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A STUDY OF MASS TRANSFER OF MOISTURE IN
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MAHESH KHURANA

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**A STUDY OF MASS TRANSFER OF MOISTURE IN BIODEGRADABLE SHEETS
AND RESINS**

By

Mahesh Khurana

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

A STUDY OF MASS TRANSFER OF MOISTURE IN BIODEGRADABLE SHEETS AND RESINS

By

Mahesh Khurana

Through this research the moisture sorption of two biopolymers, Biomax[®] and Sorona[®], was investigated. DuPont Biomax[®] is a hydro-biodegradable modified polyester. Sorona[®], Poly(trimethylene terephthalate), is a thermoplastic polyester produced by condensation of terephthalic acid and 1,3-propanediol (derived from renewable sources). The moisture sorption profile of both polymers was assessed at 23 and 40°C using gravimetric technique.

The moisture sorption isotherms of both polymers showed a positive temperature dependence, i.e. more moisture was sorbed at higher temperature. The solubility, diffusion and permeability coefficients of both polymers were also determined. The impact of processing was evaluated by comparing the sorption of moisture on resin and sheet of both polymers. The moisture sorption in resins was significantly lower than in sheets at either temperature, which is due to the morphological changes during the extrusion.

The effect of moisture on physical and mechanical properties of both polymers was evaluated. Moisture sorption in Sorona[®] has little or no impact on the tensile strength, T_g and crystallinity. In Biomax[®], the water acts as a plasticizer as shown by a drop in glass transition temperature from 40 to 30°C. Also, the mechanical properties of Biomax[®] were drastically reduced after the moisture sorption.

To my family and friends

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Chapter 1

Introduction

1. Background

The US packaging industry uses around one-third of the total plastics produced in the country.¹ Plastic is the largest segment of the packaging industry, accounting for approximately 50% of the total materials used in industry.² Most of the plastics used currently are derived from the petroleum sources and do not degrade easily after disposal. In 2006, only 10% of the total packaging plastic was recycled; the remainder landed in landfills, accounting for 6% of the total Municipal Solid Waste (MSW).³ Dwindling petroleum sources and landfill sites have prompted the development of alternative and environmentally friendly polymers. In the past few years, many new alternative polymers have been developed that are either derived from non-petroleum sources or are biodegradable. A few examples of such polymers are Poly(lactic acid) (PLA), Poly(ϵ -caprolactone)(PCL), and Polyhydroxyalkanoates (PHA).⁴ The global production of biodegradable polymers in 2006 has increased 20-folds since 1995,⁵ but it is still just a small fraction of the total polymer production. The major obstacle to commercialization of these ‘novel’ polymers in the packaging industry is their cost and the limited knowledge about their performance properties. Especially the barrier properties of such polymers to different gases and vapours dictate the use of polymer in food and pharmaceutical industry.

Polymeric packaging materials are permeable to small molecules like water vapour, organic vapours, and gases. Because these permeants are often responsible for

product deterioration, their permeation through the polymer determines the shelf life of the product. Water is one of the permeants responsible for the deterioration of most food and pharmaceutical products. Therefore, a thorough understanding of water vapour permeation through the new alternative biodegradable polymers is of great commercial importance.

Permeation process in polymers is characterized by the sorption of compounds by the polymer, their diffusion through the polymer, and finally desorption of the permeant from the polymer to product or environment. Sorption is the uptake of the permeant, water vapour, gases, or liquid, by the polymer membrane. Sorption of the permeant molecule depends on the affinity between permeant and polymer.⁶ After sorption, the permeant diffuses through the polymer's free volume from the high concentration to low concentration (or chemical potential) side and polymer characteristics also play an important role. Thus permeability of gases through common packaging polymers can be defined as:

$$P = D * S \quad (1)$$

where P is the permeability coefficient, D is the Fickian diffusion coefficient and S is the solubility coefficient.

Extensive research had been conducted for the evaluation of mass transfer properties of polymers using various methods. While isostatic and quasi-isostatic methods are generally used to evaluate the permeation of the permeant through the polymer membrane;⁷⁻¹¹ gravimetric methods, using a spring balance, an electrobalance, or a quartz crystal microbalance, evaluate the permeant sorbed in the polymer.¹¹⁻¹⁶ The gravimetric sorption method has the advantage that it can record real time mass

(moisture) uptake in a controlled environment at both the steady state as well as during the transient state. The moisture content at steady state at different water activities can be used to generate the moisture sorption isotherm, defined as the relation between the moisture and polymer membrane at a constant temperature and pressure. The moisture content at the steady state is used to determine the solubility coefficient (S) by the following relation:

$$S = \frac{M_{\infty}}{v \cdot p} \quad (2)$$

where M_{∞} is mass at steady state, v is the volume of the polymer and p is the permeant force in unit of concentration or pressure. The transient state and the steady state data can be used in determination of diffusion coefficient (D).¹⁷

As discussed earlier, several alternative polymers have recently been developed. Biomax[®] and Sorona[®] are two such alternative polymers developed by DuPont. Biomax[®] is an aliphatic-aromatic hydro-biodegradable polyester.^{18, 19} It is a co-polymer of polyethylene terephthalate (PET), produced by adding up to three different monomers to make this polymer degradable through hydrolysis.¹⁹ Biomax[®] can be used for oriented films, blown films, molded plastic articles, or coating in disposable products such as bowls, plates, cups, and sandwich wraps.²⁰ To the best of the author's knowledge no research has been conducted to study the moisture uptake of Biomax[®]. Sorona[®], Poly(trimethylene terephthalate) (PTT), derived from renewable corn sugar, is a thermoplastic polyester produced by condensation of 1,3-propanediol and terephthalic acid.²¹ PTT was developed several years ago but was not commercialized due to high cost of production. However recent developments have reduced the cost significantly.

Sorona[®] has several unique characteristics such as high elasticity and recovery as compared to PET or nylon and better chemical properties as compared to PET,²² hence it is gaining a lot of attention in packaging and textile industry. Research had been conducted to tailor the physical and mechanical properties of Sorona[®] through blending it with other polymer or nano-composites,^{21, 23} but fewer researchers have studied the moisture uptake of Sorona[®].

2. Scope of the Study

The main goal of this study was to generate a moisture sorption profile for Biomax[®] and Sorona[®] sheets and resins using a gravimetric method and to generate the moisture sorption isotherms of both polymers sheets at 23 and 40°C. The effect of processing, from resin to polymer, on the moisture sorption was evaluated. Lastly, the effect of moisture sorption on physical and mechanical properties of both polymers was investigated.

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Chapter 2

Background and Methodology

1. Introduction

The first part of this chapter presents an overview of biodegradable polymers and their classification based on raw materials. The second part focuses on the mass transfer phenomenon, followed by sorption and diffusion kinetics. The last part includes the details of the gravimetric equipment used for this study and noise quantification.

2. Biodegradable Polymers

Biodegradable polymers can be define as polymers whose chemical structure changes significantly under specific environment condition as the action of natural occurring micro-organisms. Bio-based polymers can be defined as polymers produced from renewable agricultural or biomass feedstock. Biodegradable or bio-based polymers can make the base for environment friendly and eco-efficient products that can compete and capture current market dominated by petroleum-based polymers.

2.1 Classification of Biodegradable Polymers

Different approaches have been used to formulate biodegradable polymers. Depending on the sources of raw materials, biodegradable polymers can be divided in three categories:^{1, 2} a) Renewable source-based biodegradable polymers b) Petroleum-based biodegradable polymers c) Polymers from mixed petroleum and renewable sources

2.1.1 Renewable Source-based Polymers

Poly(lactic acid) (PLA) obtained from a renewable agricultural source (corn) is synthesized by condensation polymerization of lactic acid or ring opening polymerization of lactide.²⁻⁴ PLA is currently used in packaging as thermoformed containers for fresh produce and short shelf life products.^{3, 5} Poly hydroxyalkanoates (PHA) is a class of biodegradable polymers produced from renewable resources by microbial fermentation. PHA alone is very brittle and difficult to process, therefore various copolymers have been biosynthesized.⁶

2.1.2 Petroleum-based Biodegradable Polymers

Petroleum-based biodegradable polymers can be divided into two main categories: aliphatic biodegradable polyesters and aromatic-aliphatic co-polyesters.

Aliphatic Polyesters: Poly(ϵ -caprolactone) (PCL), is a biodegradable thermoplastic obtained by ring opening polymerization of ϵ -caprolactone (obtained from crude oil) using a catalyst.⁷ PCL has good barrier properties and is easy to process, but due to the high cost it is generally blended or copolymerized.^{5, 8} Poly(butylene succinate) (PBS) is a petroleum-based polymer made by condensation polymerization of 1,4-butanediol with aliphatic dicarboxylic acids.

Aliphatic-Aromatic Co-polyesters: These are generally based on terephthalic acid. Poly(butylenes adipate-co-terephthalate) (PBAT) is a thermoplastic co-polyester produced by condensation of 1-4-butanediol, terephthalic acid and adipic acid. PBAT has barrier and mechanical properties similar to LDPE and has been approved for food contact applications.⁹ Easter Bio[®] from Eastman Chemicals and Biomax[®] from DuPont, a hydro-biodegradable polyester, also belong to petroleum-based polymer category.¹⁰

Other petroleum based polymers are Polyesteramides (PEA), made by copolycondensation of polyamide and adipic acid.¹¹ Poly(vinyl alcohol) (PVOH) is manufactured by hydrolysis of poly(vinyl acetate) in alcohol and has been reported to be biodegradable.¹²

2.1.3 Polymers from Mixed Petroleum and Renewable Sources

Poly(trimethylene terephthalate) (PTT), tradename Sorona[®] from Dupont, is a 3-carbon glycol terephthalate (3GT) synthesized by condensation of 1,3-propanediol and terephthalic acid.¹³ Propanediol can be produced from renewable sources (corn). PTT has mechanical and barrier properties similar to PET.¹⁴ Other polymers in this class are Polyurethanes (PU) manufactured from polyols (vegetable oil based) and isocyanate.⁷ Various biodegradable blends have been studied, such as starch based blends, PLA based blends or PHA based blends.

In this study we focused on two of the alternative polymers—Biomax[®] and Sorona[®].

2.2 DuPontTM Biomax[®]

Biomax[®] (4026) is a hydro-biodegradable modified polyester, developed by E.I. DuPontTM de Nemours & Co. (Wilmington, DE). The material is based on polyethylene terephthalate (PET) and is synthesized by the polymerization of terephthalic acid, ethylene glycol, glutaric acid, and sulfonic acid salt.^{10, 15} Properties of Biomax[®] are shown in Table 2.1.

Table 2.1: Physical and mechanical properties of Biomax[®] 4026*

Properties	
Density, g/cm ³	1.35
Glass Transition Temperature (T _g), °C	30
Melting Temperature (T _m), °C	195
Decomposition Temperature, °C	340
Flexural Modulus, GPa	3
Tensile Strength at Break, MPa	30

* Published on Matweb¹⁶

Biomax[®] has been awarded a ‘COMPOSTABLE’ logo by The Biodegradable Products Institute (BPI),¹⁷ because it meets ASTM D 6400-99 “Standard Specification of Compostable Plastics”.¹⁸ The polymer can be incorporated with up to three aliphatic monomers according to the end-use. These monomers create weak spots, thus making Biomax[®] degradable through hydrolysis. The moisture cleaves the polymer’s larger molecules into smaller molecules, which are then consumed by natural micro-organisms. Although Biomax[®] is intended mainly for composting, it can also be recycled, incinerated, or landfill.¹⁹

Biomax[®] has been blended with soy proteins and polycaprolactone (PCL), and with cotton (Bionature by Kurabo, Japan).^{20, 21} It is easy to process and can be processed in standard PET equipment with minor changes. It can be used as blown film, oriented film, or molded articles. Its major applications can be single-use products, such as waste bags, blister packs, geotextiles, seed mats and coating for disposable eating utensils (cups, bowls or plates).^{19, 22}

2.3 DuPont™ Sorona®

Sorona® is the trade name for Poly(trimethylene terephthalate) (PTT) manufactured by E.I. DuPont™ de Nemours & Co. (Wilmington, DE). PTT is a condensation polymer of 1,3-propanediol (PDO) and terephthalic acid (TPA). DuPont has developed a technique to produce PDO from renewable resources (corn) or via biological processes.¹³ Sorona®, a three carbon glycol terephthalate (3GT), can also be produced using only petroleum resources. Both type of polymers, petroleum-based and bio-based, are expected to have similar properties as they have the same chemical structure.

Table 2.2: Physical and mechanical properties of Sorona®, PTT^{13, 14}

Properties	
Density, g/cm ³	1.33
Glass Transition Temperature (T _g), °C	45-55
Melting Temperature (T _m), °C	228
Flexural Modulus, GPa	3.76
Tensile Strength, MPa	67.6

Sorona®, 3GT is member of the thermoplastic aromatic polyester family, which includes polyethylene terephthalate (PET)-2GT and polybutylenes terephthalate (PBT)-4GT.^{13, 23} Sorona® glass transition temperature is in the range of 45-55°C, which is lower than that of PET (80°C), but higher than that of PBT (25°C).¹⁴ Sorona® has a semi-crystalline molecular structure with a zigzag shape that gives it excellent stretch recovery and tensile and compressive properties. Sorona® has comparable strength, stiffness, and heat resistance as of PET. As expected from linear aromatic polyesters, Sorona® has a good barrier to moisture, is dimensionally stable, and has good weather and chemical

resistance. Sorona[®] can also be used as engineering thermoplastics because of its good thermal and mechanical properties.^{13, 24}

Sorona[®] can be cast into films at a setting comparable to polypropylene. Sorona[®] has been blended with other polymers to offset its relatively high cost and tailor to specific performance-cost profile.¹⁴ Sorona[®] has also been used as Polymer/Clay nanocomposites (PCNs), produced by dispersing nanoscale composites in a polymer matrix. PCN possesses the excellent combination of barrier and mechanical properties, which may eliminate the need for multilayer polymers for packaging application (reviewed by Khonakdar, et al.).¹⁴

3. Mass Transfer Phenomenon

Historically, the main purpose of a package was containment (cellophane used for bread in 1930's), but today packaging plays more active role in protecting the product, providing utility and communication. One of the major roles of packaging is to provide shelf life to the product. Currently, plastic is the leader in packaging industry because of its benefits like light weight, appearance, aesthetics, economy, and many others. Plastics allow permeability of small molecules to through them. Polymer allows moisture, aroma, and gases to pass through them, which can modify or deteriorate the product contained by the package. Although this mass transfer can also be used to improve shelf life of some products, for example modified-atmosphere packaging (MAP).²⁵ Mass transfer or permeation processes in polymers is characterized by the sorption of compounds by the polymer, their diffusion through the polymer, and finally their desorption from the polymer to product or environment.

