acculon dermatome. This skin piece was about 2 by 2 cm with thickness of 0.2 mm. The hair specimens for impedance measurements were prepared by arranging bundle of hairs (more than 5000 hairs) of length 2.5 cm parallel to each other and they hold together by 60 minute conductive epoxy. The 60 Minute Conductive Epoxy is a two parts, silver epoxy used in prototype, strong mechanical and conducting bonds, high electrical conductivity. Before gluing up them the hair was treated (washed) by pure water and then dried. After drying the bundle hair middle part was covered by plastic and paper to protect any contact of conducting glue. The other sample which was used in the project was nail which was obtained from volunteers.This nail piece was about 1 by 0.8 cm. Before measurement it was properly washed by pure water and dried. The picture of all the three sample of the project is presented in figure 3.1

3.2 Impedance Spectroscopy

Impedance spectroscopy is a powerful and a non-destructive method for characterizing the electrical properties of materials and their interfaces with a single experimental procedure encompassing a sufficiently broad range of frequencies, It includes the small-signal measurement of the linear electric response of the materials of interest (including electrode effects) and the subsequent analysis of the response to yield useful information about the physicochemical properties of the

Figure 3.1: Hair, Nail and Stratum Corneum(SC).

systems, and the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential [53, 54]. Analysis is generally carried out in the frequency domain. The measurement and analysis of the data at the impedance level such as impedance vs. frequency.

Over the last few years the importance of this technique has been grown, and is now being widely employed in a wide variety of scientific fields such as fuel cell testing [**?**], biomolecular interaction, and microstructural characterization [53]. It is also an experimental method of characterizing electrochemical systems as well as employed to studies of inorganic semiconductors, solid-liquid interfaces and bound or mobile charge in the bulk or interfacial regions.

The fundamental approach of all impedance methods is to apply a small amplitude sinusoidal excitation signal to the system under investigation and measure the re-

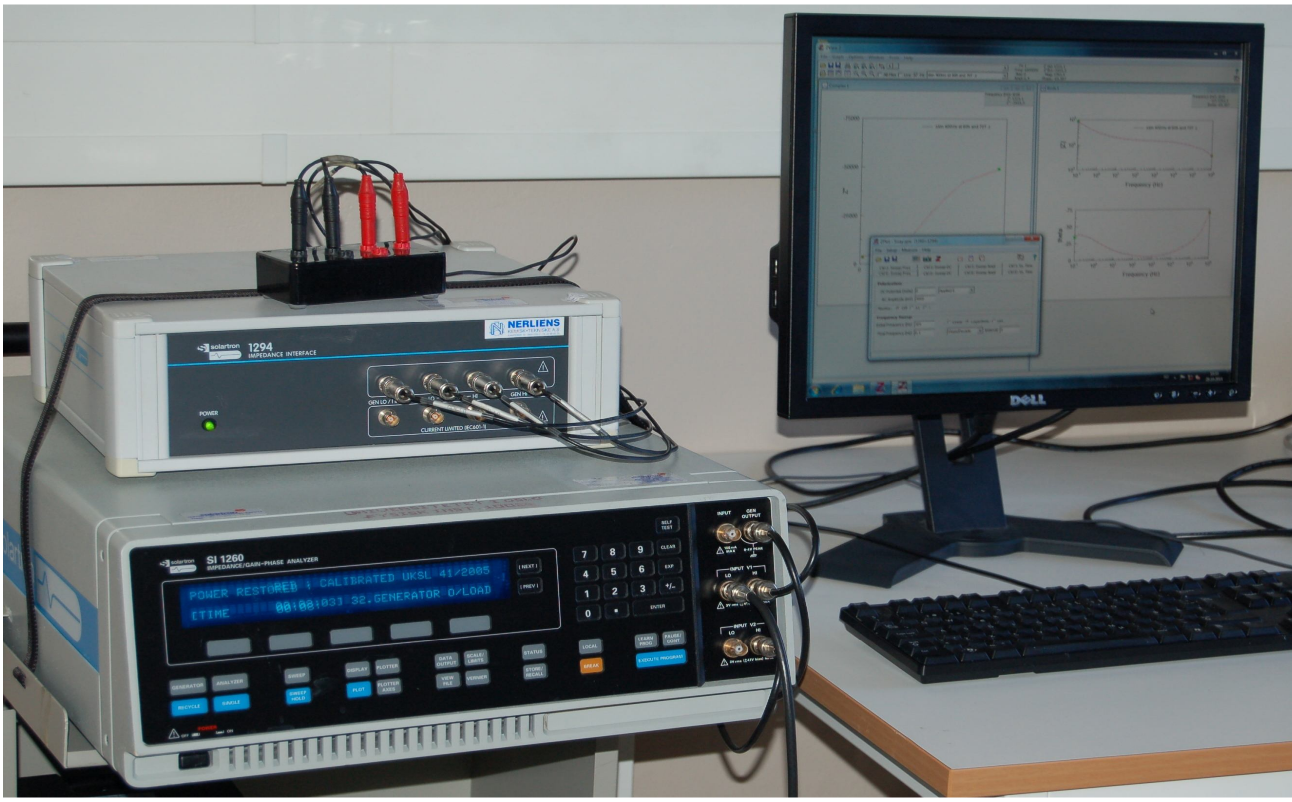

Figure 3.2: Solartron 1260 Impedance/Gain-Phase Analyzer.

sponse (current or voltage or another signal of interest). This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties, is revealed.

Biological tissue possesses energy storage and dissipation properties, and the impedance spectroscopy examines them and reveal information about the reaction mechanism of an electrochemical process. This information is expressed graphically in a Bode plot or a Nyquist (Wassel) plot.

In this project we used a Solartron 1260 Impedance/Gain-Phase Analyzer which is one of the most common and powerful, accurate and flexible frequency response analyzer available today. It has very good resolution and wide range of frequencies.

3.2.1 Bode plot

Bode plots are log-log plots named after Dr. Bode [55]. It use frequency as the horizontal axis and use two separate plots to display amplitude and phase of the frequency response. Because both the impedance and the frequency often span orders of magnitude; they are frequently plotted on a logarithmic scale. Bode plots explicitly show the frequency-dependence of the impedance of the device under test. The plot can be used to interpret how the input affects the output in both magnitude and phase over frequency.

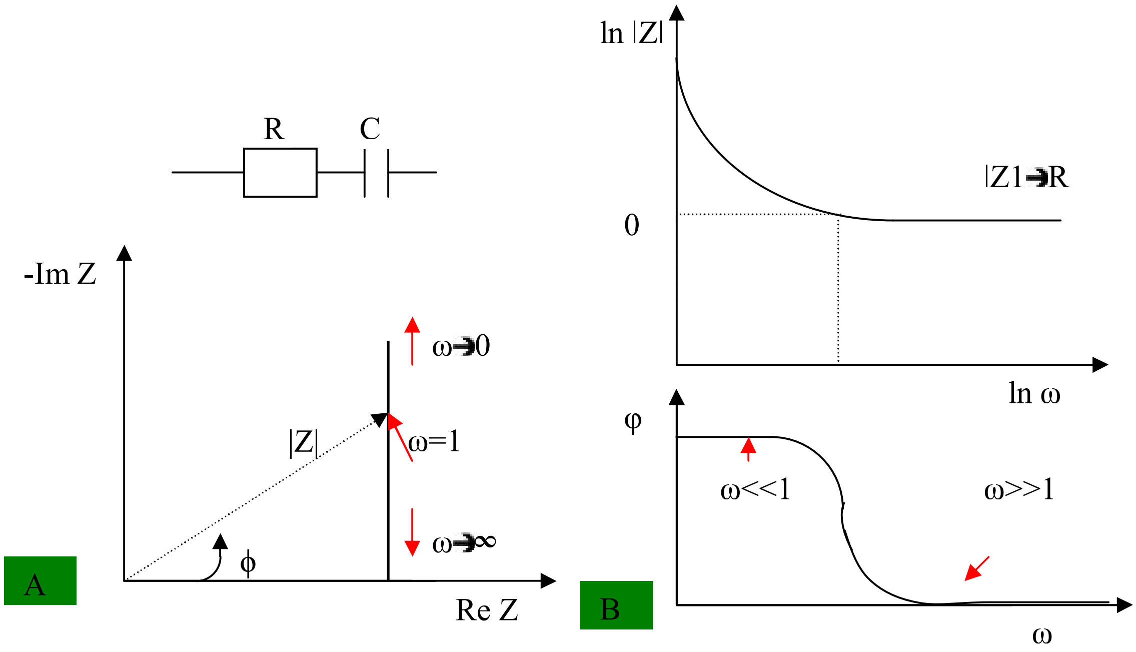

Figure 3.3: (A) wessel plot for series RC circuit. (B) Bode plot for series RC circuit.

The Bode plot for an ideal resistor R and capacitor C with a series and parallel combination is shown in the figure 3.3 and 3.4 respectively. when we consider the parallel combination and the graph plotted based on the impedance and the phase angle ϕ.

$$Z(\omega) = \frac{R}{1+(\omega RC)^2} - i\frac{\omega R^2 C}{1+(\omega RC)^2} \tag{3.1}$$

and

$$\phi = \frac{Z_{im}}{Z_{Re}} \tag{3.2}$$

where Z_{im} and Z_{Re} are imaginary and real part of the impedance in equation 3.1

3.2.2 Nyquist plot

A complex plane or Nyquist plot is also called Wessal plot is a parametric plot of a frequency response used in automatic control and signal processing of a linear system. In this plot the data are presented as a locus of points, where each data point corresponds to a different measurement frequency. Nyquist plots display both amplitude and phase angle on a single plot, using frequency as a parameter in the plot.

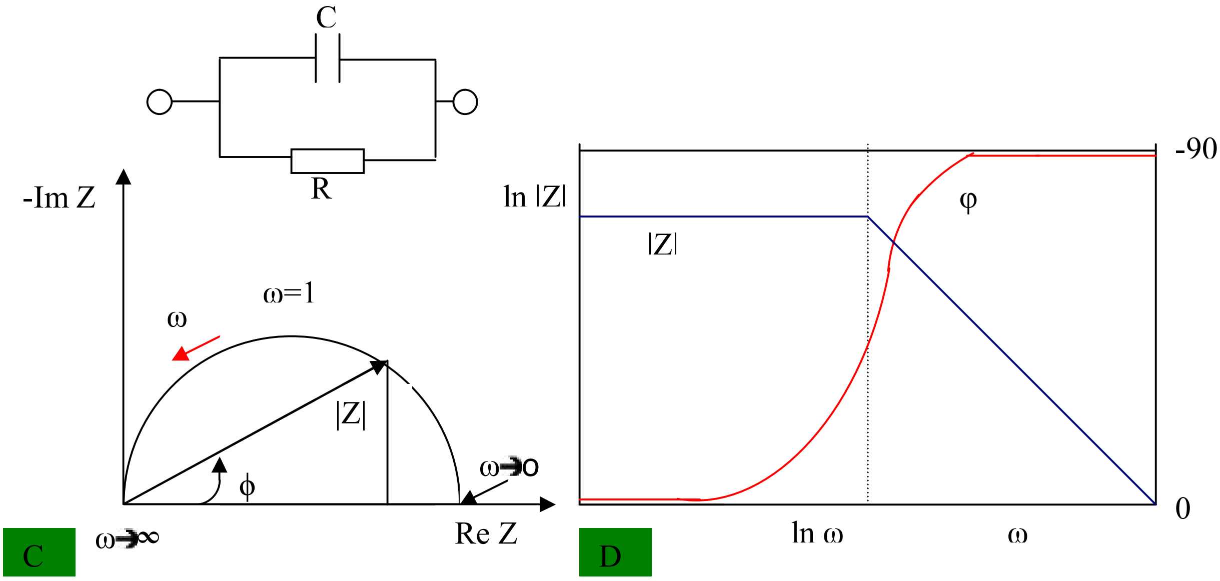

Figure 3.4: (C) wessel plot for Parallel RC circuit. (D) Bode plot for parallel RC circuit.

