MECHANICAL AND OPTO-ELECTRICAL CHARACTERIZATION OF
CHITOSAN - A MARINE BASED BIOMATERIAL

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July 2016
Declarations

Declaration by the Candidate

I hereby certify that, the work presented in this thesis entitled "Mechanical and Opto-electrical characterization of chitosan - a marine based biomaterial" is my original work done under the supervision of Prof. Gabriel Katana of Pwani University and Dr. Abdalla Merenga of Kenyatta University and that it has not been used in any previous application for a degree.

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DEDICATION

This thesis is dedicated to my loving family and Lecturers
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ABSTRACT
Mechanical, electrical and optical properties of chitosan thin films extracted from the squid gladius found along the coastal areas of Kilifi and Mombasa were investigated in this study. The films were prepared by the solution cast technique. The room temperature ionic conductivity of the film was measured by the two electrodes conductivity measurement technique and was found to be ca.1525μScm$^{-1}$. DMA analysis showed two dynamic processes; the beta relaxation process which generally seemed to increase with frequency and chitosan concentration and the alpha relaxation process ($T_g$). The temperature range between these two transitions (30 - 120°C) gave an insight of the operating temperature range of the biomaterial. Arrhenius plots gave the activation energy of the biomaterial at ca.259kJ/mol which increased with chitosan concentration. Structural characteristics of the sample were discussed on the basis of the DMA, AFM, X-ray, infrared and NMR analysis data. DMA results showed that the material under investigation is viscoelastic with very low mechanical damping which means its rigidity and resistance to deformation is very high. X-ray diffraction indicated the molecular form at two strongest peaks; 2θ ≈ 10.5° and 2θ ≈ 19.8° with minor reflections at 2θ = 6° and 2θ = 35° and crystalline structure with an index of ca:66%. A DDA value of ca:75% was obtained from the integral values of proton NMR. Optical properties obtained from the UV vis absorbance spectra gave the optical density of the material at about 0.8, the absorption coefficient of ca.2.909 and the band gap of ca.2.75eV. The refractive index of the chitosan thin films was determined by the real and apparent depth method using a traveling microscope. To determine the relaxation time and frequency, the permittivity of the material was plotted as a function of frequency and gave a value of ca:1.58μs. Measured value indicates the dielectric loss decreases with increasing frequency and temperature. The activation plot confirms that the relaxation processes follow the Arrhenius law and gave the activation energy of the squid pen gladius at ca.54.7kJ/mole.

Key Words: Tapping mode AFM, Deacetylation, Biomaterial, Cantilever.
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<thead>
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<th>Description</th>
<th>Notes</th>
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<tbody>
<tr>
<td>δ</td>
<td>Delta</td>
<td>Phase angle or phase lag. Delay between applied force and material response.</td>
</tr>
<tr>
<td>E</td>
<td>Young Modulus</td>
<td>Modulus measured in flexure, tension or compression geometry.</td>
</tr>
<tr>
<td>E’</td>
<td>Storage modulus</td>
<td>A measure of the elastic response of a material but not the same as Young’s modulus. Also called the in-phase component.</td>
</tr>
<tr>
<td>E”</td>
<td>Loss modulus</td>
<td>A measure of the viscous response of a material. Also called the imaginary modulus or out of phase component.</td>
</tr>
<tr>
<td>E*</td>
<td>Complex modulus</td>
<td>The sum of the in and out of phase components.</td>
</tr>
<tr>
<td>Eₐ</td>
<td>Activation Energy</td>
<td>Energy needed to cause a transition or reaction.</td>
</tr>
<tr>
<td>ε</td>
<td>Epsilon</td>
<td>Strain measured in flexure, tensile or compression geometry.</td>
</tr>
<tr>
<td>G</td>
<td>Shear modulus</td>
<td>Modulus measured in shear geometry.</td>
</tr>
<tr>
<td>G’; G”</td>
<td>Bulk Modulus</td>
<td>Real and imaginary parts of the complex shear modulus</td>
</tr>
<tr>
<td>γ</td>
<td>Gamma</td>
<td>Strain measured in shear geometry.</td>
</tr>
<tr>
<td>J</td>
<td>Creep Compliance</td>
<td>The ratio of sample strain to sample stress in the linear region of Creep Ramp.</td>
</tr>
<tr>
<td>Λ</td>
<td>Lambda</td>
<td>Modulus measured in torsion pendulum geometry, similar to E.</td>
</tr>
<tr>
<td>η</td>
<td>Eta</td>
<td>Viscosity.</td>
</tr>
<tr>
<td>σ</td>
<td>Sigma</td>
<td>Stress applied to a sample in flexure, tension, compression or shear.</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Alpha Transition Temperature</td>
<td>See $T_g$ (The next transition in temperature below the melt. Normally the Tg)</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------</td>
<td>---------------------------------------------------------------------</td>
</tr>
<tr>
<td>$T_\beta$</td>
<td>Beta Transition Temperature</td>
<td>The temperature at the onset of decrease in storage modulus during heating, accompanied by peak in tan delta during a temperature scan. Found above the Tg, this is associated with localized backbone or side chain motions.</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition Temperature</td>
<td>The temperature indicating the relaxation in a polymer where a material changes from a glass to a rubber.</td>
</tr>
<tr>
<td>$\tan \delta$</td>
<td>Tan delta</td>
<td>Loss Factor or Damping – The tangent of the phase angle and the ratio of $E''/E'$.</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Free volume</td>
<td>The space inside a polymer between molecules.</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Omega</td>
<td>Angular Frequency in radians per second.</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tau</td>
<td>Relaxation time; Transmission time</td>
</tr>
<tr>
<td>A</td>
<td>Amplitude; Pre-exponential factor in Arrhenius equation</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Attenuation; degree of Cure (Conversion)</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>Wave number; reaction rate</td>
<td></td>
</tr>
<tr>
<td>$C_1; C_2$</td>
<td>Parameters in WLF equation</td>
<td></td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Reflection factor; gas constant (8.314 JK$^{-1}$mol$^{-1}$)</td>
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### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>A-Scan</td>
<td>Amplitude Scan or Oscillogram</td>
</tr>
<tr>
<td>Ch</td>
<td>Chitosan</td>
</tr>
<tr>
<td>ChAcOH</td>
<td>Chitosan Acetic Acid</td>
</tr>
<tr>
<td>CNMR</td>
<td>Carbon Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic Mechanical Thermal Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
</tr>
<tr>
<td>DEA</td>
<td>Di-Electric Analysis</td>
</tr>
<tr>
<td>DES</td>
<td>Di-Electric Spectroscopy</td>
</tr>
<tr>
<td>DETA</td>
<td>Di-Electric Thermal Analysis</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transformation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra Red</td>
</tr>
<tr>
<td>HNMR</td>
<td>Proton Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infra Red</td>
</tr>
<tr>
<td>RTD</td>
<td>Resistance Temperature Detector</td>
</tr>
<tr>
<td>SG</td>
<td>Squid Gladius/Pen</td>
</tr>
<tr>
<td>SGP</td>
<td>Squid Gladius Powder</td>
</tr>
<tr>
<td>TTT</td>
<td>Time Temperature Transformation</td>
</tr>
<tr>
<td>UV Vis</td>
<td>Ultra Violet and Visible</td>
</tr>
<tr>
<td>VFT</td>
<td>Vogel Fulcher Tammann</td>
</tr>
<tr>
<td>WLF</td>
<td>William Landel Ferry</td>
</tr>
<tr>
<td>WAXRD</td>
<td>Wide Angle X-Ray Diffraction</td>
</tr>
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</table>
1 INTRODUCTION AND MOTIVATION

1.1 General Introduction

Progress in soft condensed matter surfaces at the molecular level is today forming the building blocks for the creation of the next generation materials and devices in practically all scientific areas. In recent years, significant development has been achieved in biomaterials for various bioelectronics and biomedical applications. In particular, there is huge interest in marine-derived polymers and ceramics for biomedical applications. If properly investigated and implemented, marine-derived biomaterials will be promising materials for mankind in various fields of electronics and biomedical applications[18, 99]. The study of thin film has greatly broadened the study of biomaterials by giving a clear indication of their chemical and physical properties. They have mechanical, electrical, magnetic and optical properties which differ from those of the bulk material. Currently, changes in the needs for thin film materials and devices are creating new opportunities for the development of new processes, materials and technologies. Knowledge of the physical, chemical and optical properties of any biomaterial thin films has to be established correctly in order to assign it to a given application. In particular, optical properties are directly related to structural and electronic properties of materials, and hence very important in device applications. Such knowledge provides a huge amount of information about their structure, optoelectronic behavior and transport of charge carriers [100,76].

1.2 Motivation

The driving force towards this project was to gain an understanding of the material world. Specifically, the attention of this work was the crystal clear appearance of the material under study making it transparent at visible wavelength. Another important motivation was the fact that the biomaterial was readily and locally available as a marine waste material. Similarly, the material is pliable since its biocompatibility and also biodegradability. This challenge
provides an opportunity to solve a problem of environmental pollution resulting from ignorance and use of industrial products that are non-biodegradable.

1.3 Background Information

Chitin is a polymer of un-branched chains of $\beta$- (1 - 4) - linked 2 – acetamido - 2-deoxy-D-glucose (N-acetyl-D-glucosamine). It is widely distributed in nature, especially in marine invertebrates, insects, fungi and yeast [44]. Chitin occurs naturally in the crystalline state, and X-ray diffraction studies of diverse supporting structures indicate three different types of crystallographic patterns among chitins [71]. Pure chitin is completely acetylated; when deacetylated, its derivative is known as chitosan. Chitosan is a polysaccharide. Structurally, it is very similar to cellulose. The molecular structure of chitin, chitosan and cellulose is shown in Figure 1.1. There is no set definition in the literature for the acetylation/deacetylation cut-off between chitin and chitosan but it is generally accepted that chitin must be at least 30–40% acetylated, though natural samples are typically 85–95% acetylated [94].

![Figure 1 Structure of cellulose, chitin and its chitosan](image)

Chitosan can be found in nature in some fungi, including Mucorales and a few Basidiomycetes, the majority however is produced industrially [89]. The preference of chitosan in industry is in part due to its solubility, which increases with the degree of deacetylation within the molecule [72]. The suitability and effectiveness of chitosan in its applications depends on an understanding of the relevant physicochemical properties such as the degree of deacetylation, crystallinity, conductivity, solubility and molecular weight.
Therefore, exact determination of physicochemical properties is a subject of utmost importance and in this study several techniques have been used to assess these properties precisely. Chitin and chitosan have been extracted from the squid gladius by the alkaline deacetylation process. Thin films were then cast from it by the solution/solvent casting method and the resulting biomaterial thin film characterized by Nuclear Magnetic Resonance (NMR), Fourier transform infrared spectroscopy (FTIR), Atomic Force Microscopy (AFM) and Dynamical Mechanical Analysis (DMA) techniques. Its electrical, optical and dielectric properties were also investigated.

1.4 Problem Statement

A lot of research work have been done on extraction and characterization of polymers for various applications. Scientific studies on marine based polymers have specifically concentrated on α-chitin/chitosan extracted from readily accessible crab or shrimp shells. Studies about β-chitin/chitosan from squid have been rare in comparison with α-chitin/chitosan. It has also been demonstrated that the different geographical sources and species are able to alter the functional properties of resulting chitin and chitosan [1, 82]. This study has revealed the physiochemical characteristics of the chitosan extracted from the squid gladius found in Kenya. In Coastal Kenya and in particular Kilifi County, marine solid waste disposal is carried out negligently and without proper understanding of the nature of these materials. Therefore, the purpose of this study was to investigate the mechanical and optoelectronic properties of marine based biomaterial from squid gladius found along the Kenyan Coast. The investigation covered physical, mechanical, electrical and optical properties of the marine based biomaterial derived from squid gladius found along the Kenyan Coast. It is hoped that the results will shed light on potential applications as biomaterials for bio-batteries, biosensor devices and biomedical applications and hopefully mitigate environmental pollution and degradation in Kilifi County.
1.5 Justification

The recent surge in interest in bioelectronics and the drive towards cheap, biocompatible and biodegradable components has increased the search for materials from natural, widely available and sustainable sources. Therefore, exact determination of the physicochemical properties of biomaterials is a subject of utmost importance for providing eco-friendly alternative materials for industrial applications. Squid gladius are readily available as a waste material from the local fish industry along the Kenyan Coast.

1.6 Significance of the Study

This research on the mechanical, electrical and optical properties of a marine based biomaterial is targeted at enhancing the understanding of its mechanical, optical and electric characteristics hence making biomaterial thin film for device application. Knowledge of the biomaterial properties would provide critical information about its structure, optoelectronic and transport behaviour. Therefore, exact determination of physicochemical properties is vital.

1.7 Objectives

1.7.1 General Objective:

The main objective of this study is to characterize the mechanical and opto-electrical properties of marine biomaterial chitosan extracted from the squid gladius found along the Kenyan coast with the aim of applying them in batteries and biosensors.

1.7.2 Specific Objectives:

1. To extract chitin and chitosan from the squid gladius found along the coastal areas of Kilifi and Mombasa
2. To fabricate chitosan films by solution casting method
3. To characterize chitosan films by the dynamic mechanical analysis, atomic force microscopy, x-ray diffraction, nuclear magnetic resonance and infrared spectroscopy
4. To determine the molecular dynamics of chitosan by dielectric spectroscopy, its electrical and optical properties using the four point probe method and UV Vis spectroscopy
2 LITERATURE REVIEW

2.1 History of Chitosan

Chitin (the origin of chitosan) is naturally distributed as the second most abundant bio-polymer on earth behind cellulose and is ordinarily discovered in lower end species such as fungi, insects and crustaceans, yet not in mammal [16]. Chitin is an “old” polymer that has been found in fossil insects with chemically detectable remains back to the Oligocene period (25 million years ago) [39]. The first explicit depict of chitin was not until 1811, attributed to a French scientist Henri Braconnot, who observed that a certain material (chitin) derived from mushrooms was resistant to sulfurous acid and named it “fungine”[36]. In 1823, the name “chitin” was designated by Odier from the Greek word “chiton” that implicated “coat of mail” referring to the cuticle, who found the same substance as fungine from the cuticle of beetles. In 1843, Payen indicated that chitin differs from cellulose owing to the existence of nitrogen [22], and later in 1876 Ledderhose acquired a crystalline material (glucosamine) from the acid hydrolysis of chitin which varied from glucose in replacing one hydroxyl by an amine group [35]. In 1859, the discovery of “modified chitin” (chitosan) was attributed to Rouget who reported that the chitin compound became soluble in dilute organic acid solutions after boiling chitin in concentrated potassium hydroxide in water.

It was not until 1894 that Hoppe-Seiler renamed “modified chitin” as “chitosan”. From early to mid-1900s, chitin and chitosan research had been apparently accelerated. By 1916 a researcher indicated that certain bacteria contain chitin, and by 1930 the chemical character (i.e.,\(\beta\)- (1 → 4 linkage and its \(\beta\)-D conformation) of chitin was confirmed by X-ray diffraction showing considerable similarity to patterns of cellulose which the crystallographic results were later summarized in a book in 1942 [68, 69]. In the early 1930s more works showed that some bacteria possess enzymes which degrade chitin. Meanwhile, Rammelburg confirmed more chitin sources not only form fungi but also crab shells. The first patent on chitin and chitosan were filed in 1936 in the United State by Rigby who was an employee of Du Pont de Nemours & Co [21]. The patent described from large-scale methods of isolating
chitin from crustaceans’ shells to manufacturing chitosan based films, emulsions and filaments. At the same time, other researchers were continuing the work of the occurrence of chitin in enormous type of microorganisms [34]. Studies were also proceeding on the physical and chemical properties of chitin and chitosan [34, 15]. Except for the 1940s which were plagued by World War II, the published work related to chitin and chitosan had increased each decade beginning from the 1930s. In 1951, the first book related to chitin and chitosan was written by Richards which was 140 years after the discovery of Braconnot. In 1977, the first comprehensive and interdisciplinary book on chitin was published by an Italian professor, Muzzarelli [98].

2.2 Structure of Chitosan

Chitosan (a partially N-deacetylated derivative of chitin) is a polysaccharide consisting of D-glucosamine and N-acetyl-D-glucosamine units, connected via $\beta$ (1 - 4) glycosidic linkages. When the overall portion of D-glucosamine units is more than the N-acetyl-D-glucosamine units within the chitin polymer (i.e. degree of deacetylation (DDA) of chitin is above 50%) throughout the deacetylation process, the product becomes soluble in selective diluted acid by salt formation and is defined as chitosan [82, 95]. The distribution of the D-glucosamine and N-acetyl-D-glucosamine units was suggested to be random and the repeating units were not blocked together within the chitosan molecule [37]. Most commercial grade chitosan product comprises 75 – 95% D-glucosamine and 5-25% N-acetyl-glucosamine units[54]. The structure of chitosan is very similar to cellulose with the only difference that at the C-2 position of each glucose ring of chitosan contains an amine (-NH$_2$) group instead of a hydroxyl (-OH) group. Chitosan is known to exist in three polymorphic forms as chitin; $\alpha$, $\beta$ and $\gamma$ which differ in the arrangement of the piles of molecular chains, whereas the crystalline structures of chitin are presented differently based on the raw materials [85].

Generally, the individual chains are assumed to possess an essentially linear structure which adopts one full helical (a twofold-screw, cellulose-like) conformation every 10.1-10.5 Å
along the chain axis. For each polymer chain, a distinct “left” and “right” direction is assigned owing to each glycosidic unit in the linear chain being chiral and all units are linked by an oxygen atom which connects one glycosidic unit in the C1 position to C4 of an adjacent one. The most common allomorph that chitin and chitosan occur is α conformation, where each unit cell is “orthorhombic” with a P2₁2₁2₁ space group [14] and the individual chain segment is packed in an anti parallel fashion (i.e. adjacent chains arranged in opposite directions) inside a polymer sheet along the c axis, although parallel arrangement existed between two consisted sheets of chains along the a axis, while b represents the fiber axis (Figure 2.2). The packaging structure of α-form chitosan is highly stabilized by inter-sheet, intra-sheet, and intra-chain hydrogen bonds in the directions of three unit cell. A less common allomorph exhibited by chitin and chitosan is β conformation, which possess “monoclinic” unit cells with a P2₁2₁2₁ space group [80] and the individual chain oriented in a parallel fashion. Since all linear chains are parallel along a and c axes (b indicates the fiber axis), no hydrogen bonds exist between two successive chain segments along the c axis. The least common allomorph is γ conformation, where two chains oriented in one direction and another chain runs in the opposite way [92]. The distinct allomorphs were examined by X-ray diffraction patterns and NMR spectrophotometers [85, 84].

2.3 Sources of Chitosan

Similar to cellulose in plants, chitin (precursor of chitosan) widely distributes in nature in a wide variety of species from microorganisms to sea animals, which perform as a reinforcement substance for cell wall in lower animals and plants in cuticular and exoskeletons of invertebrates like insects, crabs, and shrimps (Table 2.1). Commercial chitosan products from chitin are principally produced from shell wastes of shrimps, crabs, lobsters and krills generating by the seafood industries due to the readily accessibility with considerable quantities, where estimated chitosan use in year 2000 was approximately 2,073 tons [59]. Generally, chitin (15-40%) exists in the arthropod skin or shells as a composite
with 20 – 40% proteins and 20 – 50% calcium carbonate that are the two major substances, while pigments and various metal salts are the minor components [59].

Table 1: Showing the different sources of chitin and chitosan

<table>
<thead>
<tr>
<th>Sea animals</th>
<th>Insects</th>
<th>Microorganisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annelida</td>
<td>Scorpions</td>
<td>Green algae</td>
</tr>
<tr>
<td>Mollusca</td>
<td>Spiders</td>
<td>Yeast (β-type)</td>
</tr>
<tr>
<td>Coelenterat</td>
<td>Brachiopods</td>
<td>Fungi (cell walls)</td>
</tr>
<tr>
<td>Crustaceans:</td>
<td>Ants</td>
<td>Mycelia Penicillium</td>
</tr>
<tr>
<td>Lobster</td>
<td>Cockroaches</td>
<td>Brown algae</td>
</tr>
<tr>
<td>Crab</td>
<td>Beetles</td>
<td>Spores</td>
</tr>
<tr>
<td>Shrimp</td>
<td></td>
<td>Chytridiaceae</td>
</tr>
<tr>
<td>Prawn</td>
<td></td>
<td>Ascomydes</td>
</tr>
<tr>
<td>Krill</td>
<td></td>
<td>Blastocladaceae</td>
</tr>
<tr>
<td>Squid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oyster</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cray fish</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jelly fish</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other promising sources for chitin and chitosan production include oysters, clams, krill, crayfish, jellyfish, algae, insects, and fungi [60]. Like chitin, chitosan is also naturally existed worldwide but limited to specific species such as cell walls of some fungi (Zygomycetes), green algae (Chlorella sp.), yeast, protozoa and cuticles of insects. Advances in fermentation technology with controlling process indicated that fungi (Aspergillus niger) cultivation may supply as an attractive alternative source of chitosan. Nevertheless, chitosan produced from various source is slightly different, whereas the amino groups in chitosan isolated from crustacean chitin are uniformly distributed along the linear chain, a chitosan derived from fungal cell walls with a similar degree of deacetylation may own amine residues which are grouped into clusters.
Table 2: Showing the different contents of chitin and calcium for each source

<table>
<thead>
<tr>
<th>Carbonate Source</th>
<th>Chitin (%)</th>
<th>CaCO₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crab cuticle</td>
<td>15-30</td>
<td>40-50</td>
</tr>
<tr>
<td>Shrimp cuticle</td>
<td>30-40</td>
<td>20-30</td>
</tr>
<tr>
<td>Krill cuticle</td>
<td>20-30</td>
<td>20-25</td>
</tr>
<tr>
<td>Crab cuticle</td>
<td>20-40</td>
<td>Negligible</td>
</tr>
<tr>
<td>Shrimp cuticle</td>
<td>3-6</td>
<td>85-90</td>
</tr>
<tr>
<td>Krill cuticle</td>
<td>5-25</td>
<td>Negligible</td>
</tr>
<tr>
<td>Squid pen</td>
<td>10-25</td>
<td>Negligible</td>
</tr>
<tr>
<td>Clam/oyster shell</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insect cuticle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fungi cell wall</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Adapted from Kurita [59]

Comparing to shrimp cuticle, squid pen also contains high content of chitin (20 – 40%) which is classified as $\beta$-form but with negligible amount of calcium carbonate and pigments of a lipidic nature such as carotenoids [59] (Table 2.2). $\beta$-chitin is distinguished from the common $\alpha$-chitin from crustacean shells based on the distinct crystalline structure, where $\beta$-chitin possess a weaker intermolecular forces between the successive chain segments and is quite attractive as an alternative source of chitin with some unique characteristics different from $\alpha$-chitin [85]. Although $\beta$-chitin and chitosan is less abundant than $\alpha$-ones from crustacean source, the ease and mild isolation process from the raw squid pen material and remarkable affinity toward solvent such as organic acids and water suggested the potential and commercial value of $\beta$-chitosan [60]. In summary, source of chitin and chitosan can mainly be classified into three categories namely; sea animals, insects and microorganisms as given in table 2.2. In addition, commercial sources of chitin and chitosan in the 1990s are particularly from shell wastes of crustaceans, while krills (cell wall of fungi) and Mycelia
Penicillium were suggested as future potential sources. Several previous studies have demonstrated that the functional properties of chitin and chitosan depend on their originated marine sources and species [82, 5].