3.1 Sorption

Sorption is the uptake of the permeant, such as moisture, flavor, aroma or colorant by the polymeric packaging material. Sorption of the permeant molecule depends on the affinity between permeant and polymer. When a polymer comes in contact of a liquid or vapour phase, sorbates in both phases are exchanged until their potentials become equal. The equilibrium of every sorbate can be established by a partition coefficient. At low concentration levels, as in case in packaging, the mixing of permeant with polymers behaves as ideal solution. The relationship between sorbate concentration and partial pressure follows Henry's law of linear sorption isotherm:²⁶

$$C_i = S \cdot p_i \quad (1)$$

where C_i is concentration of the permeant

S (Solubility Coefficient) is Henry's Law proportionality constant and

p_i is the equilibrium vapor pressure of the permeant.

Henry's law holds only at low concentration or when there is no interaction between the polymer and permeant, as in case of O_2 and N_2 at low pressures or moisture sorption in hydrophobic polymer.^{26, 27} The solubility coefficient (S) is an equilibrium partition coefficient for distribution of the penetrant between polymer phase and vapor phase and is given as:

$$S = \frac{C_p}{C_v} \quad (2)$$

where C_p is the concentration of penetrant in the polymer and C_v is the concentration of penetrant in the vapor phase at the steady state.

3.2 Diffusion

Diffusion can be defined as the movement of substance within itself or another substance. Diffusion, for polymeric packaging materials, can be defined as the process through which the matter (permeant) transport from high concentration side to low concentration side as a result of random molecular motions. Diffusion coefficient (D) is the quantitative measurement of the rate at which a penetrant diffuses. D is defined as the rate of transfer of the penetrant across unit area of a section, divided by the space gradient of concentration. This definition holds good only for the one dimensional diffusion and when diffusion is normal to the section. The basic equations describing above definition are Fick's first law:²⁸

$$F = -D \frac{\partial C}{\partial x} \quad (3)$$

where F is the rate of transfer,

D is the diffusion coefficient,

C is the concentration of penetrant,

x is space coordinate

The negative sign in Eq. 3 indicates that the permeant molecules flow from high concentration side to low concentration side. For unsteady or transient state, the rate of flow of permeant can be described by Fick's second law which can be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (4)$$

where t is the time. To obtain the flux (F) or D from above equations, initial and boundary conditions associated with the experimental method are needed. The solution of

Eq. 4 is given analytically and a power-series of solution is derived. Crank²⁸ presented simplified equations related to the first approximation of the power series. Thus the values of D obtain through these equations are only approximate values. Mass sorbed on the polymer film as a function of time provides the necessary information to calculate the diffusion coefficient of the permeant in the polymer.

3.3 Permeability

Permeability can be defined as the transfer of gases, vapors, liquid through a homogeneous packaging material. It is the mass transfer of the permeants from higher concentration side to the lower concentration side through the polymer. Mass transfer of permeant through cracks, perforation or other defect is not considered as permeability. Permeability is the overall process of sorption of permeant in the polymer, its diffusion through the polymer and finally desorption on other side. Permeability of simple gases through common packaging polymer at steady state is given by following relation:

$$P = D \cdot S \quad (5)$$

where P is the permeability coefficient, D is the Fickian diffusion coefficient and S is the solubility coefficient. The above equation holds at low concentrations of the permeant and when there is no interaction between permeant and polymeric material.

The permeability diffusion and solubility coefficients of a material are dependent on the temperature and sometimes the environment relative humidity (RH). The dependence of P, D and S can be described by a Van't Hoff-Arrhenius equation:

$$S(T) = S_0 \exp(-\Delta H_s / RT) \quad (6)$$

$$D(T) = D_0 \exp(-E_D / RT) \quad (7)$$

$$P(T) = P_0 \exp(-E_p / RT) \quad (8)$$

where ΔH_s = enthalpy of sorption

E_D = activation energy of diffusion

E_p = activation energy of permeation

R = Gas constant and,

T = Temperature

Enthalpy of sorption (ΔH_s) can also be considered as sum of two terms

$$\Delta H_s = \Delta H_c + \Delta H_m \quad (9)$$

where ΔH_c is the enthalpy of condensation of pure gaseous penetrant to the liquid phase and ΔH_m is the partial molar enthalpy of mixing the condensed penetrant with polymer segments. As the solubility depends on the heat of sorption and unlike activation energy of diffusion, it can take positive or negative values.

3.4 Fickian and Non-Fickian Kinetics

The diffusion behavior of polymer films can be classified in three classes on the basis of relative rates of diffusion and polymer relaxation:²⁹

- a) Case I or Fickian diffusion in which diffusion is a function of concentration, diffusion is much less than relaxation.
- b) Case II diffusion, where the diffusion is very rapid as compared to relaxation.
- c) Non-Fickian or anomalous diffusion, where the rate of polymer relaxation is almost same as rate of diffusion.

According to Fick's law, distribution of diffusant during sorption is governed by the one-dimensional differential equation for diffusion, given by Eq. 3. Assumption for Eq. 3 is that when the ambient pressure changes from a initial to a final value, concentration at the film surface also changes to final value instantaneously. A sorption

curve is a plot of the amount of vapor absorbed or desorbed as a function of square root of time. Sorption curve which follows the above-mentioned assumption of D and surface concentration is known as Fickian or normal type sorption.

The Fickian sorption kinetics was also explained on the basis of sorption and desorption curves by Crank.²⁸ If diffusion is only dependent on the concentration, then in the initial stage the curves are linear; for absorption this is true up to 60% or more of M_{∞} . Above the linear portion the sorption curves become concave towards $t^{1/2}$ axis and steadily approaches the final steady state value.

Diffusion in some systems is found to be dependent on other factors such as time, polymer relaxation, etc. Generally, this is the case in glassy polymer systems and is called anomalous or non-Fickian diffusion. In such cases the diffusion rate is on the order of the polymer relaxation time scale. A simple deduction of diffusion coefficients from experiment showing this behavior is difficult and often explained by Flory Huggins³⁰ and clustering effect;³¹ wherein the first mechanism accounts for increase in diffusion coefficient, the other explains decrease in diffusion coefficient.

3.5 Parameters Affecting Permeability

There are many factors that affect the permeability, sorption and diffusion, of packaging materials towards moisture, gases, and organic vapors; these factors can be environmental (temperature, relative humidity), polymer (chemical structure and morphology), permeant (molecular size, concentration).

Permeability or sorption in polymers has been found to be different in the regions below and above T_g of polymer. As also explained above in case of glassy polymer, below T_g , diffusion is generally found to be anomalous or non-Fickian. Glassy polymers are

not in a state of true thermodynamic equilibrium and have very long relaxation times. These long relaxation times let the polymer to homogenize with the penetrant environment. Generally, to define the sorption and diffusion in this state a dual mode sorption model theory is used.³² Normally the diffusion at temperature above T_g is rather simple and follows Fickian kinetics. At temperature above T_g , the polymer is in rubbery state and its molecular chains are free to move. The micro-Brownian motion of polymers molecules at temperature above T_g enable the polymer to reach the equilibrium rapidly and diffusion is not time dependent. Diffusion in semi-crystalline polymers and polymers with rigid chain conformations is usually found to non-Fickian even above the T_g .

The barrier properties of a polymer also depend on its chemical structure and morphology. The barrier properties of polymer will increase with the increase in the crystallinity and orientation. It has been proved that the permeation of molecules take place only through the amorphous region of the polymer, thus increasing the crystalline region will increase the barrier properties.³³ Orientation of polymer brings the chains closer and the molecular mobility in oriented region decreases, thus decreasing the permeability.

Generally with the increase in temperature the segmental motion of polymer chains increases and thus increasing the free volume of the polymer and the diffusion of penetrant through the polymer. Also with the increase in temperature the permeant molecules have the required energy to diffuse through a polymer. The effect of temperature is best defined by the Arrhenius-type relationships given by Eq. 6-8. Generally barrier properties of the polymer decreases with increase in temperature. But few polymers have been reported which do not follow this trend. Polystyrene and

Poly lactide have been reported to have negative activation energy.³ Temperature also affects the partition coefficient, thus affecting solubility. With the increase in temperature the solubility decreases. There are few exception to this rule also, e.g., the partition coefficient of SARAN and ethyl acetate, n-hexanal and d-limonene were found to decrease at 0.2 vapor activity.³⁴

The diffusion of a penetrant through any polymer will be governed by the molecular size and vapor pressure of the penetrant. As the energy required by a smaller and lighter molecule to move is low, therefore they can easily diffuse through polymers.²⁶ Diffusion of permeant through polymer is also affected by the vapor pressure of the permeant, which defines the mobility of permeant at particular temperature. The sorption of a molecule in a polymer will be affected by the affinity of the penetrant and polymer.

4. Methods for Studying the Sorption in Polymeric Materials

The first study of gas permeation through a polymer was conducted by Thomas Graham in 1829.³⁵ Since then extensive research had been conducted for the evaluation of mass transfer properties of polymers using various methods. While isostatic and quasi-isostatic methods are generally used to evaluate the permeation of the permeant through the polymer membrane;³⁶⁻⁴⁰ gravimetric methods, using a spring balance, or an electrobalance, or a quartz crystal microbalance, evaluate the permeant sorbed in the polymer.⁴⁰⁻⁴⁵ For this research the moisture sorption in two polymers was evaluated using a gravimetric method.

4.1 Gravimetric Method

Gravimetric technique is considered as a type of isostatic technique. In this technique the polymer sample is exposed to the permeant and weight change is recorded as the function of time. The gravimetric sorption method has the advantage that it can record real time mass (moisture) uptake in a controlled environment at both the steady state (M_{∞}) as well as during the transient state (M_t). Thus it is possible to obtain both sorption isotherms (from steady state uptake) and the diffusion coefficient (from transient state sorption). The gravimetric sorption method has been adopted by many researchers to measure the sorption of moisture or organic vapors in polymer.

Different types of balance for this technique have been reported, such as Cahn suspension electrobalance,^{40, 41, 43, 46, 47} quartz crystal microbalance,^{45, 48, 49} Rubotherm magnetic suspension balance,⁵⁰ or spring balance.⁵¹⁻⁵³

The appropriate solution of the diffusion equation (Fick's laws) for a gravimetric technique, given by Crank,²⁸ can be written as:

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{l^2} \right\} \quad (11)$$

where l is thickness of the sheet,

M_t is the amount of penetrant sorbed by polymer sheet sample at time t ,

M_{∞} is steady state sorption after theoretical infinite time

Assumptions for Fick's equations and Eq. (11) are: temperature and pressure remains constant, polymer sheet has a constant thickness, during the experiment, moisture uptake follows fickian behavior (D is independent of concentration), vapor

concentration on both sides of the sheet is constant, and sheet is initially free of penetrant^{26, 28}. The Eq. 11 can be solved for $M_t/M_\infty=0.5$ with approximate error of 0.001 %:

$$D = 0.049 \frac{l^2}{t_{1/2}} \quad (12)$$

where $t_{1/2}$, half time, is the time when $M_t/M_\infty=0.5$ and can be determined experimentally by plotting M_t/M_∞ vs. square root of time.

The solubility coefficient (S) is defined as the equilibrium partition coefficient for the distribution of permeant between the polymer phase (C_p) and vapor phase (C_v) and is expressed as the mass of permeant sorbed at steady state by a unit volume of polymer per unit of driving force (partial pressure).

$$S = \frac{C_p}{C_v} = \frac{M_\infty}{v.P} \quad (13)$$

where M_∞ is the mass of the vapor absorbed by the polymer at equilibrium, v is the volume of the polymer, p is the permeant force in units of concentration or pressure. S is calculated from the sorption experiments by dividing the steady state sorption (kg of sorbate / kg of polymer) by density of polymer and vapor pressure. Once the solubility and diffusion coefficient are determined, the permeability coefficient can be calculated using Eq. 1.

For this study a symmetrical gravimetric analyzer (SGA-100) from VTI Corp was utilized.

5. Symmetrical Gravimetric Analyzer (SGA-100)

A Symmetrical Gravimetric Analyzer (SGA-100, from VTI Corp., Hialeah, FL) equipped with a Cahn Electrobalance Model D-200 (Cahn Instruments Co., Cerritos, CA) was used to measure moisture sorption in the polymer sheets and resins. The SGA-100 uses a continuous flow method for the sorption studies,^{40, 54} and is capable of generating relative humidity from 2 to 98% with variability of $\pm 1.0\%$ RH. The operational temperature range of the equipment is from 5° to 60°C with variability of $\pm 0.1^\circ\text{C}$. The main components of the SGA-100 are shown in Fig. 2.1. The equipment is divided into three different sections each of which is maintained at different, constant temperature.

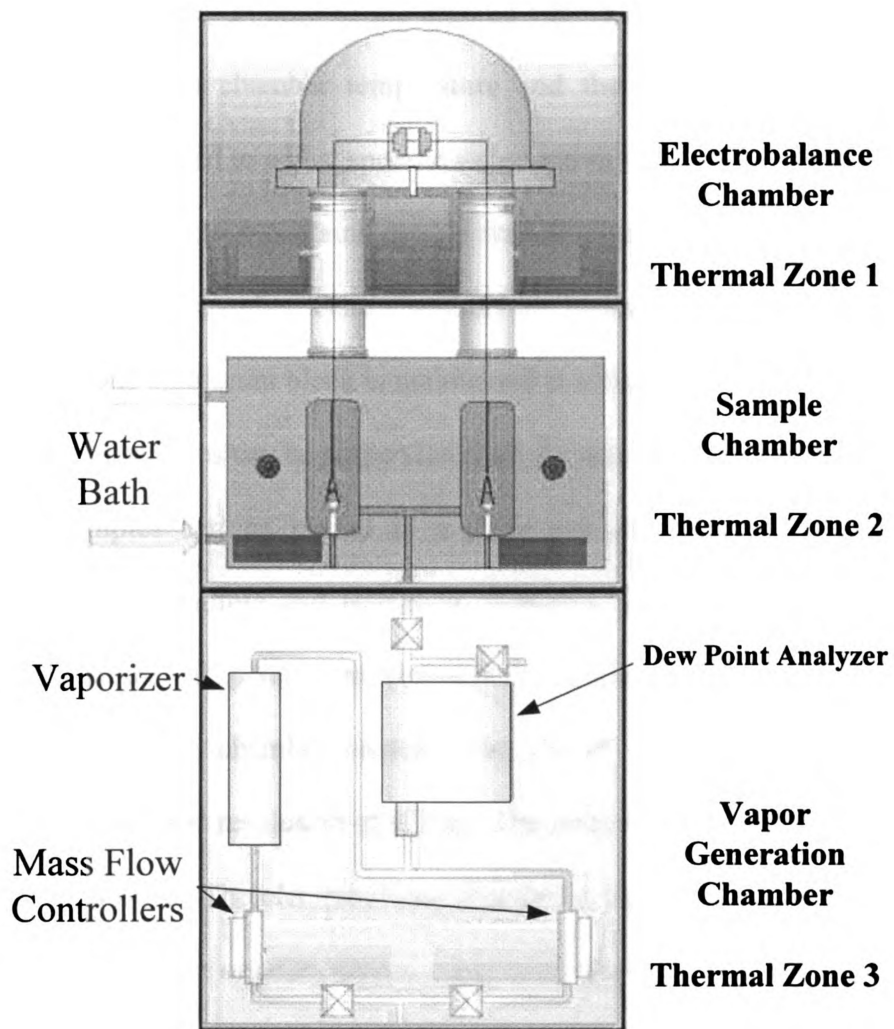


Figure 2.1: Schematic of Symmetrical Gravimetric Analyzer (SGA-100)

The lower section is the vapor generation chamber, which includes a vaporizer, a chilled mirror Dew Point Analyzer (DPA) and the mass flow controllers. The temperature of this section is maintained at 15°C above the experiment temperature, to prevent vapor condensation in the tubing. The water vapor activity is monitored by a chilled mirror dew point analyzer (DPA), which measures the dew point of the vapors before it enter into the sample chamber and send a signal to the software. Software then send the signals to the mass flow controllers, which generates the target relative humidity by mixing wet and dry

streams of nitrogen gas. In case of the organic vapors, the vapor activity is monitor by measuring the sample chamber temperature and the vaporizer temperature and the Wagner Equation is used to adjust specific vapor activity.^{50, 55}

The middle section contains double walled aluminum block which includes the sample and reference chamber. Both chambers are insulated and of identical size (10.8 x 3.8 x 3.8 cm). The aluminum block is maintained at constant temperature by a circulating water bath. Film samples can be suspended from the arm of the microbalance, while resin or powder samples can be placed in a glass pan suspended form the arm of the microbalance. Both sample and reference chambers have a platinum thermometer to measure the chamber temperature as well as the incoming vapor stream temperature.