The advantage of Nyquist representation is that it gives a quick overview of the data and one can make some qualitative interpretations. For example, if the locus of points traces a perfect semicircle the impedance response corresponds to a single activation-energy-controlled process. A depressed semicircle indicates that a more detailed model is required, and multiple peaks provide clear indication that more than one time constant is required to describe the process. Since the shape of the curve is important in making qualitative interpretations of the data. Therefore for plotting data in the Nyquist format the scale of the real axis must be equal to the imaginary axis so as not to distort the shape of the curve. While using the Nyquist representation care has to be taken not to lose the frequency dimension of the data [53, 55, 56]. The Nyquist plot for an ideal resistor R and capacitor C in series and parallel connection is shown in the figure 3.3 and 3.4

3.3 CTS-Temperature Test

Some systems allow temperature and humidity control to be added to the materials impedance test system to characterize the way that materials change with temperature and humidity. There are wide ranges of temperature controllers available from various manufacturers. In this work we use CTS-temperature test chamber which has a high temperature adjustment rate, simple programming on a colored touch panel. In addition to this CTS-temperature test chambers are also control the relative humidity (RH) very accurately.

3.4 Dynamic Vapor Sorption (DVS)

Another important instrument that we used in our work is the dynamic vapor sorption (DVS) which is developed by Surface Measurement System (London, UK, 1997). DVS is a temperature-controlled incubator that contains two chambers, the reference chamber and the sample chamber, within which the specified relative humidity is produced. The changes in relative humidity in each chamber occur by mixing a specific ratio of saturated vapor (100 percent relative humidity generated by passing the air (nitrogen gas) through a vapor humidifier) and the dry air is controlled by mass flow controller. Temperature and relative humidity probes monitor the conditions in each chamber. Within each respective chamber, a reference pan and a sample pan are hanging on a wire that is attached to a Cahn microbalance. The balance is highly sensitive to the changes in moisture that occur throughout the incubator.

In this study, the pieces of the three samples was placed onto a cleaned sample pan. A constant flow of dry nitrogen gas (200 cm^3min^{-1}) is mixed into a stream of nitrogen containing water vapor at saturation and this mixed stream passes through the measurement chamber to maintain a set RH.

Furthermore this device is an automated apparatus that can change the relative humidity or temperature according to specification set by the user. The software

Figure 3.5: CTS-temperature test chamber.

of the DVS apparatus is user-set to terminate a sorption run and move to the next RH step. The instrument maintained the sample at a constant RH until the rate of change in mass (dm/dt) was less than 0.002 % per min. The change in weight was recorded and saved every 20 s. The sample mass readings from the microbalance then reveal the vapour adsorption or desorption behaviour of the material.

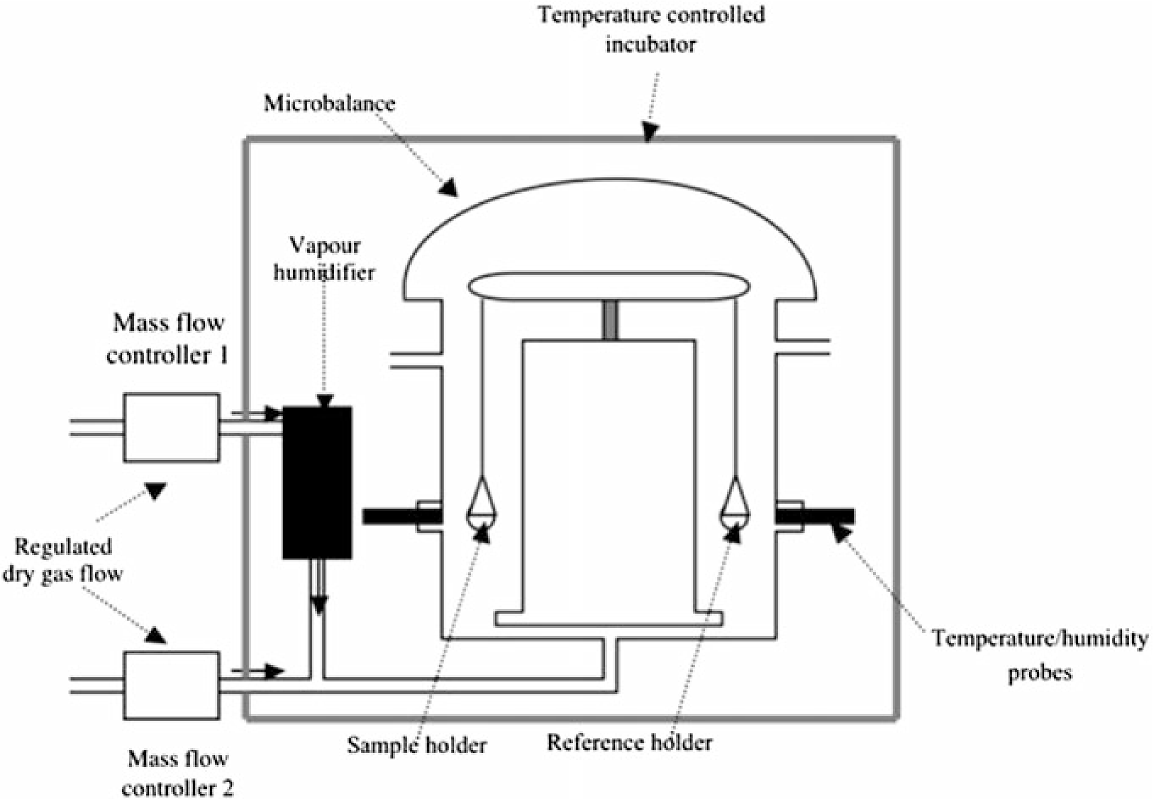

Figure 3.6: Schematic diagram of the operation of dynamic vapor sorption (DVS).

3.5 Measurement and Procedure

In this study we pass through the following procedure to measure the impedance and conductivity of the sample.

After preparing the sample nail and SC and sandwiched them between the two stainless steel electrodes of sample holder. In order to avoid any physical and structural damage due to pressure on the sample, the contact was made smoothly and carefully by putting a small weight approximately 10 gm of stainless steel on the top of the upper electrode. The electrodes have a cylindrical shape with circular electrode surface area approximately 20 mm^2 and due to the mass on the top, the electrode created contact to the sample with a constant pressure of around 5000 $\frac{N}{m^2}$. But for hair the crocodile clipper was used to hold the sample at the two ends and then put the sample inside the moisture chamber for controlling the humidity and the temperature.

The sample stayed approximately 24 hours inside the moisture chamber to be stabilized in the required state before any electrical measurement and immediately after measurement was carried out either temperature or RH was increased again.

AC impedance at different calibrated temperature and relative humidity was measured using a Solatron 1290 (Hampshire, UK) impedance analyzer with 1294 dielectric interface. During impedance measurement the sample scanned at 36 frequency points over the frequency range 0.01 Hz to 1 MHz with employing constant voltage signal amplitude of 400 mV for skin and 2000 mV for hair and nail at 5 permutations settings.

Electrical impedance was displayed as Real Z (R,resistive component in ohms) and Im Z ,capacitive reactance component in ohms. Finally we can change the impedance measurement in to admittance which is composed of real part(conductance), this paper main target and imaginary part (susceptance) measurement using the Zview software setup which use the mathematical relation between impedance and admittance.

Chapter 4

Results

4.1 Time Constant of Sorption of water in keratinized tissue

The aim of this section is to present the dynamic vapor sorption (DVS) measurement results of stratum corneum, hair and nail

The DVS measurement on the sample stratum corneum (SC), nail and hair are used to determine the relationship between water activity and moisture content at a constant temperature. And the time constant of the absorption process as a function of the sample relative humidity. The time needed for hair, nail and SC to reach equilibrium with the environment in the DVS measurement chamber was highly dependent on the relative humidity of the surrounding air [57]. The schedule for the DVS was set to record the sample mass at each of the following RH steps of adsorption at 0, 20, 40, 60, 80 and 95$\%$ RH and at a constant temperature of 25 ± 0.1 ^0C and in reverse sequence at 95, 80, 60, 40, 20, 0$\%$ RH for the desorption.

4.1.1 DVS Measurement of Stratum Corneum Sorption

The SC is naturally poor in water; water is essential to maintenance of normal function and structure of SC. Due to this it has properties of sorbance. It is a thermodynamic rule that water can diffuse from more wetted area to less one until the system reach equilibrium. The SC took and released water with a certain time constant.

The data of DVS absorption measurement of the skin sample had been taken by

Martinsen $et.al$ [37]. According to their result shown on the figure 4.1 the absorption process was not completed at each step in RH before the next step was introduced. Hence, a regression method was used to calculate the time constant(see section 5.1.1)

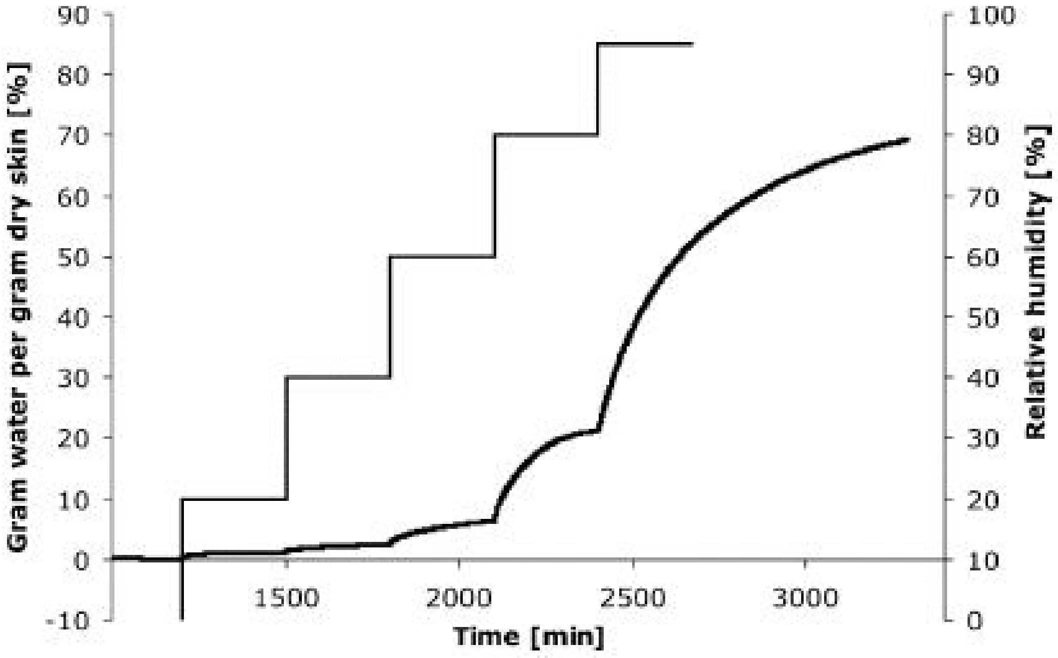

Figure 4.1: Steps in chamber RH (left curve) and resulting change in skin sample mass (right curve)([37]).