2.4 Chitosan Preparation

Chitosan derived from deacetylated chitin may be approached by several methods, including alkaline deacetylation [70], enzymatic deacetylation, intermittent water washing [104], flash treatment [9], and organic solvent used [43]. Among the methods mentioned above, alkaline deacetylation process has been mostly used. Chitosan is produced from the chitin hydrolysis in hot alkaline medium (i.e. deacetylation reaction), in which KOH or NaOH at high temperature are commonly used as strong alkaline reagents [58]. The deacetylation process removed the acetyl groups (-COCH$_3$) in N-acetyl-D-glucosamine units in chitin and converted to D-glucosamine units with free amine groups (-NH$_2$) to acquire chitosan product that are highly soluble in selective dilute acids. Characteristics of the final chitosan product in terms of molecular weight and degree of deacetylation are based on the used reagents and treatment conditions. For $\alpha$-chitin from shrimp shells, the typical deacetylation conditions were suggested by using 40-50% NaOH at 80 – 100°C for 6 - 12 h [5].

The source of the raw material is also a critical factor in the development of the N-deacetylation reactions of chitin and the degree of deacetylation of resulting chitosan, where $\alpha$ and $\beta$-chitin are mainly found in crustacean shells and squid pens, respectively [80]. Since $\beta$-chitin (squid chitin) chains are arranged in a parallel fashion with relatively weak intermolecular force and loose package comparing to $\alpha$-chitin [67] (Fig. 2.1), the deacetylation process of $\beta$-chitin are able to manipulate under relatively mild conditions by using alkali medium at lower temperature [5, 58] which indicates $\beta$-chitosan possesses a much greater affinity to various solvents and higher reactivity than $\alpha$-chitosan.
For example, Kurita [58] showed the degree of deacetylation (DDA) of squid pen chitosan reached as high as 70% with 30% NaOH at 100°C in 2 h, whereas DDA of shrimp chitosan was only 20%. Recently, the optimal deacetylated conditions for seeking high molecular weight and high degree of deacetylation of β-chitin were suggested by adopting 40 – 50% NaOH at 90°C for 6 h with one step or three separate steps (2 h + 2 h + 2 h). Also, squid pens have low mineral content, which eliminates the demineralization step in the preparation of β-chitosan [5, 56].

2.5 General Properties of Chitosan

2.5.1 Degree of Deacetylation

The degree of deacetylation is an indicator of the number of free amino groups on the polysaccharide, and can be used to differentiate between chitin and chitosan. Chitin with a degree of deacetylation 75% or above is generally known as chitosan [90]. Various methods have been employed to determine the degree of deacetylation of chitosan. These methods involve Fourier Transform Infrared Spectroscopy (FTIR), first derivative UV-spectrophotometry, hydrogen bromide titrimetry, nuclear magnetic resonance (NMR) spectroscopy and by acid base titration [4]. It appears that degree of deacetylation is highly dependent on the analytical method used for its determination. Out of many analytical methods mentioned above, the degree of deacetylation determination by FTIR is the most
common and simple. The degree of deacetylation of chitosan can be determined by IR spectroscopy using the formulae:

\[
DDA = 100 \times \left(1 - \frac{A_{1655}}{A_{3450}} \times 115\right)
\]

where \(A_{1655}\) and \(A_{3450}\) refer to the absorbance value at 1655 cm\(^{-1}\) and 3450 cm\(^{-1}\) which can be estimated from properly base lined FTIR spectra and \(A_{1655}/A_{3450}\) is the absorbance ratio [4].

### 2.5.2 Crystallinity

The biological and chemical reactivity of chitosan strongly depends on the extent of hydration and crystallinity. Ogawa [63] reported that anhydrous chitosan is insoluble and complexation of transition metals is strongly inhibited. Mochizuki has reported that water and ethanol molecules permeate through amorphous forms of chitosan and not through crystalline ones [3]. Therefore, crystallinity of chitosan becomes a very important aspect for coating formulations and for effective inhibitor release kinetics. Crystallinity of chitosan can be determined using X-ray diffraction studies on chitosan samples. Four crystalline polymorphs of chitosan are distinguished in the literature. They are tendon, Form I, Form II, and annealed chitosan [90]. Annealed chitosan is anhydrous; the other polymorphs are hydrated. Among chitosan polymorphs, tendon chitosan is the most common. There are two other polymorphs of chitosan that can be found in the literature. They are “L-2” and “1-2” chitosan. Sakurai reported that “L-2” chitosan is very similar to the Form II chitosan [64]. Similarly, Ogawa reported that “1-2” chitosan is the mixture of “L-2” and annealed crystals [4]. Basic to the proposed structure of chitosan is the presence of sheets of chitosan chains linked through hydrogen bonds. Chitosan polymorphs mainly differ in the sense of chains in the successive sheets. A unit cell of tendon chitosan, which is the most commonly found polymorph of chitosan, in this structure, different chitosan chains are arranged in anti-parallel (having opposite sense) fashion in successive sheets [90].
2.5.3 Molecular Weight

Precise determination of the average molecular weight of chitosan is difficult. The usual average molecular weight reported in the literature for chitosan is of the order of $10^5$ g/mole. Many treatments like acid or alkaline treatments are possible for the deacetylation of chitosan [81]. Chitosan deacetylated using a particular approach may have higher chain degradation and lower molecular weight compared to the chitosan deacetylated using another approach for the same degree of deacetylation. The molecular weight of chitosan can be determined by the measurement of intrinsic viscosity of the solution [81]. Different authors reported different relationships between intrinsic viscosity and viscometric average molecular weight ($M_v$) of chitosan. The most commonly used expressions for determination of molecular weight are:

\[
[\eta](\text{cm}^3/\text{g}) = 1.81 \times 10^{-3} M_v^{0.93} \text{ in } [0.1M \text{ AcOH} - 0.2M \text{ NaCl}] \tag{2.2}
\]

\[
[\eta](\text{cm}^3/\text{g}) = 3.04 \times 10^{-5} M_v^{1.26} \text{ in } [0.1M \text{ AcOH} - 0.02M \text{ NaCl}] \tag{2.3}
\]

Where $\eta$ is the intrinsic viscosity of the chitosan solution and $M_v$ is the viscometric average molecular weight of chitosan. Further, the above equations indicate the dependence of molecular weight of chitosan on the solvent used for the preparation of the solution. Due to the dependence of various chitosan properties on molecular weight, attempts have been made to manufacture well-characterized samples of known molecular weight using methods such as alkaline and acid hydrolysis.

2.5.4 Solubility

Chitosan is insoluble in pure water, alkali or organic solvents but is soluble in aqueous solutions of organic or mineral acids under specific conditions. Chitosan is insoluble in pure and organic solvents, but is readily soluble in most organic acid aqueous media at pH below 6 [18] due to the presence of the primary aliphatic amino groups of chitosan [53]. The amino groups (pKa from 6.2 to 7.0) are completely protonated in acids with pKa smaller than 6.2 making chitosan soluble. Hence, at low pH, amines on each D-glucosamine residue are partially protonated (i.e. from $-\text{NH}_2$ to $-\text{NH}_3^+$) and become positively charged which drives
chitosan as a cationic water-soluble polyelectrolyte owing to the repulsion between positively charged chains that allows water molecules to diffuse. In contrast, when pH increases above 6, the amines become deprotonated (i.e., the chitosan molecular loses its charge) and become insoluble. The soluble-insoluble transition exists at the pKa value of chitosan which ranges from 6.3 to 6.5. Since the pKa value is highly depending on the degree of N-acetylation, the solubility of chitosan is according to the degree of deacetylation and the method of deacetylation, where degree of deacetylation could be affected by time and temperature of deacetylation, alkali concentration, ratio of chitin to alkali medium, prior treatments adopted to chitin, and particle size of chitin [18]. At low pH environment, chitosan can readily form quaternary nitrogen salts with organic acids such as formate, acetate, lactate, citrate, pyruvate, maltase, and citrate, which are soluble in water [103]. Formic acid was found to be the best solvent to dissolve chitosan with a large range of concentration from 0.2 to 100%, while 1% acetic acid (as a reference) is the most commonly used solvent which may cause chitosan depolymerization at high temperature when concentrated as β-glycosidic linkages hydrolysis occurs.

Acid concentration is also an important factor to impart desired property [9], while solubility is based on the ionic concentration and salting-out effect. The acid amount needed is related to the chitosan quantity to be dissolved, where required proton concentration is at least to be equal to the amine concentration involved. As a result, the solubility of chitosan is quite a difficult parameter to control when it involves a complex solvent system of controlling factors [81]. Chitin is difficult to dissolve in many solvents due to the presence of strong molecular bonding between acetyl groups. Chitosan is not soluble in water at neutral pH. Below pH 6.5, chitosan can be dissolved in aqueous solution and the free amino group present in chitosan becomes protonated to form cationic amine group [107];

\[ Gl\textsubscript{c} - NH\textsubscript{2} + AH \rightleftharpoons Gl\textsubscript{c} - NH\textsubscript{3}^+ + A \]  

(2.4)

The average value of degree of acetylation (DA) and dissociation constant of the above equation controls chitosan solubility and hydrophilicity. Based on potentiometric titration
curves prepared using fully deacetylated chitosan in 0.1 M KClO₄ using 0.1 M NaOH as the titrant, Domard reported the variation of pKa value with degree of dissociation as in the following relation [1];

\[ pK_a = pH + \log((1 - \alpha)/(\alpha)) \]  

(2.5)

Where \( pK_a \) is the dissociation constant and \( \alpha \) is the degree of dissociation. The above equation shows that dissociation constant (\( pK_a \)) is not a constant and depends on the degree of dissociation (\( \alpha \)) at which its value is determined and the degree of deacetylation of chitosan. Extrapolation of a plot of pH versus \( \alpha \) to \( \alpha - 1 \) gives the \( pK_0 \) value that is the intrinsic dissociation constant value which is independent of degree of deacetylation of chitosan. Domard has reported an intrinsic dissociation constant of 6.5 on the basis of this analysis. The total solubility of chitosan can be calculated using this dissociation constant. For the known dissociation constant (\( pK_a \)) of chitosan, degree of dissociation (\( \alpha \)) can be calculated at different pH using the above equation. Values of dissociation constants (\( \alpha \)) at different pH can be used to calculate variation of protonated amine functional group of the chitosan with pH of the solution.

### 2.5.5 Molecular Structure

The molecular structure of chitosan has been studied using a range of different spectroscopic techniques including FTIR, XPS and solid-state NMR spectroscopy. Infrared energy corresponds to the energy required to stretch or bend molecular bonds. In infrared spectroscopy, monochromatic radiation of IR energy is passed through the sample. A molecule absorbs energy at wavelengths where incident energy corresponds to the energy of stretching or bending motion in a bond in the molecule. In FTIR spectroscopy, a radiation with all wavelengths of IR energy is applied on the sample. It allows rapid measurement of data that can later be transformed mathematically to obtain the spectra. FTIR spectroscopy uses the difference in vibration frequencies of different bonds of the molecule for the determination of its molecular structure. On this basis, bands in FTIR can be assigned to the
chemical bonds of the molecule. However, interpretation of the spectrum is difficult due to overlap in vibrational frequencies of bonds. Further, absorption of radiation may not take place if the energy of a stretching or bending motion in a molecular bond matches the incident energy. Absorption of energy at a certain wavelength is governed by quantum mechanical selection rules. This makes the determination of molecular structure even more complex. Nonetheless, if identification of certain functional group is the aim of an analysis, rather than determination of three-dimensional structure of the molecule, FTIR spectroscopy is fairly straightforward, cheap and reliable. NMR spectroscopy, on the other hand, exploits the magnetic properties of the nucleus of an atom to provide information on the structure of the molecule.

While FTIR spectroscopy is used to identify functional groups, NMR spectroscopy is used to identify individual atoms and the environment of an atom. When used properly, it is probably the only technique that can provide detailed information on three-dimensional structure of molecules. Intermolecular and intra-molecular bonding between chains of chitosan has been characterized by FTIR spectroscopy, which shows that covalently bonded molecular chains in chitosan are linked together in sheets by hydrogen bonding. Because chitin with a degree of deacetylation of 75% or above is chitosan, many of the studies aimed at understanding bonding have been done on chitin [4]. Infrared spectra of chitin showed the presence of intra sheet hydrogen bonds between C=O and NH groups of chitin. The spectra also showed the presence of intra sheet hydrogen bonds between C=O and HO groups of chitin. Spectra of chitosan showed a loss in the intensity of bands corresponding to the C=O…HO and C=O…HN bonds, and the appearance of new absorption bands corresponding to the OH…HO bonds. The disappearance of the bands corresponding to C=O…HO and C=O…HN in FTIR spectra of chitosan has been attributed to the deacetylation of chitin molecule [67]. The most definitive characterization of chitosan by optical spectroscopy is found in the work of Samuels who performed FTIR spectroscopy on Form I and From II chitosan molecules. Different chemical bonds of a molecule vibrate at specific frequencies
corresponding to their vibrational energy level. Samuels performed a detailed characterization of the chitosan in 1650 cm\(^{-1}\) to 1020 cm\(^{-1}\) frequency range and identified bands and assigned them to the different bonds in the chitosan structure.

### 2.5.6 Film Forming Ability

The linear chitosan polymer has excellent film and coating forming capacity owing to the \(\beta-(1\rightarrow4)\) glycosidic linkages between the sugar monomers making the chain. This biodegradable film is usually fabricated by evaporation of dilute organic acid mixture with the chitosan polymer i.e. transferring hydrocolloids from aqueous suspension leading to change in phase by solvent evaporation [101]. Generally, \(\alpha\)-chitosan films were reported to be transparent, flexible, tough, durable and hard to tear with several permeable properties. Most of the mechanical properties of the films were comparable to various commercial polymers with medium strength such as cellulose. However, the elongation of \(\alpha\)-chitosan films was much less compared to plastic synthetic films which ideally would be in a range of 250 to 300\%. The elongation characteristics of \(\alpha\)-chitosan films can however be ameliorated by implanting plasticizers such as polyols which were indicated to be the most effective plasticizers for hydrocolloid-based films since its structure is similar to the polymer matrix. For food applications, chitosan edible films were mostly made from dilute carboxylic acids such as formic, acetic, propionic, and lactic acid [103], where the mechanical and barrier properties (i.e. water vapor permeability) of these \(\alpha\)-chitosan films could be controlled by selecting the film forming compositions such as chitosan molecular weight and degree of deacetylation, solvent type, adjusting the pH, and adding plasticizer agents, etc. Chitosan films possessing moderate water permeability were suggested to be used to extend the shelf life of fresh produce and foodstuffs with high water activity [26]. Like \(\alpha\)-chitosan based films, \(\beta\)-chitosan film characteristics such as tensile strength, elongation at break, and water vapor permeability were also affected by chitosan molecular weight and degree of
deacetylation with similar trends as α-form. However, to the best of my knowledge, the influence of solvent type and plasticizer on β-chitosan based films are still unknown.

2.6 β-Chitosan and its Recent Studies

β-chitosan derived from deacetylated squid (Ommastrephes bartramii) chitin was reported as a versatile polysaccharide due to the much greater affinity to various solvents and higher reactivity than α-chitosan [60]. The difference between α- and β-chitin and chitosan are generally based on the crystalline structure of the molecule. The β-chitin chains are arranged in a parallel arrangement with relatively weak intermolecular forces and loose package [67], while the α-structure is aligned in an antiparallel fashion responsible for a stronger intermolecular hydrogen bonding [67, 56]. Accordingly, the deacetylation process of β-chitin can be operated under mild conditions by using alkali solution at relatively low temperature [5, 70]. Moreover, squid pens having low mineral content, eliminated the demineralization step in the preparation of β-chitosan [5]. Comparing to α-chitosan obtained from crustacean shells, related works of β-chitosan derived from squid pens were limited and mostly from the species of Loligo and the focus of the studies were mainly on the optimization of deacetylation process of preparing the β-chitosan from chitin [5].

To the best of my knowledge, no studies had demonstrated further potential usage and application of the β-chitosan products from Loligo squid pen which only had approximately 9% of world cephalopod catch. In contrast, Illex argentinus and Todarodes pacificus, which were the first (16.1%, 511,087 tons) and second (15.9%, 504,438 tons) respectively and the largest harvested squid species in the world[27]. Moreover, the characteristic of β-chitosan films prepared by these two species were comparable to common α-chitosan films from crustacean in regard of barrier and mechanical properties. However, no work has indicated the optimized deacetylation condition for each specific squid species to obtain the β-chitosan products in the studies above. Jumbo squid (Dosidicus gigas) had taken the third place of squid catch (12.8%, 406,356 tons) worldwide and several studies had demonstrated the potential usage of β-chitosan from other squid species in the aspect of film-forming and
antibacterial properties [60]. Moreover, a comprehensive study has evaluated the deacetylation and depolymerization of $\beta$-chitin from jumbo squid pens and suggested the optimal treatment conditions to obtain a wide range of molecular weights and degrees of deacetylation of $\beta$-chitosan [5].
3 THEORETICAL BACKGROUND

3.1 Film Formation Techniques

The physical properties of polymer film depend basically on the film preparation and formation technique. There are several methods that can be used for formation of polymer thin film. The formation of synthetic polymer is a process which occurs via chemical connection of many hundred to thousand of monomer molecules. As a result, macromolecules are formed. The important thin film formation processes are based on liquid phase chemical techniques, gas phase chemical processes, glow discharge processes and evaporation methods [19]. The methods employed for thin film deposition can be divided into two groups based on the nature of deposition process, namely physical or chemical.

3.1.1 Physical Vapour Deposition (PVD) Processes

Physical vapour deposition is a technique whereby physical process, such as evaporation, sublimation or ionic impingement on a target, facilitates the transfer of atoms from a solid or molten source onto a substrate. Evaporation and sputtering are the most widely used PVD methods for depositing films [75]. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousand of nanometers; however, they can also be used to form multilayer coatings graded composition deposits, very thick deposits and freestanding structures. The substrates can range in size from very small to very large such as the 10’ × 12’ glass panels used for architectural glass. The substrates can range in shape from flat to complex geometries such as watchbands and tool bits.

Typical PVD deposition rates are 10-100Å (1-10nm) per second. PVD processes can be used to deposit films of elements and alloys as well as compounds using reactive deposition processes. In reactive deposition processes, compounds are formed by the reaction of depositing material with the ambient gas environment such as nitrogen in forming titanium nitride (TiN) or with a co-depositing material. (e.g. titanium carbide, TiC). Quasi-reactive deposition is the deposition of films of a compound material from a compound source where
loss of the more volatile species or less reactive species during the transport and condensation process, is compensated for by having a partial pressure of reactive gas in the deposition environment. For example, the quasi-reactive sputter deposition of ITO (indium-tin oxide) from an ITO sputtering target using a partial pressure of oxygen in the plasma. The main categories of PVD processing are vacuum evaporation, sputter deposition, arc deposition and ion plating.

### 3.1.2 Vacuum Deposition

Vacuum deposition which is sometimes called vacuum evaporation is a PVD process in which material from a thermal vaporization source reaches the substrate with little or no collision with gas molecules in the space between the source and substrate. The trajectory of the vaporized material is “line-of-sight”. The vacuum environment also provides the ability to reduce gaseous contamination in the deposition system to a low level. Typically, vacuum deposition takes place in the gas pressure range of $10^{-5}$ to $10^{-9}$ Torr depending on the level of gaseous contamination that can be tolerated in the deposition system. The thermal vapourization rate can be very high compared to other vaporization methods. The material vapourized from the source has a composition which is in proportion to the relative vapour pressure of the material in the molten source material. Thermal evaporation is generally done using thermally heated sources such as tungsten wire coils or by high energy electron beam heating of the source material itself. Generally the substrates are mounted at an appreciable distance away from the vaporization source to reduce radiant heating of the substrate by the vaporization source. Vacuum deposition is used to form optical interference coating, mirror coating, decorative coatings, permeation barrier film on flexible packaging materials, electrically conducting films, wear resistant coatings, and corrosion protective coatings.

### 3.1.3 Sputter Deposition

Sputter deposition is the deposition of particles vaporized from a surface (“target”), by the physical sputtering process. Physical sputtering is a non-thermal vaporization process where
surface atoms are physically ejected from a solid surface by momentum transfer from an atomic sized energetic bombarding particles which is usually a gaseous ion accelerated from a plasma. This PVD process is sometimes just called sputtering i.e. “Sputtered films of –” which is an improper term in that the film is not being sputtered. Generally the source-to-substrate distance is short compared to vacuum deposition. Sputter deposition can be performed by energetic ion bombardment of a solid surface (sputtering target) in vacuum using an ion gun or low pressure plasma (<5 m Torr) where the sputtered particles suffer few or no gas phase collisions in the space between the target and the substrate. Sputtering can also be done in a higher plasma pressure (5-30 m Torr) where energetic particles sputtered or reflected from the sputtering target are “thermalized” by gas phase collisions before they reach the substrate surface. The plasma used in sputtering can be confined near the sputtering surface or may fill the region between the source and the substrate.

The sputtering source can be an element, alloy mixture, or a compound and the material is vapourized with the bulk composition of the target. The sputtering target provides a long lived vapourization source that can be mounted so as to vapourize in any direction. Compound materials such as titanium nitride (TiN) and zirconium nitride (ZrN) are commonly reactively sputter deposited by using a reactive gas in the plasma. The presence of the plasma “activities” the reactive gas (“plasma activation”) making it more chemically reactive. Sputter deposition is widely used to deposit thin film metallization on semiconductor material, coatings on architectural glass, reflective coatings on compact discs, magnetic films, dry film lubricants and decorative coatings.

3.1.3.1 Arc Vapour Deposition

Arc vapour deposition uses a high current, low-voltage arc to vaporize a cathodic electrode (cathode arc) on anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions (“film ions”) to the substrate surface.
3.1.3.2 Ion Plating

Ion plating which is sometimes called Ion Assisted Deposition (IAD) or Ion Vapour Deposition (IVD) utilizes concurrent or periodic bombardment of the depositing film by atomic-sized energetic particles, to modify and control the properties of the depositing film. In ion plating the energy, flux and mass of the bombarding species along with the ratio of bombarding particles are important processing variables. The deposition material may be vaporized either by evaporation, sputtering, arc erosion or by decomposition of a chemical vapour precursor. The energetic particles used for bombardment are usually ions of an inert or reactive gas, or, in some cases, ions of the condensing film material (“film ions”). Ion plating can be done in a plasma environment where ions for bombardment are extracted from the plasma or it may be done in a vacuum environment where ions for bombardment are formed in a separate “ion gun”. The latter ion plating configuration is often called Ion Beam Assisted Deposition (IBAD). By using a reactive gas in the plasma, films of compound materials can be deposited. Ion plating can provide dense coatings at relatively high gas pressures where gas scattering can enhance surface coverage. Ion plating is used to deposit hard coating of compound materials, adherent metal coatings, optical coating with high densities, and conformal coatings on complex surfaces.