The uppermost chamber encloses the CAHN electrobalance, with maximum capacity of 100 mg and resolution of 0.1 μg . This section is also thermally insulated and is maintained at 40°C. The electrobalance-chamber is purged with a dry nitrogen stream to prevent moisture or organic vapors from condensation. The weight change of the sample is recorded by the Flow System Software (developed by VTI Corporation) on a computer connected to the system. The software is also use to define the different experiment parameter like temperature, relative humidity, etc.

6. Noise Quantification

Every analytical or instrumental measurement is made up of two component—signal and noise. Noise can be defined as the unwanted, extraneous signals.^{56, 57} Noise can originate from small fluctuations of various sources like in the power provided to the instrument or from external source such as other instruments nearby or building vibration. Noise is random in nature; it can be positive or negative therefore it is treated

statistically. Ideally when no analyte is present there should be no signal, but in practice recorded signal include some random signals. There are several types of noise – white noise, drift or flicker noise, and line noise. White noise can be due to the thermal motion of charge carrier (thermal noise) or when electron crosses a junction (shot noise). Drift or flicker noise has a magnitude that is inversely proportional to the frequency of the signal being measured. It is still not understood what causes the drift. Drift becomes significant at low frequencies. Line or environmental noise can be due to the power lines, conductors in the instrument or building vibrations.^{56, 57}

Therefore, to get reliable and robust results from an analytical instrument, its noise should be quantified. The amplitude of noise and the drift of gravimetric equipment were quantified using standard stainless steel weights. Ideally, the stainless steel should not absorb any moisture, the weight change observed is the noise associated with the instrument. A least square method for regression was used to evaluate the amplitude of noise and drift. The assumptions for the hypothesis testing of regression analysis are: (i) the relationship between x and y is linear, (ii) the errors are independent and (iii) normally distributed and (iv) variances of the errors are constant across the observations. The linear model for experimental observation can be written as:⁵⁸

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon_i \quad i = 1, 2, \dots, n \quad (14)$$

where x and y represent the time and weight change respectively and β_1 is the slope of the regression line. The drift is given by the slope of the regression line and the amplitude of noise of the equipment was calculated as $3s$, where s is the square root of means squared error (MSE). Based on the empirical rule, $y_i \pm 3s$ contains 99.7% of the distribution.

7. Consistency Test

To determine the experimental data fit to the model described by Eq. 11 certain assumptions are made:²⁸

- The polymer is free of any vapor at the start of the sorption experiment.
- The vapor concentration at each side of the polymer sheets at time=0 is the same as the vapor concentration at equilibrium.
- The vapor concentration remains constant through out the experiment.
- The thickness of the polymer sheet is constant.

However, any significance variation or departure from any of these assumptions or conditions will affect the calculated value of the diffusion and permeability coefficients. Thus a consistency test was established by Hernandez et al.⁵⁹ For the consistency test, Eq. 11 was solved by keeping M_t/M_∞ equal to 0.25, 0.50, and 0.75 to obtain $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$, respectively. The basis of the test was that the ratio between $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ remains fixed, irrespective of the penetrant-polymer system:⁵⁹

$$K_1 = \frac{t_{1/4}}{t_{1/2}} = 0.250, \quad K_2 = \frac{t_{1/4}}{t_{3/4}} = 0.103, \quad K_3 = \frac{t_{1/2}}{t_{3/4}} = 0.413$$

To determine the validity of the data obtained, experimental K_1 , K_2 and K_3 were compared to the theoretical values.

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Chapter 3

A Study of Mass Transfer of Moisture in Biodegradable Sheets and Resins

1. Introduction

Dwindling petroleum sources and landfill sites have prompted the development of alternative and environmentally friendly polymers for different applications. In the past few years, many new alternative polymers have been developed that are either derived from non-petroleum sources or are biodegradable. A few examples of such polymers are Poly(lactide) (PLA), Poly(ϵ -caprolactone) (PCL), and Polyhydroxylalkanoates (PHA).¹ The global production of biodegradable polymers in 2006 has increased 20-folds since 1995,² but this represent just a small fraction of the total polymer production. The major obstacle to commercialization of these ‘novel’ polymers in the packaging industry is their cost and the limited knowledge about their performance properties.

The US packaging industry uses around one-third of the total plastics produced in the country.³ Plastic is the largest segment of the packaging industry, accounting for approximately 50% of the total materials used in industry.⁴ The barrier properties of polymer to different gases and vapors dictate the application of polymer as a package to be used in the food and pharmaceutical industries. Therefore, it is important to measure the barrier properties of these alternative polymers for their application in packaging industry.

Unlike glass or metal packaging, plastic packaging materials are permeable to small molecules like water, volatiles and gases. Extensive research had been conducted for the evaluation of mass transfer properties of polymers using various methods. While

isostatic and quasi-isostatic methods are generally used to evaluate the permeation of the permeant through the polymer membrane;⁵⁻⁹ gravimetric methods, using a spring balance, an electrobalance, or a quartz crystal microbalance, evaluate the permeant sorbed in the polymer.⁹⁻¹⁴ The gravimetric sorption method has the advantage that it can record real time mass (moisture) uptake in a controlled environment at both the steady state (M_{∞}) as well as during the transient state (M_t). The M_t and M_{∞} values can be used to determine the solubility (S) and diffusion (D) coefficients experimentally and hence calculate the permeability (P) coefficient using the following relation:

$$P = D * S \quad (1)$$

The above equation holds at low concentrations of the permeant and when there is no interaction between permeant and polymeric material. In the above equation D follows Fickian kinetics (is independent of concentration) and S follows Henry's law. In this research moisture sorption of two environment friendly polymers, Biomax[®] and Sorona[®], was studied using the gravimetric method.

Biomax[®] (4026) is a hydro-biodegradable modified polyester, developed by DuPont. The material is based on polyethylene terephthalate (PET) and is synthesized by the polymerization of terephthalic acid, ethylene glycol, glutaric acid, and sulfonic acid salt.^{15, 16} Biomax[®] has been awarded a 'COMPOSTABLE' logo by The Biodegradable Products Institute (BPI).¹⁷ Biomax[®] can be used for oriented films, blown films, moulded plastic articles, or coating in disposable products such as bowls, plates, cups, and sandwich wraps.¹⁸ Because it is modified polyester, it can be easily processed using standard PET equipment. Biomax[®] has been blended with soy proteins and polycaprolactone (PCL), and with cotton (Bionature by Kurabo, Japan).^{19, 20}

Sorona[®], Poly(trimethylene terephthalate) (PTT) is a thermoplastic polyester produced by condensation of 1,3-propanediol and terephthalic acid.²¹ The propanediol (PDO) monomer can be derived from corn (a renewable resource). PTT was developed several years ago but was not commercialized due to the high cost of production of PDO. However, recent developments have reduced the cost significantly. Sorona[®] belongs to the thermoplastic aromatic polyester family and due to three carbon glycol in its backbone it has better mechanical properties as compared to the other two members of this family (PET and PBT). Sorona[®] has high elasticity and recovery as compared to PET or nylon and better chemical properties than PET;²² hence it is gaining much attention in the packaging industry. Research had been conducted to tailor the physical and mechanical properties of Sorona[®] through blending it with other polymer or nano-composites,^{21, 23} but few researchers have studied the moisture uptake of Sorona[®].

This study aims to generate a moisture sorption profile of Biomax[®] and Sorona[®] sheets and resins using a gravimetric method. The solubility and diffusion coefficients of both polymer sheets were determined through the sorption data.

2. Theoretical Background

2.1 Sorption by Polymer Film

In a gravimetric method for moisture sorption, weight gain of polymer sample is recorded under specific relative humidity and temperature till the steady state is reached. The weight gain data is used to obtain the moisture sorption isotherm and the diffusion coefficient. Sorption during the transient state can be used to estimate the diffusion coefficient (D) using the following equation ²⁴:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-\frac{D(2n+1)^2 \pi^2 t}{l^2}\right\} \quad (2)$$

where l is thickness of the sheet, M_t is the amount of penetrant sorbed by the polymer sheet sample at time t , and M_∞ is the steady state sorption after theoretical infinite time. The fit of the experimental data model described by Eq. 2 is based on the following assumptions:^{24, 25}

- The polymer sheet has a constant thickness
- Temperature and pressure remain constant during the experiment
- Moisture uptake follows Fickian behavior (D is independent of concentration)
- Vapor concentration on both sides of the sheet is constant and the change in concentration from initial concentration to final is instantaneous
- The sheet is initially free of penetrant

The Eq. 2 can be solved for $M_t/M_\infty = 0.5$ with approximate error of 0.001 %:

$$D = 0.049 \frac{l^2}{t_{1/2}} \quad (3)$$

where $t_{1/2}$, half time, is the time when $M_t/M_\infty = 0.5$ determined experimentally.

The solubility coefficient (S) is defined as the equilibrium partition coefficient for the distribution of permeant between the polymer phase (C_p) and vapor phase (C_v) and is expressed as the mass of permeant sorbed at steady state by a unit volume of polymer per unit of driving force (partial pressure).

$$S = \frac{C_p}{C_v} = \frac{M_\infty}{v.P} \quad (4)$$

where M_∞ is the mass of the vapor absorbed by the polymer at equilibrium, v is the volume of the polymer, p is the permeant force in units of concentration or pressure. The common unit of S is $\text{kg/m}^3\text{Pa}$ and is calculated by dividing the steady state sorption ($\text{kg sorbate} / \text{kg polymer}$) by polymer density and vapor pressure. Once the solubility and diffusion coefficient are determined, the permeability coefficient can be calculated using Eq. 1.

2.2 Consistency Test

The assumptions in determining D through Eq. 2 are listed above. However, any significance variation or departure from any of these assumptions or conditions will affect the calculated value of the diffusion and permeability coefficients from experimental data. Thus to determine the fit of experimental data to the Eq 2, a consistency test for gravimetric method, established by Hernandez et al²⁶, was utilized. Eq. (2) was solved for M_t/M_∞ equal to 0.25, 0.50, and 0.75 to obtain $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ respectively. The basis of the test was that the ratio between $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$ remains fixed, irrespective of the penetrant-polymer system²⁶:

$$K_1 = \frac{t_{1/4}}{t_{1/2}} = 0.250 \quad K_2 = \frac{t_{1/4}}{t_{3/4}} = 0.103 \quad K_3 = \frac{t_{1/2}}{t_{3/4}} = 0.413 \quad (5)$$

3. Experimental

3.1 Materials

Biomax[®] (4026) and Sorona[®] resin pellets were obtained from E.I. DuPont[™] de Nemours & Co. (Wilmington, DE). Biomax[®] pellets were odourless and opaque white in appearance with density of 1344.3 kg/m³ (1.34 g/cc). Sorona[®] pellets were odourless and translucent in appearance with density of 1334.7 kg/m³ (1.33 g/cc). Both polymer types were processed using a DSM twin screw Micro-Extruder and Injection Molder (TS/I-02, DSM, Netherlands), to obtain small discs of approximately 25.4 mm diameter and 2 mm thick. A compression molding press (Carvar Hydraulic Press, Wabash, IN) was used to process the discs into sheets form, for the sorption experiments. The sheets samples were cooled quickly in the compression press by rushing cold water through the platens. The processing conditions for both polymers are given in Table 3.1. The thickness of both polymer sheets was maintained at 4 to 6 mils.

Table 3.1: Processing condition for Biomax[®] and Sorona[®]

	Biomax[®]	Sorona[®]
Micro-Extruder and Injection Molder		
Barrel Temperature, °C	200	250
Melt Temperature, °C	190	240
Screw Speed, rpm	100	150
Process Cycle Time, min	2	3
Transfer Cylinder Temperature, °C	190	240
Mold Temperature, °C	60	85
Pressure, psi	100	120
Compression Press		
Platen Temperature, °C	200	250
Compression Pressure, psi	10,000	12,000
Cooling Time, min	5	7

3.2 Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter (TA Instruments, New Castle, DE) was used to determine the percent crystallinity of both polymers' sheets and resins using one heating cycle followed by one cooling cycle. Biomax[®] samples were heated from 10°C to 210°C at a rate of 10°C/min and then cooled down to 10°C at a rate of 5°C/min. Sorona[®] samples were heated from 10°C to 265°C at a rate of 10°C/min and then cooled to 10°C at a rate of 5°C/min. The data were analyzed with Universal Analysis software (TA Instruments).

3.3 Instrument SGA-100

A Symmetrical Gravimetric Analyzer - SGA-100 (VTI Corp., Hialeah, FL) equipped with a Cahn Electrobalance Model D-200 (Cahn Instruments Co., Cerritos, CA) was used to measure the sorption of moisture in the polymer sheets and resins. It is capable of generating relative humidity from 2 to 98% with variability of $\pm 1.0\%$ RH. The instrument is divided into three thermally isolated sections: a vapor generation chamber, sample chamber, and electrobalance chamber. The aluminum sample chamber (10.8 x 3.8 x 3.8cm) can be maintained at a constant temperature with variability of $\pm 0.1^\circ\text{C}$. The relative humidity inside the sample chamber is obtained by mixing wet and dry streams of nitrogen using mass flow controllers. The electrobalance has a maximum capacity of 100 mg with resolution of 0.1 μg . The main components of the SGA-100 are shown in Fig. 3.1.