4.1.2 DVS Measurement of Nail And Hair Sorption

The result shown in the figures 4.2 and 4.3 are from the DVS sorption measurement of samples of hair and nail respectively. Each measurement was carried out with RH steps of 20%. The blue one is the target relative humidity and the red shows the increment and decrement of the mass of the sample due to adsorption and desorption of moisture. According to the result shown in the figure 4.2 and 4.3, the RH of the sample did not always reach the targeted RH when the testing program changes the RH from one value to the next. But the change in weight in the sample clearly seen as having an exponential curve (the adsorption part shows exponential growth and desorption part exponential decay).

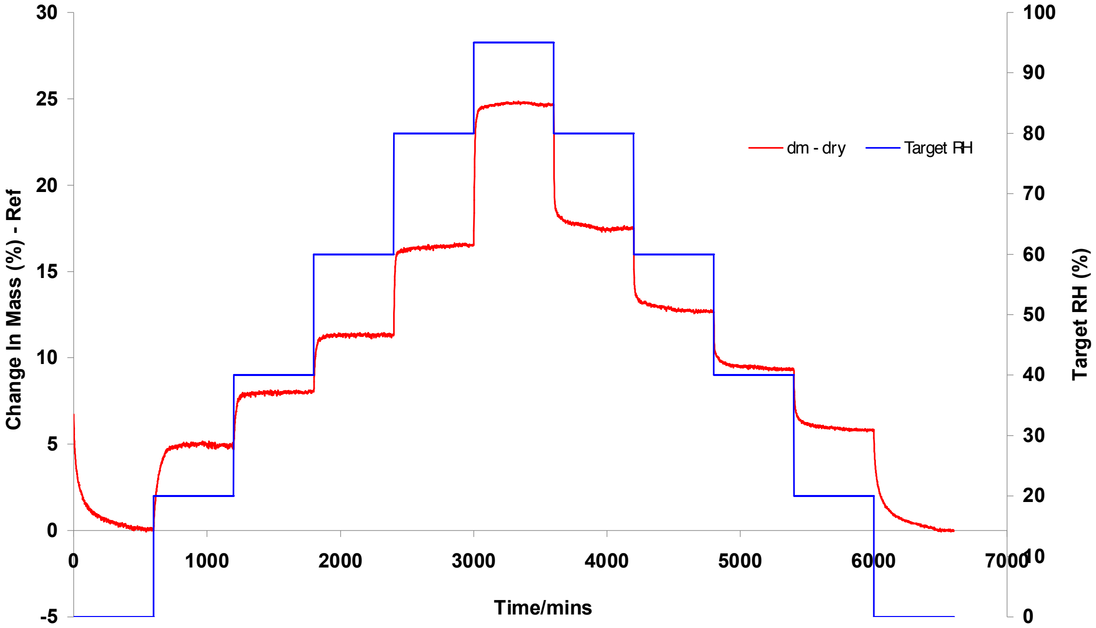

Figure 4.2: Steps in chamber RH and resulting change in hair sample mass.

4.2 Impedance of Keratins Tissue

Hair Impedance: The impedance of the hair was measured in vitro and the result is presented graphically in the figure 4.4 and 4.5. Before we got the presented results we tried to measure the impedance of hair by putting the sample on the flat wood. this was done to prevent the effect of the metal rod of the moisture chamber. But the result shows that the flat wood has also a certain effect. To avoid this we suspend the sample inside the moisture chamber.

The graph shows the measurement result of a bundle of hair fibers connected parallel to each other and measured in different relative humidity and temperatures.

Skin Impedance: Here we measured the impedance of SC in vitro. Electrical impedance measurements were conducted by varying two different parameters. The first measurement was at 25 ^0C in different relative humidity and the second was at 80% relative humidity in different temperatures. The result presented in the figure 4.6 and 4.7.

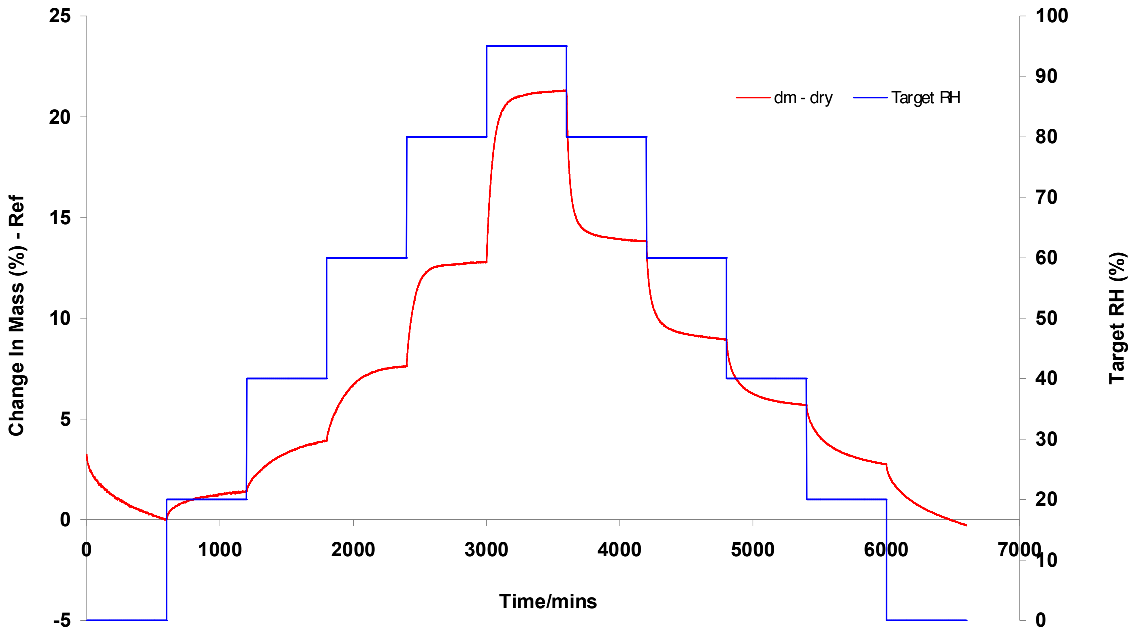

Figure 4.3: Steps in chamber RH and resulting change in nail sample mass.

Nail Impedance: The measurement was done in vitro and upon two different varying parameters (Temperature and RH). The results from the impedance spectroscopy measurements on nail are presented graphically in the figure 4.8 and 4.9.

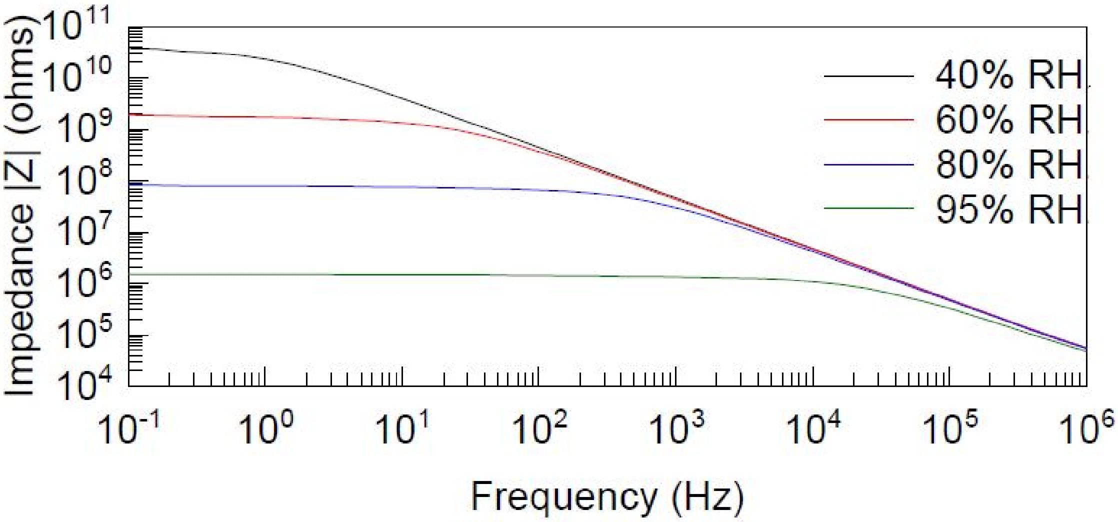

Figure 4.4: Impedance of hair at a constant temperature of 25 ^0C in different RH.

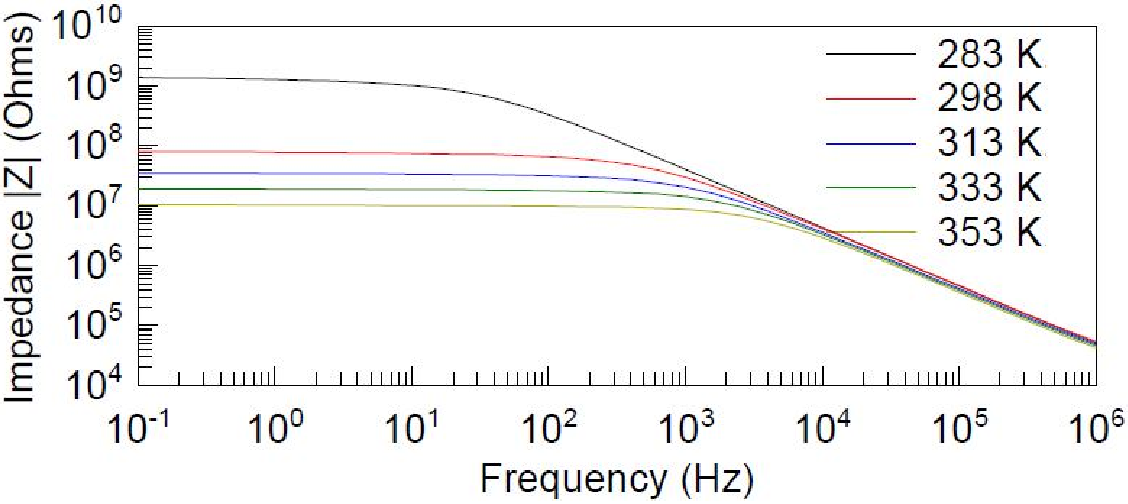

Figure 4.5: Impedance of hair at a constant RH of 80$\%$ in different temperature.

