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EVALUATION OF THE MOISTURE PERMEABILITY CHARACTERISTICS OF CONFECTIONERY PRODUCT PACKAGES WITH A COLD SEAL CLOSURE

By

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ABSTRACT

EVALUATION OF THE MOISTURE PERMEABILITY CHARACTERISTICS OF CONFECTIONERY PRODUCT PACKAGES WITH A COLD SEAL CLOSURE

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The water vapor transmission rate and permeance constants were determined for the seven commodity films. The moisture isotherm of the confectionery product was developed at a temperature of 23°C, to allow the selection of storage conditions, in which the product would gain moisture as well as lose moisture. The extent of moisture uptake by a confectionery product packaged in the respective commodity packaging structures was also evaluated over a storage period of 115 days, at ambient temperature and low (20 %) and high (75%) relative humidity conditions. Hardness of the nougat phase was determined to evaluate the effect of moisture and relative humidity. Based on the statistical analysis, no statistically significant differences between the performance of the respective package film structures were observed over the storage period. The moisture loss or gain of the packaged product at the two different relative humidity conditions, was assumed to pass through micro-voids in the cold seal closure area. The packaging structures were found to have no significant effect on the hardness of the nougat phase of the product over the storage conditions studied. The storage conditions however, had a statistical significance difference on the hardness in all packaged products.

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INTRODUCTION

The quality or shelf life of a food product is determined by a number of interactions between parameters related to the product itself and/or associated with the external storage environment. The interaction between moisture and the food product is critical, and moisture transfer in food products, to include confectionery products, frequently leads to deleterious changes in product quality. Moisture transfer can occur between a food product and its environment, and/or within a non-homogeneous structured food product. In either situation, moisture transfer results in a change of the water activity (a_w) and the moisture content of the product.

Preventing such undesirable effects are dependent on the nature of the product, its sensitivity to the gain or loss of moisture, the package system and the storage environment. Selecting a package system of appropriate moisture barrier characteristics, in general, provides adequate protection to prevent the gain or loss of moisture by the product and allows maintenance of product quality. Implicit in this assumption is that the package is hermetically sealed and that diffusion through the package structure, as described by Fick's First and Second Laws, is the principle mechanism resulting in water vapor transfer through the package structure.

Alternatively, if the package system had serious leakage or seal integrity problems, the assumption that water vapor transfer is the result of diffusion through the package structure is erroneous. In this case, a process involving flow or transfer through micro-voids in the seal area would be the principle mechanism of moisture gain or loss.

Precedence for a mechanism involving the flow or transfer of water vapor through micro-voids in the package seal area, accompanied by a concomitant change in the moisture content of the packaged product is found in the studies recently reported by Lin (1995), who studied the extent of toluene vapor uptake by a packaged confectionery product. The results of these studies indicated that for a confectionery product packaged in a series of commodity package structures, permeant flow or transfer through micro-voids in the cold seal closure area was the predominant mechanism of toluene ingression. Since cold seal closures are widely employed in the packaging of confectionery products, evaluation of seal performance or seal integrity for the cold seal closure warrants further investigation.

This study represents an extension of the studies reported by Lin (1995) and considers the effect of storage conditions and package structure on the quality of a chocolate based confectionery product, over a six month storage period. The moisture content of the packaged products was determined as a function of storage time and conditions (i.e. temperature and relative humidity), due to its dominant role in product quality.

Two analytical procedures, namely moisture content determination by the Karl Fischer method and texture Profile Analysis using the Instron

Universal Tensile Tester, were employed. The results of the tests were applied to assess the relative performance of a series of commodity package structures, sealed by a cold seal closure procedure, on the moisture content change of a chocolate based confectionery product, where quality is dependent upon the moisture content of the non-homogeneous product.

The results of the objective and subjective tests performed were evaluated to establish a relationship between the change in moisture content of the packaged product and the moisture barrier characteristics of the respective package structures, as well as the affect of moisture content on the texture of the packaged product. Further, by analyzing the numerical consistency of the product water activity, information on the mechanism associated with water vapor transfer was obtained.