3.1.3.3 Chemical Vapour Deposition

Chemical vapour deposition (CVD) processes are widely used in industry due to their versatility for depositing a very large variety of elements and compounds covering a wide range from amorphous deposits to epitaxial layers having high degree of perfection and purity. CVD can be defined as a process in which the gaseous chemical reactants are transported to the reaction chamber, activated thermally (conventional CVD) or by other than thermal means (plasma assisted CVD or laser induced CVD), in the vicinity of the substrate, and made to react to form a solid deposit on the substrate surface. It is possible to deposit films of uniform thickness and low porosity even on substrates of complicated shape in this process. A major area for utility of CVD is in microelectronics applications, such as gate
insulating layers, passivation layers, oxidation barrier, polycrystalline silicon, etc. CVD techniques are also extensively employed for protective coating for a variety of operating environments where, for example, protection is required against wear, erosion, and high temperature oxidation. CVD has numerous other names and adjectives associated with it such as Vapour Phase Epitaxy (VPE) when CVD is used to deposit single crystal films, Metal-organic CVD (MOCVD) when the precursor gas is a metal-organic species, Plasma Enhanced CVD (PECVD) when a plasma is used to induce or enhance decomposition and reaction, and Low Pressure CVD (LPCVD) when the pressure is less than ambient. Plasmas can be used in CVD reactors to activate and partially decompose the precursor species. This allows deposition at a temperature lower than thermal CVD and the process is called plasma-enhanced CVD (PECVD) or plasma-assisted CVD (PACVD). The plasmas are typically generated by radio-frequency techniques. At low pressures, concurrent energetic particle bombardment during deposition can affect the properties of films deposited by PECVD. Plasma based CVD are also used to deposit polymer film (Plasma polymerization). In this case the precursor vapour is a monomer that becomes cross linked in the plasma and on the surface to form an organic or inorganic polymer film. These films have very low porosity and excellent surface coverage. When plasma depositing films from organo-silane precursors, oxygen can be added to the plasma to oxidize more or less of the silicon in the film.

3.1.4 Electroplating

Electrolysis Plating and Displacement Plating Electroplating is the deposition on the cathode of metallic ions from the electrolyte of an electrolysis cell [83]. Only about 10 elements (Cr, Ni, Zn, Sn, In, Ag, Cd, Au, Pb, and Rh) are commercially deposited from aqueous solutions. Some alloy composition such as Cu-Zn, Cu-Sn, Pb-Sn, Au-Co, Sn-Ni, Ni-Fe, Ni-P and Co-P are commercially deposited, Conductive oxides such as PbO₂ and Cr₂O₃ can also be deposited by electroplating. A thin film of material deposited by electroplating is often called a “flash” and is on the order of 40 thousandths of an inch thick. Typically, the anode of the
electrolytic cell is of the material to be deposited and is consumed in the deposition process. In some cases, the anode material is not consumed and the material to be deposited comes only from solution. For example, lead oxide, PbO₂ can be electrodeposited from a lead nitrate plating bath using carbon anodes. Stainless steel and platinum are also often used as non consumable anode materials. In electroless or autocatalytic plating no external voltage/current source is required. The Voltage/current is supplied by the chemical reduction of an agent at the deposit surface.

The reduction reaction is catalyzed by a material, which is often boron or phosphorous. Materials that are commonly deposited by electroless deposition are Ni, Cu, Au, Pd, Pt, Ag, Co and Ni-Fe alloys. Displacement plating is the deposition of ions in solution on a surface and results from the difference in electro negativity of the surface and the ions. Electrophoresis is the migration of charged particles in an electric field. Electrophoretic deposition, or electro-coating, is the electro deposition of large charged particles from a solution. The particles may be charged dielectric particles (glass particles, organic molecules, paint globules, etc.) which are non soluble in the aqueous electrolyte. Alternatively some of the components can be treated so that they are soluble in water but will chemically react in the vicinity of an electrode and their solubility is decreased. Particles are usually deposited on the anode but sometimes on the cathode.

3.1.5 Films from Polymer Solution

The techniques of film formation described above are not expected to give useful films for research purposes. Further, the polymer films formed by these techniques may have different degree of polymerisation and may contain undesired impurities. Polymer films formed by vacuum deposition technique are also not quite useful as these have pin holes. Films of doped polymer cannot be obtained by above mentioned methods since it is difficult to control the quality of dopant both during evaporation as well as during polymerisation. Film with uniform degree of polymerisation and high purity can be prepared from polymer solution
using highly pure polymer as solute and inert solvents of AR grade. The doping percentage can be controlled easily by dissolving known amount of dopant in the solution. There are two main methods available for preparing thin films from polymer solution:

### 3.1.5.1 Isothermal Immersion Technique

Solution of suitable concentration is kept at a desired temperature and substrate is immersed into it vertically for a given period of time depending upon the required film thickness. When the film is deposited, the substrate is slowly taken out and dried by hot air. The deposited film is then gently detached using a sharp knife edge. Doped films can also be prepared using desired quantity of dopant in solution. Rastogi and Chopra [57] found that the thickness of film depends upon concentration of the solution, its temperature, nature of the substrate, and the time for which the substrate is kept immersed in the solution. This method requires a great care in selecting the temperature and concentration of the solution. Also, sophisticated mechanical instrumentation is required for taking out the substrate from the solution and keeping them exactly vertical to the solution surface. Lack of proper instrumentation and precautions may result into the films containing air bubbles and non-uniform thickness.

### 3.1.5.2 Casting from the Solution

Polymer solution of known concentration and quantity is spread over plane clear glass plate of known surface area which is made to float in a mercury pool. Solvent is allowed to evaporate at a suitable constant temperature and the resulting film is gently detached from the substrate. Films of different thickness may be obtained using solution of different concentrations. The films obtained by this technique are of uniform thickness and perfectly plane. Also, an elaborate cleaning procedure must be adopted for substrate in order to eliminate any possible impurity and deformation.

### 3.2 Thermodynamics of Polymers

Equilibrium properties of materials can be sufficiently predicted when their Gibbs free energy $G$ is known as a function of independent variables such as temperature, pressure.
and composition. In the thermodynamics of mixtures the relevant quantity is the change in the Gibbs function due to the process of mixing defined as:

$$\Delta G_{\text{mix}} = G - \sum n_i G_i^0$$  \hspace{1cm} (3.1)

where $n_i$ is the number of moles of component $i$, $G_i$ is the molar Gibbs function (chemical potential) of the pure component $i$. If the free energy of mixing can be calculated for all possible compositions of the mixture, then it is easy to calculate the values of temperature, pressure and composition at which the mixture will either form a single stable phase or separate phases. There are several theoretical procedures for predicting $\Delta G_{\text{mix}}$. Among them, the more frequently used theories are the Flory-Huggins theory based on a lattice model, perturbation or excluded-volume theories which treat the spatial and energetic interaction of polymer segments and the equation-of-state and phenomenological theories which consider aspects such as the volume changes on mixing and compressibility. In the following, the basic thermodynamic principles of Polymer-Polymer mixtures will be treated according to the Flory-Huggins theory.

### 3.2.1 Thermodynamic Theories

#### 3.2.1.1 Relations Amongst Thermodynamic Quantities at $T_g$

Many experimental results suggest that the glass transition phenomenon has the nature of a second order thermodynamic transition. A good test for this would be the application of the second order transition thermodynamic relations first formulated by Ehrenfest. The Ehrenfest relations derived were analogous to the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$  \hspace{1cm} (3.2)

and for a second order phase transition the following relations result:

$$\frac{dP}{dT} = \frac{\Delta \alpha}{\Delta \kappa}$$  \hspace{1cm} (3.3)

and;
Combination of equation (3.3) and (3.4) gives for $T_g$;

$$T_g = \left[ \frac{\Delta \kappa \Delta C_p}{V (\Delta \alpha)^2} \right]_{T=T_g}$$

where $\Delta C_p$, $\Delta k$ and $\Delta \alpha$, are the changes in heat capacity, the compressibility and the thermal expansion coefficient respectively which occur at the second order transition temperature $T_2 = T_g$. Without invoking second order thermodynamic transitions, it can generally be shown that if a single ordering parameter determines the position of equilibrium in a relaxing system, the following relation holds [46];

$$\frac{\Delta \kappa \Delta C_p}{TV (\Delta \alpha)^2} = R = 1$$

where $R$ is called the Prigogine - Defay ratio. If more than one ordering parameter is required, as seems to be the case with glass - formers, then the thermodynamic stability requires that $R > 1$. This requirement can be expressed as;

$$\frac{\Delta \kappa}{\Delta \alpha} \geq \frac{TV \Delta \alpha}{\Delta C_p}$$

3.2.1.2 Gibbs and DiMarzio Theory

The thermodynamic theory of the glass transition was first formulated for systems of chain polymers by Gibbs and DiMarzio [49] based on lattice calculations. The theory predicts a true second order transition at a temperature $T_2 = T_g - 50$ K when a material finally reaches equilibrium albeit at infinitely long times. A basic premise of the theory is that, a given conformation by one molecule places restrictions on the conformations which could be taken by others, and this restriction of the total number of configurations increases with a decrease in temperature. The transition from one configuration to another is associated with an energy barrier $\Delta E$ and determines the transport or relaxation properties of a glass-forming material. Central to the Gibbs-DiMarzio theory is the determination of a configurational partition
function $Q$, from which the expression for configurational entropy can be calculated. The application of the partition function assumes an equilibrium state. Accordingly, the glass transition is predicted to occur when the configurational entropy $S_c$ reaches a critical small value. According to Meyer- Flory-Huggins lattice calculations, $S_c$ becomes zero at a finite temperature $T_2$ at which a second order transition in the Ehrenfest sense occurs. At this temperature the number of accessible configurations $W$, allowed by the amorphous phase partition function appropriate to higher temperatures tends to unity. Once the partition function $Q$ is formulated, the entropy can be calculated from statistical thermodynamics as;

$$S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,n} + k \ln Q$$

(3.8)

from which all the necessary calculations can be made. In infinitely slow experiments, a glassy phase should eventually emerge where the entropy of the amorphous phase compares to that of the crystalline phase. This was the resolution of the Kauzmann [112] paradox in which it was noted that, for most glass formers, an extrapolation of the super cooled entropy below $T_g$ crosses the associated crystalline value at a non zero temperature $T_K$ (the Kauzmann temperature) [112]. This would require that some changes in thermodynamic and inferentially relaxation properties of the equilibrium liquid must change in some way at or above $T_K$ to avoid this paradoxical situation. $T_K$ is identified as the equilibrium glass transition temperature. Although the thermodynamic theories are successful in determining the quantitative correlations of the glass temperature with molecular weight [77], random copolymer composition and diluents and with known chain stiffness parameters, they do not provide the form of heat capacity temperature relation to be expected near $T_g$ partly because of the difficulty in deciding the exact form of the partition function as $W \rightarrow 1$. Moreover, they suffer a great drawback in that a true equilibrium second order glass transition is experimentally yet to be observed. They also lack information about the kinetics involved in the transition region with which experimental observations can be compared.
3.2.1.3 Free Volume Theories

The glass transition exhibits certain kinetic characteristics in that it is strongly influenced by the rate of cooling or heating as well as the duration of loading and frequency of an applied stress. In this respect, the glass state in polymers is thermodynamically a non-equilibrium state. In order to describe such a state an internal order parameter in addition to the usual variables of state is necessary. Fox and Flory[108] proposed that this order parameter should be a free volume and they hypothesised that the glass transition results from the decrease of the free volume of the amorphous phase below some characteristic value. Consequently the molecular mobility at the glass transition is drastically reduced so that a non-equilibrium state would become frozen resulting to an iso-free volume state. There are many theories[48] which require, as prerequisite of the glass transition, the existence of a free volume. These theories generally apply the lattice model and base their arguments on the temperature dependence of molecular transport properties such as fluidity ($\Phi$ – which is related to viscosity) and the self-diffusion constant $D$ in the glass transition region. In this section a detailed outline of the free-volume theory of Sanchez [55] is given. Basing on the hole theory of the liquid state proposed by Erying [25], Sanchez treats the liquid or polymer melt as a mixture of molecules and holes, with the molecules occupying some lattice sites while the other sites are empty. The holes are considered to be pseudo-particles with zero chemical potential ($\mu = 0$). The number $N_0$ of the holes is temperature dependent and Sanchez’s theory [48] calculates among others the energy change due to the introduction of new holes in a glass forming system. By assuming a random mixing of the holes and the molecules, the change in entropy is approximated by;

$$\Delta S = -R \left( N_0 \ln v_0 + N_1 \ln v_1 \right) \quad (3.9)$$

where $N_0$ and $N_1$ are the numbers of holes and molecules respectively and $V_0$ and $V_1$ are the volume fractions of the holes and the molecules. The total change of the Helmholtz free energy $\Delta F$ that is associated with the introduction of $N_0$ holes in a liquid initially free of holes is given by;
\[ \Delta F = v_1 N_0 E_h + RT (N_0 \ln v_0 + N_1 \ln v_1) \]  

(3.10)

where \( E_h \) is the energy required to produce a hole and \( R \) is the gas constant. The equilibrium number of holes is determined by minimizing the free energy functions with respect to \( N_0 \). This is satisfied by either;

\[
\frac{\partial \Delta F}{\partial N_0} = 0 \quad \text{or} \quad \frac{\partial \Delta G}{\partial N_0} = 0
\]  

(3.11)

where \( \Delta G \) is the change in the Gibbs energy. Equation (3.11) is equivalent to the requirement that the chemical potential \( \mu \) of the holes be zero and for a small hole fraction the minimization of the free energy leads to;

\[ v_0 \approx \exp \left\{ 1 - \frac{1}{r} - \frac{E_h}{RT} \right\} \]  

(3.12)

where \( r \) is a measure of the molecule size and is proportional to the molecular weight.

To obtain a complete equation of state, the hole volume fraction \( V_0 \) must be related to the macroscopic volume \( V \). By using the lattice model, the following relations are obtained;

\[ V = [rN_1 + N_o] V_h \]  

(3.13)

where \( V_h \) is the hole volume and;

\[ N_0 = v_0 \left( \frac{rN_1}{1-v_0} \right) \]  

(3.14)

Substitution of equation (3.14) into equation (3.13) yields;

\[ \frac{1}{V} = \frac{1-v_0}{V_0} = \frac{v_1}{V_0} \]  

(3.15)

with \( v_1 = 1-v_0 \) and \( V_0 = (rN_1)V_h \) being the hard core volume of the \( N_1 \) molecules. The thermal expansion coefficient for a glass forming liquid can be expressed as;

\[ \alpha = \alpha_h + \alpha_0 \]  

(3.16)

where \( \alpha_h \) is the thermal expansion of the liquid associated with the changes in the hole concentration and \( \alpha_0 \) is the contribution due to the thermal expansion of the occupied volume.
It is in fact assumed that below $T_g$, the thermal expansion of the glass is equal to $\alpha_0$ and above $T_g$ the thermal expansion of the glass is equal to the value given by equation (3.16). This assumption is justified by the fact that below $T_g$ the holes are frozen in the glass matrix, whereas above $T_g$ changes in the hole concentration will occur. Since the hard core volume $V_0$ and $\alpha_o$ are considered to be independent of temperature and pressure, it follows from equation (3.15) that:

$$\alpha_h = \frac{\partial \ln V}{\partial T} \Big|_P = \frac{\partial V_0}{\partial T} \Big|_P \cdot \frac{1}{1 - V_0}$$

(3.17)

Substitution of equation (3.12) into equation (3.17) leads to:

$$T \alpha_h = \frac{E_h}{RT} \cdot \frac{1}{\exp \left\{ 1 - \frac{1}{r} + \frac{E_h}{RT} \right\} - 1}$$

(3.18)

For polymeric liquids $(1)/(r) \approx 0$, and $T \alpha_h$ is mainly a function of $(E_h)/(RT)$. The change in the thermal expansion coefficient $\Delta \alpha$ occurring in the glass transition can thus be identified with $\alpha_h$ and at $T_g$:

$$T_g \alpha_h = T_g \Delta \alpha$$

(3.19)

Sanchez has shown that $T_g \Delta \alpha$ has a maximum value of 0.159 corresponding to $(E_h)/(RT) = 0.841$. By utilizing the viscosity theory of Cohen and Turnbull in which it is required that a critical volume $v^*$ must be available to a molecule before a diffusive motion can occur, and the temperature dependence of the viscosity given by the Doolittle [7] equation:

$$\ln \eta = \ln A + \frac{B}{T + T_0}$$

(3.20)

the viscosity $\eta$ can be expressed explicitly as a function of free volume:

$$\eta = A \exp \left[ \frac{B v^*}{V_f} \right]$$

(3.21)

where $B = 2.303 C_1 C_2$ and $C_2 = T_g - T_0$ and $C_1, C_2$ are the WLF constants [86]. The total probability of finding a hole of size exceeding $v^*$ is;
\[ p(v > v^*) = \exp \left( -\frac{\gamma v^*}{v_f} \right) \]  
\hspace{1cm} (3.22)

where \( v_f \) is the average free volume associated with a molecule, \( v \) is the volume of the hole, and \( 0.5 < \gamma < 1 \). The viscosity expression obtained by relating the viscosity and diffusion is;

\[ \ln \eta = \ln \eta_0 + \frac{\gamma v^*}{v_f} \]  
\hspace{1cm} (3.23)

Defining \( N \) as the number of diffusive segments in a polymeric molecule of size \( r \), and \( r_m \) as the size of the mobile segment such that;

\[ N = \frac{rN_1}{r_m} = \frac{V_0}{v_m} \]  
\hspace{1cm} (3.24)

where \( v_m \) is the hard core volume of the mobile segment and further using the definition of the average free volume \( v_f \) according to Gibbs and DiMarzio[49], Sanchez obtained an expression for the average free volume by postulating that the temperature \( T_2 \) where the viscosity should become infinity is equivalent to the Vogel temperature \( T_0 \);

\[ v_f = v_m \left( \frac{V - v_\infty}{V_0} \right) \]  
\hspace{1cm} (3.25)

\( v_\infty \) is the macroscopic volume of the liquid at \( T_0 \). Substituting equation (3.25) into equation (3.23) gives;

\[ \ln \eta = \ln \eta_0 + \left( \frac{\gamma v^*}{v_m} \right) \times \left[ \frac{v_\infty}{v-v_\infty} \right] \]  
\hspace{1cm} (3.26)

or from equation (3.15);

\[ \ln \eta = \ln \eta_0 + \left( \frac{\gamma v^*}{v_m} \right) \times \left[ \frac{1 - v_0(T)}{v_0(T) - v_0(T_0)} \right] \]  
\hspace{1cm} (3.27)

Equation (3.26) is significant because it shows that the fundamental relaxation time associated with diffusive motions is determined by the excess volume \( (V_0 - v_\infty) \) above \( T_0 \). This is a postulate similar to the one of Adams and Gibbs [29] except that they argued that the relaxation time is governed by the excess configurational entropy above \( T_2 \) or \( T_0 \). Expanding equation (3.26) in a Taylor series about \( T_0 \) one obtains;
\[
\ln \frac{\eta}{\eta_\infty} = \gamma \frac{v^*}{v_m} \frac{V_\infty}{\alpha_\infty V_\infty} \frac{1}{T - T_0} \quad (3.28)
\]

where \( \alpha_\infty = \alpha_0(T_0) \). With \( E_h = 2RT_0 \), the higher terms in the Taylor series go to zero and equation (3.26) compares with the Vogel equation to give for the parameters;

\[
A = \ln \eta_\infty B = \gamma \frac{v^*}{v_m} \frac{V_0}{\alpha_0 V_\infty} \quad (3.29)
\]

and the Cohen Turnbull parameter;

\[
\gamma \frac{v^*}{v_m} = 0.254 \frac{C_1C_2}{T_0} = 1.01 \frac{C_1C_2}{E_h} \quad (3.30)
\]

The hole energy \( E_h \) thus completely characterizes the volume-temperature behaviour of the polymer. Assuming that the relaxation times associated with mechanical or dielectric relaxation processes are proportional to the viscosity, then the relation;

\[
\eta \propto \zeta \propto \tau \quad (3.31)
\]

holds where \( \zeta \) is the coefficient of friction. This relation follows directly from the Rouse [29] model and has been experimentally shown to hold for a number of polymers. Further comparison with the Vogel equation gives for the activation parameter;

\[
B = \gamma \frac{v^*}{v_m} \frac{V_0}{\alpha_0 T_g V_\infty} \quad (3.32)
\]

According to Ferry [48];

\[
C_1^g = \frac{1}{2.303 \frac{f_g}{T_g}} \quad (3.33)
\]

and;

\[
C_2^g = \frac{f_g}{\Delta \alpha} \quad (3.34)
\]

Knowing the free volume fraction at \( T_g \), the change of the thermal expansion can be determined. Sanchez [55] obtained expressions for the volume fraction of the holes at \( T_g \) and the change of the thermal expansion coefficient as;

\[
v_0(T_g) = \exp\left(1 + \frac{2T_0}{T_g}\right) \quad (3.35)
\]

and;
3.2.1.4 Relaxation Behaviour of the Glass-Formers near the Glass Transition: The Concept of Co-operativity

The peculiar slowing down of the relaxation processes at $T_s$ in under-cooled liquids is a characteristic behaviour of most glass formers within the glass transition region. This effect has been identified as being due to a co-operative phenomenon such that the inter-atomic and spatial correlations in the glass state are determined by the extent of co-operative molecular rearrangements. One of the problems which has become of primary interest in the recent times, for both experimental and theoretical work, is to determine the length scale of the spatial correlations leading to co-operativity. The concept of co-operativity was first used by Adam and Gibbs [29] to interpret relaxation and viscosity properties of glass forming liquids. These authors derived an expression for the probability of the co-operative rearrangement involved in the relaxation or viscous flow process by finding the minimum size of a molecular group capable of independent rearrangement at a given temperature. The temperature dependence of the relaxation behaviour is governed by the temperature variation of the size of the cooperatively rearranging region (CRR). This cooperatively rearranging region is defined to be the smallest unit that can undergo a transition to a new configuration without simultaneous configurational change on or outside its boundary (no interaction). The main idea of AG is that the number of units that co-operatively rearrange increases with decreasing temperature, and the potential energy barrier for the transition is proportional to the number $z$;

$$E_a = z\Delta \mu$$  \hspace{1cm} (3.37)

where $z$ is the size/number of co-operative units, $\Delta \mu$ is the potential energy per molecule hindering rearrangement and is independent of $z$ and $T$. The rearrangement probability and

$$\alpha_h(T_s) = \Delta \alpha = \frac{2(T_0/T_s)}{\exp(1+2T_0/T_s)-1}$$  \hspace{1cm} (3.36)
hence the size of each CRR could be expressed as a function of the total configurational entropy $S_c$ given by;

$$W(T) = A \exp \left( \frac{-C}{T S_c} \right)$$

and

$$z^*(T) = \frac{N_A S^*}{S_c(T)}$$

where in equation (3.38) $C$ is a constant containing the term $\Delta \mu$ and in equation (3.39) $z^*(T)$ is the minimum size of a co-operative unit, $S^*$ is the entropy of the smallest CRR, and $N_A$ is the Avogadro number. $S_c$ is a function of $\Delta C_p$ (the change in heat capacity) given by;

$$S_c = \int_{T_0}^{T} \Delta C_p \, d \log T$$

where $T_0$ is the temperature at which $S_c = 0$. A general relationship between the relaxation time $\tau$, the temperature $T$ and heat capacity change $\Delta C_p$ can be obtained since $\Delta C_p$ can be measured at $T_g$. Assuming that $\Delta C_p$ is entirely configurational, $\Delta C_p$ can be approximated as;

$$\Delta C_p(T) = (c)/(T)$$

where $c$ is a constant. This approximation leads to a relaxation time $\tau$ given by;

$$\tau = \tau_0 \left( \frac{D T_0}{T - T_0} \right)$$

Equation (3.42) is equivalent to the Vogel equation with the parameter $D$ determining the fragility of a glass former. Using similar thermodynamic and molecular arguments (isomeric-state theory) Matsuoka [86, 109] has derived a relation of the size of the domain of co-operatively relaxing dipoles with temperature as;

$$z^* = \frac{T^* - T_0}{T^*} \cdot \frac{T}{T - T_0}$$

where $T^*$ is the temperature at which co-operativity starts to set in. According to Matsuoka this temperature should be universal for most glass formers and should be
approximately equal to 500°C which however is questionable. Miller et al [111] have applied the Adams-Gibbs and free-volume theories of polymer melt viscosity to Polyethylene chain and obtained \( z^* = 5 \) as the number of monomer segments \((-CH_2-)\) in a co-operative unit at \( T_g \).