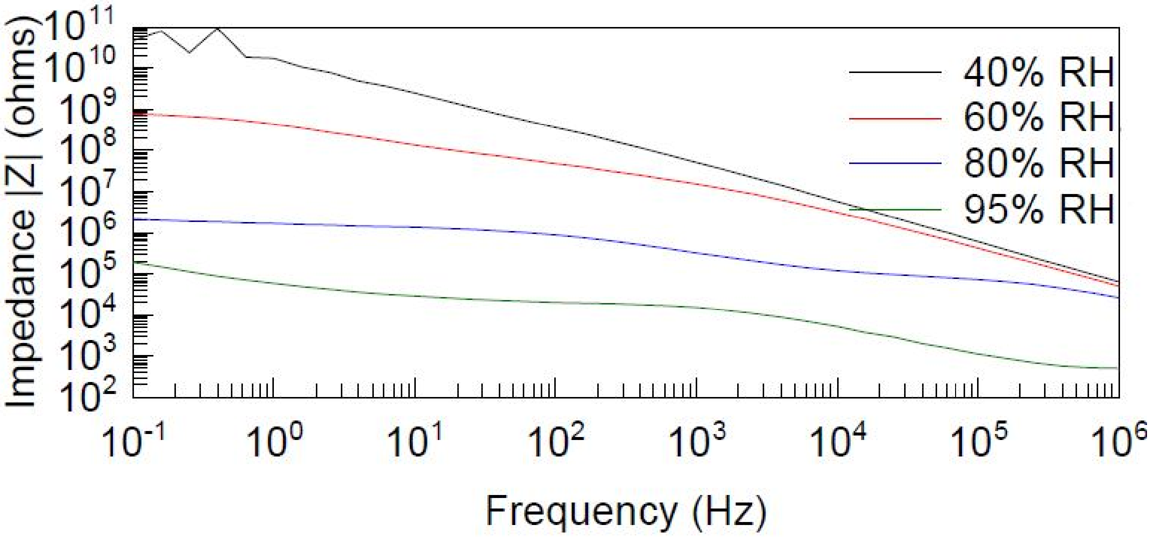

Figure 4.6: Impedance of skin at a constant temperature of 25 ^0C in different RH.

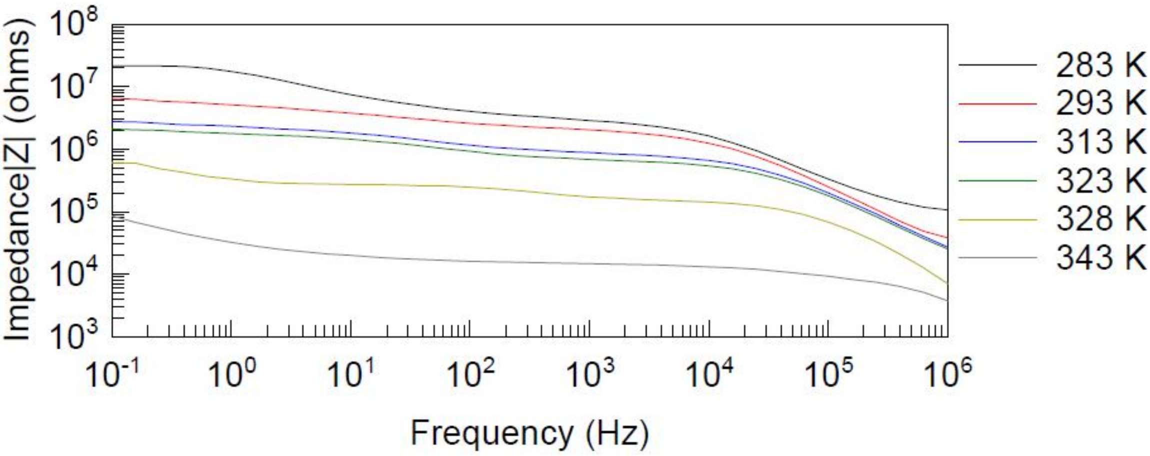

Figure 4.7: Impedance of skin at a constant RH of 80$\%$ in different temperature.

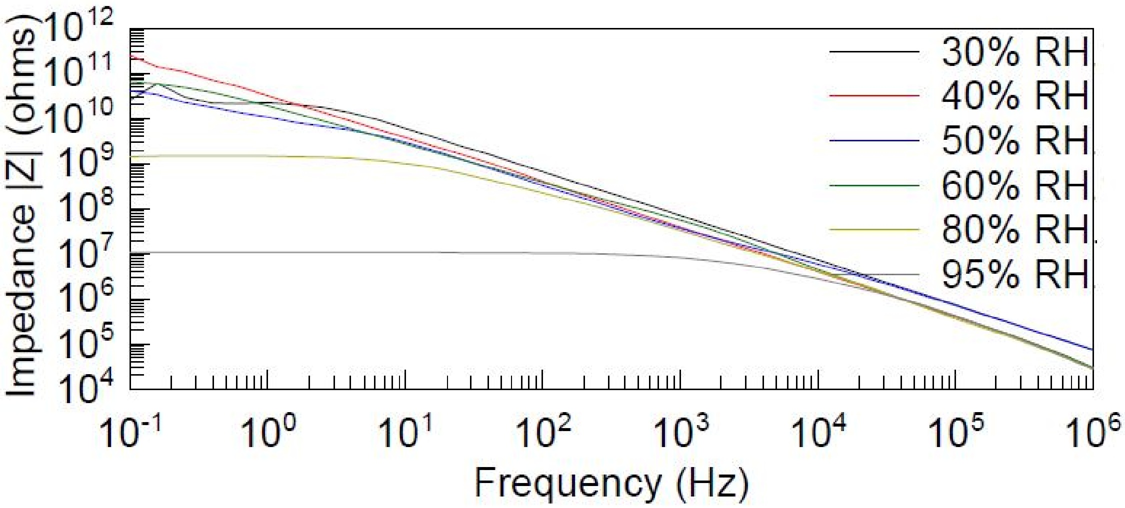

Figure 4.8: Impedance of nail at a constant temperature of 25 ^0C in different RH.

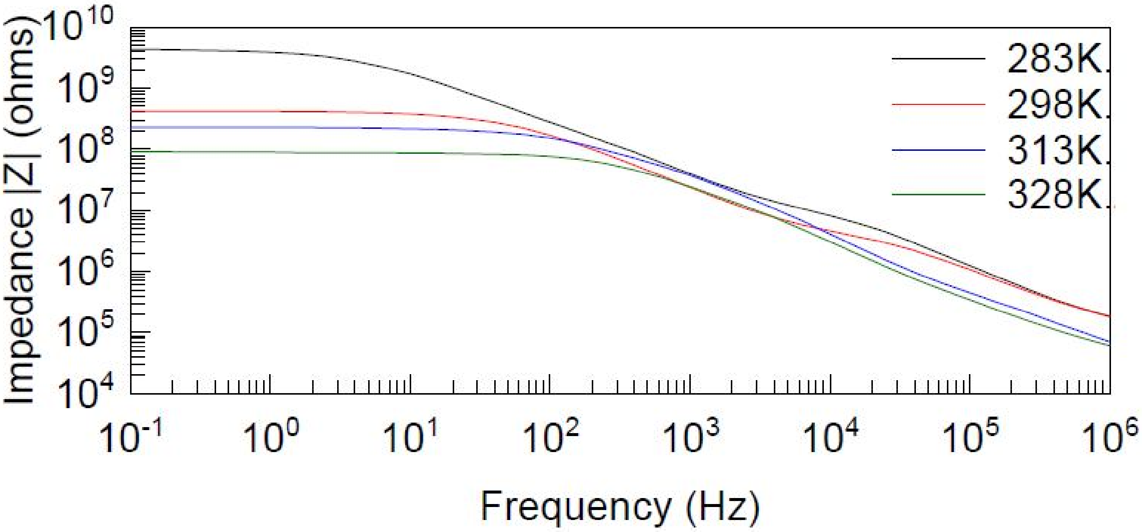

Figure 4.9: Impedance of nail at a constant RH of 80$\%$ in different temperature.

Chapter 5

Analysis and Discussion

5.1 Time Constant of Sorption of water in keratinized tissue

The aim of this topic is not to describe the detail of sorption of keratins tissue, but to determine the time constant that this tissues required to reach to equilibrium with the targeted relative humidity.

5.1.1 Time Constant of Stratum Corneum Sorption

It is a thermodynamic rule that water can diffuse from more wetted area to less one until the system reach equilibrium. The SC uptake and released water with a certain time constant. Time needed for the SC to reach equilibrium with the environment calculated using the numerical extrapolation of this data and the solution of Ficks second law. According to the result shown in the figure 5.1 the time constant has triphasic behavior. The time constant for the absorption process varies as a function of hydration level. The time constant increases with increasing target RH up to about 50%, then decreases up to about 80% and finally increases again above 80%. The more detailed analysis of the skin absorption can be found in [37, 57].

In general the time constant increases very rapidly at very low and high values of RH and with slower changes at mid-range values. The time constant ranges from 5 to 256 minutes. This means, waiting for 24 hours is more than enough and appropriate to reach the targeted ambient relative humidity to be stable for this project AC conductivity measurement. As mentioned in the report [37] the SC needs or some one has to wait at least 17 hours to reach 98% of the final weight

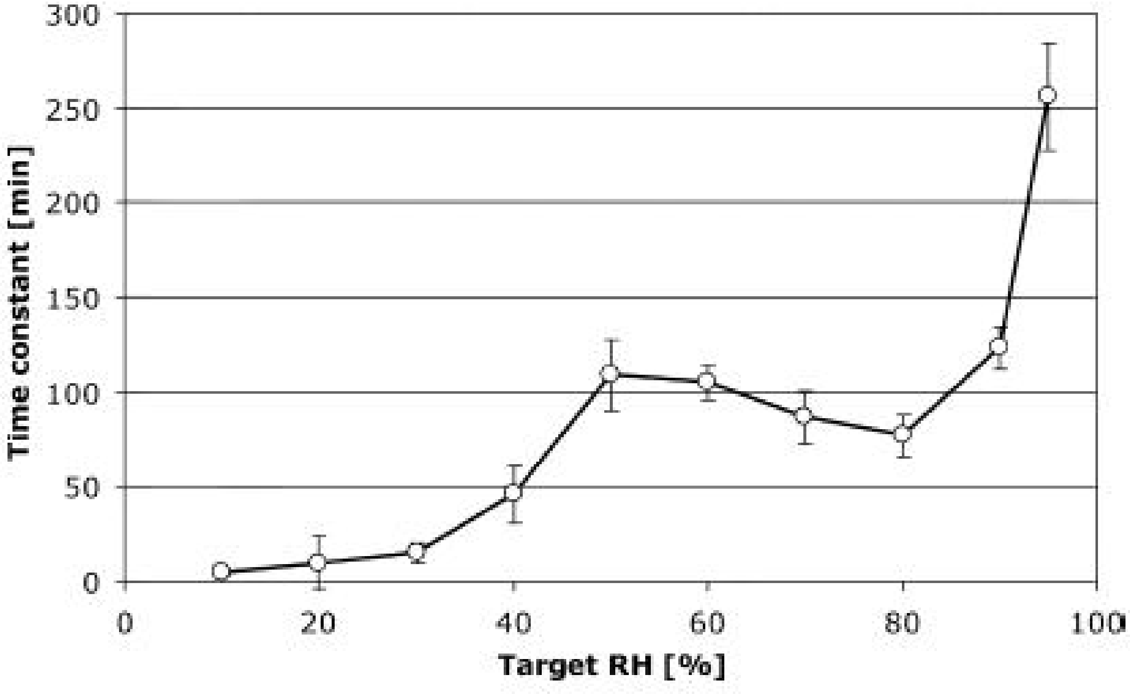

Figure 5.1: Time constant for the absorption process as a function of target RH([37]).

when going from 90%to 98% RH

5.1.2 Time Constant of Nail And Hair Sorption

The result shown in the figures 4.2 and 4.3 are from the DVS sorption measurement of samples of hair and nail respectively. According to this measurement result the RH of the sample did not always reach the targeted RH when the testing program changes the RH from one value to the next. But the change in weight in the sample is clearly seen as having an exponential curve.