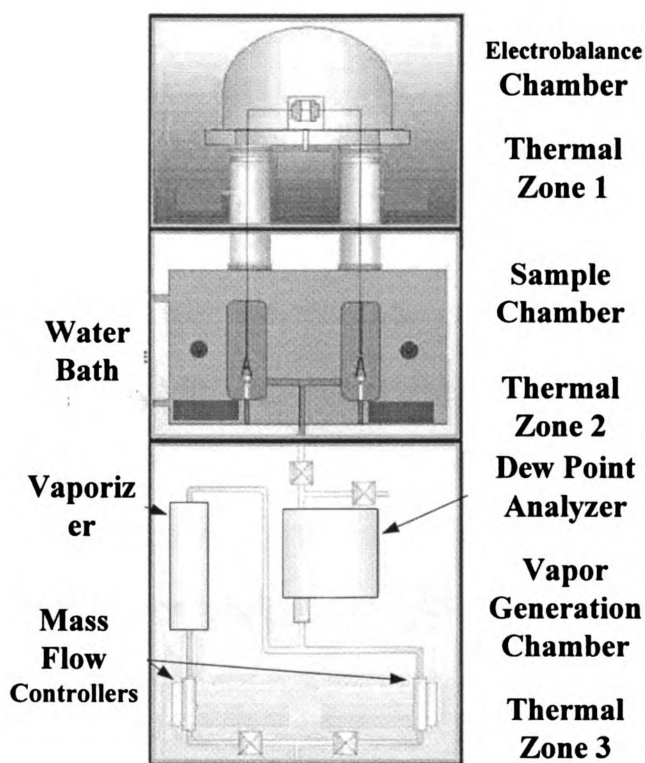


Figure 3.1: Schematic of Symmetrical Gravimetric Analyzer (SGA-100)

3.4 Noise Quantification

Every measurements carried out by an analytical instrument is made up of two components - signal and noise. Noise can be defined as the unwanted, extraneous signals which can make the actual signals indiscernible.^{27, 28} A protocol was implemented to quantify the noise level associated with the SGA-100 by measuring the amplitude of the noise and the drift. To quantify the noise level, three standard stainless steel weights of 20, 50, and 100mg were exposed to 5%, 50%, and 90% at three different temperatures. Weight change of the standard stainless steel weight was recorded every 10 minutes for 72 hours.

3.5 Sorption Experiment

The sheet and resin samples were stored in a desiccator to remove the moisture from the samples at 23°C. To minimize the variation in thickness within the sample, small pieces of the sheets (around 1 cm² and 30 mg) were used. The samples were suspended on the arm of the electrobalance. After conditioning at 60°C and 0% RH for 1h, the sheet samples were exposed to a specific relative humidity (10, 30, 50, 70 and 90%) at a constant temperature (23 and 40°C). The weight gain (moisture uptake) was recorded, from t=0 to the time at which no more weight gain was observed (steady state), at 2 min interval thus providing a detailed information about the transient state. In this sorption study, the steady state was determined by a specific equilibrium criterion. The resin samples of both polymers were exposed (after conditioning) to specific relative humidity of 50 and 90 % RH at two different temperatures (23° and 40°C). All the sorption experiments of sheets and resins of both polymers were done in triplicate and standard error was calculated.

4. Results and Discussion

4.1 Physical Properties

The thickness of the processed Biomax[®] sheets was measured as 0.14 ± 0.03 mm (5.5 ± 1 mil) and for Sorona[®] as 0.11 ± 0.03 mm (4.5 ± 1 mil). The density of Biomax[®] and Sorona[®] sheets was measured at 23°C as 1344.3 kg/m^3 (1.34 g/cc) and 1334.7 kg/m^3 (1.33 g/cc), respectively (in accordance with ASTM D792-00). The percent crystallinity of polymer sheet and resin was calculated using the following formula:

$$\chi_c = 100 \times \frac{\Delta H_m}{\Delta H_o} \quad (6)$$

where ΔH_m is enthalpy of fusion and ΔH_o is the heat of melting of purely crystalline polymer. The percent crystallinity of Biomax[®] resin was found out to be around 18.3 % and after processing the percent crystallinity of Biomax[®] sheets dropped to 9.5 %. The percent crystallinity of Sorona[®] polymer was found to be 42 % for resin and 26 % for sheets. The drop in percent crystallinity after processing is due to the quenching of the polymer samples during sheet making in the compression press.

4.2 Instrument Noise and Drift:

To evaluate the amplitude of noise and drift of the equipment, a least squares method for regression was adopted.²⁸ The assumptions for the hypothesis testing of regression analysis are: (i) the relationship between x and y is linear, (ii) the errors are independent and (iii) normally distributed and (iv) variances of the errors are constant across the observations. The linear model for experimental observation can be written as²⁹:

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon_i \quad i = 1, 2, \dots, n \quad (7)$$

where x and y represent the time and weight change respectively and β_1 is the slope of the regression line.

The percent weight change vs. time graph of 50 mg standard weights at 40°C and 90% RH is shown in Fig. 3.2. The drift of the equipment is given by the slope of this regression line. The noise residual output vs. time plot for the same experiment is shown in Fig. 3.3.

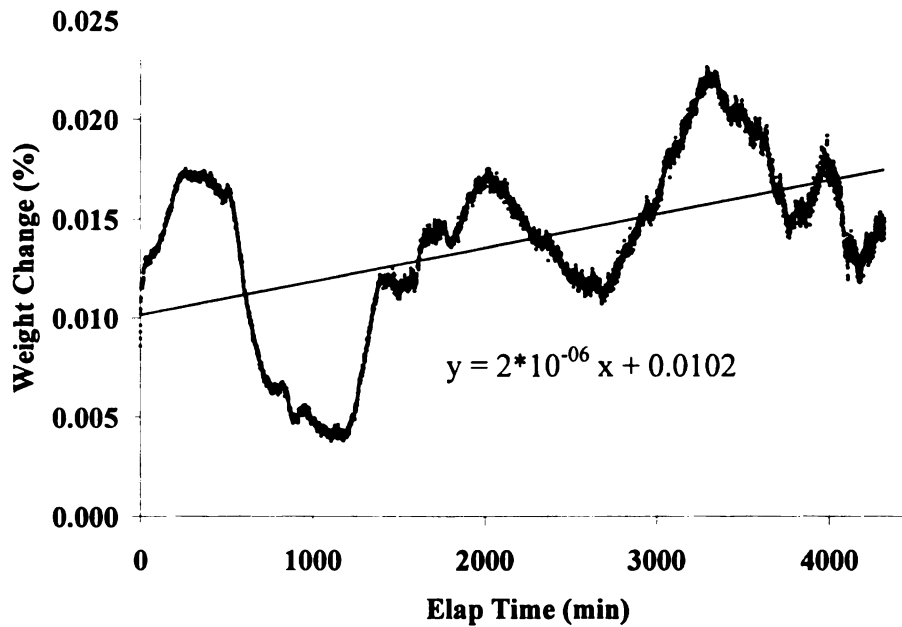


Figure 3.2: Percent weight change vs. time and linear regression line for a 50 mg standard weight at 40°C, 90% RH

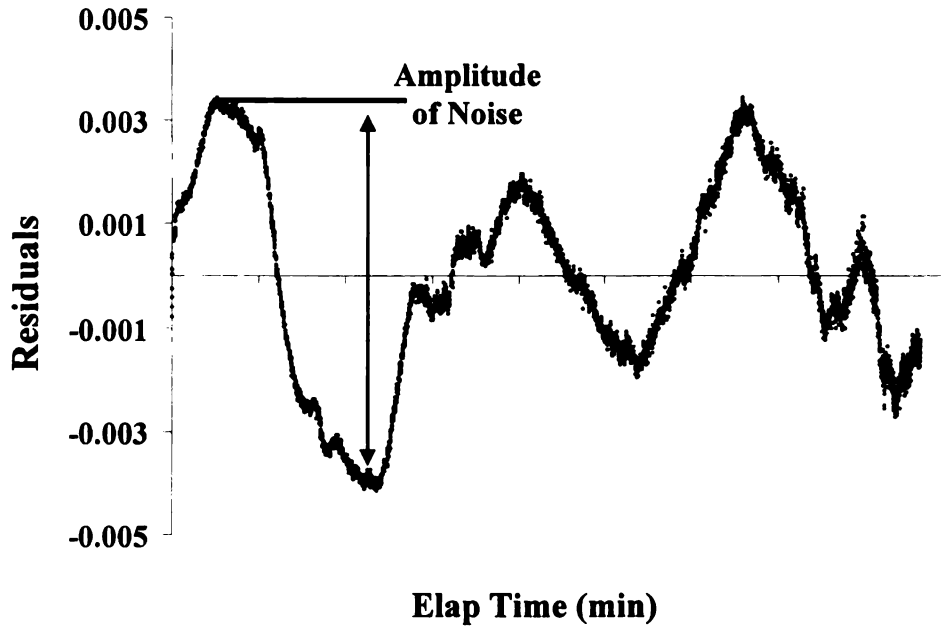


Figure 3.3: Residual output vs. time for 50 mg standard weight at 40°C, 90% RH

The results from linear regression statistical analysis are given in Table 3.2. The significant F values of all the experiments (not shown in table) were found to be very close to 0, thus null hypothesis H_0 ($\beta_1 = 0$) was rejected, concluding that the weight change (y) and time (x) are not independent ($\alpha = 0.05$). A small drift ranging from 10^{-06} to 10^{-07} was observed in the equipment at different experimental conditions. Both positive and negative drift was observed during the experiments. The drift of the equipment was not found to be dependent on either weight or experimental conditions.

The amplitude of the noise was calculated as the difference between the experimental values and the predicted value (std. metal weight's actual weight). The amplitude of noise of the equipment can be given as $3s$, where s is the square root of means squared error (MSE) from the residual analysis. Based on the empirical rule, $y_i \pm 3s$ contains 99.7% of the distribution. The amplitude of noise under different conditions is given in Table 3.2. The noise level was found to be very low as compared to the signal.

Although the noise amplitude increased with weight, the Signal to Noise ratio (S/N) was improved. The noise was independent of humidity and temperature, except for 20 mg weight, where an increase in noise was observed with increase in temperature.

Table 3.2: Regression analysis of the equipment's noise and drift

Standard				Amplitude of	
Weight	Condition	Regression Line	MSE (s ²)	noise (3s) %	S/N
20 mg	10°C 90%	$y = 1 \cdot 10^{-06}x + 0.0183$	$1.10 \cdot 10^{-06}$	0.003145	6359.30
	23°C 90%	$y = -4 \cdot 10^{-06}x + 0.0269$	$1.56 \cdot 10^{-06}$	0.003744	5341.88
	40°C 90%	$y = -6 \cdot 10^{-06}x + 0.0185$	$2.10 \cdot 10^{-06}$	0.004351	4596.64
50 mg	10°C 5%	$y = -4 \cdot 10^{-06}x - 0.0062$	$5.02 \cdot 10^{-06}$	0.006723	7437.16
	10°C 50%	$y = -2 \cdot 10^{-07}x - 0.0083$	$2.37 \cdot 10^{-06}$	0.004615	10834.24
	10°C 90%	$y = -5 \cdot 10^{-06}x + 0.0107$	$3.85 \cdot 10^{-06}$	0.005890	8488.96
	23°C 5%	$y = -3 \cdot 10^{-06}x + 0.0091$	$4.67 \cdot 10^{-06}$	0.006481	7714.86
	23°C 50%	$y = -3 \cdot 10^{-06}x + 0.0064$	$3.62 \cdot 10^{-06}$	0.005710	8756.57
	23°C 90%	$y = -6 \cdot 10^{-06}x - 0.0093$	$6.84 \cdot 10^{-06}$	0.007847	6371.86
	40°C 5%	$y = -4 \cdot 10^{-07}x - 0.0026$	$3.61 \cdot 10^{-06}$	0.005697	8776.55
	40°C 50%	$y = -1 \cdot 10^{-06}x + 0.0007$	$5.31 \cdot 10^{-06}$	0.006916	7229.61
	40°C 90%	$y = 2 \cdot 10^{-06}x + 0.0102$	$3.56 \cdot 10^{-06}$	0.005661	8832.36
100 mg	23°C 90%	$y = -7 \cdot 10^{-06}x - 0.0063$	$1.58 \cdot 10^{-05}$	0.011923	8387.15

4.3 Equilibrium Criterion Determination

The fundamental driving force that promotes the diffusion of a molecule through a polymer is the difference between the chemical potential of the fluid and the polymer phase. When the chemical potential of permeant in the fluid and polymer phase becomes equal, an equilibrium or steady state is reached.²⁵ In the gravimetric method, the steady state is said to be reached when the weight gain of the sample is zero or negligible.

In this study, the steady state is controlled and determined by an equilibrium criterion, provided in the flow system software of the SGA-100. The equilibrium criterion for both polymer types was set as 'weight change of 0.005% in 30 min'. It means if the weight change of the polymer is less than 0.005 % for continuous 30 minutes, the steady state or equilibrium is considered to be reached.

4.4 Moisture uptake in Sheets

The moisture sorption in both polymer sheets followed Fickian kinetics. The average percent moisture uptake for the triplicate runs vs. time (min) for Biomax[®] sheets at 23°C and 40°C for different water activities is shown in Fig. 3.4. The time taken to reach the steady state increased with relative humidity. The time to reach the steady state at 40°C was less than that at 23°C, due to higher saturated vapor pressure at higher temperatures.