### 3.2.1.5 Thermo-Kinetic Fluctuation Theory

The thermokinetic fluctuation theory of the glass transition proposed by Donth [24] bases on the higher intermolecular correlations at \( T_g \) which lead to sizes of cooperatively rearranging regions large enough that thermodynamic analysis can be applied. By applying thermodynamic fluctuation theory, Donth derived an expression for the volume of a CRR taking temperature as the thermodynamic activity.

\[
V_a(T_g) = \frac{kT_g^2 \Delta C_p^{-1}}{\rho \delta T^2} \tag{3.44}
\]

where \( \rho \) is the density of the bulk material and \( \Delta C_p^{-1} \) is the relaxation strength of the reciprocal specific heat at constant pressure. Considering \( V_a \) as a sphere with radius \( \xi \), the characteristic length scale of the glass transition is obtained from;

\[
\xi = \frac{V_a}{4\pi} \tag{3.45}
\]

Different thermodynamic activities such as pressure and concentration should yield different characteristic lengths however their temperature dependence should be the same since according to Donth all activities are guided by the same WLF scaling. For example the volume of co-operativity is related to fluctuation of concentration as;

\[
<\delta \phi^2> = \frac{kT}{\nu(V_a)} \Delta \left( \frac{\partial^2 G}{\partial \phi^2} \right)^{-1} \tag{3.46}
\]

The temperature dependence of \( V_a \) is given by;

\[
V_a \propto N_a \propto (T - T_0)^2 \tag{3.47}
\]

Therefore the characteristic length should scale with temperature as;

\[
\xi \propto (T - T_0)^v \tag{3.48}
\]
with exponent \( v = 2/3 \) or \( 2/d \) for any dimension \( d \geq 1 \) [24]. For a thin film in our case, \( d = 2 \) and \( v = 1 \).

### 3.2.1.6 The Coupling Scheme

In order to describe segmental relaxation and glass transition behaviour of polymers, Ngai [61] developed the coupling scheme which bases on the fact that relaxation processes in complex systems are co-operative. The essence of the model is that conformational relaxation of a single chain in bulk is unobserved because this primitive relaxation is retarded by inter-chain interactions and correlations among the elements comprising the system. The coupling among the primary species provides a time-dependent effect on the relaxation rate.

The theoretical context of a time dependent relaxation rate is based on classic Liouville dynamics [42] supplemented by an extension of the Dirac constraint theory to time dependent constraints [93]. At times longer than time \( t_c = (1)/(\omega_o) \) characteristic of the strength of intermolecular coupling, the initially constant relaxation rate \( \omega_0 \) slows down. For thermorheologically simple systems, the effect of the coupling in the relaxation rate is given by:

\[
\omega(t) = \omega_0 f(t)
\]  

(3.49)

where:

\[
f(t) = \begin{cases} 1 & \text{for } \omega_c t < 1 \\ \frac{w_c}{(w_c t)^n} & \text{for } \omega_c t > 1 \text{ and } 0 < n < 1 \end{cases}
\]  

(3.50)

In these expressions, \( (\omega_c)^{-1} \) is the time characteristic of the system and \( n \) is a parameter characterizing the coupling strength between the primary species. This same parameter also measures the extent of co-operativity. If the time-temperature correspondence holds, the evolution of the normalized relaxation function \( \Phi(t) \) for a single relaxation mechanism can be written as:

\[
\frac{d\phi}{dt} = -W_0 f(t) \phi
\]  

(3.51)
For polymers around the dynamic glass transition and above, intermolecular coupling or co-operativity is important so that,

\[
\frac{d\phi(t)}{dt} = -W_0(W_c t)^{-n} \phi
\]

(3.52)

From equations (3.51) and (3.52), the KWW equation is obtained;

\[
\phi(t) = \exp\left(\frac{t}{\tau}\right)^{-n}
\]

(3.53)

with

\[
\tau^* = \left[ (1 - n) (W_c)^n \tau_0 \right]^{(1 - n)}
\]

(3.54)

where \(\tau\) is the effective relaxation time of a complex system, and \(\tau_0 = (\omega_0)^{-1}\) is the primitive relaxation time. The predictions of the coupling model for relaxation times in dielectric, mechanical and density fluctuations [61] variables are given by;

\[
\tau_i^* = \left[ (1 - n_i)(W_c)^{n_i}(W_{0i})^{-1} \right]^{1-n_i}
\]

(3.55)

where \(i\) stands for the type of variable used. Since the friction coefficient near \(T_g\) varies rapidly with temperature and as was shown in equation (3.48), \((\omega_0)^{-1}\) are proportional to friction coefficient \(\xi\), with

\[
\zeta = \exp\left(\frac{B_0}{T-T_0}\right)
\]

(3.56)

so that equation(3.55) becomes;

\[
\tau_i^* \approx \exp\left\{ \left[ \frac{B_0}{(1 - n_i)} \right] / (T - T_0) \right\}
\]

(3.57)

where \(i\) represents dielectric, mechanical and density fluctuation relaxations respectively.

Since \(\tau_i^*\) is related to the mean relaxation time \(\tau_i\) by [61];

\[
\tau_i = \int_0^\infty \exp\left[ -\left( \frac{t}{\tau_i^*} \right)^{1-n_i} \right] dt = \frac{\tau_i^*}{1-n_i} \Gamma\left( \frac{1}{1-n_i} \right)
\]

(3.58)

where \(\Gamma\) is the gamma function, and \(\tau\) is given by the Vogel equation;

\[
\tau = \tau_0 \exp\left[ \frac{B}{\alpha (T - T_0)} \right]
\]

(3.59)
where $\alpha$ is the coefficient of thermal expansion. Substituting equation (3.59) in equation (3.58) one obtains for the activation parameter $B$ from the three relaxation processes;

$$B_{\text{dielectric}} = \frac{B_0}{1 - n_{\text{dieel}}}$$

$$B_{\text{mechanical}} = \frac{B_0}{1 - n_{\text{mech}}}$$

$$B_{\text{density}} = \frac{B_0}{1 - n_{\text{dens}}}$$

leading to the invariant relation;

$$(1 - n_{\text{dieel}})B_{\text{dieel}} = (1 - n_{\text{mech}})B_{\text{mech}} = (1 - n_{\text{dens}})B_{\text{dens}} = B_0$$

which allows for comparison of data obtained using different techniques. $B_0$ can for example be determined using Brillouin-Scattering. Ngai et al [61] have applied this model to describe relaxation behaviour in polymer mixtures. The conclusions drawn from this model are based on the requirement that the system in question should be thermorheologically simple so that the time-temperature superposition holds. This requirement is however not satisfied in most polymer mixtures that the time-temperature superposition holds.

### 3.3 Relaxation in the Linear Response Regime

#### 3.3.1 Linear Relations

Systems whose responses can be described by relations linear in the external forces imposed on them are called linear systems. Denoting the displacement of a system at time $t$ by $R(t)$ and the corresponding external action by $A(t)$, the linear relation for an isotropic system can be expressed in the form;

$$R_{\mu}(t) - < R_{\mu} >_0 = L_{\mu\mu} A_{\mu}(t)$$

where $\mu$ distinguishes the kinds of vector or tensor components and $< R_{\mu} >_0$ is the equilibrium value in the absence of external forces. In the case in which various processes coexist, the effect of the various kinds of forces is obtained by using the Boltzmann superposition principle [12];
\[ R_\mu(t) - < R_\mu >_0 = \sum_\nu L_{\mu \nu} A_\nu(t) \]  

(3.63)

with \( L_{\mu \nu} \) being identified as the kinetic coefficients. Equation (3.63) is however only applicable to slowly varying linear irreversible processes with an instantaneous response to the forces. When the response lags the forces, all after effects due to forces prior to time \( t \) must be superposed. This follows from the principle of causality, according to which the present state results from the past cause. The system in question becomes non-Markovian [105] and equation (3.63) takes the form:

\[ R_\mu(t) - < R_\mu >_0 = \sum_\nu \chi_{\mu \nu} A_\nu(t) + \int_{-\infty}^t dt' \sum_\nu \Phi_{\mu \nu}(t-t') A_\nu(t') \]  

(3.64)

The first term on the right-hand side denotes a contribution whose delay can be neglected while the delay of the second term cannot be neglected. Macroscopic systems with a large number of degrees of freedom lose memory of the effect of the past values of the forces with time so that:

\[ \lim_{t \to \infty} \Phi_{\mu \nu}(t-t') = 0 \]  

(3.65)

For the case where the temporal variation of the forces are so slow that the forces may be regarded constant during a time interval \( \tau \) above which the convergence to zero in equation (3.65) holds, the following expression is obtained:

\[ R_\mu(t) - < A_\mu >_0 = 4 \sum_\nu \chi_{\mu \nu} A_\nu(t) + \int_0^\infty ds \sum_\nu \Phi_{\mu \nu}(s) A_\nu(t-s) \]  

(3.66)

where \( s = t - t' \) is the integration parameter in the second term of equation (3.66). The main contribution to the integral comes from range of \( s < \tau \). By considering the action to be instantaneous in a given time scale, the time dependence of the force may be expressed by the Dirac \( \delta \) function (Figure 3.1a):

\[ A_\nu(t) = \delta(t-t_1) \]  

(3.67)

where \( z \) denotes the direction of action of the external force. Substituting equation (3.67) into equation (3.66) and introducing a step function external force:

\[ A_\nu(t) = \theta(t_1 - t) \]  

(3.68)

with \( \theta \) being the Heaviside unit step function defined as;
\[ \theta(x) = \int_{-\infty}^{x} dx' \delta(x') = \begin{cases} 1 & (x > 0) \\ 0 & (x < 0) \end{cases} \] (3.69)

which leads to;

\[ R_\mu(t) - < R_\mu >_0 = \chi_\mu \delta(t-t_1) + \Phi_\mu(t-t_1) \theta(t-t_1) \] (3.70)

with \( R_\mu(t) = < R_\mu > \) (at \( t < t_1 \))

The first term in equation (3.70) represents the instantaneous response to the pulsed force, while the second is the effect of the pulsed force remaining after time \( t_1 \) at which;

\[ R(t) - < R > = \Phi_\mu(t-t_1) \theta(t-t_1) \] (3.71)

From equation (3.71), the system will return to thermal equilibrium in long time \( t \) (Figure 3.1b). The function \( \Phi \) is called the after effect (Nachwirkungs funktion) or the linear response function.

![Figure 3.1: Showing the response to a pulsed force](image)

### 3.3.2 Relaxation

Relaxation means the time-dependent return to equilibrium of a system that has been perturbed by a change in an applied constant field. Among the common fields are mechanical, thermal as well as electrical and magnetic stresses, for each of which a given system will exhibit a characteristic frequency-dependent response. The integral of the response function \( \Phi(t) \) gives a relaxation function \( \Psi(t) \);
\[ \psi_{\mu\nu}(t) = \int_{s_{\text{t}}}^{\infty} ds \Phi_{\mu\nu}(s) \]  

(3.72)

The inverse gives the response function as;

\[ \Phi_{\mu\nu}(t) = -\frac{d\psi_{\mu\nu}(t)}{dt} \]  

(3.73)

When the convergence of the response function is sufficiently rapid and the integral in equation (3.72) converges then,

\[ \lim_{t \to \infty} \psi_{\mu\nu}(t) = 0 \]  

(3.74)

which means that \( R_{\mu}(t) \) converges towards \( \langle R_{\mu}\rangle > 0 \). Response due to a harmonically oscillating force can be described by a superposition of harmonic oscillations;

\[ A_{V}(t) = \int_{-\infty}^{\infty} d\omega e^{-i\omega t} A_{V, \omega} \]  

(3.75)

\[ R_{\mu}(t) - \langle R_{\mu}\rangle > 0 = \int_{-\infty}^{\infty} d\omega e^{-i\omega t} R_{\mu, \omega} \]  

(3.76)

with;

\[ A_{V, \omega} = \int_{-\infty}^{\infty} dt e^{i\omega t} A_{V}(t) \]  

(3.77)

\[ R_{\mu, \omega} = \int_{-\infty}^{\infty} dt e^{i\omega t} \{ R_{\mu}(t) - \langle R_{\mu}\rangle > 0 \} \]  

(3.78)

Substituting equations (3.75) in (3.77) and (3.76) into the right hand side of equation (3.78) gives the Fourier transform of the linear relation;

\[ R_{\mu, \omega} = \sum_{V} \chi_{\mu V}(\omega)A_{V, \omega} \]  

(3.79)

where the formula for the Dirac \( \delta \)-function;

\[ \delta(x) = \int_{-\infty}^{\infty} d\omega e^{i\omega x} \]  

(3.80)

was used and;

\[ \chi_{\mu\nu}(\omega) = \chi_{\mu\nu}^{\infty} + \int_{0}^{\infty} dt e^{i\omega t} \Phi_{\mu\nu}(t) \]  

(3.81)
is the complex admittance. The characteristic relaxation frequencies are of particular importance because unlike resonance frequencies, they are highly temperature dependent. Experimentally it is easier to measure either the relaxation function or the response to harmonic forces by measuring the complex admittance. In particular the part of the complex admittance related to energy dissipation is of great interest because the energy dissipation in relaxation processes is associated with long-range irreversible motion of particles. Thus, the relaxation spectra provide a means of studying mass transport and configurational rearrangements mechanisms, occurring during the glass transition, of the molecular constituents of glass-forming materials induced by the external fields.

![Diagram of Broad-band dielectric Spectroscopy](image)

Figure 3.2: Range of frequency accessible to some techniques for studying responses of systems to external exciting external stresses. FI stands for free induction decay and SE for solid echo.

Many different techniques may be applied in the study of system responses to each of the various stresses referred above and the choice of a particular technique will usually depend on the frequency range being investigated.

### 3.2.2.1 Dielectric Relaxation

When the constraint that undergoes a change is an electric field, the observable quantity that varies with time is the polarization \( \rightarrow P \) giving rise to dielectric relaxation. Among the contributions to the total polarization, orientation polarization is most important because it depends directly on the internal structure of the molecules of the dielectric. The application
of a constant electric field $\vec{E}$ to a dielectric, results into the development of an electric displacement $\vec{D}$ that increases with time until a constant value is reached at sufficiently long time (Figure 3.3a). After the removal of the electric field, the electric displacement returns to zero with time. For sufficiently small electric displacements $e = \vec{D} / \vec{E}$ the system can be treated as linear and consequently conforms to the superposition principle (Figure 3.3b).

The electric displacement can be expressed as a function of the applied field as:

$$
\mathbf{D}(t) = \left[ \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \Phi(t) \right] \mathbf{E}(t)
$$

(3.82)

where $\Phi(t)$ is a built-up normalized dielectric function (Figure 3.4) whose extreme values are:

$$
\Psi(t) = 1 - \Phi(t) = 0 \quad \text{for} \quad t = 0
$$

(3.83)

and

$$
\Psi(t) = 1 - \Phi(t) = 1 \quad \text{for} \quad t = \infty
$$

(3.84)

and
Figure 6: Normalized Correlation functions of the polarization when a steady macroscopic electric field is removed from the medium

\( \Phi(t) \) is the normalized decay or response function of the polarization when a steady macroscopic electric field is removed from the medium. If an electric field is applied at time \( t = 0 \) and it increases by an infinitesimal amount \( dE \), at \( t = t' (0 < t' < t) \), the increase in electric displacement at time \( t \) is given by

\[
D(t) = \varepsilon_\infty dE + (\varepsilon_0 - \varepsilon_\infty) \Phi(t - t') dE
\]

(3.65)

In linear systems, the total displacement at a time \( t \) caused by a variable electric field \( E(t') \) is the result of superposition of all the increments, \( dD \) and

\[
D(t) = \varepsilon_\infty E(t) + (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{t} \frac{dE(t')}{dt'} \Phi(t - t') dt'
\]

(3.86)

By making the substitution \( t - t' = u \) and integrating by parts, one finds

\[
D(t) = \varepsilon_\infty E(t) + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{d\Phi(u)}{du} E(t - u) du
\]

(3.87)

For an alternating field, \( E = E_0 \exp(i\omega t) \) and equation (3.87) leads to

\[
\varepsilon^*(\omega) = \frac{D(t)}{E(t)} = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \exp(i\omega u) \left[ - \frac{d\Phi(u)}{du} \right] du
\]

(3.88)

where;
\[-\frac{d \phi(u)}{du} = \frac{d \Phi(u)}{du}\]  
\tag{3.89}

and:

\[\varepsilon^*(\omega) = \varepsilon'\omega - i\varepsilon''\omega\]  
\tag{3.90}

is the complex dielectric permittivity. Rearrangement of terms of equation (3.88) leads to:

\[\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_{0}^{\infty} \left(-\frac{d \phi}{dt}\right) \exp(-i\omega t) dt = \mathcal{L}\left(-\frac{d \phi}{dt}\right)\]  
\tag{3.91}

The first term of equation (3.91) is related to \(-d\Phi/dt\) through a Laplace transform. Thus by one sided Fourier transformation of the time derivative of the decay or time correlation function \(\Phi(t)\) into the frequency domain one obtains the complex permittivity \(\varepsilon\) of the system. This enables the direct comparison of dielectric spectroscopy and photon correlation data where the correlation function can directly be measured. The real part \(\varepsilon'\) and the imaginary part \(\varepsilon''\) of the complex permittivity are connected by the Kramers-Kronig dispersion relations:

\[\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \int_{0}^{\infty} \frac{x\varepsilon''(x)}{x^2 - \omega^2} dx\]  
\tag{3.92}

\[\varepsilon''(\omega) = \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega\varepsilon'(x)}{x^2 - \omega^2} dx\]  
\tag{3.93}

This shows that one of these quantities may be determined from the other if data over a sufficiently wide range of frequencies are available. Here \(x\) indicates the Cauchy principal value \([97]\). These relations apply only for pure relaxation processes. If the dielectric is lossy, conductivity contributions at frequencies lower compared to the relaxation processes have to be subtracted. In order to solve the integral equation (3.88) one requires knowing the decay function over the entire relaxation range. For an ideal relaxation, the rate of return to equilibrium value of an observable quantity \(P\) is dependent on the deviation from the equilibrium value \(P_{eq}\) and for small fluctuations the response may be described by a linear first order approximation with the solution:
\( P - P_\infty \approx \exp \left( \frac{1}{\tau} \right). \) \hfill (3.94)

\( \tau \) is the relaxation time, which may be defined as the time in which the observable quantity is reduced to \( 1/e \) times the original value. For a dielectric relaxation involving a single relaxation time (Debye process);

\[ \varphi(t) = \exp \left( -\frac{t}{\tau} \right) \] \hfill (3.95) 

and equation (3.91) becomes;

\[ \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega \tau} \] \hfill (3.96)

from which the real \( \varepsilon' \) and loss \( \varepsilon'' \) components of \( \varepsilon \) are given by;

\[ \varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \] \hfill (3.97) 

\[ \varepsilon''(\omega) = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2} \] \hfill (3.98)

In the limit of low and high frequencies, equations 3.97 and 3.98 lead to;

\[ \lim_{\omega \to 0} \varepsilon'(\omega) = \varepsilon_0 \quad \text{and} \quad \lim_{\omega \to 0} \varepsilon''(\omega) = \varepsilon_\infty \] \hfill (3.99)

It can be seen from Figure 3.5 that \( \varepsilon' \) is a continuously decreasing function of frequency and \( \varepsilon'' \) approaches zero both for small and for large values of frequency, reaching a maximum at \( \omega \tau = 1 \).

![Figure 3.5: Variation of the real \( \varepsilon' \) and imaginary \( \varepsilon'' \) components of the complex dielectric constant \( \varepsilon \) with frequency for an ideal dielectric with a single relaxation time.](image)
The ratio $\varepsilon''/\varepsilon'$ is defined as the loss tangent or $\tan \delta$. Although very simple liquids obey the above equations, in polymers, the dispersion usually occurs over a wider frequency range than predicted by equation (3.95).

This behaviour is commonly interpreted to be a result of many relaxation mechanisms involved in the relaxation with a different relaxation time $\tau_i$. Accordingly, $\Phi(t)$ should be expressed as a weighted sum of exponential decay functions [32]:

$$\phi(t) = \sum n_i \exp(-t/\tau_i)$$  \hspace{1cm} (3.100)

where $\sum n_i = 1$. This leads to the integral involving a normalized continuous distribution of relaxation times $g[\ln(\tau)]$, so that:

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{\infty} \frac{g[\ln(\tau)]d[\ln(\tau)]}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (3.101)

and:

$$\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{\infty} \frac{g[\ln(\tau)]\omega \tau d[\ln(\tau)]}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (3.102)

Knowledge of the relaxation function is paramount to interpret the dielectric behaviour of most polar systems including macromolecules. From equations (3.92) and (3.93) the real and the imaginary parts of the normalized complex dielectric constant are given by:

$$\frac{\varepsilon'(\omega)}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] \cos \omega t \, dt$$

And

$$\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] \sin \omega t \, dt$$  \hspace{1cm} (3.103)

Equations (3.103) may be inverted giving:

$$\frac{d\phi(t)}{dt} = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \cos \omega t \, d\omega = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} \sin \omega t \, d\omega$$  \hspace{1cm} (3.104)
Thus if one of the components of the complex dielectric function is known over the entire relaxation range, the relaxation function $\Phi(t)$ can be determined. Integration of equation (3.103) gives:

$$
\Phi(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon'(\omega)}{\epsilon_0 - \epsilon_{\infty}} \sin \alpha \sin(\omega t) \, d\omega = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_{\infty}} \sin \alpha \cos \alpha \, d\omega
$$

(3.105)

Since the normalized decay function is unity at $t = 0$, the relaxation strength $\Delta \epsilon = \epsilon_0 - \epsilon_{\infty}$ is related to the loss permittivity by the expression;

$$
\Delta \epsilon = \epsilon_0 - \epsilon_{\infty} = \frac{2}{\pi} \int_{-\infty}^{\infty} \epsilon''(\omega) \cos \alpha \, d\omega
$$

(3.106)

Several relaxation functions have been proposed to fit experimental data for real systems whose dispersions and absorption cannot be described by a single relaxation function. Among the most important are the Cole-Cole [65], Davidson-Cole [20] and the Kohlrausch-Williams-Watts [31] functions. A more generalized relaxation function was proposed by Havriliak and Negami [102] and formulated as a combination of the Cole-Cole and the Davidson-Cole equations. This function reads;

$$
\epsilon^*(\omega) = \epsilon'(\omega) - i \epsilon''(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + (i \omega \alpha)^\gamma)^\beta}
$$

(3.107)

with $0 < \alpha < 1$ and $0 < \gamma < 1$. When $\gamma = 1$ and, equation (3.107) reduces to a Cole-Cole equation and when $\alpha = 1$ and $0 < \gamma < 1$, it leads to the Davidson-Cole equation. When both $\alpha, \gamma = 1$, the single time relaxation function is obtained whereas the KWW stretched exponential function is gained numerically as a Fourier transform of equation (3.107) in the time domain. The Cole-Cole equation describes data well where the relaxation behaviour is symmetrical about the logarithm of the maximum loss. For non-symmetrical processes the Davidson-Cole, the Havriliak Negami and the KWW functions represent the experimental data well. The real and imaginary parts of the HN function are given by;
\[ \varepsilon_{HN}^\prime (\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{\cos (\gamma \varphi)}{\left(1 + 2(\omega \tau_0)^\alpha \cos \frac{\pi \alpha}{2} + (\omega \tau_0)^{2\alpha}\right)^{\frac{\gamma}{2}}} \] (3.108)

\[ \varepsilon_{HN}^{\prime\prime} (\omega) = (\varepsilon_0 - \varepsilon_\infty) \frac{\sin (\gamma \varphi)}{\left(1 + 2(\omega \tau_0)^\alpha \cos \frac{\pi \alpha}{2} + (\omega \tau_0)^{2\alpha}\right)^{\frac{\gamma}{2}}} \] (3.109)

with \( \psi = \arctan[(\omega \tau_o)^\alpha \sin (\pi \alpha/2)/(1 + (\omega \tau_o)^\alpha \cos (\pi \alpha/2))] \)

The parameters \( \alpha, \gamma \) and \( \tau \) can be determined at a given temperature either from a complex-plane plot as proposed by Cole [65] or directly by fitting experimental data.