This moisture gain or loss from one region to another region will continuously occur in order to reach thermodynamic equilibrium between the different domains involved. The time needed by both sample to reach equilibrium with the environment was calculated using exponential curve fitting. The fitting equation was

$$y = y_0 \pm A \exp(-\frac{t}{\tau}) \tag{5.1}$$

where y is the change in mass, t is time and y_0, A and τ are constants. The curve-fitting parameters τ is the time constant for the sorption process. All the statistics produced from the precis fit to the measured date was with a standard error of less than 0.8 percent of the curve-fitting parameters. The curve fitting was performed using Origin which is good for interactive scientific graphing and data analysis. It is produced by OriginLab Corporation.

As shown in the figure 5.2 the adsorption of nail increase up to 40% and then decrease linearly up to 80%, finally it has a small increment. That means nail needs longer time to up take water to reach equilibrium with the 40% RH and then the time constant decrease as the percentage of RH increase which implicate that nail takes water more easily in the higher humidity. In the contrary time constant of the adsorption of hair has very small negative slope, hair required a longer time to up take water in lower humidity then after when humidity increase hair needs a comparably small time to reach equilibrium with the targeted RH.

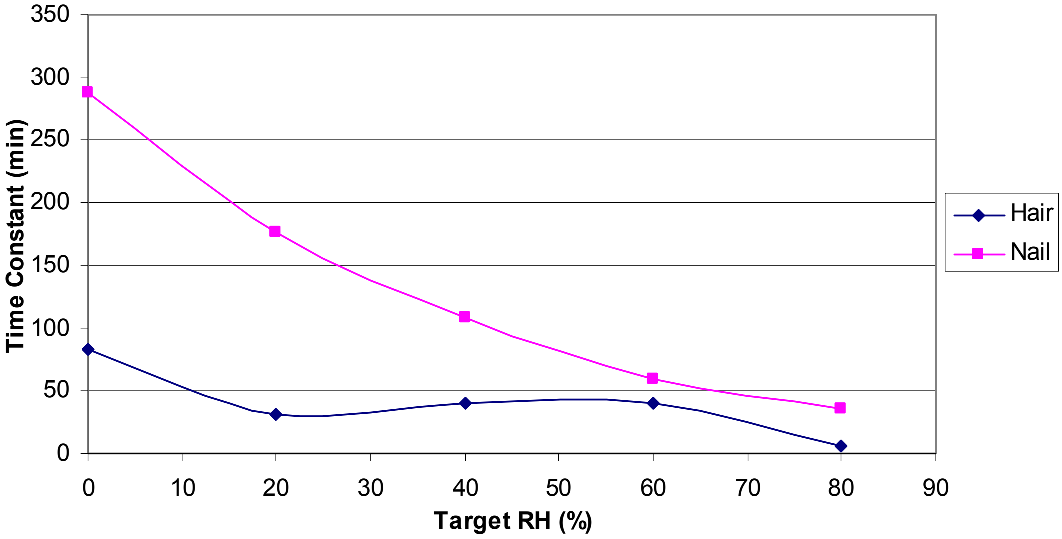

Figure 5.2: Time constant for the absorption process as a function of target RH.

As shown in the graph of figure 5.3 the time constant of desorption of nail has three phases, nail release water quickly in the higher humidity but it needs a little longer time in the 40-60% humidity, as shown in the graph nails need very long time to release the water completely from its system.

In the other hand hair need short time to release the water in the higher humid but as the humidity decrease it holds the water a longer time. Nail needed a very long time to release the water completely from its system, that means nail need long time to be dried out with zero relative humidity.

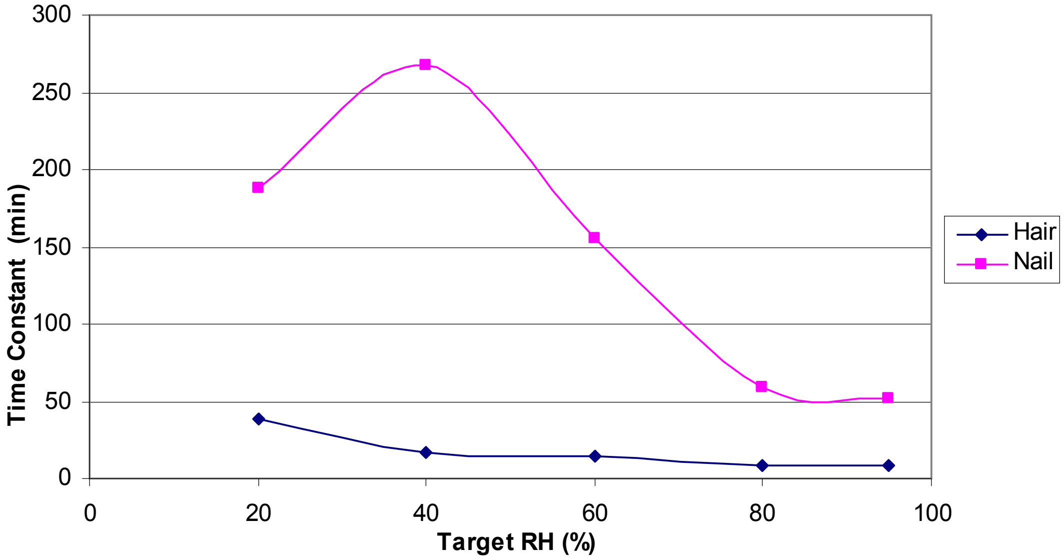

Figure 5.3: Time constant for the desorption process as a function of target RH.

In general to answer the question that why both nail and hair needed more time to uptake water in the lower humidity, release water quickly in higher humidity requires detail microscopic study of their structure, furthermore the activity of water as well as the interaction of water molecules and keratin.

Different literature [35, 58] summarized the nature of the relationship between water molecules and lipid and protein that constitute the keratins. Keratins (protein part) and water molecules have high interaction binding energy which used to form a double hydrogen bond among them. According to different research report which are summerized in [35], at the beginning of sorption process there is creation of condensation of water molecules on the other hydrophilic site via hydrogen bond. After that there is a gradual decrease in binding energy that allows water molecules to be inserted between polypeptide chains.

Water found in biological materials are hydrogen bonded either with protein or intermolecular to other water molecules. The hydrogen bonded water with protein (bimolecules) are known as bounded and those which are non-hydrogen bonded with biomolecules are free water. Therefore nails and hairs release the free waters quickly and takes longer time for bounded water to release.

As shown in the graph the time constant ranges 7 to 39 minutes and 51 to 268 minutes for absorption of hair and nail respectively. Similarly the time constant of hair and nail desorption ranges 6 to 83 minutes and 36 to 287 minutes respectively. In conclusion, it seems waiting 24 hours is more than enough and appropriate time to get the target RH to be stable for conductivity measurement.

5.2 Impedance of Keratins Tissue

Hair Impedance: As shown in figure 4.4 and 4.5 the impedance of the hair varies according to the variation of humidity and temperature. It has inverse relation to both humidity and temperatures. It decreases as relative humidity and temperature increase and vice versa. This properties is more pronounced in the lower frequency region below 10 kHz but when we move to the higher frequency region above 10 kHz the impedance of hair in different condition seems the same and become equal around 1 MHz. At lower temperature and RH the impedance is almost independent of frequency which indicate that it is dominated by resistance.

Skin Impedance: As shown in the figure 4.6 and 4.7 the impedance of the stratum corneum is affected by temperature and relative humidity. The variation of temperature and water content of the skin (SC) has pronounced effect on the impedance of the skin, the impedance of the SC decrease with increments of temperature and moisture. Detail investigations is needed to know the SC molecular dynamics caused by the hydration and dehydration as well as change temperature that influences the impedance. Unfortunately this was beyond the available research resource as well as outside of the project target. It is well known that the stratum corneum has both capacitance and resistance nature. This capacitance and resistance nature of the SC is dependent on the mobility of the keratin chains and water molocules [37].

Nail Impedance: As shown in figure 4.8 and 4.9 the nail electric impedance is affected by moisture and temperature variation as that of hair and skin. The impedance of nail decrease as the temperature and the percentage of RH increased. The nail impedance in the lower relative humidity shows a small variation but above 60 % relative humidity the impedance shows large variation

5.3 Conductance of Keratins Tissue

Different materials display different electrical properties; conductivity is one of the electrical properties which determine the behaviors of materials under the influence of external electric fields.

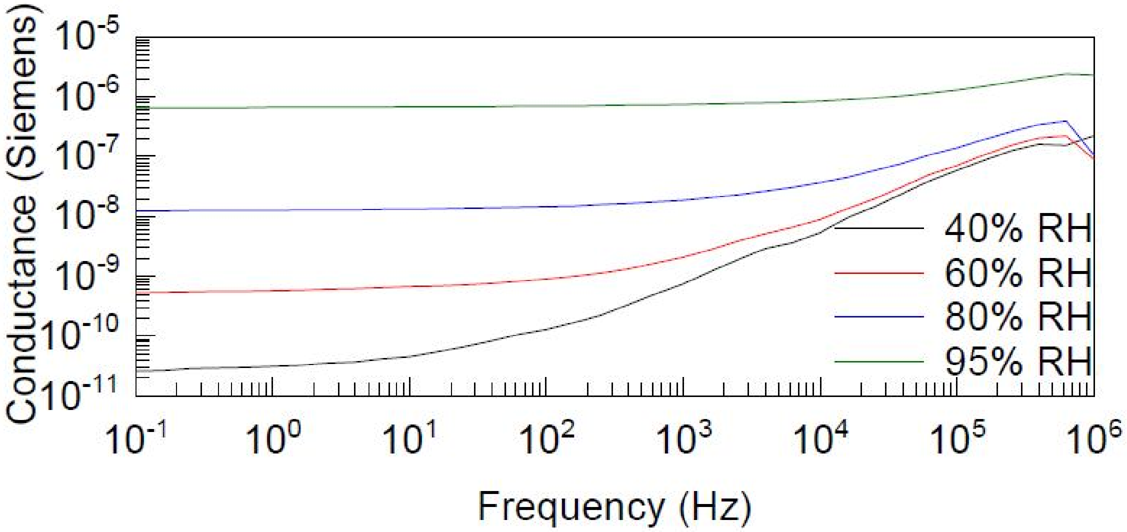

Figure 5.4: Conductance of nail at a constant temperature of 25 ^0C in different RH.