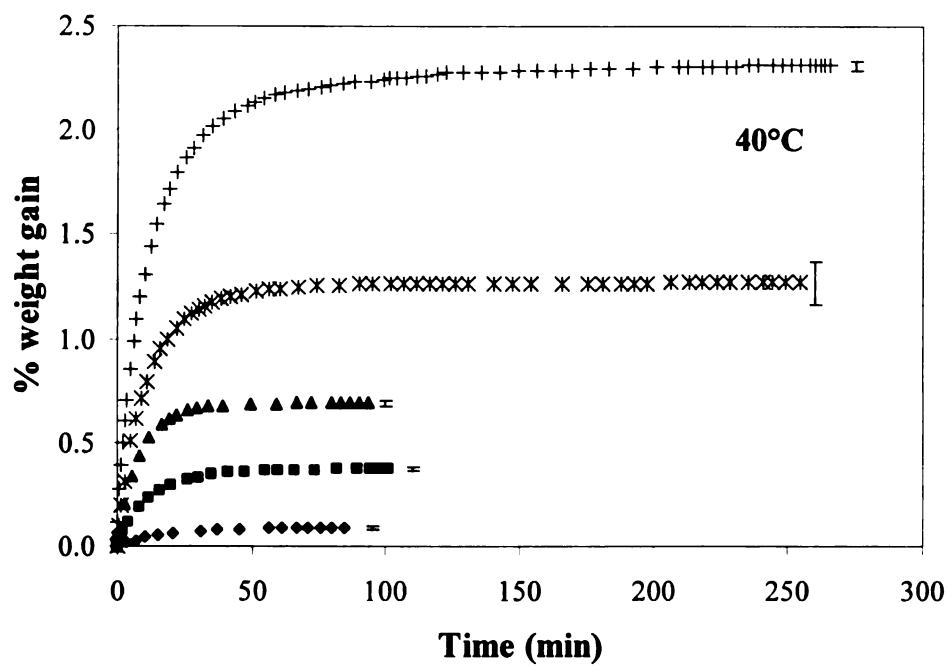
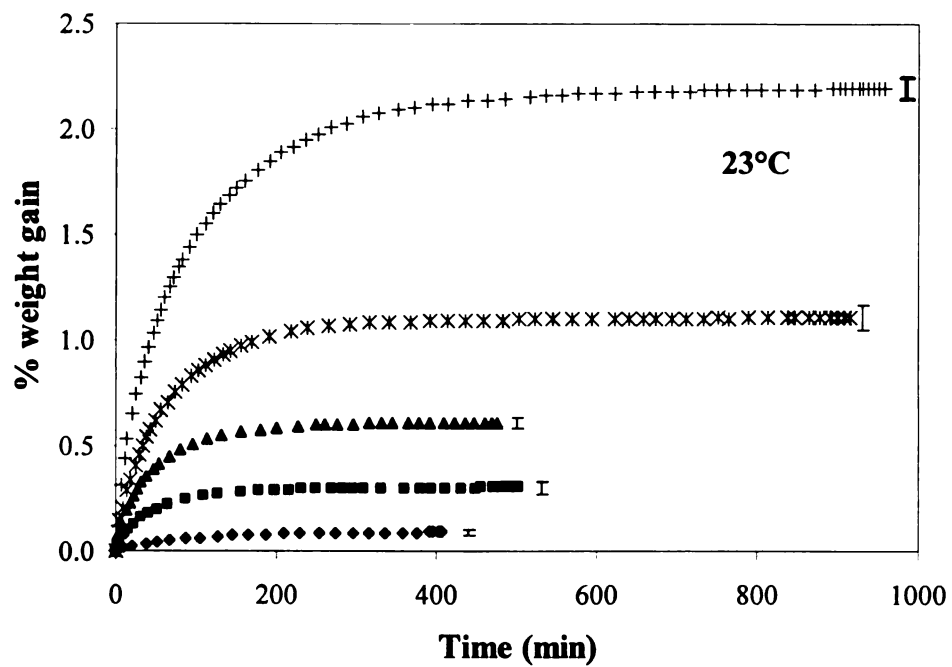


Figure 3.4: Average percent weight gain (3 runs) vs. time (min) for **Biomax[®]** sheets at 23°C and 40°C, S.E. bars are shown only for the last data point.

◆ 10% RH ■ 30%RH ▲ 50%RH × 70% RH + 90%RH

The average percent moisture uptake vs. time for Sorona® sheets at 23°C and 40°C at different relative humidities is shown in Fig. 3.5. Moisture uptake increased with the increased water activity and temperature. The moisture uptake in Sorona sheets (0.03-0.5%) was much lower than in Biomax sheets (0.1-2.5%) due to lower affinity to water of Sorona than Biomax® to water.

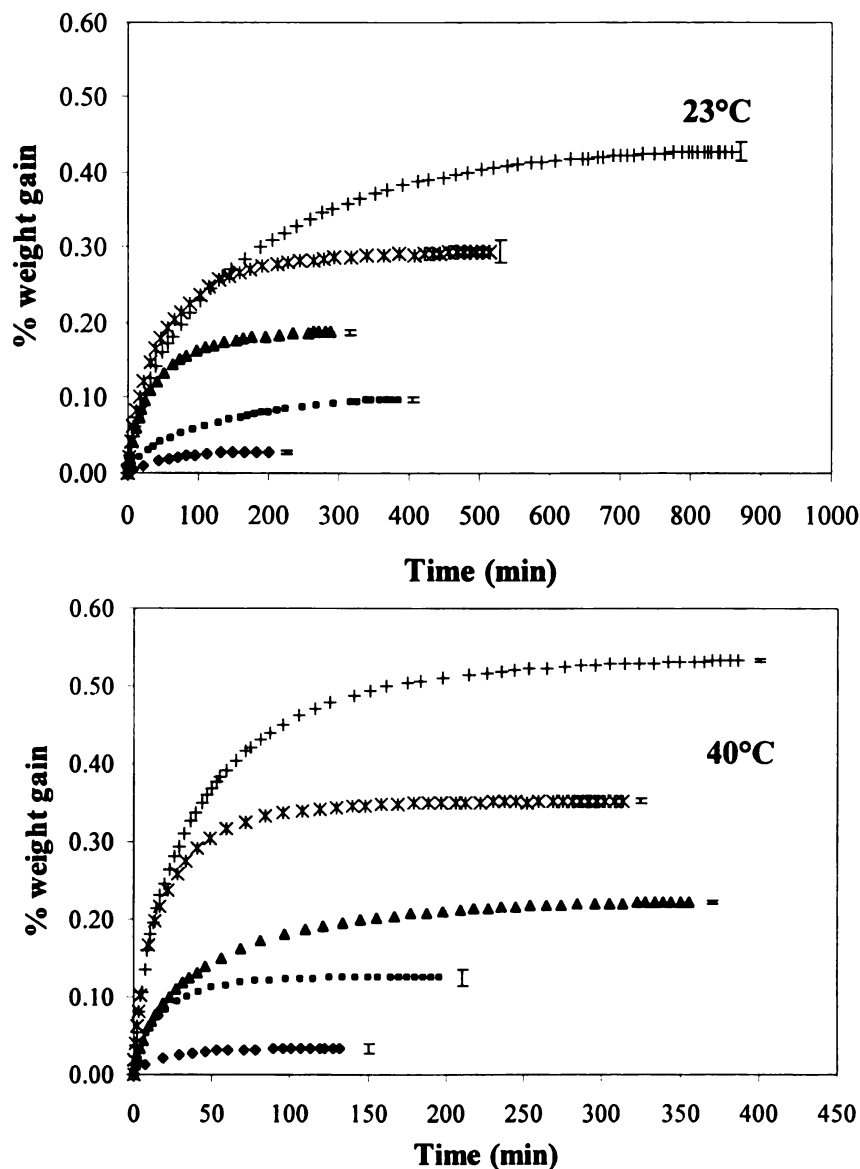


Figure 3.5: Average percent weight gain (3 runs) vs. time (min) for Sorona® sheets at 23°C and 40°C, S.E. bars are shown only for the last data point.

◆ 10% RH ■ 30%RH ▲ 50%RH × 70% RH + 90%RH

4.5 Consistency Test and Correction

To determine the fit of the experimental data to the model defined by Eq. 2, theoretical M_t/M_∞ values were calculated using Eq. 2. The experimental M_t/M_∞ and theoretical M_t/M_∞ vs. square root of time ($\text{second}^{1/2}$) are shown in Fig. 3.6.

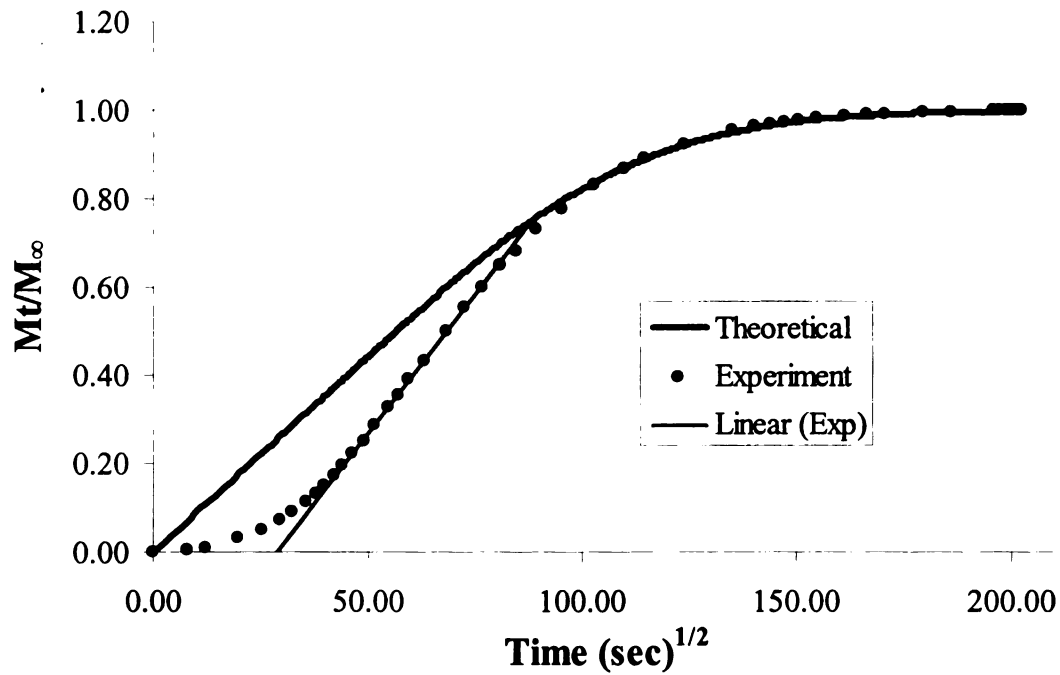
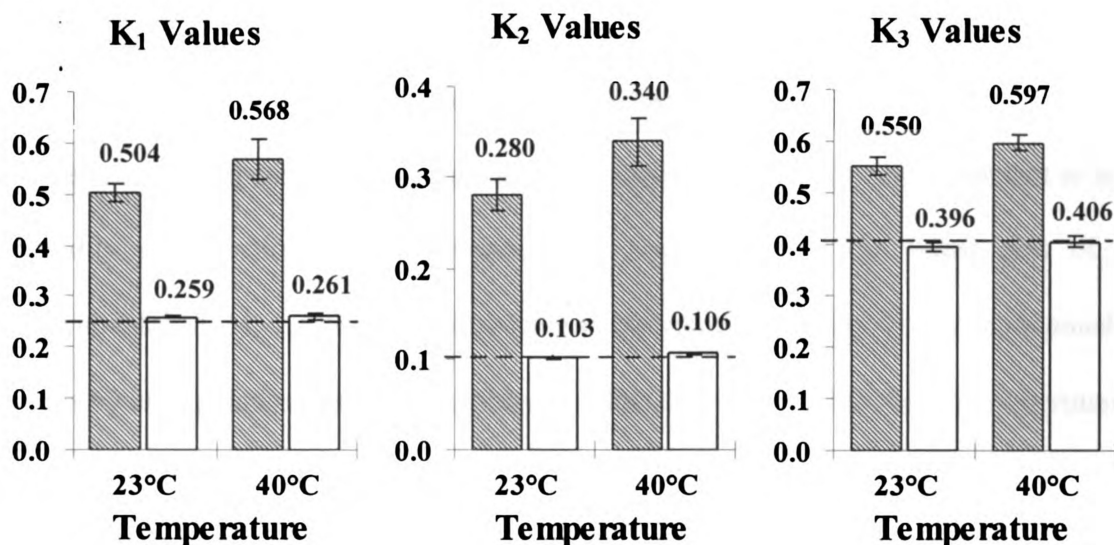


Figure 3.6: Experimental M_t/M_∞ (before correction) and theoretical M_t/M_∞ vs. square root of time ($\text{second}^{1/2}$) for a Biomax[®] sheet at 23°C and 30% RH

The initial part of the curve was concave and a large difference was observed between experimental and theoretical values. A similar difference was found for all the sorption experiments for both polymers. K_i parameters, for consistency test, of each sorption experiment were calculated for both polymers sorption runs (Fig. 3.7). As seen,

for both polymers experimental the K_1 and K_2 values differed from the theoretical values by more than 100%.

Biomax[®]



Sorona[®]

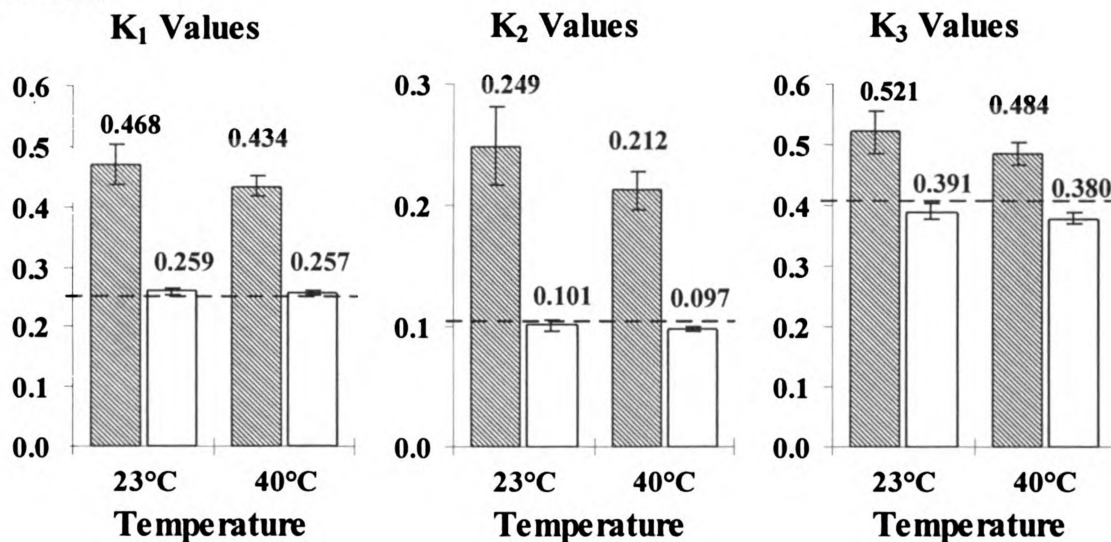


Figure 3.7: Average of K_i values of different relative humidities for Biomax[®] and Sorona[®] sheets before and after correction at 23°C and 40°C, dotted line represents the theoretical K_i value.

■ Before correction □ After correction

This deviation of experimental data from the theoretical model could be related to the time taken by the vapors inside the sample chamber to reach the target experimental vapor activity, as one of the assumptions for Eq. 2 is that the sorbate concentration around polymer sample changes stepwise from the initial zero concentration to the target experimental concentration. However, this is hardly possible in actual experiments. Therefore, to compensate for the time taken by vapors to reach the target constant relative humidity a correction in experimental data was proposed. The linear part of the experimental M_t/M_∞ curve was extrapolated to the x-axis (Fig. 3.6). The time obtained on x-axis by extrapolation was then considered as the zero time for the sorption experiments. After the correction, the experimental M_t/M_∞ and theoretical M_t/M_∞ (from Eq. 2) values were obtained. A very good fit was observed between the time-corrected experimental and the theoretical values for the same Biomax[®] sheet (Fig. 3.8).