The specific objectives of the study include:

- Determination of the water vapor permeability of a series of commodity packaging structures used for packaging confectionery products.
- Development of a test system to allow determination of the change in product moisture content of a packaged confectionery product stored at conditions of constant temperature and relative humidity.
- Evaluation of the relative performance of the package systems with respect to variation in the moisture content of the packaged product, as a function of storage time and conditions.

- Evaluation of the quantitative relationship between the respective package structures as regards product moisture content and the sensory responses (i.e. texture profile) to product quality, as a function of storage time and conditions.

LITERATURE REVIEW

The Mechanism of Water Vapor Transmission Through Polymeric Packaging Materials

The deterioration of food quality during storage may be due in part to the loss of moisture or flavor compounds from the packaged food product, or to the uptake of moisture or volatile contaminants permeating from the external environment. Therefore, measurement of the rate of permeation of water vapor and organic vapors through polymeric packaging materials is of significant importance.

Permeability is the phenomenon of transmission of a gas or water vapor through a polymer. This process may be characterized by three basic steps, which are summarized below:

1. Adsorption, the dissolution of a gas or vapor into the polymer matrix at the high penetrant concentration surface.
2. Diffusion, the movement of a gas or water vapor penetrant through the polymer bulk phase, along a concentration gradient.
3. Desorption, the desorption or evaporation of the penetrant from the low concentration surface of the polymer membrane.

Mass transfer in polymeric packaging materials can be referred to as either permeability, sorption or migration. When small molecules permeate through a polymeric membrane, the rate of permeation is governed by the physical and chemical nature of the penetrant and the polymer membrane, as well as external factors, which include: temperature, vapor pressure, and relative humidity.

The permeability of a gas or vapor through a polymeric film is a function of two fundamental parameters: the diffusion coefficient (D), and the solubility coefficient (S). Functionally, the diffusion coefficient is a kinetic term and describes how rapidly permeant molecules advance and the time required to reach steady state. The solubility coefficient is a thermodynamic term, describing how permeant molecules are sorbed by the barrier structure. The diffusion process is the result of polymer molecules having a random kinetic agitation or heat motion. Above the glass transition temperature (T_g), polymer chain segments have vibration, rotation, and translation properties, which continually create temporary holes or voids within the polymer matrix. The holes allow penetrant molecules to pass through the matrix under a concentration gradient. For polymer membranes below T_g, the rate of diffusion will be a function of the size and frequency of pre-existing holes or the void volume between polymer chains. Whereas, solubility involves the affinity of the permeant for the polymer (Baner, 1984 and Imbalzano et al., 1991).

Permeation is a measure of the steady-state transfer of the permeant, which is usually described by the permeability constant, P. The permeability constant can be expressed in terms of two fundamental parameters: the diffusion coefficient (D) and the solubility coefficient (S). Their relationship is described by Equation A.

$$P = D \times S \qquad (A)$$

Where the diffusion coefficient (D) is a measure of the rate at which penetrant molecules advance through the polymer, and the solubility coefficient (S) describes the amount of permeant dissolved in the polymer matrix at equilibrium conditions (Crank, 1968).

The mass transfer of organic volatiles is a major concern with polymeric packaging films. There is potential loss of aroma/flavor compounds due to their permeation through the film, or to their sorption by the polymeric packaging material. Another reason for concern involves the possibility of contamination of the food due to the permeation of organic vapor from the external environment through the packaging film, with sorption by the product (Mohney et al., 1988; Tou et al., 1990; and Franz, 1993).

To understand the sorption mechanism in food product /package systems, it is necessary to assure quality control and prediction of product shelf life. Measurement of the loss of product volatiles by permeation is also associated with product shelf life. Sorption can be described as a function of sorbate concentration by a sorption equilibrium isotherm that can be presented by Henry's law or other mathematical models. Specifically, Henry's law describes the relationship between the vapor pressure of the organic penetrate and the mole fraction of penetrant sorbed by the polymer membrane at equilibrium.

The partition coefficient K is defined as the ratio of the equilibrium concentration of a component in a fluid phase and the equilibrium concentration of the component in a polymeric material. For a specific concentration, the partition coefficient K provides a practical way to calculate the change in a component concentration, either in the food or packaging material, from the time that the food product and packaging material are contracted, up to the moment they reach equilibrium, provided the initial concentrations are known.