Electrical conductivity is a measure of how well materials transmit the electric current. For example, conductive materials have a high electrical conductivity and both direct and alternating currents flow easily through them. Dielectric materials have a large electric permittivity and they allow passage of only alternating electric currents. The electrical conductance of human skin (SC), hair and nail obtained from Zview software mathematical calculation of the impedance measurement in a frequency range of 0.1 Hz to 1 MHz with two different varying parameters, temperature and RH and the result presented graphically. As the result shown in the figures from 5.4 to 5.9 for the three samples the conductivity varies with variation of both temperature and RH. At a constant temperature the conductivity increase with relative humidity and in the similar measurement at a constant relative humidity the conductivity increase with the temperature. That means both temperature and relative humidity play a vital role on the conductivity properties of all the three samples. But the main question is how? It is obvious that electrical conductivity of a material is determined by two factors: the concentration of free carriers available to conduct current and their mobility. In metals the conductivity decrease when temperature increases, while the conductivity of semiconductors increases as the temperature increase.

The reason that metals conductivity decrease with increasing temperature is that

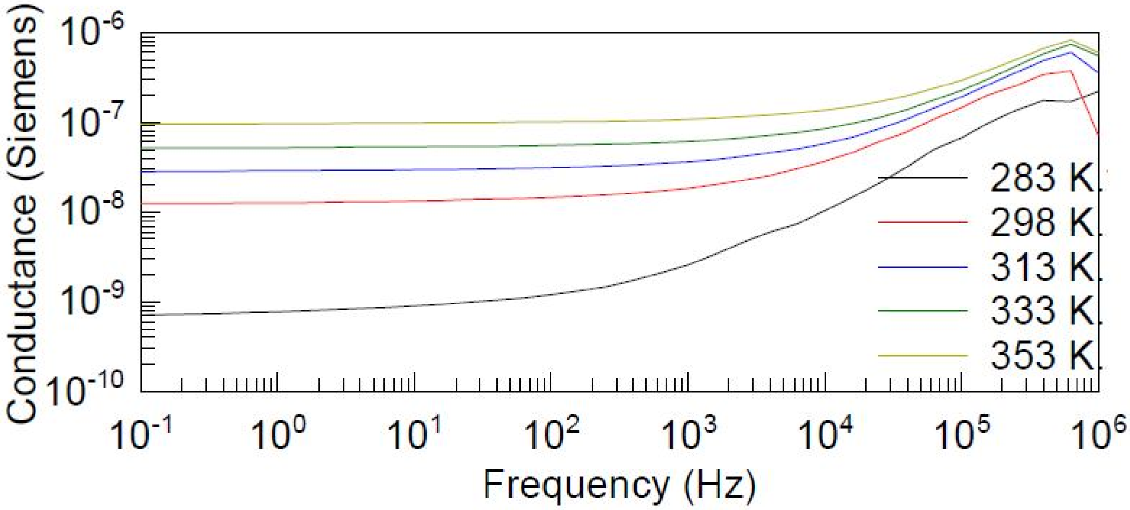

Figure 5.5: Conductance of hair at a constant RH of 80% in different temperature.

it does not affect the number of charge carriers (electrons) as well as the amount of charges but it has effects on mobility which is related to the drift velocity of the electrons. As temperature increase the atomic vibration increase which will cause more collision of electrons within the crystal lattice. As a result drift velocity decrease. But in semiconductor materials temperature causes electrons in the valance band to gain energy to be promoted to the conduction band and from donor levels, or holes to acceptor levels.

In the other hand the conductivity of the solutions also increases as temperature increase. When the temperature of the solution increases, it will cause a decrease in viscosity and an increase in the mobility of the ions in solution. In addition to this an increase in temperature can also cause an increase in the number of ions in solution due to dissociation of molecules.

As shown in the graph of figure 5.4, 5.6 and 5.8, Ac conductance correlated positively with moisture content. Increase of water content in keratin tissue has been found to increase the conductivity of the materials. This increment is as a result of molecular mobility and ionic conduction as more water molecules added to the system that create good environment for the free oscillations of the molecules. In fact the water is found in the body in three different states, free, loosely bounded and tightly bounded. The variations of water state can affect the relaxation time of water and its ability to polarize in an electric field. Thus, the water content-dependent electrical conductivity may be due to the existence of these ionic mobilities in the water-swollen keratin tissues.

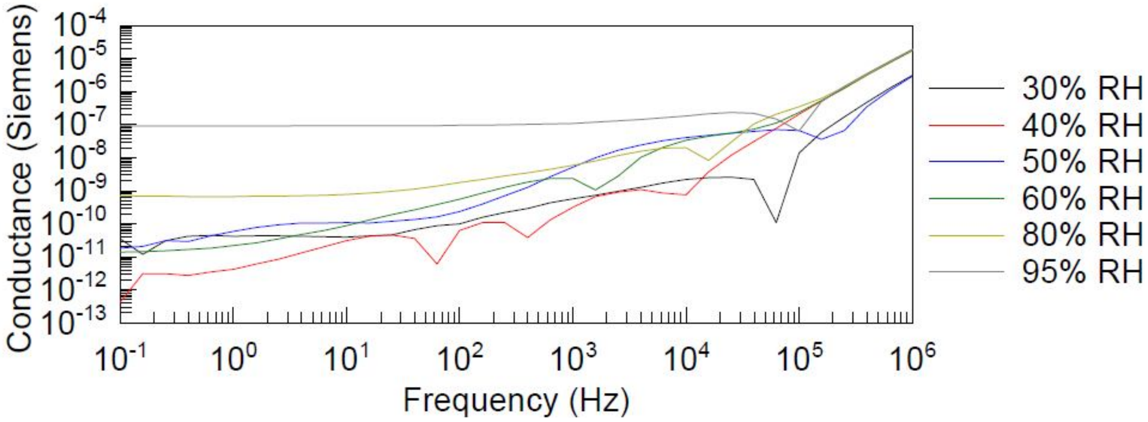

Figure 5.6: Conductance of nail at a constant temperature of 25 ^0C in different RH.

In addition to this keratins are composed of polypeptide chains made from different amino acids. Parts of these polypeptides can form structures (such as, α-helical and β-pleated configurations) with different chemical nature of many side chain endings of keratins. These properties of keratins can form bond to the surrounding water molecules that leads different arrangement and internal reorganization. This kind of reorganization can cause some kind of conduction energy change and introduce new donor/acceptor levels, thereby considerably modifying the electronic structure and conduction properties of keratins.

5.4 AC Conductance Universality In Keratins Tissue

In the previous section we discussed the conductivity of hair, nail and SC and its dependence on the temperature and the relative humidity. It is clearly shown in the graph of figure 5.4-5.9 the AC conductivity of all the three samples of the project depends on both temperature and RH. Here the main target of the project and this topic is to investigate the universality of the measured AC conductance of the hair, nail and SC. Universality is a phenomenon which occurs in any condition. Here the condition is AC conductance spectra of different temperatures or different RH. These conductance spectra are normalized (each measured value divided by the DC conductivity) and the frequency is normalized with regard to both DC conductivity and temperature or RH fall on a single master curve (over-

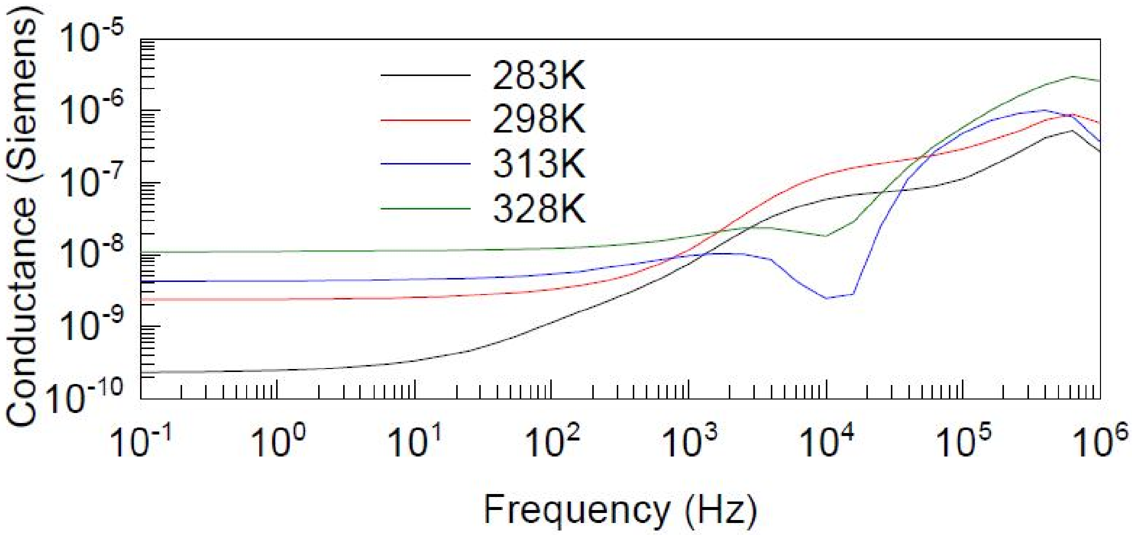

Figure 5.7: Conductance of nail at a constant RH of 80% in different temperature.

lap each other). Such behavior is observed in different types of materials, such as glasses, amorphous semiconductors, electron conducting polymers etc. But to our knowledge it has never been checked the existence of this behavior in biological materials.

The real part of the electrical conductivity σ' is plotted as a function of frequency and normalized with regard to both DC conductivity and temperature or RH. Here we used Summerfield scaling method which is described in equation 2.26, because it has the advantage of using directly accessible quantities such as DC conductivity (σ_{DC}), temperature (T) and ambient relative humidity ($\%RH$) the conductivity axis was scaled by DC conductivity (σ_{DC}) and the frequency axis by $\sigma_{DC}T$ different temperature or $\frac{\sigma_{DC}}{\%RH}$ different RH.

5.4.1 AC Conductivity Scaling Result of Hair

The electrical conductivity of hair is clearly dependent on both temperature and RH. Here the hair electrical conductivity measured at a constant temperature of 25 ^{0}C in different relative humidity and another measurements was taken by keeping the relative humidity constant at 80% for different temperatures.