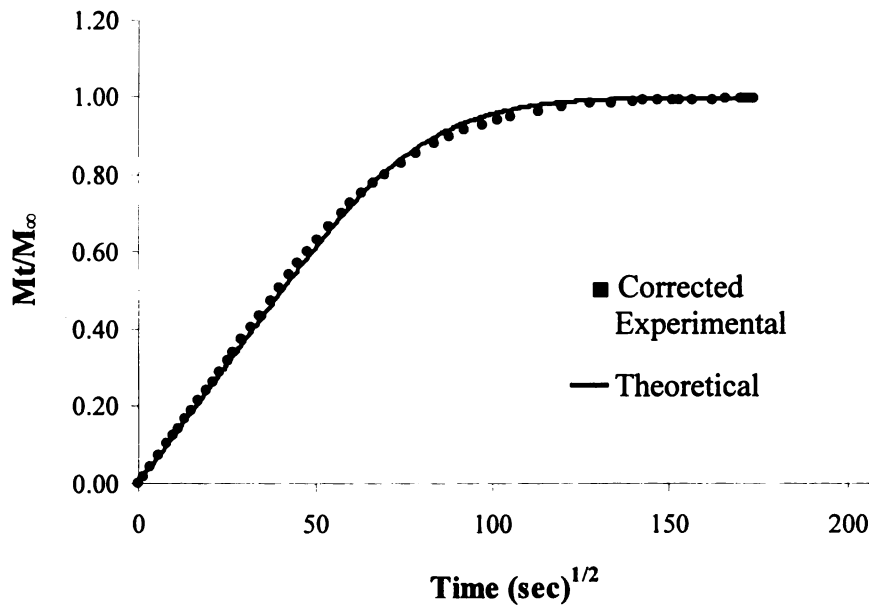
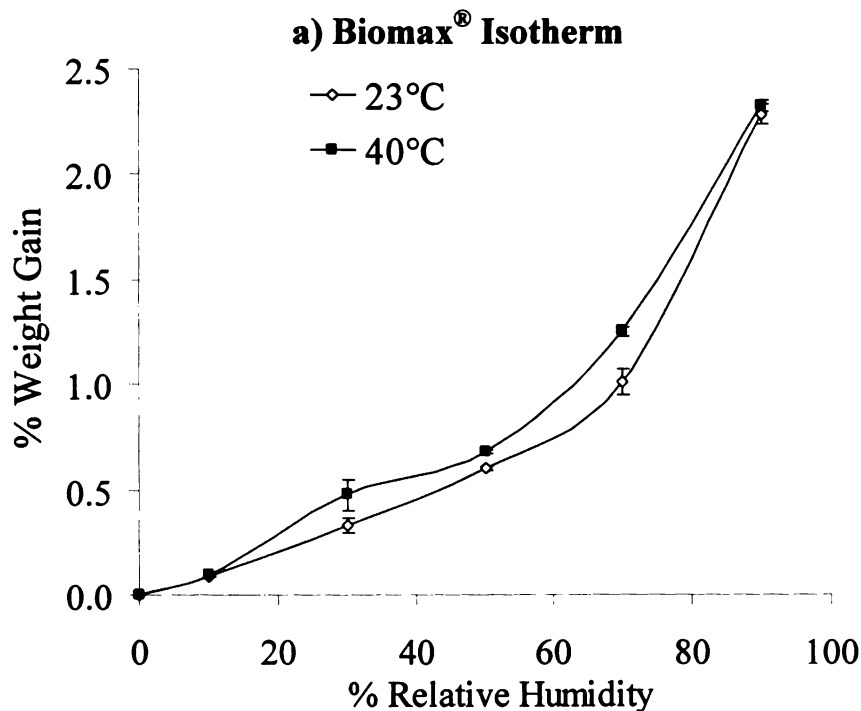


Figure 3.8: Experimental M_t/M_∞ (after correction) and theoretical M_t/M_∞ vs. square root of time ($\text{second}^{1/2}$) for a Biomax[®] sheet at 23°C and 30% RH

The K_i parameters were also calculated using the new corrected $t_{1/4}$, $t_{1/2}$, and $t_{3/4}$. As seen in Fig. 3.7, the difference between the experimental and theoretical K_i values was reduced to 0-10%, hence verifying the validity of corrected experimental data. A similar correction was applied to all sorption experiments of both types of polymer sheets. The corrected data were used to calculate the solubility and diffusion coefficients.

4.6 Sheet Moisture Sorption Results

The moisture sorption of the polymer sheet at the steady state was used to generate the moisture sorption isotherms for Biomax[®](a) and Sorona[®](b) sheets at 23°C and 40°C (Fig. 3.9). The polyester Sorona[®] sheets had low moisture sorption (0.5% at 40°C, 90%RH) as compared to Biomax[®] (2.5% at 40°C, 90%RH), which is a hydro-biodegradable polymer. Moisture sorption in both polymers was dependent on the RH. For Sorona[®] sheet the moisture sorption increased significantly with increase in temperature, except at 10% RH. For Biomax[®] moisture sorption was found to be slightly dependent on temperature only in the middle range of the relative humidities.



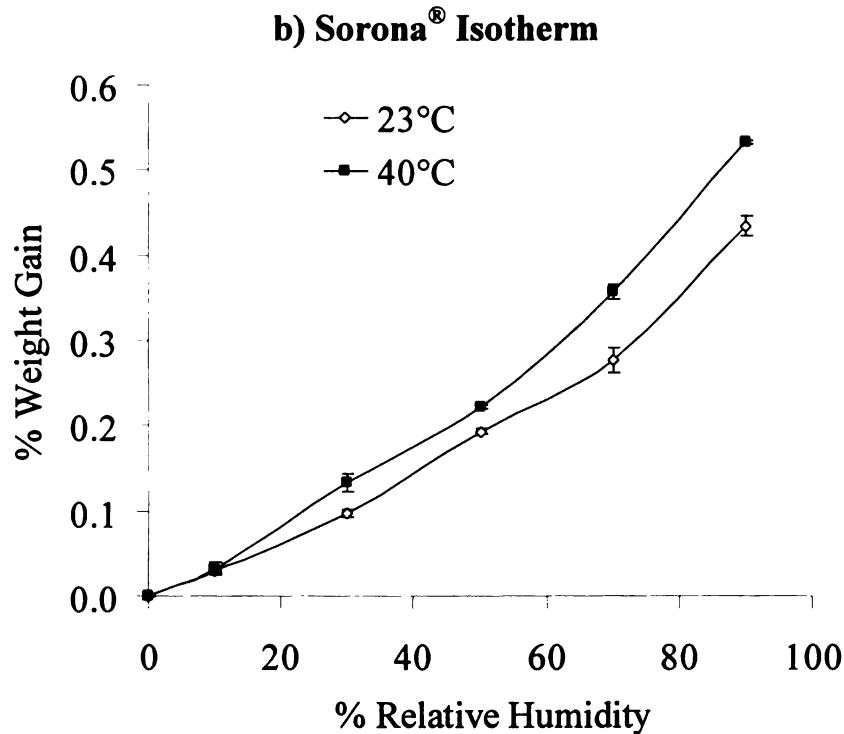


Figure 3.9: Moisture sorption isotherm of Biomax[®] (a) and Sorona[®] (b) sheets at 23°C and 40°C, error bars are S.E. for 3 runs

Most food and biomaterials are characterized by negative heat of sorption, which means equilibrium moisture sorption isotherm corresponding to lower temperature is situated above to that corresponding to higher temperature.³⁰ But both Biomax[®] and Sorona[®] did not followed this pattern, the moisture sorption at 40°C was more as compared to 23°C. Though not common but similar isotherms with such a positive temperature dependence have been reported previously.³¹⁻³³ For Biomax[®] sheets this behavior may be due to two reasons: (1) it is a hydro-biodegradable polymer and 40°C is above the glass transition temperature; thus, increasing the movements within the chain and allowing more moisture to be sorbed; and (2) the moisture sorption is driven by the hydrolysis of the ester linkages, as also seen in the case of PLA films.³²

A sum of square technique was applied to determine the best estimated diffusion from the experimental data.⁹ The best estimated diffusion coefficient can be defined as diffusion coefficient for which the difference between the experimental and the theoretical curve (Eq. 2) is least. A representative plot of the sum of squares values as function of diffusion coefficient values (calculated around $t_{1/2}$) was used, from which the best estimated diffusion coefficient was determined from minimum sum of square value (plot not shown).

Table 3.3 presents the best estimated diffusion, solubility, and permeability coefficients of Biomax[®] and Sorona[®] sheets at 23°C and 40°C. As the temperature increases the mobility of the chain and free volume increases, so more permeant can pass through the sheet easily. Hence, diffusion coefficient of both polymer sheets increased with increase in temperature. For Biomax[®] sheet, the diffusion coefficient drops at 90% RH which can be related to the condensation of vapors on the sheet at high water activity. The solubility coefficient of both polymers increased with relative humidity. A statistical analysis, Least Square Means Difference (LSMD),²⁹ was conducted to determine whether the solubility and diffusion coefficients of both polymers differed as a function of relative humidity. The solubility coefficient of Biomax[®] was found to be slightly dependent on the RH and temperature. The S increased significantly with increased in RH from 10% to 50% and from 50% to 90%. The diffusion coefficient of Biomax[®] slightly increased with increase in RH except at 90% RH at both temperatures, where a drop in D was observed which could be related to the condensation of vapors on the sheet at high humidity. The changes in diffusion coefficient of Sorona[®] sheets were not statistically significant (LSMD results) because of the unequal residual variance at different RH. The solubility

coefficient of Sorona[®] sheets at 23°C increased significantly with increase in RH from 10% to 50% and 50% to 90% and at 40°C a significant increased was observed from 10% to 70% and higher RH.

Table 3.3: Average Solubility, Diffusion and Permeability coefficients for Biomax[®] and Sorona[®] sheets at 23°C and 40°C
 (± S.E. of 3 runs) with LSMD results (means followed by same letter are not significantly different, $\alpha=0.05$)

BIOMAX [®]						
RH (%)	$S \times 10^{-3}$ (kg/m ³ pa)	$D \times 10^{-13}$ (m ² /sec)	$P \times 10^{-15}$ (Kg.m/m ² secPa)	$S \times 10^{-3}$ (kg/m ³ pa)	$D \times 10^{-13}$ (m ² /sec)	$P \times 10^{-15}$ (Kg.m/m ² secPa)
		23°C			40°C	
10	4.19 ± 0.17 a	4.09 ± 0.3 ab	1.56 ± 0.3	1.73 ± 0.14 a	19.70 ± 4.4 a	3.37 ± 0.7
30	5.28 ± 0.53 ab	6.62 ± 0.1 abc	3.49 ± 0.3	2.71 ± 0.51 b	26.00 ± 2.0 a	7.24 ± 1.9
50	5.92 ± 0.24 bc	8.18 ± 1.3 bc	4.90 ± 1.0	2.49 ± 0.04 ba	36.20 ± 4.4 b	9.03 ± 1.2
70	6.90 ± 0.44 c	8.86 ± 2.6 c	6.13 ± 1.8	3.02 ± 0.29 b	40.40 ± 4.5 c	12.00 ± 1.2
90	12.16 ± 0.27 d	3.70 ± 0.6 a	4.53 ± 0.8	4.71 ± 0.05 c	22.50 ± 1.1 a	10.60 ± 0.5
SORONA [®]						
RH (%)	$S \times 10^{-3}$	$D \times 10^{-13}$ 23°C	$P \times 10^{-16}$	$S \times 10^{-3}$	$D \times 10^{-13}$ 40°C	$P \times 10^{-16}$
10	1.36 ± 0.08 a	2.22 ± 0.4 a	2.99 ± 0.5	0.59 ± 0.11 a	6.40 ± 1.2 a	3.47 ± 0.1
30	1.54 ± 0.07 a	1.36 ± 0.2 a	2.06 ± 0.3	0.80 ± 0.06 b	4.77 ± 1.7 a	3.70 ± 1.2
50	1.84 ± 0.03 b	2.63 ± 0.5 a	4.64 ± 1.4	0.80 ± 0.01 b	4.44 ± 1.3 a	3.54 ± 1.0
70	1.87 ± 0.10 b	2.23 ± 0.6 a	4.05 ± 0.9	0.93 ± 0.01 bc	4.75 ± 0.8 a	4.40 ± 0.6
90	2.28 ± 0.06 c	1.57 ± 0.3 a	3.59 ± 0.7	1.07 ± 0.02 c	2.70 ± 0.4 a	2.87 ± 0.4

4.7 Effect of Temperature on Permeability, Diffusion, and Solubility

The temperature dependence of transport parameters are usually described by Arrhenius-type relationships, and are given as

$$S(T) = S_0 \exp(-\Delta H_s / RT) \quad (8)$$

$$D(T) = D_0 \exp(-E_D / RT) \quad (9)$$

$$P(T) = P_0 \exp(-E_P / RT) \quad (10)$$

where ΔH_s is the enthalpy of sorption, E_D is the activation energy of diffusion, E_P is the activation energy of permeation.

The ΔH_s , E_D , and E_P for polymeric sheets were determined and are reported in Table 3.4. The enthalpy of sorption was determined from the experiment runs at 23 and 40°C and was averaged over the whole range of RH. The enthalpy of sorption of Biomax[®] is lower than Sorona[®] suggesting that there is a higher interaction between the moisture and Biomax. While the E_D of Sorona was significantly lower than that of Biomax indicating that diffusion of moisture through Biomax is more temperature dependant. The enthalpy of mixing (ΔH_M) was determined as 16 and 7.8 kJ/mol for Biomax and Sorona respectively confirming the different interaction with moisture.

Table 3.4: Enthalpy of sorption and activation energy of Biomax[®] and Sorona[®] sheets (average of 3 runs $\pm$ S.E.)

	ΔH_s kJ/mol	ΔH_M kJ/mol	E_D kJ/mol	E_P kJ/mol
Biomax [®]	-38.03 $\pm$ 2.1	16.0	70.23 $\pm$ 3.3	32.92 $\pm$ 1.8
Sorona [®]	-34.20 $\pm$ 1.6	7.8	37.48 $\pm$ 6.5	2.93 $\pm$ 6.9

4.8 Resin Moisture Sorption Results

To determine the effect of processing on the moisture sorption, the sorption experiments were also done using the resin pellets of both polymers. For both polymers, moisture uptake by resin did not follow fickian kinetics and did not reach steady state within the allowable time range of the equipment. To compare the sorption of moisture in polymer sheets and resin, moisture uptake after 1400 minutes was recorded for the resin (Table 3.5). Moisture sorption in resin was observed to be very low as comparable to sheets for both polymers, at both temperatures. When the polymer is processed into sheets, it undergoes some morphological changes depending on processing conditions such as temperature, cooling rate, orientation, and pressure. During the processing the polymer is heated above its melting temperature and then cooled down. The cooling time, during which the polymer chains rearrange themselves, affects the crystallinity of the processed polymer, hence affecting the sorption properties.