### 3.3.2.2 Distribution of Relaxation Times

As already pointed out, the decay functions in real systems are not simple exponential and the imaginary part of the HN function is usually broader in frequency than given by equation (3.109) and is also skewed to high frequencies. In such cases \( \varepsilon'' \) must be described by the inclusion of a distribution function \( g(\tau) \) or \( g(\tau/\tau_o) \) for the relaxation times such that:

\[ \frac{\varepsilon^* (i \omega \tau_0) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_{-\infty}^{\infty} \frac{g(\tau/\tau_0)}{1 + i \omega \tau} d \ln(\tau/\tau_0) \] (3.110)

with:

\[ \varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{g(\tau/\tau_0)}{1 + \omega^2 \tau^2} d \ln(\tau/\tau_0) \] (3.111)

\[ \varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{g(\tau/\tau_0) \omega \tau}{1 + \omega^2 \tau^2} d \ln(\tau/\tau_0) \] (3.112)

Key to relaxation spectroscopy on polymers is the determination of the functions \( g(\tau) \) or \( g(\tau/\tau_o) \) and examining their relationships to the glass transition, the liquid or glass structure and the molecular interaction potentials therein. By solving equation (3.110) for \( g(\tau/\tau_o) \), Davidson and Cole [20] obtained the expression;
\[ g(y) = \frac{1}{2\pi i (\varepsilon_y - \varepsilon_{0})} \left[ \varepsilon_y^{*} \left( \frac{1}{y e^{i\pi}} \right) - \varepsilon_{0}^{*} \left( \frac{1}{ye^{-i\pi}} \right) \right] \]  \hspace{1cm} (3.113)

where \( y = (\tau)/(\tau_o) \). Havriliak and Negami \[102\] substituted for \( iy, ye^{\pm i\pi} \) and obtained;

\[ \varepsilon_y^{*} \left( \frac{1}{ye^{i\pi\alpha}} \right) = \varepsilon_y + \frac{\varepsilon_y - \varepsilon_{0}}{1 + \left( \frac{1}{ye^{i\pi\alpha}} \right)^{\gamma}} \]  \hspace{1cm} (3.114)

with the solution;

\[ g \left( \frac{\tau}{\tau_o} \right) = \frac{(\tau/\tau_o)^{\alpha\gamma} \sin (\gamma \theta)}{\pi \left[ (\tau/\tau_o)^{2\alpha} + 2(\tau/\tau_o) \cos (\pi\alpha) + 1 \right]^{\frac{\gamma}{2}}} \]  \hspace{1cm} (3.115)

where;

\[ \theta = \arctan \left( \frac{\sin (\pi \alpha)}{((\tau/\tau_o) \alpha + \cos (\pi \alpha))} \right) \]  \hspace{1cm} (3.116)

When \( \alpha = 1 \), equation (3.115) leads the Davidson-Cole distribution function;

\[ g \left( \frac{\tau}{\tau_o} \right) = \frac{1}{\pi} \sin \pi \gamma \left( \frac{\tau}{\tau_o} \right)^{\gamma} \]  \hspace{1cm} (3.117)

for \( \tau < \tau_o \) and \( g((\tau)/(\tau_o)) = 0 \) for \( \tau > \tau_o \). For \( \gamma = 1 \), equation (3.117) yields the Cole-Cole time distribution function;

\[ g \left( \frac{\tau}{\tau_o} \right) = \frac{1}{2\pi} \sin \pi \alpha \left\{ \cosh \left[ \alpha \ln \left( \tau/\tau_o \right) \right] \cos \pi \alpha \right\}^{-1} \]  \hspace{1cm} (3.118)

Figure (3.6) shows the three normalized distribution functions evaluated for the parameters \( \gamma = 0.5, \alpha = 0.5 \) and \( \tau_o = 103s \). The two parameters \( \alpha \) and \( \gamma \) therefore uniquely represent the distribution of relaxation times with \( \alpha \) determining the width while \( \gamma \) reflects the skewness of the distribution. An important quantity which characterizes a dielectric relaxation process is its relaxation time. The determination of the mean relaxation time has recently received close attention with respect to the question as to which of the averages physically represents the relaxation processes.
Figure 3.6: Normalized relaxation time distributions corresponding to (1) the Havriliak-Negami, (2) the Davidson-Cole and (3) the Cole-Cole relaxation functions evaluated for the parameters $\gamma = 0.5$, $\alpha = 0.5$ and $\tau_0 = 103s$.

This follows from the realization that no unique $\tau$, independent of the method of evaluation, can be obtained from the empirical relaxation functions for real systems. For example, in the case of the Havriliak-Negami function, the maxima for and the corresponding $g(\tau)$ do not coincide since

$$\omega_{\text{max}} \neq \frac{1}{\tau_{\text{max}}}$$

Although it is commonly found in literature that the characteristic time for a dielectric process is obtained from fitting the data using the Havriliak-Negami function, this value should rather be identified as being the characteristic time for this relaxation function. A different $\tau$ is obtained by taking the value at the peak maximum. From the relaxation time distribution function one can obtain the time averages $<\tau>$ or $<\log \tau>$. These two averages do not exist for the Havriliaki-Negami function. The only physical meaningful averages are obtained when one works in the logarithmic scale leading to;
A feature which reflects molecular interactions and correlation is the temperature dependence of the relaxation time distribution. A temperature dependence of the distribution will be determined by either a temperature dependence of both $\alpha$ or $\gamma$ or by temperature dependencies of the parameters which are opposite in sense. Polymer mixtures exhibit a much stronger temperature dependence of the shape parameters compared to pure components. There are other models which have been used to interpret broad dispersions and absorptions. One approach relates the dispersion to the fluctuation of the free energy of a system. According to this approach the spectral energy associated with the fluctuation is essentially the integral of the loss tangent versus logarithm of frequency curve given as:

$$< F(M^2) > - F(0) \geq \frac{3kT}{\pi} \int_0^\infty \frac{p\psi(\omega)}{p\psi(\omega)} d\omega$$

(3.121)

where $\frac{p\psi(\omega)}{p\psi(\omega)}$ is the loss tangent and $p$ stands for the polarization.

### 3.3.2.3 Chain Dynamics

Polymers in solution and in the melt continuously change their shape and position randomly by thermal agitation. Therefore the macroscopic theory outlined in the previous section should be related to the microscopic structure of the system. This is achieved by considering the fluctuations of the dipole moment $< M >$ which arise due to conformational changes resulting from thermal agitation. Usually such agitation leads to a Brownian motion which is known to dominate various time-dependent phenomena such as viscoelasticity, birefringence, polarity and light scattering. This motion is characterized by a time-correlation function $\Phi(t)$. By considering a variable $A$ for example the position $r$ or the dipole moment $\mu$, the time auto-correlation function $CAA(t)$ is given by:

$$CAA(t) = < A(0) \times A(t) > = \iint A(p, q, u) \times A(p, q, t + u) \times f(p, q) dp dq$$

(3.122)
where \( A(t + u) \) is the value for a molecule at time \((t + u)\), given that it was \( A(u) \) at time \( u \), \( f(p, q) \) is the equilibrium-phase space-distribution function and \( f(p, q)dpdq \) is the probability that a molecule has the conjugated momenta \( p \) and co-ordinates \( q \) in the intervals \( p \) to \( p + dp \) and \( q \) to \( q + dq \). For \( t = 0 \);

\[
1C_{A,A}(0) = \langle A^2(0) \rangle = \iint A^2(p, q, u) \times f(p, q)dpdq
\]

(3.123)

which is the mean square value of \( A \) in the equilibrium state that can be evaluated from time independent statistical mechanics. For large values of \( t \), the correlation between \( A(u) \) and \( A(t + u) \) vanishes and \( C_{AA}(t) = \langle A(u) \rangle > 2 \). In complex polymer systems cross-correlation between different molecules plays an important role. The time cross-correlation function is defined as;

\[
C_{A,A_j}(t) = \langle A_i(0)A_j(t) \rangle
\]

(3.124)

where \( A_i \) and \( A_j \) are the dynamic variable \( A \) of molecules \( i \) and \( j \) ( \( i \neq j \) ) According to Böttcher[13], the static dielectric permittivity \( \varepsilon_o \) for an ensemble of dipolar chain molecules and the constituent dipole moments of a polymer system are related by the expression;

\[
\varepsilon_o - \varepsilon_v = \frac{4\pi}{3k_B} \times \frac{3\varepsilon_o (2\varepsilon_o - \varepsilon_v)}{(2\varepsilon_o + 1)^2} \frac{\langle M(0) \times M(0) \rangle}{V}
\]

(3.125)

where \( M(0) \) is the instantaneous dipole moment of a microscopic sphere of volume \( V \) embedded in the system, and \( \langle M(0) \times M(0) \rangle \) is the mean-square dipole moment deduced in the absence of an applied field and evaluated over all the configurations of the ensemble contained in the sphere. The time correlation function is defined as;

\[
\Phi(t) = \frac{\langle M(0) \times M(t) \rangle}{\langle M(0) \times M(0) \rangle} = \frac{\langle \mu_1(0) \times \mu_1(t) \rangle + \sum_{j \neq k} \langle \mu_j(0) \times \mu_k(t) \rangle}{\mu^2 + \sum_{j \neq k} \langle \mu_j(0) \times \mu_k(0) \rangle}
\]

(3.126)

where \( \mu_j(t) \) denotes the elementary dipole moment in the chain at time \( t \). If \( t \) is very small so that very little change takes place in this interval, then \( M(t) \approx M(0) \) and the correlation function is close to unity. If, however, \( t \) is so large that considerable fluctuation takes place, then there will be little correlation between \( M(t) \) and \( M(0) \) and the correlation function approaches zero as \( t \to \infty \). Hence the correlation function contains all temporal information
of the system and is therefore related to the frequency dependence of the permittivity. For non-associated systems, the complex dielectric constant $\varepsilon(\omega)$ is related to the decay function:

$$\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} \rho(\omega) = \mathcal{L} \left( -\frac{d\Phi_0}{dt} \right)$$

with $\Phi_0(t) = \frac{\langle \mu(0) \mu(t) \rangle}{\langle \mu(0) \rangle}$ and $\rho(\omega)$ is an internal field factor. In this case the cross-correlation is zero. It follows from the correlation function that the differences in the dielectric behaviour of polymers and simple substances arise from the cross-correlation terms appearing in equation (3.127).

### 3.3.2.4 Typical Dielectric Spectra

In solid polymers the relaxation function shows abrupt changes in its real and imaginary parts at frequencies which may be related to the different molecular motions of the dipolar groups. The dielectric spectra obtained can be represented by either plotting isochronous permittivity as a function of temperature, or by defining a relaxation-time distribution as a function of temperature. The shape of the distribution curve gives information about the dipole-dipole interactions. Figure 3.7 shows schematically some typical dielectric transitions.

![Figure 3.7: A graph of some typical dielectric relaxation processes](image)

Three transitions are shown: the primary ($\alpha$-relaxation) which is a slow transition occurring at high temperatures, and two secondary transitions, the $\beta$ and the $\gamma$-relaxation which are fast transitions. In amorphous polymers the $\alpha$-relaxation is associated with large-scale Brownian motion involving many chain segments. In the temperature scale the $\alpha$-process corresponds
to the glass transition. The $\beta$ transition generally represents localized relaxation processes in the glassy state.

### 3.3.2.5 Temperature Dependence of the Relaxation Time

The temperature dependency of polymer properties is of great importance because the physical and mechanical properties of the polymers change drastically as temperature changes. It is important to study the relaxation behaviour of polymers at a particular temperature for a given time period. The temperature dependency of the relaxation time provides a way of varying the temperature to bring the relaxation process within a time scale that is readily accessible. Viscoelastic behaviour at short or long time periods can be predicted by extrapolation. Changes due to temperature can be described in terms of free volume or relaxation time. At temperatures below $T_g$, local chain relaxation takes place. At these temperatures motions are hindered by close presence of other molecules. For relaxation to take place a potential barrier must be surmounted. In this region the kinetics of relaxation are better described on the basis of barrier state theories and as such the temperature dependency of the relaxation time $\tau$ is often described by the Arrhenius relationship described by equation (3.128)[73];

$$\tau = \tau_o \exp \left[ \frac{E_a}{kT} \right]$$

(3.128)

where $\tau_o$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is Boltzmann constant and $T$ is the absolute temperature. In contrast to local motions, relaxation times associated with secondary motions are dependent on free volume. The presence of volume allows the molecules to relax to a new configuration. The Doolittle equation gives a relation that expresses the dependency of relaxation time on the free volume as [8];

$$\tau = \tau_o \exp \left[ \frac{BV_o}{V - V_o} \right]$$

(3.129)

where $V$ is the total volume, $V_o$ is the occupied volume, $B = \xi((V^*)(V_m))$ is a constant, $V^*$ is the minimum volume required for relaxation process to take place, $V_m$ is the mean volume of
the relaxing polymer segment, $\xi$ is a constant such that $0.5 < \xi < 1$. At temperature above the glass transition ($T_g$), the dependency follows the William - Landel-Ferry (WLF) law [45]:

$$\log \frac{\tau(T)}{\tau(T_g)} = \frac{C_1(T - T_g)}{C_2 + T - T_g}$$

(3.139)

where $\tau(T)/\tau(T_g)$ is the shift factor relative to the reference temperature $T_g$, $C_1$ and $C_2$ are empirically determined constants and $T_g$ is a glass transition temperature. For temperatures less than the reference temperature the shift factor shifts the curves to the right while for higher temperatures to the left. The values of $C_1$ and $C_2$ depend on the particular morphology or structure associated with a given sample. For amorphous materials, the best approximations for the parameters are $C_1 = 17.44$ and $C_2 = 55.6$. As the sample becomes more crystalline (e.g. polyethylene or the asphalt paraffins) or cross linked (such as a vulcanized rubber), the values of $C_1$ and $C_2$ will increase, reflecting changes in the free volume and the expansion with respect to temperature. Conversely, Vogel-Fulcher-Tamman equation [40] can also be used to explain temperature dependency above $T_g$:

$$\tau = \tau_o \exp \left[ \frac{K}{T - T_o} \right]$$

(3.131)

where $\tau_o$ is the characteristic time at which free volume would be zero, $K = (BV_o/\alpha)$ is a constant and $T_o$ is ideal (Vogel) temperature which is 50°C below $T_g$, temperature at which free volume would be zero. From Figure 3.8, it can be seen that at high temperatures the two are approximately the same but differ significantly at lower temperatures.

![Figure 3.8: A graph showing the Arrhenius and VFT/WLF relationship](image)

Figure 3.8: A graph showing the Arrhenius and VFT/WLF relationship
When measurements are taken at different temperatures the loss modulus is shifted to higher frequencies as shown in Figure 3.9.

![Figure 3.9: Variation of loss modulus against the logarithm of frequency at different temperatures](image)

3.4 Optical Characterization of Thin Films

When light is incident on a semiconductor, the optical phenomena of absorption, reflection and transmission are observed. From these optical effects, we obtain much of the information. From absorption spectrum as a function of photon energy, a number of processes can be contributed to absorption. At high energies photons are absorbed by the transitions of electrons from filled valence band states to empty conduction band states. For energies just below the lowest forbidden energy gap, radiation is absorbed due to the formation of excitants, and electron transitions between band and impurity states. The transitions of free carriers within energy bands produce an absorption continuum which increases with decreasing photon energy. Also, the crystalline lattice itself can absorb radiation, with the energy being given off as optical and acoustic phonons. Finally, at low energies, or long wavelengths, electronic transitions can be observed between impurities and their associated bands. Many of these processes have important technological applications;
for example, intrinsic photo detectors utilize band to band absorption. While semiconductor Lasers generally operate by means of transitions between impurity and band states [23].

3.4.1 Optical Properties of Amorphous and Crystalline Materials

The general theory and many of the experimental results on amorphous semiconductors have been summarized by Mott and Davis [23]. These results have shown two important features namely:

- A band structure related to these materials.
- The replacement of the sharp cut off most attributed to crystalline structures with tail or defect states in the forbidden energy gap.

They show that one feature of such materials is some sort of energy band structure, but show also that the normally sharp cut off in the density of states curves at the band edges is replaced by a tailing into the normally forbidden energy gap. Thus we expect a difference in the absorption spectra, particularly at the fundamental absorption edge, between samples of the same basic material but for which one is crystalline and the other amorphous. From the standpoint of electron motion a mobility or pseudo gap is defined and is larger for amorphous materials than for crystals having the same chemical compositions. The equivalent gaps from the optical standpoint will depend on the form of excitation process taking place in the material when photons are absorbed. Thus a variety of possibilities will arise, depending on whether the transitions involved are direct or indirect. The theory of such transitions has been presented by Davis and Mott [23] and they take account of the localized electronic states in the mobility or pseudo-gap. In amorphous materials the K-conservation rule breaks down and thus K is not a good quantum number. If we assume that the matrix element for optical transitions has the same value whether or not the initial and final states are localized, and also that the densities of states at the band edges are linear functions of the energy, then we may deduce $\alpha$. The equation for optical absorption coefficient $\alpha$ at a given angular frequency $\omega$ then reduces to the form [23]:
\[ \alpha(\omega) = \frac{A(h\omega - E_{opt})^2}{h\omega} \]  

where \( A \) is a constant equal to \((4\pi/(c)) \times (\sigma_o)/(n_o)\Delta E\) and \( \sigma_o \) is the electrical conductivity at absolute zero, \( \Delta E \) the width of the tail of localized states in the normally forbidden band gap, \( n_o \) the refractive index and \( E_{opt} \) is the optical energy gap. Thus the optical energy gap can be determined from the extrapolation to \((\alpha h\omega)^{1/2} = 0\) of a plot of \((\alpha h\omega)^{1/2} \) vs \((h\omega)\).

### 3.4.1.1 Direct and Indirect Optical Transitions

The energy gap in a semiconductor is responsible for the fundamental optical absorption edge. The fundamental absorption process is one in which a photon is absorbed and an electron is excited from an occupied valence band state to an unoccupied conduction band state. If the photon energy \((h\omega)\) is less than the gap energy, such processes are impossible and the photon will not be absorbed. That is, the semiconductor is transparent to electromagnetic radiation for which \((h\omega < E_{gap})\). For \((h\omega > E_{gap})\) on the other hand, such inter band absorption processes are possible. In high quality semiconductor crystals at low temperatures, the density of states rises sharply at the band edge and consequently the absorption rises very rapidly when the photon energy reaches the gap energy. Observation of the optical absorption edge is the most common means of measuring the energy gap in semiconductors. Now considering an inter band electronic transition, we see that such transitions must be essentially vertical on the band diagram. This is required if the process is to conserve momentum.

\[ hk_{\text{photon}} = h\Delta k_{\text{electron}} \]  

This condition is readily satisfied if the maximum of the valency band (VB) and the minimum of the conduction band (CB) occur at the same \( k \)-value (often \( k = 0 \) as in the figure 3.10. If the band structure has this feature, the gap is said to be direct as in figure 3.10 (a). Such semiconductors are suitable for optoelectronics applications. When the VB maximum and CB minimum do not occur at same \( k \)-value, the gap is said to be indirect gap Figure
3.10(b). In indirect transition, absorption over the band gap cannot conserve energy and momentum without the participation of another particle, usually a phonon. The process then corresponds to photon \( \rightarrow \) conduction electron plus phonon. Because of the participation of a third particle (the phonon), their transition probabilities are much lower than those of direct processes.

![Diagram showing direct and indirect band gap transitions.](image)

**Figure 3.10:** Schematic diagram showing direct and indirect band gap transitions.

The two step process corresponds to photon absorption to promote bound electrons in the valence band to the conduction band and with the emission or absorption of a phonon. The participation of the phonon in these absorption processes leads to lower transition probabilities and hence lower absorption coefficients compared to those of the direct interband transitions. Optical spectroscopy constitutes the most important approach to determining the band structures of semiconductors. Photo induced transitions can occur between different bands, which lead to the determination of the energy band gap or within a single band such as the free carrier absorption. Optical measurements can also be used to study lattice vibrations.

The transmission coefficient \( T \) and the reflection coefficient \( R \) are the two important quantities generally measured. For normal incidence they are given by [79]:

\[
T = \frac{(1 - R^2) \exp(-4\pi x/\lambda)}{1 - R^2 \exp(-8\pi x/\lambda)}
\]  

(3.134)

or
\[ T = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \]  

(3.135)

Where, \( \lambda \) is the wavelength, \( n \) the refractive index, \( k \) the absorption constant, and \( x \) the thickness of the sample. The absorption coefficient per unit length \( \alpha \) is given by [79];

\[ \alpha = \frac{4 \pi k}{\lambda} \]  

(3.136)

By analyzing the transmittance or reflectance with wavelength data at normal incidence, or by making observations of \( R \) or \( T \) for different angles of incidence, both \( n \) and \( k \) can be obtained and related to transition energy between bands. Near the absorption edge the absorption coefficient \( \alpha \) can be expressed as:

\[ \alpha = \left( \frac{\hbar \omega}{E_g} \right)^\gamma \]  

(3.137)

Where \((\hbar \omega)\) is the photon energy, \((E_g)\) is the band gap, and \(\gamma\) is a constant. In the one electron approximation \(\gamma - 1/(2) & (3)/(2)\) for allowed direct transitions and forbidden direct transitions, respectively.

### 3.4.1.2 Absorption Edge and Urbach Energy

The study of optical absorption and particularly the absorption edge is a useful method for investigating optically induced transitions and the band structure of crystalline semiconductors and non crystalline materials. The principle of this technique is the absorption of photons with energies greater than the band gap. The absorption edge in many disordered materials follows the Urbach rule given by:

\[ \alpha(\omega) = e \times p \left( \frac{\hbar \omega}{E_U} \right) \]  

(3.138)

Where \(\alpha(\omega)\) is the absorption coefficient at an angular frequency of \(\omega = 2\pi v\), and \(E_U\) is called 'Urbach energy'. Since;

\[ \ln \alpha(\omega) = C + \left( \frac{\hbar \omega}{E_U} \right) \]  

(3.139)

then

\[ E_U = \left[ \frac{d}{d \left( \frac{\hbar \omega}{\ln \alpha} \right)} \right]^{-1} \]  

(3.140)
Since the Urbach energy is determined indirectly by plotting the logarithm of the absorption coefficient as a function of energy. The reciprocal of the slope from this graph gives the Urbach Energy.