The scaled electrical conductance of hair is shown in figure 5.10 and figure 5.11. Each graph is a log-log plot of the real part of the normalized AC conductivity as

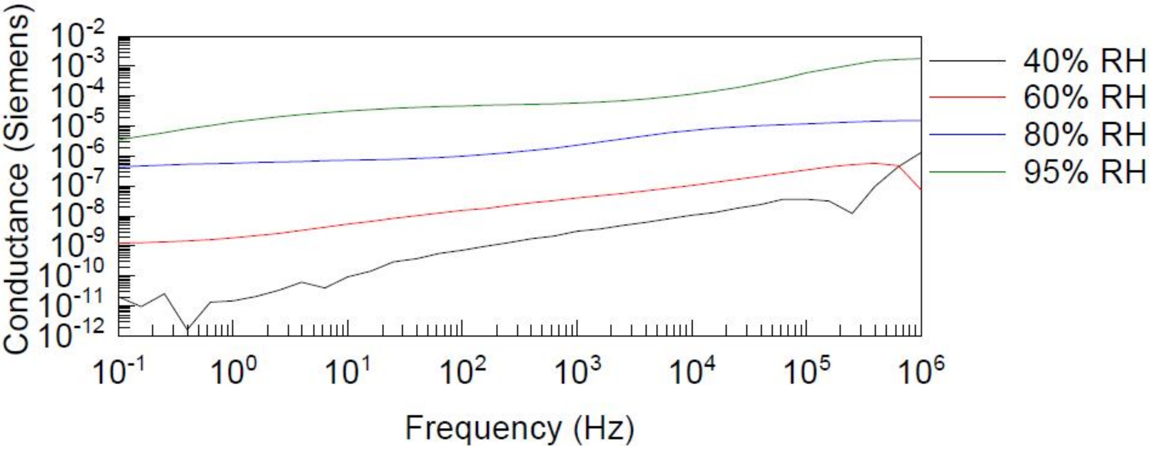

Figure 5.8: Conductance of skin at a constant temperature of 25 ^0C in different RH.

a function of scaled frequency. As the scaling result shows the electrical conductance of hair which is measured in different environmental condition (temperature and RH) almost falls in to a single curve.

It is evident that hair satisfies the so called time-temperature superposition principle. This means that the frequency dependent conductivity which measured at different temperature and RH demonstrates similar shape. In other words the shape of the frequency dependent conductivity of hair does not depend on the temperature and RH.

5.4.2 AC Conductance Scaling Result of Nail

The AC conductivity of nail also clearly demonstrates the dependence of temperature and ambient relative humidity. The electrical conductivity of the nail was measured at two different cases; the first one was at constant temperature of 25 ^0c at different ambient relative humidity and the second was at constant ambient relative humidity at different temperatures. The real part of the Ac conductivity spectra was normalized or scaled with regard to both DC conductivity and temperature or RH.

As shown in the figure 5.12 the scaled graph of the nail conductivity which is measured at a constant temperature in different relative humidities, in the higher humidity collapsed in to single curve. But there is a deviation from lower hu-

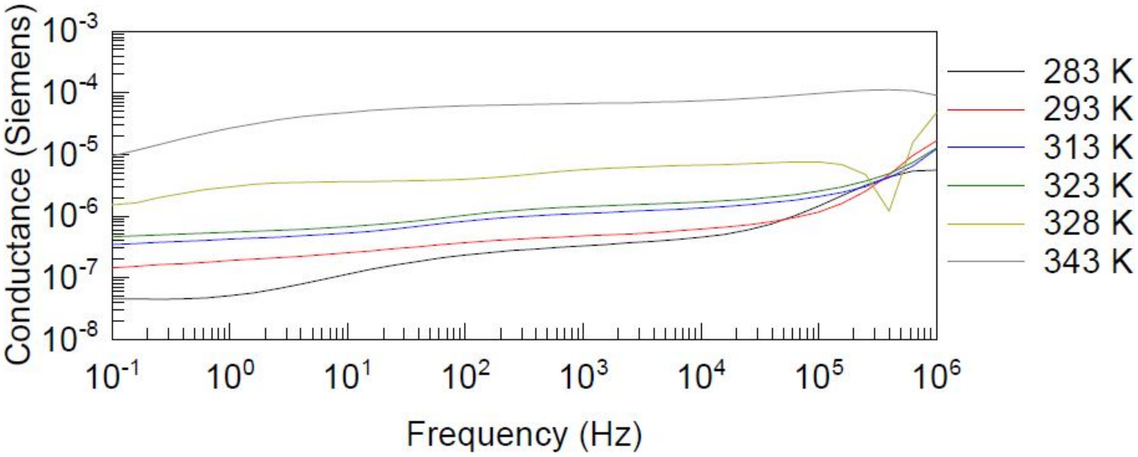

Figure 5.9: Conductance of skin at a constant RH of 80% in different temperature.

midity conductivity measurement result. In fact the curve shape seems similar however only there is shift on the frequency axis. This shows evidently that nail satisfy the so called time-temperature superposition principle to a certain extent. Shift on the frequency axis may be due to the existence of high impedance (low conductivity) on that environmental condition. Low conductivity indicates the existence of small charge transportation. This limited charge transportation can be caused by decrease in charge carrier concentration or decrease in mobility of charge carrier. Both mobility and charge carrier concentration has direct impact on the conductivity of the materials. This can be express in simple mathematical expression as $\sigma = ne\mu$ where μ is mobility (drift velocity) n is the density of free charge carriers and e is the electronic charge.

The scaled conductivity spectra of the nail which is measured at a constant relative humidity in varying temperature is presented in figure 5.13. As shown in the figure the normalized conductance more or less shows a high tendency to collapse into one curve. In fact the curve shape seems similar but it shows only a very small deviation among the graph. This shows more or less nail satisfy the so called time-temperature superposition principle to a certain extent.

5.4.3 AC Conductance Scaling Result of SC

Like nail and hair the electric conductivity of SC is clearly influenced by both temperature and ambient relative humidity. Similarly the AC conductivity of the SC was normalized with regard to DC conductivity and temperatures or relative

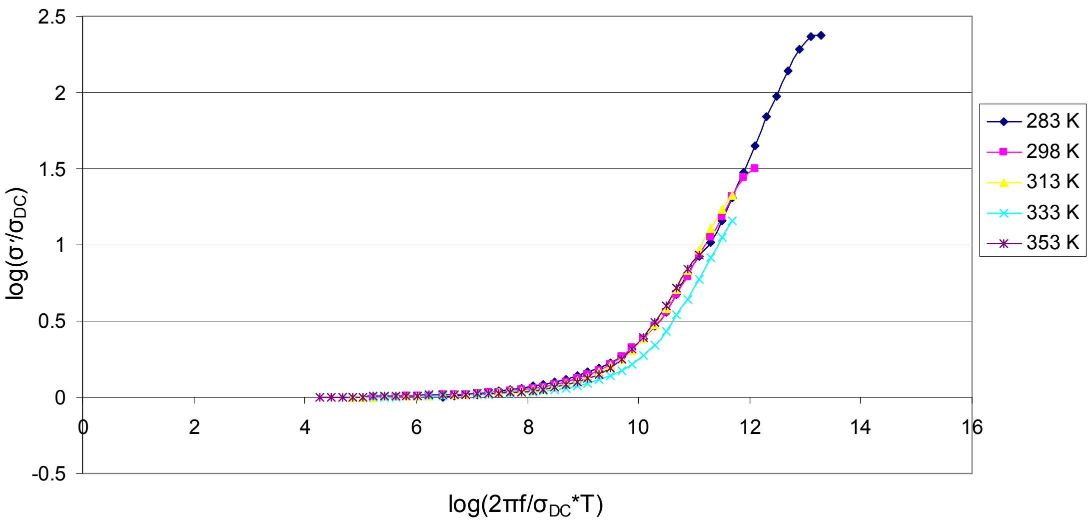

Figure 5.10: Scaled conductance spectra of hair at a constant RH of 80% in different Temperature.

humidity. The scaled conductance spectra is presented in the figure 5.14 and 5.15.

As shown in the figure 5.14 the SC scaled conductance spectra which were measured at constant temperature in arbitrary humidity did not collapsed into one single curve as the hair and nail did. The normalized curve for lower relative humidity deviated from the higher relative humidity conductance result. As clearly shown in the figure, when the relative humidity decreases the normalized curve deviation increases.

As shown in the figure 5.15 SC scaled conductivity spectra did not collapse in to one curve. But in the certain temperature range between 20 ^0C to 50 ^0C the normalized graph collapsed. The normalized graph below 20 ^0C and above 50 ^0C did come close to the other graph but the graph above 50 ^0C also overlapped to each other. It seems like some kind of regional grouping. There may be several reasons why this happened.

In both case the normalized conductance spectra which were measured at lower temperature and lower relative humidity deviated from the rest of the group. At these two conditions the SC has very high impedance and low electrical conductivity. Based on this project result it is difficult to conclude whether SC satisfies the time-temperature superposition principle or not. The deviation from a normalized curve in the lower temperature and humidity can be due to the existence of

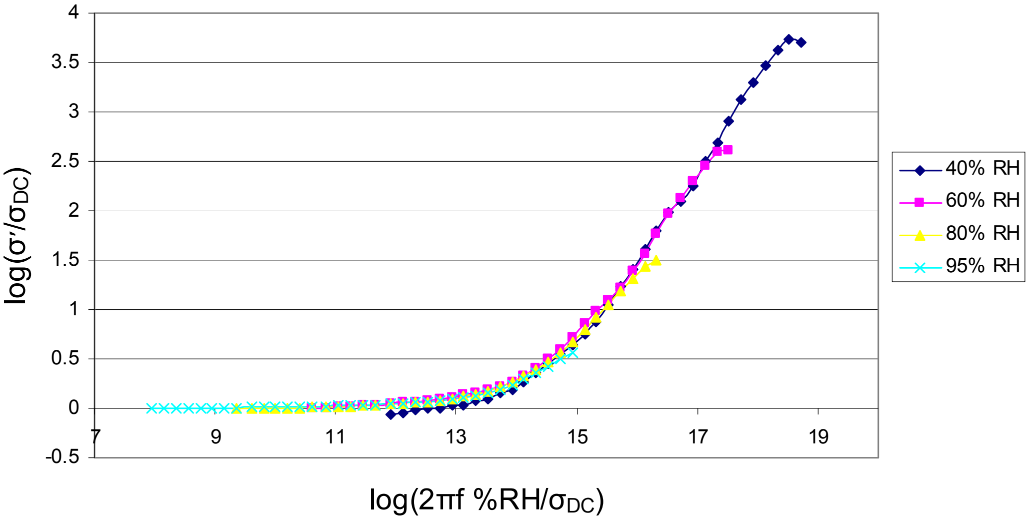

Figure 5.11: Scaled conductance spectra of hair at a constant temperature of 25 ^0C in different RH.

high impedance (low conductivity) on that environmental condition. As discussed above the low conductivity indicates the existence of small charge transportation. This limited charge transportation can be caused by a decrease in charge carrier concentration or decrease in mobility of charge carrier. Both mobility and charge carrier concentration has direct impact on the conductivity of the materials.

5.5 General Discussion

In different materials of any structure, the charge transport can be done by different charge carriers such as ions (negative and positive), protons, electrons and holes. It can be also a combination of these and the total conductivity is the sum of the contributions of each charge carrier type.