Table 3.5: Moisture uptake in Biomax[®] and Sorona[®] resin after 1400 minutes,

Average of 3 runs $\pm$ S.E.

Moisture uptake at 1400 min (kg sorbate/kg polymer)				
RH (%)	Biomax [®]		Sorona [®]	
	23°C	40°C	23°C	40°C
50	0.19 $\pm$ 0.01	0.53 $\pm$ 0.03	0.07 $\pm$ 0.01	0.13 $\pm$ 0.01
90	0.68 $\pm$ 0.03	1.86 $\pm$ 0.04	0.15 $\pm$ 0.00	0.29 $\pm$ 0.01

As seen from the DSC results, the crystallinity decreased after the processing of polymer from resin to sheet, hence moisture sorption in sheets was observed to be more

than that in the resin. For Biomax[®], the moisture uptake in resin was observed as 70% and 21% less than that in sheets at 23°C and 40°C, respectively. For Sorona[®], moisture uptake was 64% lower at 23°C and 43% at 40°C as compared to sheets at respective relative humidities.

5. Conclusions

A protocol for noise quantification of gravimetric equipment was proposed and amplitude of noise and drift associated with symmetrical gravimetric analyzer was quantified. A complete sorption profile of DuPont Biomax[®] and Sorona[®] sheets was generated at two different temperatures (23°C and 40°C) and five different water activities by gravimetric method. A time correction, supported by assumptions and consistency test, was done for all the sorption experiments of both polymers. The moisture uptake, at steady state, by Biomax[®] sheets was approximately five times as that of the Sorona[®] sheets. Both Biomax[®] and Sorona[®] sheets isotherm showed a positive temperature dependence i.e. more moisture was sorbed at higher temperature. The solubility coefficients for both polymer sheets increased with water activity and decreased with increase in temperature. The data generated would be useful in the application of these new polymers in packaging industry.

Moisture sorption in both types of resins did not follow Fickian kinetics. For Biomax[®] the moisture uptake in resins at 1400 min. was lower by 70% at 23°C and 21% at 40°C than the steady state moisture uptake of the sheets, whereas for Sorona[®] resins it was 64% lower at 23°C and 43% at 40°C as compare to steady state moisture uptake of the sheets.

6. References:

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CHAPTER 4

The Effect of Moisture Sorption on the Physical and Mechanical Properties of Biomax[®] and Sorona[®]

1. Introduction

DuPont Sorona[®], PTT, Poly(trimethylene terephthalate) is a thermoplastic polyester produced by condensation of 1,3-propanediol (derived from renewable corn sugar) and terephthalic acid (derived from fossil fuel).¹ Sorona[®] belongs to the thermoplastic aromatic polyester family and due to the three carbon glycol in its backbone it has better mechanical properties as compared to the other two members of this family (PET and PBT). Sorona[®] has a semi-crystalline molecular structure with a zigzag shape that gives it excellent stretch recovery and tensile and compressive properties.² Sorona[®] has a good barrier to moisture, is dimensionally stable, and has good weather and chemical resistance. Sorona[®] can also be used as an engineering thermoplastic because of its good thermal and mechanical properties.^{2, 3} Research had been conducted to tailor the physical and mechanical properties of Sorona[®] through blending it with other polymers or nano-composites,^{1, 4} but few researchers have studied the effect of moisture on the physical and mechanical properties of Sorona[®].

DuPont Biomax[®], polyethylene terephthalate succinate,⁵ is a hydro-biodegradable modified polyester. It is a modified polyethylene terephthalate (PET) and up to three aliphatic monomers can be added to the polyester, which creates weak spots that promote degradation through hydrolysis.⁶ Biomax[®] is one of the few polymers that have received the “COMPOSTABLE” logo from The Biodegradable Products Institute (BPI).⁷ Due to

its lower T_m as compared to PET it is easy to process into blown film, oriented film, or molded articles. Its major applications can be single-use products, such as waste bags, blister packs, geotextiles, seed mats and coating for disposable eating utensils (cups, bowls or plates).^{6, 8}

In the previous chapter, the moisture sorption profile of Biomax[®] and Sorona[®] was evaluated. This study aims to characterize the effect of moisture sorption on the physical (T_g and crystallinity) and mechanical properties (modulus of elasticity and tensile strength) of Biomax[®] and Sorona[®].

2. Methodology

2.1 Polymer processing

Biomax[®] (4026) and Sorona[®] resin pellets were obtained from E.I. DuPont[™] de Nemours & Co. (Wilmington, DE). The resin was processed using a DSM twin screw Micro-Extruder and Injection Molder (TS/I-02, DSM, Netherlands) to obtain small discs (25.4 mm dia. and 2 mm thick) and ‘dumbbell’ shaped samples. The processing temperature of the barrel of DSM micro extruder was kept at 200°C with a screw speed of 100 rpm for Biomax[®]. For Sorona[®], the barrel temperature was 250°C and the screw speed was 150 rpm. A compression molding press (Carvar Hydraulic Press, Wabash, IN) was used to process the discs into sheets. The temperature of the hydraulic press platen was kept at 200°C with 12,000 psi pressure for Biomax[®] and 250°C with 10,000 psi pressure for Sorona[®]. The sheets samples were cooled quickly in the compression press by rushing cold water through the platens. The thickness of both polymers sheets was maintained at 4 to 6 mils. Details of processing are given in the previous paper.

2.2 Conditioning of the samples

Dried and moisture-sorbed sheet and dumbbell samples were used for this study. To remove the residual moisture, the polymer sheets and dumbbell shaped samples were preconditioned in an airtight jar with desiccant at 23°C until no further weight loss was observed; these samples had been referred as dried samples throughout this chapter. A saturated salt solution of sodium chloride (Aldrich Chemical Co., Milwaukee, WI) was prepared in an airtight jar in accordance with ASTM E104-02(2007) to obtain 75±1 % relative humidity at 23±1°C. Both polymer sheets and dumbbell shaped samples were stored at 75% RH at 23°C until they had reached the steady state. These samples had been referred as sorbed samples throughout this chapter.

2.3 Physical Properties

2.3.1 Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter (TA Instruments, New Castle, Delaware) was used to determine the glass transition temperature (T_g), melting temperature (T_m), and percent crystallinity in accordance with ASTM D3418-03.⁹ For both polymer samples one heating cycle followed by one cooling cycle was used. Aluminum pans were used for the DSC experiments. Biomax[®] sheet samples were heated from 10°C to 210°C at a rate of 10°C/min and then cooled down to 10°C at a rate of 5°C/min. Sorona[®] sheets were heated from 10°C to 265°C at a rate of 10°C/min and then cooled to 10°C at a rate of 5°C/min. The data were analyzed with Universal Analysis software (TA Instruments). For both polymers, three measurements were performed on dried and sorbed sheet samples.

2.3.2 X-Ray Diffraction (XRD)

The percent crystallinity of Sorona[®] and Biomax[®] was also determined at 23°C using the X-Ray diffraction (XRD) method,¹⁰ using a Rigaku RU-200B equipped with a CuK α radiation source (λ = 0.1541 nm). The XRD tube power and current used were 45 kW and 100 mA respectively. Both dried and sorbed samples were used for XRD analysis. The measurements were done in triplicate using an angle of exposure of 10° to 30° and scan speed of 1° per min. Results consisted of a diffractogram in which peaks (crystallinity peaks) corresponds to rings shown on the diffraction image. Fractional crystallinity was determined as the ratio of the area under the crystallinity peaks and the total area (sum of crystallinity peaks and amorphous area).¹⁰ Intensity was plotted against angle (2θ) and area under curve was calculated using Jade-7 software (Materials Data Inc., Livermore, CA).

2.3.3 Dynamic Mechanical Analyzer (DMA)

For Biomax[®], due to ambiguous results of T_g from DSC, the T_g was determined using a dynamic mechanical analyzer (DMA) (TA Instruments, DE). The center part of the dumbbell shaped samples was cut (30 x 5 x 1.4 mm) and used for determination of T_g through single cantilever mode. Three samples of both dried and sorbed samples were tested at a frequency of 1 Hz and 50 μ m amplitude over the temperature range of 0° to 80°C at a ramp rate of 2°C/min. The T_g had been determined from the peak of the loss modulus.

2.4 Mechanical Properties

The mechanical properties, Young's modulus of elasticity and tensile strength, were measured on a tensile instrument model SFM-20 made by United Testing Systems (Huntington Beach, CA). To study the effect of moisture on mechanical properties, the dried and sorbed dumbbell shaped samples of both polymers were tested in accordance with ASTM D638-03.¹¹ A sample width of approx. 1.4 mm and gage length of 25.4 mm (1 in) with crosshead speed of 1.27 mm/min (0.05 in/min) was used. Five runs of each type of sample (both polymer- dried and sorbed) were examined and the average and the standard error had been reported.

2.5 FT-InfraRed

Dried and sorbed Biomax[®] sheet samples were analyzed using a Shimadzu IR Prestige-21 Spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD) to study the interaction of moisture with the polymer. The experiment was performed by first taking the background scan of air and then taking the transmission spectrum of a Biomax[®] sheet samples at room temperature (around 23°C). The spectrum was recorded in the wavenumber range from 600 to 4000 cm⁻¹, by taking 40 scans per run to get a better resolution. The sheet was then kept in a jar with water at 23°C, to let the sheet absorb the moisture. Same sheet was then again scanned to study the interaction of moisture with the polymer.

3. Results and discussion

3.1 Physical properties

The amount of moisture sorbed by Biomax[®] and Sorona[®] at 23°C and 75% RH was determined using the moisture sorption isotherms as 1.3 g/100 g of polymer and 0.3 g/100 g of polymer, respectively.

The melting temperature (T_m) of Biomax[®] and Sorona[®] sheets was determined as 198°C and 228°C respectively; no significant change was observed in T_m before and after moisture sorption for both polymers (data not shown). The results of T_g and crystallinity from DSC, XRD and DMA analysis are given in Table 4.1. As the moisture uptake in Sorona[®] was very low, no significant difference in the physical properties, T_g and crystallinity, was observed among the dried and sorbed samples. The T_g of Sorona[®] sheets was determined as 57°C for the dried samples and 54.6°C for the sorbed samples. A student's t-test showed that the change in T_g was not significant ($\alpha = 0.05$).¹²

For Biomax[®], the DSC results of T_g were ambiguous and had significant variability within different runs (data not shown). Thus the DMA single cantilever mode was used to determine the T_g , identified as the peak of loss modulus (Fig. 4.1). The T_g of Biomax[®] dropped by 10°C (from 40°C to 30°C) after moisture sorption, which shows the plasticizing effect of water. Water acts as plasticizer by reducing the inter- and intra-macromolecular forces also seen in PET.¹³ These results are also supported by the fact Biomax[®] is a hydro-biodegradable polymer; moisture lowers the T_g and thus helps in degradation of the polymer by micro-organisms.

Table 4.1: Physical properties of dried and sorbed Biomax[®] and Sorona[®] samples

Average of 3 runs $\pm$ S.E

Sample \ Property	T_g (C°)	Crystallinity (%) DSC	Crystallinity (%) XRD
Sorona[®]			
Dried Samples	57.0 ± 0.4 #	26.4 ± 0.9	22.4 ± 0.1
Sorbed Sample *	54.6 ± 0.3 #	28.5 ± 0.5	22.4 ± 1.0
Biomax[®]			
Dried Samples	39.9 ± 0.7 ^	9.5 ± 0.7	12.9 ± 0.9
Sorbed Sample *	29.7 ± 0.5 ^	3.6 ± 1.1	19.4 ± 0.6

* Samples sorbed with moisture at 75% RH at 23°C

^ For Biomax[®] T_g reported is from DMA results

For Sorona[®] T_g reported is from DSC results

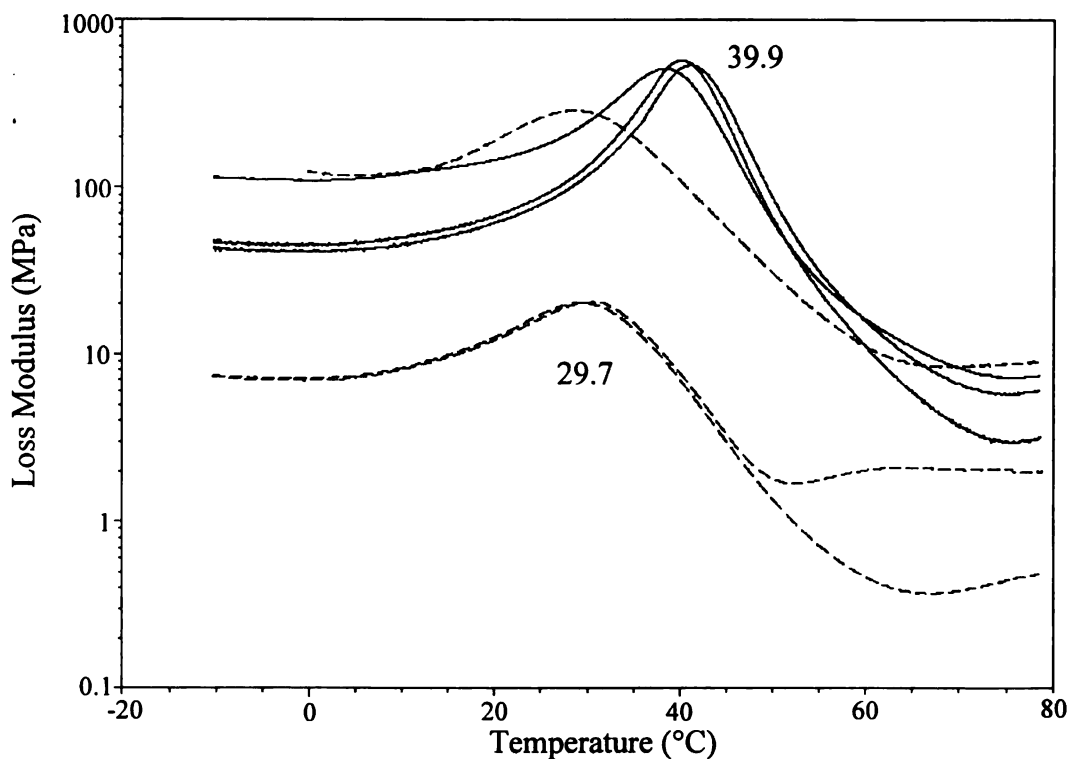


Figure 4.1: DMA results for Biomax[®] dried and sorbed samples,

solid line- Biomax[®] dried and dotted line- Biomax[®] sorbed

The percent crystallinity determined by DSC and XRD was found to be different for both polymers. This can be due to the fact that during a DSC run, the sample is heated to its melting point, which causes the sample to loose moisture. In DSC the percent crystallinity (χ_c) was calculated by using the following equation:

$$\chi_c = 100 \frac{\Delta H_m}{\Delta H_o} \quad (1)$$

where ΔH_m is enthalpy of fusion and ΔH_o is the heat of melting of purely crystalline polymer. Poly(ethylene terephthalate) ΔH_o (140 J/g) was used for calculating the percent crystallinity as ΔH_o value for both polymers was not available. The percent crystallinity was determined using the area under the crystallinity peaks and the total area (sum of crystallinity peaks and amorphous area) (Fig. 4.2).¹⁰

$$\chi_c = 100 \frac{Area_{Crystalline}}{Area_{Crystalline} + Area_{Amorphous}} \quad (2)$$