### 3.4.1.3 Optical Band Gap and Physical Models

OJL [106] model has been employed to describe inter-band transition in amorphous materials, while Drude model has been used to account for the movement of free electrons. OJL inter-band model gives expressions for the density of states for the optical transition from the valence band to conduction band. Parabolic bands are assumed with tail states exponentially decaying into the band gap. The original parameters of OJL density of states model are energy, \( E_v \) and \( E_c \), and the ‘damping constants’ of the valence and conduction bands, \( \gamma_v \) and \( \gamma_c \), respectively. Also included are the masses of the valence and conduction bands, \( m_v \) and \( m_c \). The expressions:

\[
E_{M,V} = E_v - \frac{1}{2} \gamma_v \quad \text{and} \quad E_{M,C} = E_c + \frac{1}{2} \gamma_c
\]  

(3.141)

denote the mobility edges of the valence and conduction bands respectively. The mobility gap \( E_m \) in the OJL is therefore given by:

\[
E_c + \frac{1}{2} \gamma_c - \left( E_v - \frac{1}{2} \gamma_v \right) = E_o
\]  

(3.142)

The band gap energy, \( E_g \), is the difference between \( E_c \) and \( E_v \) values, i.e. the band gap in the case of no disorder, which is realized when both \( E_c \) and \( E_v \) are zero. This gap energy is different from the mobility band gap which depends on the values of the disorder parameters \( E_c \) and \( E_v \). The optical band gap energy is simulated by SCOUT software. The energy gap (or band gap) \( E_g \), and its structure as a function of the wave vector are key characteristics of the semiconductor material and of fundamental importance to the operation of the solar cell (see Figure 3.11).
The principal features of interest are the temperature variation of the band gap energy $E_g$, and the magnitude of wave vector associated with low-energy transitions. To free an electron, the energy of a photon must be greater than the band gap energy. However, photons with more energy than the band gap energy will expend that extra amount as heat when freeing electrons. So, it’s important for a solar cell to be "tuned" – through slight modifications to the silicon’s crystal structure – to optimize the photon energy. A key to obtaining an efficient solar cell is to convert as much sunlight as possible into electricity. Crystalline silicon has indirect band gap energy of 1.1eV. The band gap energies of other effective photovoltaic semiconductors range from 1.0 to 1.6 eV. In this range, electrons can be freed without creating extra heat. The photon energy of light varies according to the different wavelengths of the light. The entire spectrum of sunlight, from infrared to ultraviolet, covers a range of about 0.5 eV to about 2.9 eV. For example, red light has energy of about 1.7 eV, and blue light has energy of about 2.7 eV. Most solar cells cannot use about 55% of the energy of sunlight, because this energy is either below the band gap of the material or carries excess energy [28].

### 3.5 Structural Properties of Thin Films

Texture can be determined by various methods. Some of them allow a qualitative analysis of the texture; others are only quantitative. Among the quantitative techniques, the most widely used is X-ray diffraction using triple axis goniometers, followed by EBSD-method (electron backscatter diffraction) and Scanning Electron Microscopes (SEM). Qualitative analysis can
be done by Laue photography, simple X-ray diffraction or with the polarized microscope. Neutron and synchrotron high-energy X-ray diffraction allow access to textures of bulk material and in-situ analysis, whereas laboratory x-ray diffraction instruments are more appropriate for thin film textures. X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system.

X-Ray fluorescence (XRF) technique is generally non-destructive, multi-elemental, fast and cost effective. High energy photons (x-rays) displace inner shell electrons. Outer shell electrons then fall into the vacancy left by the displaced electron. In doing so, they emit light (fluoresce) equivalent to the energy difference between the two states. Since each element has electrons with more or less unique energy levels, the wavelength of light emitted is characteristic of the element and the intensity of light emitted is proportional to the elements concentration. There are two types of XRF spectrometers: wavelength dispersive and energy dispersive. Wavelength dispersive system uses a diffraction crystal to focus specific wavelengths onto a detector. Energy dispersive spectrometer focuses all the emitted x-rays onto an energy analyzing detector. While this is faster and less expensive, wavelength dispersive spectrometers are more sensitive and have higher resolution.

3.6 Characterization Methods

3.6.1 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis is a technique that is widely used to characterize a material’s properties as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. DMA is a very popular and powerful technique that measures the transitions in materials because it is sensitive to side chain or main chain motions and local
models in polymers. It characterizes the mechanical responses of materials by monitoring property changes with respect to temperature and/or frequency of oscillation. The technique separates the dynamic response of materials into two distinct parts: an elastic part (E') and a viscous damping component (E’’). Specifically in DMA a variable sinusoidal strain (\(\varepsilon\)) or stress (\(\sigma\)) is applied to a sample and the resultant sinusoidal stress or strain is measured. If the material being evaluated is purely elastic, the phase difference between the stress and strain is zero (i.e. stress and strain are in phase). The stress \(\sigma\) and the deformation (strain) \(\varepsilon\) are related through the Young modulus \(E\) as follows:

\[
\sigma = E\varepsilon
\]  

(3.143)

The modulus is often known as the rigidity and is a quantity that is a representative of the materials resistance to deformation. Its reciprocal is the compliance \(J\) given by;

\[
J = \frac{1}{\sigma} = \frac{1}{E\varepsilon}
\]  

(3.144)

If a material is purely viscous, the phase difference is 90°. However, most real-world materials including polymers are viscoelastic, both behave as elastic (Hookean) solid and viscous (Newtonian) liquid, such materials exhibit a phase difference between the extremes. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of fundamental material parameters, including storage and loss modulus, loss factor (\(\tan \delta\)), complex and dynamic viscosity, storage and loss compliance, transition temperatures, creep, and stress relaxation as well as related performance attributes such as rate of degree of cure, sound absorption impact resistance, and morphology. Dynamic mechanical analysis measures the viscoelastic properties using either transient or dynamic oscillatory tests. Transient tests include creep and stress relaxation. In a creep relaxation, a stress is applied on a sample and held constant while the deformation is measured versus time. After a short time, the stress is removed and the recovery is measured as a function of time. In a stress relaxation, a deformation is applied to the sample and held constant, and the degradation of the stress required in maintaining the deformation is measured as a function of
time. The sample is then released to an unstressed state, and its recovery is measured as a function of time. The dynamic oscillatory test is the most common, where a sinusoidal stress (or strain) is applied to a material and the resultant sinusoidal strain (or stress) is measured. Most DMA measurements are made using a single frequency and constant deformation (strain) amplitude while varying temperature.

3.6.1.1 Dynamic Mechanical Measurement

An alternative experimental procedure to creep and stress relaxation is to subject the specimen to an alternating strain and simultaneously measure the stress. For linear viscoelastic behavior, when the equilibrium is reached, the stress and strain varies sinusoidal, but the strain lags behind the stress. If stress $\sigma(t)$ is applied, then altered with time $t$, and angular frequency $\omega$, the governing equation is:

$$\sigma(t) = \sigma_o \sin \omega t$$  \hspace{1cm} (3.145)

where $\sigma_o$ is the amplitude, $\sigma$ is the stress, $\omega$ is the angular frequency and $t$ is the time. An ideal elastic body deformation instantly follows an applied stress, and consequently;

$$\epsilon(t) = \epsilon_o \sin \omega t$$  \hspace{1cm} (3.146)

where $\epsilon_o$ is the amplitude. Polymers are not ideal elastic bodies; they are viscoelastic materials. In such cases the deformation (strain) lags behind the applied stress as shown in Figure 3.12. With ideal viscoelastic bodies, the resulting phase angle $\delta$ in the corresponding vector diagram can be assumed to be constant, such that the deformation follows the above equation while the stress is given by:

$$\sigma(t) = \sigma_o \sin (\omega t + \delta)$$  \hspace{1cm} (3.147)

where $\delta$ is the phase angle, $\sigma_o$ is the amplitude, $\omega$ is the angular frequency and $t$ is the time. The stress vector can be considered to be the sum of two components. The second component;

$$\sigma' = \sigma_o \cos \delta$$  \hspace{1cm} (3.148)

is in phase with the deformation, the first component, on the other hand,

$$\sigma'' = \sigma_o \sin \delta$$

is out of phase. A modulus can be assigned to each of the components.
The real modulus or storage modulus, $E'$, measures the rigidity and resistance to deformation of the sample. It is related to the complex modulus of rigidity $E^*$ by:

$$E' = \frac{\sigma'}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} \cos \delta = E^* \cos \delta$$  \hspace{1cm} (3.149)

The imaginary, or loss modulus, $E''$, on the other hand, reflects the loss of useful mechanical energy through dissipation as heat:

$$E'' = \frac{\sigma''}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} \sin \delta = E^* \sin \delta$$  \hspace{1cm} (3.150)

Similarly, $E''$ is given by:

$$E'' = \frac{\sigma''}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} \sin \delta = E^* \sin \delta$$  \hspace{1cm} (3.151)

The loss factor spectra can be quantitatively described by a superposition of model function [52]:

$$E''(T) = \sum_{i=1}^{2} A_i \exp \left\{ -\frac{E_i}{kT} - \frac{T^2}{T_{m_i}} \left[ \frac{E_i}{k} \left( \frac{1}{T_{m_i}} - \frac{1}{T} \right) \right] \right\}$$  \hspace{1cm} (3.152)

In this model function $A$ is a constant, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $T_m$ temperature representing maximum loss modulus, $E$ is the activation energy and $i$ refers to different processes which contribute to the mechanical response. Introducing the complex variables, one may express the strain $\varepsilon$ and stress $\sigma$ as follows:

$$\varepsilon^* = \varepsilon_o \, e^{i\omega t} \quad \text{and} \quad \sigma^* = \sigma_o \, e^{i(\omega t + \delta)}$$  \hspace{1cm} (3.153)
The complex modulus $E^*$ may be then expressed as:

$$E^*(\omega) = E'(\omega) + iE''(\omega)$$

(3.154)

where: $i^2 = -1$ Instead of following the deformation (strain) produced by a given stress, the sample can be strained and the resulting stress can be measured. The complex compliance defined as:

$$J^* = \frac{1}{E^*}$$

(3.155)

is obtained in this case and the storage and loss compliance are correspondingly given by:

$$E' = \frac{J'}{J^2 + J'^2} \text{ and } E'' = \frac{J''}{J^2 + J'^2}$$

(3.156)

The complex dynamic shear modulus at frequency $\omega$, $E^*(\omega)$ expressed in pascal, is given by the ratio between the magnitude of the dynamic shear stress, $\tau(\omega)$, and the magnitude of the applied dynamic shear strain, $\varepsilon(\omega)$ as depicted in the following equation:

$$E^*(\omega) = \frac{\tau(\omega)}{\varepsilon(\omega)}$$

(3.157)

The loss factor, storage modulus and loss modulus vary with frequency of loading as shown in Figure 3.13 below. At low frequency the polymer is rubber like and has a low storage modulus, which is independent of frequency. At high frequency, the polymer is glassy and the storage modulus is again independent of frequency. In the intermediate region where the material behaves viscoelastically, the storage modulus increases with increasing frequency. As the frequency is increased it becomes more difficulty for the chains to respond to the applied forces and tend to remain in a frozen state. A frozen system stores more energy than a free system [45].
Figure 15  The complex modulus, $E^* = E' + iE''$, as a function of frequency

The loss modulus is zero both at low and at high frequencies where stress and strain are in phase for the rubbery and glassy phases. In the intermediate viscoelastic region, the loss modulus increases to a maximum value then decreases. If the mechanical force applied has a low frequency compared to the transition rates in the system, establishment of a thermal equilibrium is rapid and the system can always remain in equilibrium, hence we encounter quasistatic conditions and observe the full relaxation strength. On the other hand when the frequency of the applied force is large compared to the transition rates, equilibrium cannot be established and the system reacts to the average strain only, which is zero. Crossover from one regime to the other occurs at $\omega \tau \approx 1$ [45]. The phase angle, expressed as its sine or tangent, is an important parameter for describing the viscoelastic properties of a paving material. The complex, storage and loss moduli, and the phase angle are illustrated by the trigonometry of a right triangle, as shown in Figure 3.14.
It follows that the loss tangent can be calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli:

\[ \tan \delta = \frac{E''}{E'} = \frac{1}{\omega \tau} \]  \hspace{1cm} (3.158)

and that

\[ E^* = \sqrt{E'^2 + E''^2} \]  \hspace{1cm} (3.159)

where \( E^* \) is the ratio of the peak stress to the peak strain, and reflects the total stiffness. The in-phase component of \( E^* \), that is, the shear storage modulus, \( E' \), represents the part of the input energy which is stored (the elastic portion). The out-of-phase component of \( E^* \), that is, the shear loss modulus \( E'' \), represents viscous component of it. The complex dynamic shear viscosity \( \eta^* \) can be obtained from \( E^* \) divided by the frequency, while the dynamic viscosity is:

\[ \eta = \frac{E''}{\omega} \]  \hspace{1cm} (3.160)

### 3.6.1.2 DMA Measurement System

The DMA measurement system consists of:
• A drive motor that provides precise control of all stresses applied to the sample. The high resolution of the motor allows for reproducible force control. It supplies the sinusoidal deformation force to the material;

• Furnace, this controls the temperature of the system;

• The central core rod (drive shaft) and guidance system, which transfers all stresses (forces) from the drive motor to the clamps that hold the sample;

• Mechanically controlled displacement sensor, this is the one that accurately tracks any mechanical changes occurring in the sample due to changes in the temperature atmospheric conditions and time. It then detects changes in the systems resonance frequency and supplies electrical energy needed to maintain the preset amplitude. The amount of electrical energy supplied is a measure of damping properties of the material. Changes detected are then expressed in terms of current, which are then easily separated by a phase sensitive detector and hence the signals can be measured.

The DMA 2980 dynamic mechanical analyzer (TA instrument) (Figure 3.15) is based on a patent-pending design that optimizes the combination of these critical components. Specifically, the analyzer incorporates a noncontact direct drive motor to deliver reproducible forces (stresses) over a wide dynamic range of 0.001-18 N; an air bearing shaft support and guidance system to provide frictionless continuous travel over 25 mm from evaluating polymers at large oscillating amplitude (±0.5 – 10, 000µm); and optical encoder displacement sensor to provide high resolution of oscillation amplitude, which results in excellent modulus precision and $\tan\delta$ sensitivity (0.0001); and a bifilar- wound furnace complemented by a gas cooling accessory to allow a broad temperature range ($-150°C \rightarrow 600°C$) to be covered.
The DMA 2980 also features a variety of damping configuration to accommodate rigid bars, fibers, thin films and viscous liquids in bending, compression, shear, and tension modes of deformation.

### 3.6.2 X-ray Spectroscopy

X-ray spectroscopy is unarguably the most versatile and widely used means of characterizing materials of all forms. There are two general types of structural information that can be studied by X-ray spectroscopy: electronic structure (focused on valence and core electrons, which control the chemical and physical properties, among others) and geometric structure (which gives information about the locations of all or a set of atoms in a molecule at an atomic resolution). This method encompasses several spectroscopic techniques for determining the electronic and geometric structures of materials using X-ray excitation: X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), X-ray photoelectron spectroscopy (XPS) and X-ray Auger spectroscopy. Which type of X-ray spectroscopy is employed depends on whether the target information is electronic, geometric or refers to oxidation states: for instance, XAS (first developed by de Broglie) to probe empty states and the shapes of molecules or local structures, and XPS (first developed by Siegbahn) to investigate occupied electronic states. X-ray spectroscopy is thus a powerful and flexible
tool and an excellent complement to many structural analysis techniques such as UV-Vis, IR, NMR or Raman.

3.6.2.1 Typical Conditions of X-ray Measurements

In an X-ray diffraction measurement, a crystal is mounted on a goniometer and gradually rotated while being bombarded with X-rays, producing a diffraction pattern of regularly spaced spots known as reflections. The two-dimensional images taken at different rotations are converted into a three dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with the chemical data obtained for the sample. If single crystals of sufficient size cannot be obtained, various other X-ray methods, like fiber and powder diffraction, can be applied to record less detailed information.

3.6.2.2 X-ray Diffractogram

X-ray diffractograms are recorded for comparing the crystallinity of protaned polymer sample with that of the base sample. This is carried out by using X-ray diffractometer. From the plots of intensity versus $2\theta$, the crystallinity index of the sample is calculated by employing Manjunath et al.’s formula. According to this, the resolution of the peak $R$ is given by:

$$R = \frac{m_1 + m_2 + \ldots + m_{n-1}}{h_1 + h_2 + \ldots + h_n}$$

(3.161)

where $m_1, m_2$… are the heights of minima between two peaks and $h_1, h_2$… are the heights of peaks from the base line. From the resolution of the peak ($R$), the lateral order or the index of the crystallinity can be estimated.

3.6.2.3 Bragg’s law

An intuitive understanding of X-ray diffraction can be obtained from the Bragg model of diffraction. In this model, a given reflection is associated with a set of evenly spaced sheets running through the crystal, usually passing through the centers of the atoms of the crystal.
lattice. The orientation of a particular set of sheets is identified by its three Miller indices \((h, k, l)\), and let their spacing be noted by \(d\). William Lawrence Bragg proposed a model in which the incoming X-rays are scattered specularly (mirror-like) from each plane; from that assumption, X-rays scattered from adjacent planes will combine constructively (constructive interference) when the angle \(\theta\) between the plane and the X-ray results in a path-length difference that is an integer multiple \(n\) of the X-ray wavelength \(\lambda\).

\[
2d \sin \theta = n \lambda \tag{3.162}
\]

A reflection is said to be indexed when its Miller indices (or, more correctly, its reciprocal lattice vector components) have been identified from the known wavelength and the scattering angle \(2\theta\). Such indexing gives the unit-cell parameters, the lengths and angles of the unit-cell, as well as its space group. Since Bragg’s law does not interpret the relative intensities of the reflections, however, it is generally inadequate to solve for the arrangement of atoms within the unit-cell; for that, a Fourier transform method must be carried out.

### 3.6.3 Fourier Transform Infra-Red (FTIR) Spectroscopy

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. Mid infrared spectroscopy (in the mid IR range, which runs from \(4000\text{cm}^{-1}\) to \(400\text{cm}^{-1}\)) has been widely employed to characterise various organic compounds. The spectroscopy of the coupled rotational and vibrational excitations is an exquisite probe for structural studies and also for the determination of the internal atomic motions of gas-phase molecules. This is carried out with the aid of vibrational spectroscopy and is conducted with the Fourier transform infrared (FTIR) spectrometer based on a scanning interferometer that modulates a broadband infrared source based on its optical frequency components.
3.6.3.1 The Sample Analysis Process

The normal instrumental process is as follows:

- **The Source**: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

- **The Interferometer**: The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

- **The Sample**: The beam enters the sample compartment where it is transmitted through, absorbed or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

- **The Detector**: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

- **The Computer**: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Schematic diagram of an FTIR spectrometer is as shown in Fig. 3.16a. The sample holder arrangement is comprised of a circular crystal and a solid press tip (Fig 3.16b). A small amount of the sample is placed on the top of the circular crystal to cover the crystal completely. The black tip is used to press the sample. After scanning, the data is collected in terms of transmittance and absorption as a function of wavenumbers. The ratio of the sample to reference intensity spectra gives the transmission spectrum of the sample. The absorption or transmission peaks of an infrared spectrum correspond to the frequencies of vibration between bonds of the atoms.
Films can be produced by either solvent casting or by melt casting. In solvent casting, the sample is dissolved in an appropriate solvent (the concentration depends on the required film thickness). A solvent needs to be chosen which not only dissolves the sample, but will also produce a uniform film. The solution is poured onto a leveled glass plate (such as a microscope slide) or a metal plate and spread to uniform thickness. The solvent may then be evaporated in an oven and, once dry, the film can be stripped from the plate. However, care must be taken as the heating of samples may cause degradation. Alternatively, it is possible to cast a film straight onto the infrared window to be used. Solid samples which melt at relatively low temperatures without decomposition can be prepared by melt casting. A film is prepared by ‘hot-pressing’ the sample in a hydraulic press between heated metal plates.

3.6.4 Atomic Force Microscopy (AFM)

AFM is a key instrument for evaluating polymers at small length scales. Its spatial resolution enables visualization of sub-micrometer and sub-nanometer polymer morphology. It can contribute much more information about polymers besides simple topographic morphology, including probing molecular-level forces; mapping mechanical, thermal, and electrical properties; and assessing solvent and thermal effects in near real time [74]. Force spectroscopy has proved to be one of the most promising techniques using AFM. In an AFM experiment, a tip is attached to a flexible cantilever, which is moved across the sample.
surface. During this procedure, the surface morphology is measured with a nanometer resolution. Upon contact with the sample surface, the tip experiences a force, which is monitored as a change in the deflection of the cantilever [30]. This force is a function of tip-sample separation and the material properties of the tip and the sample and can be used to investigate other characteristics of the sample, the tip, or the medium in-between [41].

The procedure of an AFM force measurement is schematically depicted in Figure 3.6.6 and goes as follows: the tip attached to a cantilever spring is moved towards the sample in a normal direction. During this movement the vertical position of the tip and the deflection of the cantilever are recorded and converted to force-versus-distance curves, briefly called force curves [87]. The AFM probe has a very sharp tip, often less than 100Å in diameter, at the end of a small cantilever beam. The probe is attached to a piezoelectric scanner tube, which scans the probe across a selected area of the sample surface. Inter-atomic forces between the probe tip and the sample surface cause the cantilever to deflect as the sample’s surface topography (or other properties) changes. A laser light reflected from the back of the cantilever measures the deflection of the cantilever. This information is fed back to a computer, which generates a map of topography and/or other properties of interest. Areas as large as 100µm square to less than 100nm square can be imaged.

Tapping mode with phase imaging has become a valuable technique for polymer characterization for it’s a simple and popular means of obtaining qualitative material property. Phase contrast in intermittent-contact atomic force microscopy (IC AFM) reveals in-plane structural and mechanical properties of polymer monolayer.
The phase shifts depend on the orientation of the cantilever relative to the in-plane polymer backbone orientation. These phase shifts arise from energy dissipation due to in-plane dissipative forces which in turn are due to tip motion parallel to the surface. Phase shifts between the drive and the response in IC AFM indicate energy loss. In IC AFM, the cantilever’s base is driven with small amplitude, resulting in a larger tip oscillation. Cleveland et al.[17] have shown that, if the tip’s motion is nearly sinusoidal, the power $P$ dissipated due to the tip-sample interaction is well described by:

$$P_{\text{tip}} = \frac{1}{2} \frac{k A^2}{Q} \omega_o \left( \frac{A_o}{A} \sin \phi - 1 \right)$$  \hspace{1cm} (3.162)

where $k$ is the cantilever stiffness, $A_0$ is the free amplitude of oscillation, $A$ is the amplitude during imaging, $\omega_o$ is the angular frequency of the cantilever, $Q$ is the quality factor of the free cantilever, and $\phi$ is the phase of the oscillation relative to the drive. From this equation, the phase shifts indicate variations in the dissipated power and is smallest when the striations are parallel to the long axis of the cantilever.

### 3.6.5 UV VIS Spectroscopy

The optical absorption is described by an absorption coefficient $\alpha$ which can be derived from transmission or absorption measurements.