In biological materials in the presence of an electric field, conduction arises in certain degree because they contain dipoles as well as charges that can move and mainly from the movement of mobile hydrated ions. In general in order to understand the conduction processes it is necessary to know the charge carrier density and the mobility of each charge carrier type. As discussed above temperature and relative humidity has higher impact on the conductivity of all the three specimen of the project. This means both temperature and humidity has influence either on the charge carrier concentration and mobility or on both.

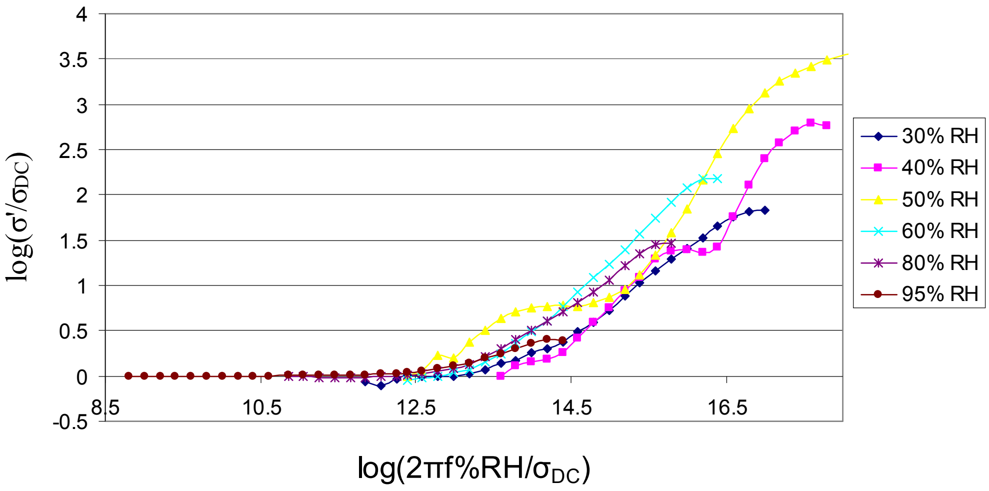

Figure 5.12: Scaled AC conductivity spectra of nail at a constant temperature of 25 ^0C in different RH.

The charge carrier increment can occur in different ways for instance in the solution due to dissociation of molecules whereas in electronic conduction due to delocalization but in the other direction the charge carrier can be lost either by recombination or localization.

In fact in addition to their conductivity contribution, charge carriers have a great role for energy transfer, information transfer, spatial separation of oxidizing and reducing entities and generation of free radicals in biology.

On the other hand in a certain degree this temperature dependent conductivity nature of the biological materials resembles the temperature dependent conductivity nature of semiconductors. It is not easy to run into a conclusion like this but there are plenty of proposals and reports which are summarized by Susheel Kalia and Luc Averous [59] that biological materials such as protein and DNA has a semi-conduction polymer nature (polymer is a large molecule, or macromolecule, composed of many repeated subunits).

Furthermore the time-temperature superposition principle which is hold by so many amorphous semiconductors and semiconductor polymers shows its existence in biological materials. Indeed no one knows the real cause of the universality of AC conductivity in disordered semiconductors but there are many assumptions and postulates reported in different literature that universality is caused by

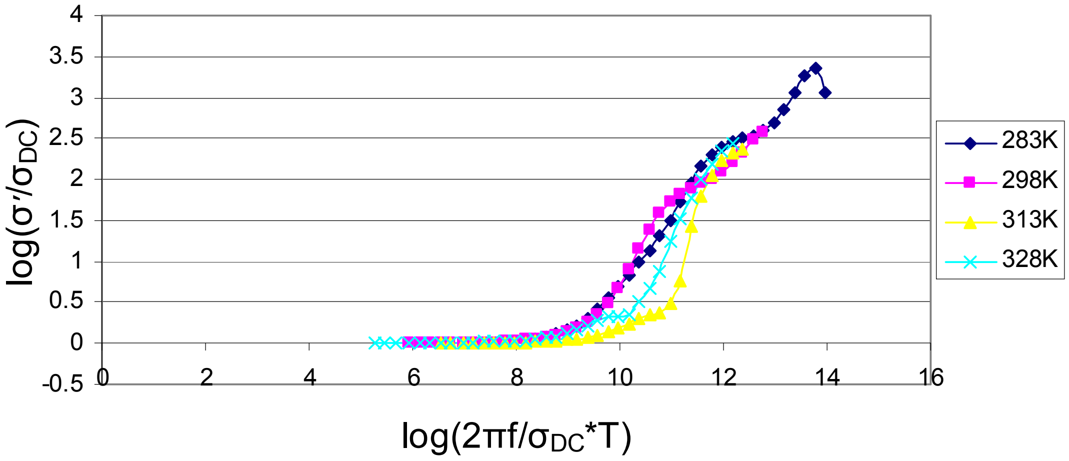

Figure 5.13: Scaled AC conductance spectra of nail at a constant RH of 80% in different Temperature.

percolations, the random variation in the degree of connectivity.

In this project we tried to show the role of temperature and relative humidity in the conductivity of the materials. This is done based on the percolation argument using resistor and capacitor circuit networks as shown in subsection 2.3.1.

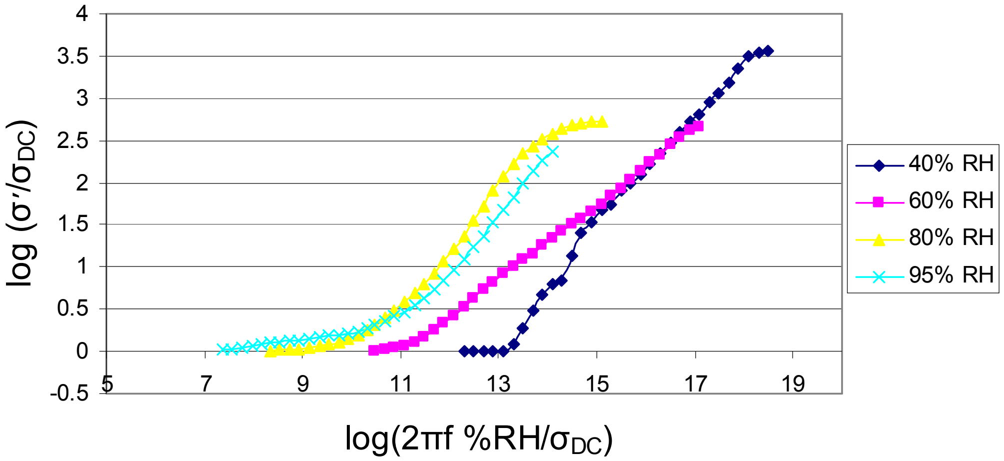

Figure 5.14: Scaled AC conductance spectra of Skin at a constant temperature of 25 ^{0}C in different RH.

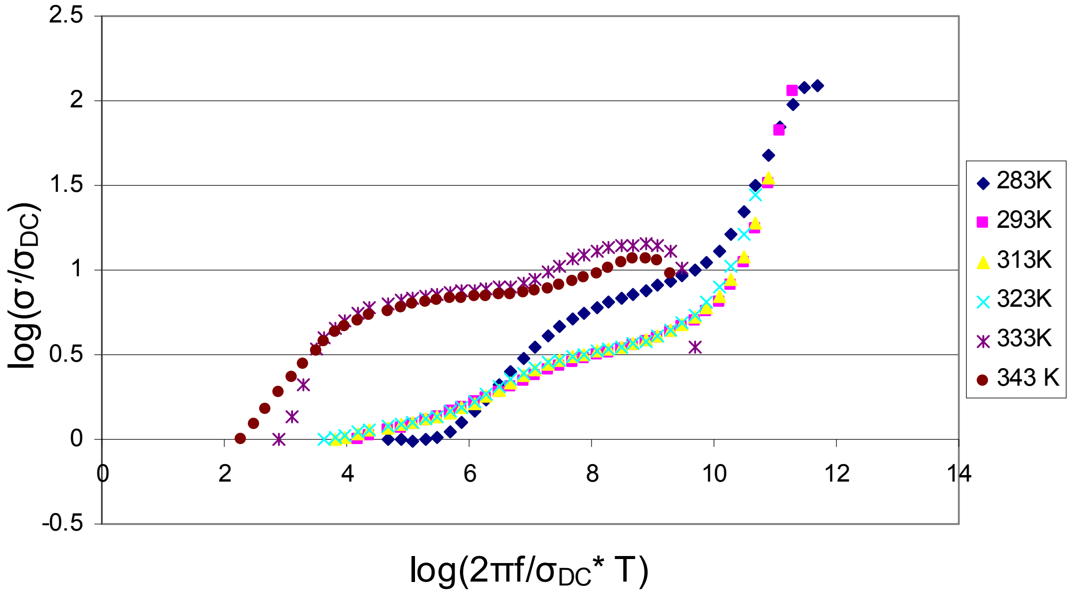

Figure 5.15: Scaled AC conductance spectra of skin at a constant RH of 80$\%$ in different temperature.

Chapter 6

Conclusion

6.1 Conclusion

Temperature and percentage of relative humidity has a pronounced effect on the electric properties of keratinazed tissues. Impedance shows inverse relation with both temperature and humidity whereas conductance shows direct relation. For all the three samples the conductance in the lower frequency (from 0.1 Hz to 10 KHz) and higher humidity (above 60%) is dominated by DC conductivity because the conductance is almost independent of frequency. On the other hand at high humidity and lower frequency (From 0.1 Hz to 1 KHz) the impedance exhibit frequency independence, that means at this situation the impedance is dominated by resistance of the resistor.

Hair and nail shows sign of the existence of universality of AC conductance. but in Stratum corneum it is hard to draw any conclusion whether this property exist or not. It needs further investigation.

The cause of this universality is still unclear even for the keratiiazed tissue. Electrical conductivity is sensitive to any change in chemical composition, structure of study material. Therefore, in order to know the exact cause of universality in AC conductance of biological materials especially on hair and nail it needs detailed microscopic studies. That means one has to know and understand what happened to the physical structure and chemical compositions of the materials due to the change of both temperature and humidity, and the mechanism and the path of the charge from one end to the other.

Finally precision is estimated by making repeated measurements on a sample under specified conditions. Repeated impedance measurements on the same samples had been done more than one at different parameters (Conditions). The result shows very small minor differences between the two measurements. This shows the result is reproducible and reliable.

6.2 Future Work

This section includes the possible improvements that could be implemented in order to make theory more powerful and more complete. In our work we limit the measurement and in two certain condition, at constant temperature for different relative humidity and vise verse. There are some interesting conditions that have to be considered in the future work. Since relative humidity is dependent on the temperature, it would be an idea to make the over all impedance and conductance measurement at constant water content instead of relative humidity. It could be possible to see the actual relation between the water content and the electrical properties of the materials. The water content value could vary depending on the needs.

Furthermore in future investigations it would be feasible to add a new temperature range (down to zero and above 60 ^0C) to perform a large temperature range AC conductance universality check of the electrical properties of biological materials.

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