Since sorption and migration are essentially the same mass transport phenomenon, migration can also be described by a partition and diffusion coefficient. The diffusion coefficient determines the dynamics of the sorption process. The larger the value of D the shorter the time to reach equilibrium. (Giacin, 1995).

Non-interactive molecules like oxygen, nitrogen, and carbon dioxide will have little or no effect on polymer morphology, when sorbed into the polymer matrix. However, organic vapors are comparable in size or larger than the polymer chain segments associated with chain segmental mobility at temperatures above T_g. These organic penetrants diffuse by a complicated mechanism, which is dependent upon the motions of both the polymer and diffusant molecules. Organic molecules may also have a higher solubility in the polymer, which can result in significant swelling of the polymer matrix by the sorbed organic molecules. Organic molecules sorbed by the polymer can act like a plasticizer, lowering the glass transition temperature (T_g) and increasing the polymer's segmental motions at any temperature. This will results in further plasticization and swelling (Meares, 1965).

Permeation Theory

For non-interactive permeants, such as gases, the rate of transfer of a diffusing substance can be expressed mathematically by Fick's first and second laws of diffusion, as described in equations B and C, respectively. The solubility can be described by Henry's law (Crank, 1975).

$$F = - D\,(dc/dx) \qquad \text{(B)}$$

$$dc/dt = d/dx\ (D\, dc/dx) = D\,(d^2c/dx^2) \qquad \text{(C)}$$

where: F = flux (the rate of transfer of the diffusing substance per unit area)

D = diffusion coefficient

c = concentration of diffusing substance

x = direction of diffusion

t = time.

When organic permeants enter the permeant molecules the polymer, a boundary layer is created. The boundary layer phase of the polymer is swollen and the diffusion coefficient of the permeant in this phase is not equivalent to that of the non-swollen phase. The diffusion coefficient in the swollen phase is larger than in the non-swollen phase. Also in such cases, Fick's laws of diffusion do not apply, since the boundary phase is changing with time (Crosby, 1981 and Maekawa, 1994).

Under low vapor concentration levels, the vapor pressure of the penetrant is proportional to its concentration in the polymer. According to Henry's law

(Equation D), the rate of transfer of a diffusing substance can be expressed in terms of the permeant partial pressure between surfaces $x = 0$ to $x = L$ by the relationship:

$$C = S \times \Delta p \qquad (D)$$

where: C = concentration of the penetrant in the polymer phase

S = solubility coefficient

ΔP = partial pressure of the penetrant in the gas phase.

At steady state, the diffusion flux (F) (equation E) of a permeant in a polymer can be defined as the amount of penetrant which passes through a unit surface area per unit time.

$$F = Q/A \times t \qquad (E)$$

where : Q = quantity of diffusing substance transferring through the film.

A = area

t = time.

Also the diffusion flux (F) (equation F) of the permeant can be integrated through the total thickness of the polymer between the two concentrations, assuming that the diffusion coefficient (D) is constant and independent of concentration.

$$F = D\,(C_1 - C_2)\,/L \qquad (F)$$

where : C_1, C_2 = concentration of gas or vapor at the surfaces $x = 0$ and $x = L$ respectively ($C_1 > C_2$)

L = film thickness.

From equations D, E and F the amount of penetrant which has transmitted at time t can be calculated by substitution in to equations (G) and (H).

$$Q = \{D(C_1 - C_2) \times A \times t\} / L \qquad (G)$$

$$Q = \{D \times S(p_1 - p_2) \times A \times t\} / L \qquad (H)$$

Using the definition of permeability:

$$P = D \times S$$

The permeability constant can be determined by substitution in to Equation I:

$$P = (Q \times L)/A \times t \times (p_1 - p_2) \qquad (I)$$

Permeability Measurement Methods

Permeability, diffusion and solubility coefficient values can be determined by the following methods: (1) the gravimetric method (2) the isostatic method; and (3) the quasi-isostatic method. Basically, each test method is designed to measure the permeability by mounting the film in a hermetic environment between two test cell chambers. A fixed and constant gas or vapor concentration is introduced into the high concentration cell chamber. The permeant then diffuses through the barrier membrane and is desorbed from the low concentration film surface into the low concentration cell chamber, where it is then quantified using an appropriate method of detection.