If $I_0$ is an incident light intensity, $I$ is the transmitted light intensity and $R$ is the reflectivity, then the transmission, $T = I/I_0$ can be written as (neglecting interference):

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}$$  \hspace{1cm} (3.163)

where $t$ is the thickness of the material. For large $\alpha t$, the expression reduces to:

$$T = (1-R)^2 \exp(-\alpha t)$$  \hspace{1cm} (3.164)

and in the absence of reflection, it further reduces:

$$I = I_o \exp(-\alpha t)$$  \hspace{1cm} (3.165)

In terms of absorbance $A$, we have;
\[ \alpha = \frac{2.303A}{t} \]  
(3.167)

The relationship between the absorption coefficient and the incident photon energy in a direct transition is given by;

\[ \alpha h \nu = A (h \nu - E_g)^n \]  
(3.168)

where \( A \) is a constant, \( E_g \) is the optical energy gap. The value of \( n \) is \( \frac{1}{2} \) or \( \frac{3}{2} \) for direct allowed and direct forbidden transitions respectively and \( n = 2 \) represents the indirect allowed transition energy gap. Thus, a plot of \( (\alpha h \nu)^2 \) versus \( h \nu \) allows us to determine the energy gap [51, 10]. Alternatively, from the relation;

\[ E_g^* = \frac{hc}{\lambda_c} \]  
(3.169)

where \( \lambda_c \) = cut-off wavelength absorbed by the sample, and \( c \) is the speed of light. The cut-off wavelength may be estimated from the intersection of the tangent line of the peak is with the wavelength axis. This wavelength is used to determine the band gap \( E_g \) of the material.

### 3.6.6 Dielectric Spectroscopy

Dielectric spectroscopy, which is based on the measurement of current and voltage (amplitude and phase AC system) is widely used to study the dielectric properties of polymers (i.e dielectric loss, dielectric storage and loss factor). The permittivity expresses the ability of a material to polarize in response to an applied field. It is the ratio of the permittivity of the dielectric to the permittivity of a vacuum. Physically it means the greater the polarization developed by a material in an applied field of given strength, the greater the...
dielectric constant will be. Under an alternative (ac) sinusoidal supplied voltage, the real part of permittivity and loss factor is computed using the following equations:

\[
\varepsilon' = \frac{C_p d}{\varepsilon_o A} \quad (3.175)
\]

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{R_p C_p \omega} \quad (3.171)
\]

where \( \varepsilon_o \) is the vacuum permittivity, \( d \) the thickness of the sample polymer, \( A \) the electrode area and \( \omega \) the angular frequency, \( C_p \) and \( R_p \) are the capacitance and the resistance measurements. The static (dc) conductivity can be derived from the (ac) conductivity measurements at low frequency using the relation [96];

\[
\sigma_{ac}(\omega) = \omega \varepsilon_o \varepsilon''(\omega) = \sigma_{dc} + K \omega^n \quad (3.172)
\]

where \( K \) is an empirical parameter and \( n \) represents the high frequency slope of the (ac) conductivity from 0 to 1. The dielectric permittivity of a material is defined as the ratio of the permittivity of the material (\( \varepsilon \)) to that of a vacuum (\( \varepsilon_o \)) and may be expressed as follows:

\[
\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} \quad (3.173)
\]

It changes with frequency, temperature, orientation, pressure and molecular structure of the materials. The dielectric permittivity studies are carried out on polymer samples (Bulk and Thin films) using a home-made four probe dielectric cell and an impedance analyser. The capacitance of the sample is calculated by using parallel plate capacitance method and is given by;

\[
c = \frac{\varepsilon_o \varepsilon_r A}{d} \quad (3.174)
\]

Where \( \varepsilon_o \) is the permittivity of air, \( \varepsilon_r \) the dielectric permittivity of the material between the parallel plates, \( A \) the area of the sample and \( d \) is thickness of the sample. By knowing thickness and area of the sample, the dielectric constant is calculated. The AC conductivity of the these samples are then evaluated by using the relation;

\[
\sigma_{ac} = 2\pi f \varepsilon_o \varepsilon_r \tan \delta \quad (3.175)
\]
Here $f$ is the frequency of the applied field and $\tan\delta$ is the loss factor. The measurement of permittivity with frequency is automated with the help of package based on graphical program called Lab VIEW.

### 3.6.6.1 Theory of Dielectric Properties in Polymer

Quantitative treatment of a dielectric in an electric field can be summarized using Clausius–Mossotti equation;

$$P = \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \times \frac{M}{\rho} = \frac{N_A \alpha}{3\varepsilon_o}$$  \hspace{1cm} (3.176)

where $P$ is the molar polarization, $\varepsilon_r$ is the relative permittivity, $\varepsilon_o$ is the free space permittivity, $M$ is molar weight of a repeat unit, $\rho$ is density, $\alpha$ is polarization and $N_A$ is the Avogadro constant. This equation shows that dielectric constant is dependent on polarizability and free volume of the constituents’ element present in the materials. The relation between polarizability with the permittivity of the dielectric material can be shown as in the following equation;

$$\varepsilon_r = 1 + \frac{N \alpha}{\varepsilon_o}$$  \hspace{1cm} (3.177)

It shows that relative permittivity is the ratio of total permittivity of one mole of material with that in vacuum. The dependency of free volume on relative permittivity thus originates from the volume involved in one mole of the material.

### 3.6.6.2 Relaxation and Dielectric Loss

Relative permittivity can be express in complex form as in the equation below:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$  \hspace{1cm} (3.178)

It consists of the real part which is dielectric constant and the imaginary part which is the dielectric loss. The ratio between the dielectric loss with the dielectric constant is quantified as $\tan\delta$ i.e.:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (3.179)
Dielectric loss result from the inability of polarization process in a molecule to follow the rate of change of the oscillating applied electric field. This arise from the relaxation time ($\tau$) in a polymer which is the time taken for the dipoles to return to its original random orientation. It does not occur instantaneously but the polarization diminished exponentially. If the relaxation time is smaller or comparable to the rate of oscillating electric field, then there would be no or minimum loss. However when the rate of electric field oscillates well faster than the relaxation time, the polarization cannot follow the oscillating frequency resulting in the energy absorption and dissipation.
4 EXPERIMENTAL METHODS

4.1 Sample Collection
The majority of the research work for the project was carried out along the Kenyan Coast (Appendix 2). Samples of squid gladius (SG) were collected from the south coast areas of Ukunda and Likoni in Kwale County, Mombasa and Changamwe in Mombasa County, Kilifi, Takaungu and Malindi in Kilifi County. They were chosen specifically because of their abundant supply of marine wastes and also due to their contrasting environmental conditions and geographical locations.

4.2 Extraction of Chitosan
The extraction process is summarized in the Figure 4.1 below and involves the following processes;

![Figure 4.1: Summary of the process of chitosan extraction](image)

4.2.1 Pre-treatment Stage
The SG samples collected were washed with water and then soaked in a mild sodium hydroxide solution, (1% w/v NaOH) to remove non-chitin rich organic material. In the pretreatment step, a small amount of proteins may also be removed, aiding in the removal of proteins in a later deproteination step. This was followed by washing and air drying at room
temperature for two days. The dry SG were then pulverized into powder using a mortar and pestle and then sieved with a 1.5mm sieve to obtain the squid gladius powder (SGP).

4.2.2 Deproteination

The deproteination step was done by putting the SGP in a mild sodium hydroxide solution of 5% w/v NaOH at 70° C at a ratio of 1:10 w/v overnight. The resulting chitin was filtered and washed with distilled water until neutral pH then dried in a hot air oven at 60° C for six hours and then weighed.

4.2.3 Deacetylation

The dry chitin powder obtained was refluxed in concentrated sodium hydroxide solution of 50% NaOH at a temperature of 100°C for six hours in the ratio 1:10 w/v. The resulting chitosan was washed thoroughly with de ionised water until neutral pH, then acetone and dried in hot air oven at 60°C for 8 hours and then weighed. The dry chitosan powder (CP) was then stored in a desiccator.

4.3 Chitosan Film Preparations

4.3.1 Preparation of Chitosan Thin Films by Solution Casting Method

Two different Chitosan film samples were made. The first one (sample A) of 0.5% concentration was made by dissolving 0.5g of chitosan powder in a 100ml of 1 % aqueous acetic acid solution with subsequent stirring to promote dissolution. The other (sample B) of 1% concentration was prepared by dissolving 1g of chitosan powder in a 100ml of 1% aqueous acetic acid. The obtained chitosan-acetic acid solutions were then filtered to remove insoluble residues. Plastic petri dishes were cleaned in soap water to eliminate any possible impurity, rinsed in distilled water then dried in hot air oven. Chitosan Films were prepared by pouring 10ml of the obtained solution into the cleaned petri dishes on a flat bench and ensuring that the solution evenly covers the whole base (Figure 4.2) [110, 88]. The solution was then allowed to evaporate naturally at room temperature for 72 hours. The resulting
chitosan films were gently detached from the petri dishes, their thicknesses measured using a digital micrometer screw gauge and then stored in a desiccator.

Figure 4.2: Solution casting method

4.3.2 Preparation of Chitosan Film (CF) by Drop Casting Method

Some other chitosan films (sample C) were prepared by the drop casting method [113]. In this method, the filtered chitosan-acetic acid (CAcOH) solution was put in a dropper and then releasing two drops on a leveled cleaned glass plate/slides (Figure 4.3) [113, 91, 11]. To ensure uniform thickness, the drops were smeared on the slides by rolling a glass rod once. The slides were then kept in a dust free area for drying at room temperature for 12h.

Figure 4.3: Drop casting Method showing the steps in preparing chitosan thin films

4.4 Sample Characterization

4.4.1 Dynamic Mechanical Analysis

Dynamic mechanical measurements were employed to investigate relaxation events and also to the study of the viscoelastic response of the chitosan film samples. Kinetic parameters such as activation energy, pre-exponential factor and reaction order, give a quantitative measure of thermal stability of a material. Normally at a lower temperature, other relaxation
processes can be observed for polymeric materials. The \( \beta \) relaxation is normally attributed to polymer backbone conformation reorganization. The DMA equipment (TA instruments DMA 2980) was calibrated according to the manufacturers’ recommended procedures. DMA measurements were conducted at a heating rate of 5\(^\circ\)C/min, testing temperature ranging from 25 – 200\(^\circ\)C and a frequency of 1 Hz. The dimensions of the testing sample were; thickness 0.07 mm, width 9.44 mm and length 15.21 mm. The loss and storage moduli were recorded in a DMA multi-frequency single cantilever mode system. The storage and loss moduli were measured in the frequency range 0.1-30 Hz.

![Figure 4.4: Front view of a single cantilever showing the sample position and the movable clamp](image)

The temperature range was from 298 to 375 K in steps of 2 K after every frequency sweep. The sample was clamped as shown in Figure 4.4. It took about 120 minutes to run a measurement.

### 4.4.2 Wide angle X-ray diffraction (WAXRD)

The crystallinity of the material was analyzed by Wide-angle X-ray diffraction (WAXRD) on a STOE (Darmstadt, Germany, STADI-P) diffractometer found at the Freiburg Materials Centre (FMF) which employs \( Cu-K_\alpha \) x-ray radiation of wavelength \( \lambda = 1.5418\text{Å} \) between a 2\( \theta \) angle of 5\(^\circ\) – 40\(^\circ\) at 40 kV. The films were adhered to glass slides before placing them to the sample chamber.
4.4.3 Fourier Transforms Infrared (FTIR) Spectroscopy

FTIR spectroscopy provides information through band properties, frequencies and intensities, and can therefore be used to identify species and predict chemical processes. For this research, formation of the N-acetyl bond was determined by FTIR spectroscopy. The samples were prepared by grinding the dry SG powder with powdered KBr, in the ratio of 1:5 and then compressed to form discs/pellets. The FTIR spectra were measured in the transmission mode in the range 400–4000 cm\(^{-1}\) using Perkin–Elmer 2000 spectrophotometer. The DDA of the samples were calculated from the IR spectra following the method of [47].

4.4.4 Nuclear Magnetic Resonance (NMR)

H-NMR spectroscopy was used for the quantitative determination of the degree of deacetylation (DDA) of chitosan. This method is also particularity useful for studying the macromolecular structure and for quick identification of impurities sometimes present in a biomaterial. The SGP was treated in 45% NaOH solution for 3 h at 90°C and then washed to neutral and dried. This process was repeated twice and white chitosan was obtained. Chitosan solutions were prepared by stirring at room temperature 30 mg of dry chitosan in a solution composed of 4.9 ml of 2% Deuterium oxide (\(D_2O\)) and 0.1 ml of Deuterium Chloride (DCl) and waiting for about one hour to ensure complete dissolution of the polymer. The experiments were run under a static magnetic field of 9.4T at 343 K (70°C), the temperature at which the solvent peak does not interfere with any of chitosan’s peaks and a better resolution of the signals is after dissolution of the polymer.

The experiments were run under a static magnetic field of 9.4T at 343 K (70°C), the temperature at which the solvent peak does not interfere with any of chitosan’s peaks and a better resolution of the signals is after dissolution. Approximately 0.7 ml of the chitosan solution was transferred to a 5 mm NMR tube. The sample tube was inserted in the magnet and allowed to reach thermal equilibrium by waiting 10 minutes before performing the experiment. \(^1H\) and \(^13C\) NMR measurements were carried out with Bruker DSX 300 spectrometer at the Freiburg Materials Centre (FMF), Germany and on a JEOL JNM-GX400
NMR spectrometer. The H NMR experiment for DDA determination was a single pulse sequence with pre-saturation of the solvent. A $90^\circ C$ pulse corresponding to a pulse width of $11\mu s$ was used. The delay before the application of the pulse was 6s and the acquisition time was 2 s for a total relaxation cycle of 8s between each transient.

### 4.4.5 Atomic Force Microscopy (AFM)

AFM technique was used to probe and map the surface and sub-surface structure of the chitosan films. Measurements were performed on dry film samples under ambient atmospheric conditions. Silicon cantilever with integrated pyramidal tip was used to image the film surface topography. A topographic image of the sample is obtained by plotting the deflection of the cantilever versus its position on the sample.

![Figure 4.5: Schematic depiction of AFM feedback loop of an AFM analyzer](image)

This height is controlled by a feedback loop, which maintains a constant force between tip and sample (Figure 4.5). The membrane surface was imaged in tapping mode so as to probe information related to surface features of the films.

### 4.5 Measurements

#### 4.5.1 UV VIS Spectroscopy

Optical absorption spectra were recorded with a Schimadzu UV-VIS spectrophotometer (model: UV mini-1800) within the wavelength range of 200–800 nm at room temperature as shown in the Figure 4.6.
4.5.2 Electrical Measurement

The resistivity and conductivity of the material was determined from the I-V characteristics of the materials by the standard four point probe measurements made up of four points - probes that touch the surface of the film. A current $I$ is passed through the outer two probes 1 and 2, while a potential difference $V$ is measured between the inner two probes 3 and 4 (Figure 4.7a) by means of the Keithley Source Meter 2400 model (Figure 4.7b).

When an electric field $E$ is applied to a semiconductor material, an electric current will flow. The current density $J$ and the electric field $E$ are given by the equations:

$$J = \frac{\sigma}{E} = \frac{I}{A} \quad \text{(4.1)}$$

$$E = \frac{V}{L} \quad \text{(4.2)}$$
where I is current, A is area, L is length, $\sigma$ is the electrical conductivity of the film. When a rectangular-shaped film with dimensions $l \times w \times d$ (where $l$ is the length, $w$ the width and $d$ the thickness of this rectangle) is considered, the resistance is given by:

$$R = \frac{\rho l}{w d}$$

(4.3)

For a square film, $l = w$, and the equation reduces to:

$$R = \frac{\rho}{d} = R_s$$

(4.4)

The quantity $R_s$ ($\Omega/m^2$) is known as the sheet resistance of one square of the film that is independent of the size of the square. For a current $I$ and potential $V$ measured between the inner probes, the Surface/Sheet resistivity is given by:

$$\rho_s = \frac{V}{I} 2\pi x$$

(4.5)

where $x$ is the distance between the probes. If the material is in the form of an infinitely thin film resting on an insulating support then this equation can be written as:

$$\rho_s = \frac{V \pi d}{I \ln 2}$$

(4.6)

or

$$\frac{\rho_s}{d} = R_s = 4.53 \frac{V}{I}$$

(4.7)

### 4.5.3 Refractive Index Measurement

A coloured piece of Manila paper with a faint cross mark was placed on a white sheet of paper on top of the table and focused using a travelling microscope (Figure 4.8a). The reading from the microscope scale was noted as ($d_1$). The chitosan thin film was then placed on top of the coloured sheet in the above set up and again focusing the mark on the writing viewed through the film. The reading from the microscope scale was noted as ($d_2$). Finally the coloured piece of Manila paper was placed on top of the film and the mark focused. The reading from the microscope scale was again noted as ($d_3$).
4.5.3.1 Alternatively

The reading of the microscope was set to 0.000mm and the length of the coloured piece of manila was measured while on the white sheet of paper (Figure 4.8b). The same length was again determined while the coloured piece of manila sheet was viewed under the film as shown by the illustration diagrams below (Figure 4.8c). A second trial was done to determine the accuracy of the measures.

4.5.4 Dielectric Measurement

Dielectric spectroscopy was used to study the dielectric properties (dielectric loss $\varepsilon''$ and loss factor (tan $\delta$) of the polymers material as a function of temperature and frequency. Measurements of the real part of the permittivity and the loss factor for polymer samples were performed with a Hewlett-Packard impedance analyzer (Figure 4.9) for the frequency range $10^3$Hz to 1 MHz. In this setup, two electrodes are configured with a test fixture sandwiching the dielectric material.
Figure 4.9: A photograph of the dielectric test fixture with impedance analyzer

In this set up, a sinusoidal field is applied to the sample and the resulting current is detected and expressed in terms of the complex admittance, the real and imaginary parts. The real part of the admittance is proportional to the current component that is in phase with voltage, while the imaginary part is 90° out of phase with the field (Figure 4.9). These two components can be separated easily by a phase-sensitive detector and hence the admittance components can be measured. By this digital integration technique, the signal is analyzed using an online Fourier analysis.

Figure 4.10: A schematic diagram of the frequency response analyser Solartron- lumberger

FRA 1260 and the Chelsea - Dielectric -Interface
5 RESULTS AND DISCUSSION

5.1 Mechanical Properties

5.1.1 Effects of Temperature, Concentration and Frequency on the Relaxation Processes

To observe the effects of factors on relaxation processes, graphs of storage modulus, loss modulus and loss factor against temperature at various frequencies and concentration were plotted as shown below.

![Figure 5.1: Effects of Temperature, Concentration and Frequency on the Relaxation Processes](image)

From Figures 5.1a and 5.1b, we see the first transition marked by tan delta peaks for the films ranging between 30°C - 50°C which generally seem to increase with frequency and chitosan concentration. This is the β-relaxation which normally occurs at a lower temperature and is assigned to the local side-chain movement of the polymer. This is in agreement with values obtained from literature where chitosan films is reported to exhibit two tan δ peaks with one at around 30 –50°C. According to Mucha and Pawlak [78], these peaks are attributed to relaxation processes.
Figure 5.2: Graphs showing the variations (a) of Loss factor and (b) Loss modulus with temperature for different loading times for Ch

Another transition can be seen in Figure 5.2a between 125 -150°C which is the glass transition ($T_g$) which also shifts with frequency. This is confirmed by the peak of the loss modulus plot in Figure 5.2b. The figure shows that $\alpha$-process (loss modulus peaks) shifts to higher temperature with increasing frequency and this indicates a true relaxation process. This shift can be attributed to the fact that at low frequency, almost all the chains are able to follow movement of the oscillations.

Figure 5.3: Graphs showing the variation of Storage modulus with temperature for various frequencies and loading time for Ch
At higher frequency however, it becomes very difficult for all the chains to follow the movement of the oscillations. This can be explained by the fact that when the timescale of molecular motion coincides with that of mechanical deformation, each oscillation is converted into the maximum-possible internal friction and nonelastic deformation. The loss modulus, which is a measure of this dissipated energy, also reaches a maximum. Toffey and Glasser[6] noticed \( \alpha \)-relaxation between 60 and 94°C for ionic complexes of chitosan. The temperatures of relaxations increase for amidized chitosan derivatives [6].

There are some ranges of \( T_g \) values reported by other researches mainly due to the difference in sample and instrumental methods. For example, the \( T_g \) of chitosan is reported to be about 150°C by Kakizaki et al 1988 and 141.2°C by Nelly et al, 2005. Ratto et al [50] reported glass transition temperature at 30° C, Lazaridou and Biliaderis 2002 found \( T_g \) ranging from \(-23° - 67°C\) as per the water content in them. This indicates plasticizing effect of water in both the above cases. Whereas Sakurai [66] reported \( T_g \) of chitosan at 203° C. Two other transitions were observed at 280 and 321°C associated with a partial and total decomposition of the chitosan. Thus knowing the temperature at which the two transitions occur can give us an insight of operating temperature range of the biomaterial, in this case our material has an operation temperature range of 50°C - 120°C .

Figure 5.3 shows plots of the storage modulus against temperature for different frequencies of the samples. The storage modulus decreased gradually with temperature which shows that a transition takes place within the 120 - 200 temperature range. The value of \( E' \) tends to increase with frequency which is attributed to the lesser mobility of polymeric chains at higher frequency. That is, as frequency is increased it becomes difficult for the chain to respond to the applied forces and tend to remain in a frozen state. A frozen system stores more energy than a free system. It is observed that storage modulus of the material decreases with increasing temperature which is related to the increase in viscosity and polymer chain mobility of the matrix at higher temperatures.
5.1.2 Time-Temperature Dependence of Relaxation Time

The other important parameter which we investigated for our material was its activation energy since if the value of $E_a$ is greater than about $20kJmol^{-1}$, it is possible that processes that involve the breaking of primary chemical bonds may occur. The activation energy of these processes was determined by performing an Arrhenius plot of the data. As frequency is essentially a rate expression with units of $s^{-1}$, the natural log of frequency was plotted against temperature. The slope of this line is equal to negative the activation energy divided by the gas constant.

\[
\ln f = \ln f_o - \frac{E_a}{kT}
\]

Time-temperature dependence of mean relaxation time for the Ch films follows the Arrhenius law and VFT law as seen in the Figures 5.4 confirming that these are dynamic glass transition processes. The regression value, $R^2$ of 0.99 implies that the plotted points can be said to lie in a straight line. The red lines have been fitted using the Arrhenius model while the green and black curves are fitted with the VFT model with the fit parameters given in table 5.1 below. In the VFT relation we have;

Figure 5.4: Temperature dependence of the relaxation processes (a)1%Ch and (b)2% Ch
\[ \tau = \tau_0 \exp \left[ \frac{B}{T - T_0} \right] \]  
(5.1)

Where \( \tau_0 \) is the pre-exponent factor or the relaxation time in the absence of energy barrier. \( B \) is a constant, \( T \) is the absolute temperature and \( T_0 \) is the ideal Vogel temperature which is 50°C below \( T_g \). Since the relaxation time is inversely proportional to the frequency, we can have;

\[ \ln f = \ln f_0 - \frac{B}{T - T_0} \]  
(5.2)

In the Arrhenius relation we have;

\[ f = f_0 \exp \left[ \frac{E_a}{RT} \right] \]  
(5.3)

where \( f_0 \) is the pre-exponential or frequency factor and \( E_a \) is the activation energy, \( R \) is the gas constant which is 8.314J/Mol.K and \( T \) is the temperature in Kelvin. This can also be written as;

\[ \ln f = - \frac{E_a}{R} \left( \frac{1}{T} \right) + \ln f_0 \]  
(5.4)

The Arrhenius plot of the logarithm of frequency against the reciprocal of temperature is shown in figures 5.4a and 5.4b which gave the fit parameters as shown in the table 5.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arrhenius Model</th>
<th>VFT Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1% Ch</td>
<td>2% Ch</td>
</tr>
<tr>
<td>( f_0 )</td>
<td>5.44 ( \times 10^{37} )</td>
<td>2.4 ( \times 10^{33} )</td>
</tr>
<tr>
<td>( E_a )</td>
<td>272.7KJ/Mol</td>
<td>279.4KJ/Mol</td>
</tr>
<tr>
<td>( B )</td>
<td>588</td>
<td>540</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>289</td>
<td>255</td>
</tr>
<tr>
<td>( T_g )</td>
<td>239</td>
<td>205</td>
</tr>
</tbody>
</table>
The values of $E_a$ and $T_g$ obtained are slightly higher due to the high concentration of chitosan used. Dong et al, 2004. studied the glass transition of chitosan using different thermal analysis techniques and reported $T_g$ values between 140°C and 150°C. Peniche and Covas et al. 1993 found $E_a = 181$ kJ/mol and $E_a = 183–227$ kJ/mol, respectively.