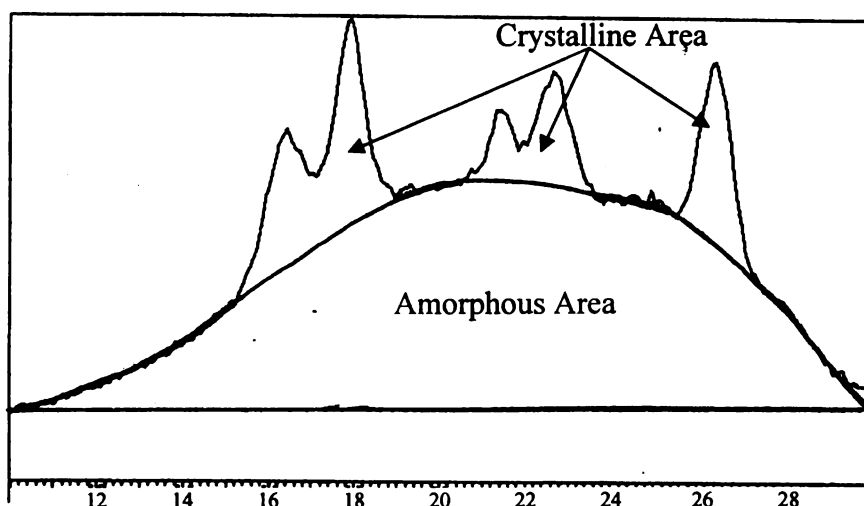


Figure 4.2: Refractogram from XRD analysis for Biomax[®] dried sample

For Sorona[®], the percent crystallinity determined by DSC was close to the results from XRD. No significant effect of moisture on the crystallinity of Sorona[®] sheets was observed through either technique.

3.2 Mechanical Properties

The mechanical properties of the polymers were evaluated by the stress and strain characteristics under tensile deformation (Fig. 4.3). The modulus of elasticity is given by the slope of the initial linear portion of the curve and tensile strength is given as the highest point of the curve. Modulus of elasticity and tensile strength of Sorona[®] dried samples were determined as 2.2 GPa and 60 MPa, respectively (Fig. 4.4).

Tensile strength and modulus were found to be very close to the values reported in the literature.^{3, 4} The effect of moisture on the mechanical properties in case of Sorona[®] was not significant. Modulus of elasticity and tensile strength of Biomax[®] dried samples was determined as 2.2 GPa and 52 MPa, respectively. Mechanical properties of Biomax[®] samples were reduced drastically after exposure to moisture, which could be the result of cleaving of the larger polymer molecules into smaller molecules by moisture.⁶ The modulus of elasticity and tensile strength of Sorona[®] samples and dried Biomax[®] samples was found to be close to that of PET.^{14, 15}

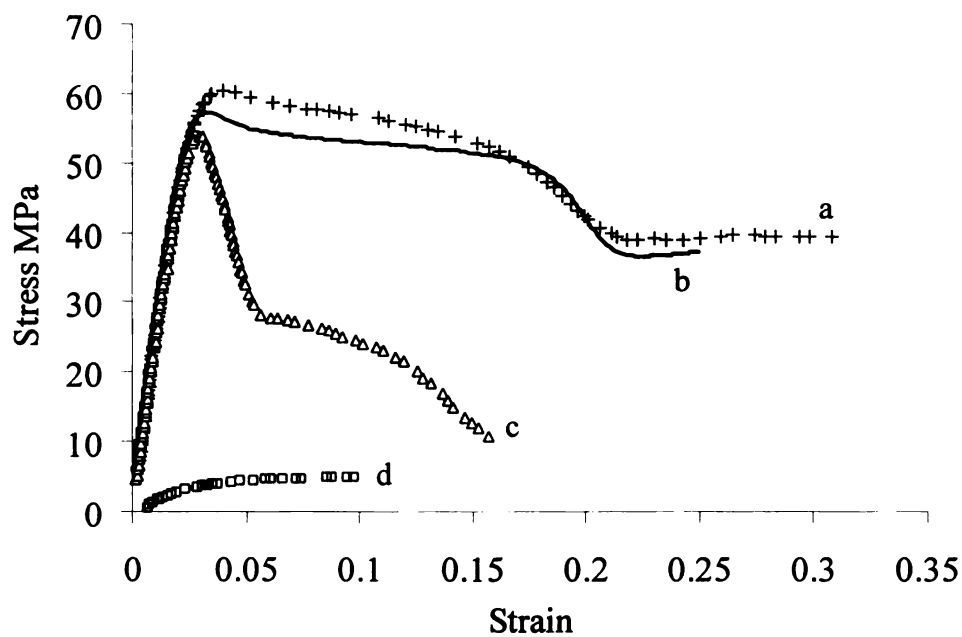


Figure 4.3: Stress-strain curves for Biomax® and Sorona® samples;

a) Sorona® dried, b) Sorona® sorbed, c) Biomax® dried, and d) Biomax® sorbed

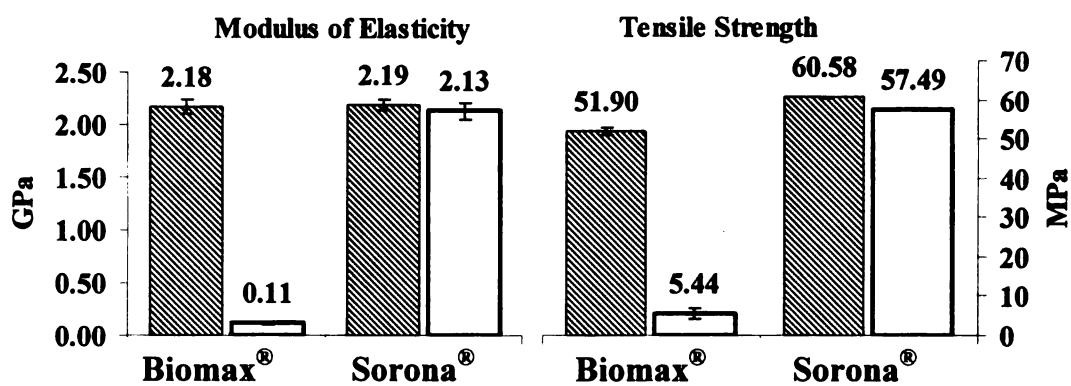


Figure 4.4: Mechanical properties of dried and sorbed Biomax® and Sorona® samples,

Average of 5 runs $\pm$ S.E

▨ Dried samples

□ Sorbed samples

3.3 FT-IR Results

The transmission spectrum of a dried Biomax[®] sheet is shown in Figure 4.5. Also shown is the scan of the same sheet when exposed to moisture for 1710 min and 4080 min. As seen in the spectrum an increase in transmission was observed around 3300 cm⁻¹. The broad peak in this 3200 to 3600 cm⁻¹ is attributed to the stretching of OH bonds. The center peak of this region was around 3400 cm⁻¹, which corresponds to the intermolecular hydrogen bonding.¹⁶ The FTIR results confirm that the water is interacting with the polymer and is bonded with the polymer.

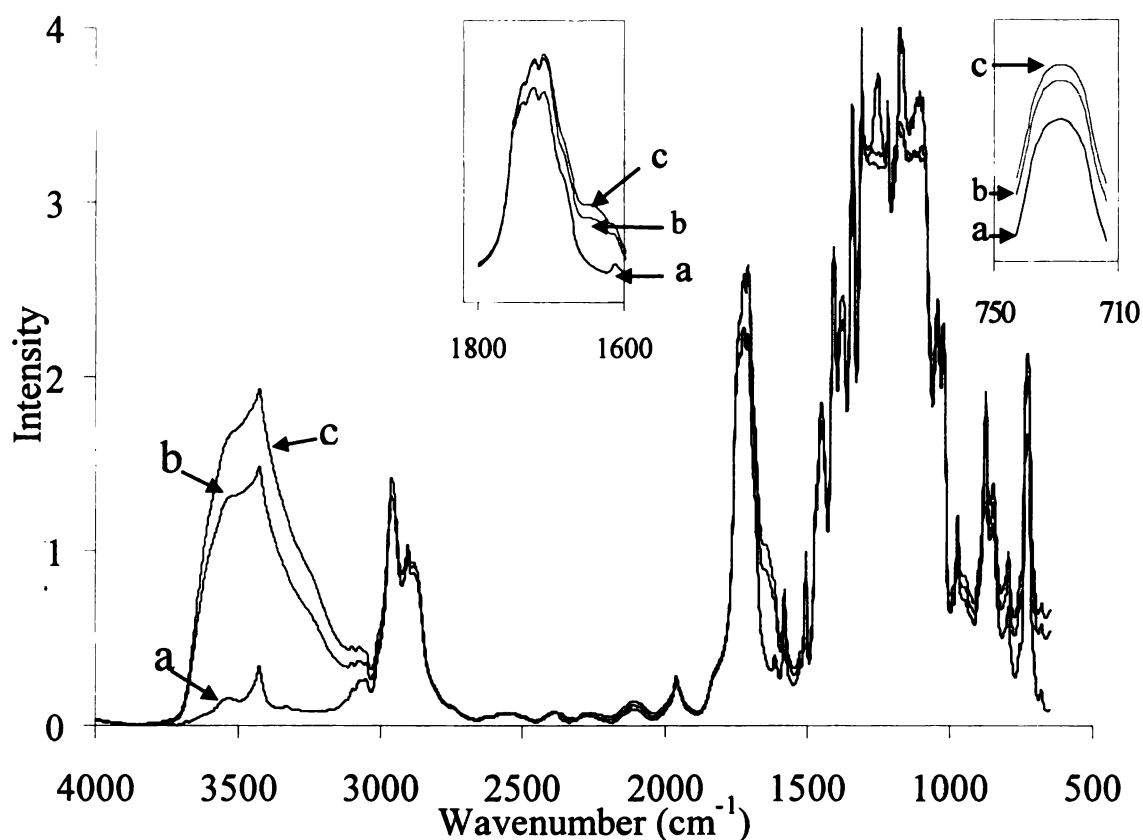


Figure 4.5: IR Spectrum of Biomax[®] sheet before and after moisture sorption; a) dried sample, b) exposed to moisture for 1710 min, and c) exposed to moisture for 4080 min.

4. Conclusions

The mechanical and physical properties of Biomax[®] and Sorona[®] were evaluated using DSC, XRD, DMA and UTS. Furthermore, the effect of moisture sorption on the physical and mechanical properties of both polymers was evaluated. Moisture sorption had little or no impact on the mechanical and physical properties of Sorona[®]. These results indicate that Sorona[®] would be useful as a packaging polymer or an engineering thermoplastic.

In Biomax[®], the water acts as a plasticizer as shown by a drop in glass transition temperature after moisture sorption. A drastic drop in mechanical properties of Biomax[®] samples was observed after exposure to moisture, possibly due to cleaving of the larger molecules into smaller molecules and reduction in molecular weight.

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Chapter 5

Conclusions

1. Conclusions

DuPont Biomax[®] and Sorona[®] are two of many newly developed biopolymers which are gaining attention in the packaging industry. Through this research the moisture sorption in these polymers was studied using a gravimetric technique. Furthermore, the effect of moisture on mechanical and physical properties of these two polymers was also assessed. The main conclusions of this study can be summarized as follow:

- ✓ A protocol for the noise quantification of gravimetric equipment – Symmetrical Gravimetric Analyzer (SGA-100) was proposed. The drift of the instrument was observed in the range of $-7 * 10^{-6}$ to $2 * 10^{-6}$ within the working range. The amplitude of noise was found to be in the range of 0.0031 to 0.0119 %.
- ✓ A complete sorption profile of DuPont Biomax[®] and Sorona[®] sheets was generated at two different temperatures (23°C and 40°C) and five different water activities by gravimetric method.
- ✓ The moisture sorption data obtained did not fit the theoretical data. Hence a time correction of the data, supported by the assumptions and a consistency test, was done for all the sorption experiments of both polymers. The time taken by the vapors to reach the experimental relative humidity was subtracted from the experimental time.
- ✓ Moisture sorption isotherms of both polymers sheets were generated at 23°C and 40°C. Both Biomax[®] and Sorona[®] sheet isotherms showed a positive temperature dependence, i.e., more moisture was sorbed at higher temperature.

- ✓ The moisture uptake, at steady state, by Biomax[®] sheets was approximately five times that of Sorona[®] sheets. The moisture sorption in both polymer sheets followed Fickian kinetic.
- ✓ Solubility coefficients were determined from the steady state moisture uptake. The solubility coefficients for both polymer sheets increased with water activity and decreased with increase in temperature.
- ✓ A sum of square technique was used to determine the best estimated diffusion coefficients from the transient state sorption data. The diffusion coefficient of Biomax[®] slightly increased with increase in RH except at 90% RH at both temperatures. For Sorona[®] sheets the diffusion coefficient was found to be independent of relative humidity.
- ✓ Moisture sorption of both polymer resins was evaluated at two temperatures and two water activities. Moisture sorption in resin did not follow Fickian kinetics. For Biomax[®] the moisture uptake in resins at 1400 min was lower by 70% at 23°C and 21% at 40°C than the steady state moisture uptake of the sheets, whereas for Sorona[®] resins it was 64% lower at 23°C and 43% at 40°C as compared to steady state moisture uptake of the sheets.
- ✓ Moisture sorption had little or no impact on the mechanical and physical properties of Sorona[®].
- ✓ In Biomax[®], the water acts as a plasticizer as shown by a drop in glass transition temperature after moisture sorption. A drastic drop in mechanical properties of Biomax[®] samples was observed after exposure to moisture, possibly due to

cleaving of the larger molecules into smaller molecules and reduction in molecular weight.

The moisture sorption and its impact on properties studied in this research would be useful in application of these novel polymers in packaging industry.

2. Future Work Recommendations

This work studied moisture sorption and its effect on the properties of the Biomax[®] and found that moisture is interacting with polymer. However, the exact interaction of moisture with polymer on molecular level could not be evaluated due to the lack of information about the chemical structure of Biomax[®]. A study can be conducted to examine this interaction on the molecular level and the structure of polymer in more details.

Due to the lack of the information about the interaction parameters of both polymers, the experimental moisture sorption isotherms were not fitted to any sorption model. To fit the sorption models such as BET or Flory Huggins, a study could be conducted to determine the interaction parameters experimentally.

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