To determine the viscoelastic properties, a plot of the storage modulus against the loss modulus was made (Figure 5.5). It gave a straight line graph whose slope gave the loss factor ($\tan \delta$), which is a measure of the mechanical damping or internal friction of the material under a load. The phase angle also tells us whether a material is purely elastic, purely viscous or is viscoelastic. From

$$E' = E^* \cos \delta$$

and

$$E'' = E^* \sin \delta$$

then

$$\tan \delta = \frac{E''}{E'}$$

and

$$E^* = \sqrt{E'^2 + E''^2}$$

where $E'$ is the storage modulus, $E''$ is the loss modulus, $E^*$ is the complex modulus and $\delta$ is the phase angle.

From Figure 5.5 there is a linear relationship between $E''$ and $E'$ giving the phase angle ($\delta$) as $4.8^\circ (\pi / 38\text{rad})$. The phase angle $\delta$ is the phase difference between the dynamic stress and the dynamic strain in a material subjected to a sinusoidal oscillation. If the material being evaluated is purely elastic, the phase difference between the stress and strain is zero (i.e. stress and strain are in phase) while if a material is purely viscous, the phase difference is $90^\circ$. However, the material under investigation is viscoelastic (i.e. it both behaves as elastic (Hookean) solid and viscous (Newtonian) liquid, since it exhibits a phase difference between $0 – 90^\circ$. 

The loss factor \((\tan \delta) = 0.084\) which is the ratio of loss modulus to storage modulus gives us a measure of the energy lost, expressed in terms of the recoverable energy, and represents mechanical damping or internal friction in a viscoelastic system. It is a measure of how well a material can get rid of energy and it tells us how good a material will be at absorbing energy. Thus the material under study has very low mechanical damping which means its rigidity and resistance to deformation is very high.

### 5.2 WXRD Spectra of Chitosan

X-ray spectroscopy was employed to determine the crystallinity of the chitosan films. Crystallinity is an important structural or physical characteristic influencing the various properties of the polymer. Figure 5.6 shows the X-ray diffraction pattern of chitosan.

The spectra showed distinct crystalline peaks at around \(2\theta = 10.5^\circ\) and \(2\theta = 19.8^\circ\) with minor reflections at \(2\theta = 6^\circ\) and \(35^\circ\). This is because of presence of plenty of \(-OH\) and \(-NH_2\) groups in the chitosan structure, which could form stronger inter and intramolecular hydrogen bonds and making the chitosan structure have certain regularity. Moreover, the peaks were less sharp indicating that the crystal structure of \(\beta\)-chitosan is less rigid and less stable or semi-crystalline. One can use Focher et al. equation [9] for determining the crystallinity index (CrI):
Crystalinity Index \( C_I \) = \( \left[ \frac{I_{110} - I_{am}}{I_{110}} \right] \times 100 \) \hspace{1cm} (5.5)

where \( I_{110} \) is the maximum intensity of the (110) peak at around \( 2\theta = 20^\circ \), and \( I_{am} \) is the amorphous diffraction at \( 2\theta = 10^\circ \).

From equation 5.9 and the values from Figure 5.6 we have \( C_I I = 66\% \).

Yin et al and Ogawa et al [63, 62, 114] reported that chitosan exhibited diverse structural types depending on the experimental conditions (kind and concentration of acid, temperature and salt preparation) used for the conversion of chitin into chitosan. Study of crystallinity index of chitosan samples showed that depending on the calculation method for the same sample different values of crystallinity index ranging from 0.4 to 0.8 can be obtained [38].

5.3 FTIR Spectra of Chitosan

Fourier transform infrared (FTIR) spectroscopy was used to identify the chemical structure and the identification of the functional groups present in chitosan macromolecules. Figures 5.7 and 5.8 show the FTIR spectra for both the squid pen and chitosan respectively.
The characteristic bands for the sample were observed in the infrared spectrum which showed strong and broad hydroxyl (O-H) stretch absorption at around 3400 cm\(^{-1}\) combined with the primary amine (NH). Presence of this band above 3000 cm\(^{-1}\) corresponds to the intermolecular crystal lattice of the sample as a result of hydrogen bonds and also a sign of the presence of water molecule in the structure. The peak at 2876 cm\(^{-1}\) was assigned to the aliphatic hydrocarbon (C-H) stretching. The double peak of frequencies 1680 – 1595 cm\(^{-1}\) corresponds to the acetylated amino group (NH\(_2\)-amine) absorption, with the amide (C=O) absorption occurring at 1680 cm\(^{-1}\) and the amide II (NH\(_2\) – NH\(_3\)^+\) bend of the amide occurring at 1595 cm\(^{-1}\) while the peak at 1383 cm\(^{-1}\) was assigned to the amide III (CH\(_3\)) bend.
The absorptions in the fingerprint region include a very weak peak at 663 cm\(^{-1}\) assigned to the hydroxyl bend and the peak at 1421 cm\(^{-1}\) is due to C-H bending for methyl and methylene (\(CH_2\)) group which is supported by the existence of the absorptions peaks at 630 cm\(^{-1}\) and 896 cm\(^{-1}\). The strong absorption appearing at the frequency of 1079 cm\(^{-1}\) was assigned to the asymmetric stretching of C-O vibration of the alcohols ethers or esters [47]. These results conform to the literature results by Singh et al [100], whose absorption bands were at 3429 cm\(^{-1}\) (O-H stretching overlapping the N-H stretching), 2921 cm\(^{-1}\) and 2867 cm\(^{-1}\) (C-H stretching), 1640 cm\(^{-1}\) (amide II band, C-O stretching of the acetyl group), 1592 cm\(^{-1}\) (amide II band, N-H stretching) 1485–1380 cm\(^{-1}\) (asymmetrical C-H bending of the \(CH_2\) group) and 1035 cm\(^{-1}\) (O bridge stretching) of the glucosamine residue.

### 5.4 NMR Spectra of Chitosan

The \(^1\)H – NMR spectrum of chitosan is shown in the Figure 5.9. The chemical shift of the internal standard appears at 5.35 parts per million (ppm). The chemical shift of the acetal proton (-CH) of the glucosamine overlaps the chemical shift of the internal standard and appears at 5.08 ppm. The –\(CH – NH_2\) proton appears at 3.66 ppm. The –\(CH – OH\),

![Figure 5.8: FTIR Spectra for Chitosan film 1% form 500 to 4000 cm\(^{-1}\)](image-url)

Figure 5.9: Proton NMR Spectra for CH 1%

Figure 5.10 shows a resonance H-1(D) at 5.33 ppm which is due to 2-amino-2-deoxy- D-glucopyranose. Peak H-1(A) at 5.05 ppm is as a result of (-CH) of glucosamine. (-CH-NH₂) proton is represented by a peak at 4.435 ppm.

Figure 5.10: A graph showing NMR Spectrum with labels for the Proton NMR

Chemical shift at 3.65 ppm corresponds to protons of – CH₂–OH. Chemical shifts from 3.5 - 3.95 ppm correspond to HOH2C-CH-, CH-CH₂- and -CH₂-OH protons of glycoside ring.
The peak at 2.45ppm is due to presence of the acetyl proton (H-Ac). The C-NMR chemical shifts for the chitosan are as shown in figure 5.11 with the shift at 26ppm attributed to the methyl group (CH$_3$).

![Figure 5.11: A graph showing NMR Spectrum with labels for the Carbon NMR](image)

The shifts from 59 - 62ppm are assigned to C2 and C6 respectively, while C3 and C5 are observed at around 77ppm. C4 and C1 have their chemical shifts at 84ppm and 107ppm respectively. The peak appearing at 176ppm corresponds to the C=O group.

![Figure 5.12: A graph showing Proton NMR spectra with labels](image)

The DDA was calculated using integrals of the peak of proton H1 of deacetylated monomer (H1-D) and of the peak of the three protons of acetyl group (H-Ac) i.e. the integral intensity
for $CH_3$ residues of N-acetyl and of acetic acid as shown in figure 5.12 using the formula 5.10 which gave a DDA value of 66.15%.

$$DDA(\%) = \left( \frac{H1D}{H1D + HAC/3} \right) \times 100$$  \hspace{1cm} (5.10)

For comparison, the DDA was also calculated with the method proposed by Hirai et al.[2] by using the integral intensity for 6 protons H2-H6 i.e. the signal from protons H2, H3, H4, H5, H6, H6' (H2-6) of both monomers and the integral of the peak of acetyl group (HAc) which gave a value of 75.44% using formula 5.11

$$DDA(\%) = \left( 1 - \frac{\frac{1}{3}HAc}{\frac{1}{6}H2-6} \right) \times 100$$  \hspace{1cm} (5.11)

where 3 represents the number of acetyl protons while 6 is the number of amine protons. The two values of DDA obtained are different which according to Ogawa et al[11], these values depend on the calculation method adopted.

5.5 Atomic Force Microscopy (AFM)

The AFM was used to probe information on structure through nanoscale imaging of topography (height), acquired in tapping mode with phase imaging.

![Figure 5.13: Atomic Force Microscopy images of SG (a) Scale bars 1µm (b) Scale bars 100nm](image)

Figures 5.13 and 5.14 show the AFM scans illustrating surface structural characteristics of the squid gladius. The AFM topographic scan shows that the films have a highly oriented surface topography. The interstitial regions between the ridges represented by dark area are
cavities on the films having an approximate width of 100nm. The surface profile of the films shows loose and uneven surface with many small crater-valley type structures. The scan size for figures 5.13 is $1\mu m \times 1\mu m$, and the contrast variations from white to black are 285 nm for the height images and 90° for the phase image and that for figures 5.14 is $200nm \times 100nm$, with a contrast variation of 100 nm and phase image 86°.

**Figure 5.14: AFM image of the Ch Film** (scale bars 40µm)

Figure 5.15 shows the topographic image of the chitosan film surface at a scale of 5µm and on a scan size 20 x 20µm$^2$. The image reveals highly ordered domains which are parallel arranged stacked in form of terraces.

**Figure 5.15: AFM height image of the Ch Film** (scale bars 5µm)

Ogawa *et al* [115] observed that, chitosan is characterized by an ordered fibrillar structure with a high degree of crystallinity and polymorphism with its structure formed by chains arranged in a parallel fashion for $\beta$-chitosan. They attributed this to the presence of free
amino groups in the structure which gives rise to different types of helical conformations. They concluded that the diversity of chitosan structural types depend on the experimental conditions (kind and concentration of acid, temperature and salt preparation) used for the conversion of chitin into chitosan.

5.6 UV VIS Spectra (Optical Properties)

UV-VIS spectroscopy was used to study the electronic transitions of molecules as they absorb light in the UV and visible regions of the electromagnetic spectrum. The visible region of the spectrum comprises photon energies of 36 to 72 Kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. This energy is enough to promote the outer electrons to higher energy levels. As a rule, the energetically favoured electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The absorbance spectra in the spectral region of 200–800 nm at room temperature are as shown in figure 5.16.

![Absorption spectrum for Ch 0.5%](image)

Figure 5.16: Absorption spectrum for Ch 0.5%

The spectrum for the chitosan shows that there is absorption in the near ultra-violet region (200nm–400nm) with “lambda-max” ($\lambda_{max}$) at around 230nm and maximum absorbance or optical density of 0.8, involving a non-bonded (n) orbital to an antibonding pi
(\pi) orbital transitions. Non-conjugated interacting chromophores of the amino group attached to the carbonyl group. Compounds that absorb light in the visible region (that is, colored compounds) have more-easily promoted electrons than compounds that absorb at shorter UV wavelengths. The absorption coefficient \( \alpha \) at various wavelengths was calculated from absorbance (A) and thickness (d) of the sample using the relation:

\[
\alpha = \frac{2.303 \ A}{d}
\]

and gave a value of 184.12. The absorption coefficient, \( \alpha \), is related to the extinction coefficient (absorptivity coefficient), \( k \), by the following formula:

\[
\alpha = \frac{4\pi k}{\lambda}
\]

where \( \lambda \) is the wavelength. If \( \lambda \) is in nm, multiply by \( 10^9 \) to get the absorption coefficient in the units of \( \text{cm}^{-1} \). Using this relationship, the value of the extinction coefficient was \( 3.37 \times 10^{-6} \). Usually, energy absorption is reported as molar absorptivity \( \varepsilon \) (also called molar extinction coefficient) rather than the actual absorbance. The magnitude of \( k \) reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore (the structural unit associated with an electronic transition). Using this result, the concentration of the sample was obtained at \( 2.37 \times 10^5 \text{ g/mol} \) from the Beer–Lambert law:

\[
c = \frac{A}{\varepsilon l} = \frac{0.8}{3.37 \times 10^{-6} \times 1}
\]

where \( A \) is the absorbance, \( \varepsilon \) is the absorptivity or absorption coefficient and \( l \) is the optical path length (width of the cuvette). The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. In a material with a low absorption coefficient, light is only poorly absorbed, and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. Materials with higher absorption coefficients more readily absorb photons, which excite electrons into the
conduction band. Knowing the absorption coefficients of materials aids engineers in determining which material to use in their solar cell designs. The band gap $E_g$ of the material was estimated from the experimental UV-Vis absorption spectrum using the following expression:

$$E_g = \frac{hc}{\lambda_c}$$  \hspace{1cm} (5.15)

where $\lambda_c$ is the cut-off wavelength absorbed by the sample, and $c$ is the speed of light and $h$ is the Planck’s Constant, $h = 6.625 \times 10^{-34}$ J.s. The cut-off wavelength was estimated from the intersection of the tangent line of the peak with the wavelength axis where the absorbance value is minimum. From figure 5.14 and equation 5.15, $E_g$ was $ca.4.413 \times 10^{-19}$ J$\approx 2.758$ eV. This value agrees with literature values because the band gap energy of insulators is large ($> 4$eV), but lower for semiconductors ($< 3$eV).

### 5.7 Electrical Measurements

The voltage –current relationship for the film using the four point probe method are shown in Figure 5.17. The graph shows that there was very little current initially but later increased as the voltage was increased. The resistances in the two linear regions AB and CD were respectively obtained as $R_{AB} = 2M\Omega$ and $R_{CD} = 1.15M\Omega$ which show that there was a change in resistance by $8.5M\Omega$ which accounted for the increase in current from AB to CD. For a square shaped probe;

$$R = \frac{\rho l}{wd} = \frac{\rho}{d}.$$  \hspace{1cm} (5.16)

where $l = w$ and $d$ is the film thickness. The value of $d$ as measured using a digital micrometer screw gauge was $ca.0.5mm$. The resistivity in the two regions was obtained using the relations;
\[ \rho_1 = R_1 \times d = 2 \times 10^6 \times 5 \times 10^{-4} = 1000 \Omega \text{m} \quad (5.17) \]

\[ \rho_2 = R_2 \times d = 1.15 \times 10^6 \times 5 \times 10^{-4} = 575 \Omega \text{m} \quad (5.18) \]

This gave the conductivity as:

\[ \sigma = \frac{1}{\rho} = 0.001 \Omega^{-1} \text{m}^{-1} \text{ using } \rho_1 \text{ and } 0.002 \Omega^{-1} \text{m}^{-1} \text{ using } \rho_2 \quad (5.19) \]

The obtained value of resistivity was less than that of silicon (2300 \( \Omega \text{m} \)) but greater than that of Germanium (0.46 \( \Omega \text{m} \)) showing that the material is a semiconductor. The value of the conductivity as measured using the conductivity meter was \( \text{ca.} 900 \mu \text{scm}^{-1} \) for 1% acetic acid and \( \text{ca.} 1525 \mu \text{scm}^{-1} \) for the chitosan acetic acid (ChAcOH) solution. This showed that Ch enhanced the conductivity of the solution. The improved conductivity of the sample extract is as a result of the transition state of the deacetylation reaction where the development of ionic charges was initiated by the nucleophilic addition of amide functions on carbonyl groups and favoured by the high dielectric constant of the solvent [5]. Chitosan dissolved in dilute acetic acid is polycationic due to the hydrogen ions and free amine group combining to form a cation ion (\( NH_3^+ \)) with the key charge carriers being oxygen and hydrogen from the hydroxyl groups (\( OH^- \)) and nitrogen and hydrogen from the positively charged amino groups (\( NH_3^+ \)).
5.8 Dielectric Spectroscopy Data

The relaxation processes in the sample material were studied by dielectric spectroscopy. The dielectric spectra were measured in the frequency range from 0.1 Hz to 10 MHz and in the temperature range from 100 to 450K. The temperature and frequency dependence of the imaginary part dielectric constant is shown in figures below. The description of the relaxation processes is given by the model function of Havriliak-Negami [102];

\[
\varepsilon = \frac{\Delta \varepsilon_i}{[1 + (i\omega \tau_i)^{a_i}]}^{b_i} \tag{5.20}
\]

where \(\Delta \varepsilon\) is the relaxation strength, \(\tau\) is the relaxation time, \(\alpha\) is the distribution broadness or with parameter of \(\tau_i\) and \(\beta_i\) is a parameter reflecting the skewness of the relaxation spectra/process. A very important quantity is the dielectric loss tangent given by;

\[
\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \tag{5.21}
\]

which measures directly the phase difference due to loss of energy within a sample at a particular frequency. Figures 5.18 show the variation of tangent loss with frequency and temperature of chitosan. Figures 5.18 shows the loss factor as a function of frequency and temperature. Three relaxation processes are observed; process I, which is the \(\beta\)-relaxation which is normally broader and occurs at lower temperatures. It is related to segmental motion of the polymer chain via the glucosidic bond and therefore corresponds to the local chain motion. Process II is the \(\alpha\)-relaxation which is normally picked than either \(\beta\) or \(\gamma\) relaxations and occurs at higher temperatures. It is related to the longer scale segmental motion of the side groups attached to the glucosidic unit of the polymer. While process III is the \(\sigma\)-relaxation process, which is normally observed at higher temperatures and involves proton migration or ion hopping in amorphous polymers.
Figure 5.18: Graphs showing (a) the variations of log $\varepsilon^-$ with T (K) at different Frequencies, (b) $\varepsilon''$ with frequency at different Temperatures for the SG.

At high frequencies, process III is not visible due to the local chains motion relaxation which overlaps the side group mobility. The broadness for each peaks signify dispersion in relaxation time as the result of different local environment of polarisable groups.

Figure 5.19: Variation of log $\varepsilon''$ with the logarithm of frequency (a) and $\varepsilon''$ with frequency (b) at various Temperatures for the Ch films.

Figures 5.19a and 5.19b, show the variations of the loss factor with frequency for process II and I respectively at the region of glass transition. In this frequency range, the loss factor decreases monotonically with increasing frequency due to the presence of free ions and ionic...
conduction in the sample showing that the loss factor has very high values at the lower frequencies.

With the increase in temperature, chain mobility begins to increase thus reducing the relaxation time. The dipole polarization of the polymer chain is better able to align in phase with the changing frequency and this account for the increase in dielectric constant as the temperature is increased. At frequencies below relaxation frequency the alternating electric field is slow enough that the dipoles are able to keep pace with the field variations. Because the polarization is able to develop fully, the loss modulus ($\varepsilon''$) is directly proportional to the frequency. Above relaxation frequency $\varepsilon''$ drops off as the electric field is too fast to influence the dipole rotation and the orientation polarization disappears. Relaxation frequency was obtained at the peak of the loss modulus as a transition occurring near the relaxation frequency. The relaxation frequency $f_c$ is inversely related to relaxation time as seen from the relation,

$$\tau = \frac{1}{\omega_c} = \frac{1}{2\pi f_c}$$

(5.21)

Figure 5.20: Showing the variation of $\varepsilon''$ with $f$ at different temperatures for process I (a) Activation Plot for the SG for process I and (b) Activation Plot for the Chitosan film for processes I and II
Figures 5.20a and 5.20b are the activation plots for processes I and II respectively which also confirm that the $\alpha$-relaxation processes follow the Arrhenius law and gave the activation energy of the squid gladius at ca.54.7 kJ/mole and that of the chitosan films at ca.31.01 kJ/mole for the $\alpha$ process and about ca.73 kJ/mole for the $\beta$-process.
6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This work presented the extraction and characterization of biopolymer chitosan found along the Kenyan coast as promising candidate for batteries and biosensor application.

1. Chitosan was successfully extracted and found to have an average DDA value of about 70.8% from the NMR results from which thin films were cast by the solvent casting method.

2. DMA results showed the material to be viscoelastic with very low mechanical damping.

3. The chitosan acetic acid solution showed improvement in ionic conductivity than pure acetic acid, due to the presence of the free -NH$_2$ groups, primary and secondary –OH groups which lead to enhancement in number of charge carriers provided by ionic liquid. This means the material has electrolytic properties which can be improved for energy storage batteries.

4. The UV Vis results showed the material with optical density of 0.8, $\lambda_{\text{max}}$ 230nm and an optical band gap value of 2.758eV which compares well with literature values because the band gap energy of insulators is large (> 4eV), but lower for semiconductors (< 3eV).

These results show that chitosan is a potential biomaterial for biotechnological industries especially for the fabrication of biobatteries and biosensor devices. Extraction of $\beta$-chitosan from squid pens is cost-effective and can be beneficial to the industrial-scale production since it needs smaller amount of reagents and shorter reaction times thus low production cost than $\alpha$-chitin/chitosan from crustacean shells. Five consecutive processes are required to extract $\alpha$-chitosan from crab and shrimp shells, including demineralization, deproteinization, decolouration, deacetylation, and depolymerization. In contrast, only three stages are necessary to isolate $\beta$-chitosan from squid pens, including deproteinization, deacetylation and depolymerization due to the ignorable mineral content and pigment in squid pens. The average market price of chitosan ranges from $10 - $1,000 per kilogram depending on the product quality and source.
6.2 Recommendations

This research has specifically looked at the mechanical and optoelectronic characteristic of chitosan of DDA 70%. The researcher recommends the following:

1. The molecular weight ($M_w$) of this material be determined

2. The effect of higher DDA values on these characteristics be explored

3. Doping or copolymerization of this material with other material to improve its opto-electric and mechanical properties

4. More precise characterization methods be used
APPENDICES

Appendix 1: Photos showing the stages of the chitosan sample from the source animal (i) then pens (iii) to the final product (ix)

(i) Squid in water  (ii) Squid out of water  (iii) Squid Gladii (SG)  (iv) SG Powder

(v) Chitin  (vi) Chitosan (Ch)  (vii) Ch Powder  (viii) Ch Solution  (ix) Ch Thin Film

Appendix 2: Map showing the sample collection area (Region shaded orange)
REFERENCES