Gravimetric Method

In this procedure, permeation values are determined by observing the change in weight of a test cell or intact package system, as a result of the diffusion process. An example is the method described in ASTM E-96 (ASTM, 1988), where an aluminum dish containing desiccant is covered with a packaging material, weighed and placed in a constant temperature and humidity chamber. The samples are then weighed periodically, and the water vapor transmission rate is determined by the weight gain over time.

Recently, an electrobalance method has been used to measure the sorption and diffusion of organic vapors by polymeric materials (Berens and Hopfenberg, 1982; Choy et al., 1984). The experiments are carried out at equilibrium vapor pressure, using an electrobalance, which continually records the gain or loss of weight, by a test specimen, as a function of time. The Gravimetric methods in general have low sensitivity, especially for high barrier polymer films, and are applicable over a limited vapor pressure range. However, application of the electrobalance negates these limitations and provides for high sensitivity and utility over a wide range of temperature and sorbate vapor pressure (Hernandez et al., 1986).

More recently, the isostatic and quasi-isostatic procedures have become widely employed for measuring permeability. Since organic vapor and aroma permeability measurement involve complicated procedures, there is no standard analytical technique. Also, there is very limited number of commercial instruments available for measuring organic vapor permeability. To date, most research in this area has been conducted using a permeation system of the investigator's own design (Blaskesley, 1974; Niebergall et al., 1979; Baner, 1987; Hernandez et al., 1986; Hatzidimitriu et al., 1987; Liu et al. 1991; and Franz, 1993). Most of these have been designed to measure the transmission rate of organic vapor through barrier membranes by maintaining a constant partial pressure differential across the test membrane.

Isostatic Method

The total pressure in both chambers of the permeation cell is kept constant by maintaining the same atmospheric pressure in both chambers of the test cell. The permeability measurement involves maintaining a constant permeant partial pressure, or a concentration gradient between the two cell chambers. The permeant which has permeated through the film and into the lower concentration chamber is then conveyed by a carrier gas to a detector where it is quantified. The permeability measurement involves determining the change in the ratio of $[(\Delta M / \Delta t)_t / (\Delta M / \Delta t)_\infty]$, as a function of time.

Equation J, which was derived by Pasternak et al. (1970), describes the transmission rate profile curve (Hernandez et al., 1986):

$$(\Delta M / \Delta t)_t / (\Delta M / \Delta t)_\infty = (4 / (\Pi)^{1/2}) (L^2 / 4Dt)^{1/2} \exp(-L^2/4Dt) \qquad (J)$$

where: $(\Delta M / \Delta t)_t$ and $(\Delta M / \Delta t)_\infty$ = the transmission rate of the penetrant at time (t) and at steady state (∞) respectively.

t = time

L = film thickness

D = diffusion coefficient.

A value of $(L^2 / 4Dt)$ can then be calculated for each value of $[(\Delta M / \Delta t)_t / (\Delta M / \Delta t)_\infty]$. A straight line can be obtained by plotting $(4Dt / L^2)$ as a function of time. From the slope of the straight line, the diffusion coefficient (D) was obtained from Equation K.

$$D = [(\text{slope}) \times (L^2)] / 4 \qquad (K)$$

Ziegel et al. (1969) derived Equation L, from a different expression for $[(\Delta M / \Delta t)_t / (\Delta M / \Delta t)_\infty]$ (Hernandez et al., 1986), to solve for D.

$$D = L^2 / (7.199 \times t_{0.5}) \qquad (L)$$

where : $t_{0.5}$ = the time required to reach a rate of transmission $(\Delta M / \Delta t)_t$ value equal to half the steady state $(\Delta M / \Delta t)_\infty$ value.

Finally, the permeability coefficient (P) can be calculated from data obtained using the isostatic method by substituation into Equation M.

$$P = (\Delta M / \Delta t)_\infty \times (L / A. \Delta p) \qquad (M)$$

Where : A = area of the film exposed to permeant in the permeation cell

L = film thickness

Δp = partial pressure gradient.

Various detector devices have been used in isostatic permeability studies. Thermal conductivity detectors and thermistors were used to measure single permeants (Pasternak et al., 1970; Ziegel et al., 1969; Yasuda and Rosengren, 1970). Flame ionization detectors (FID) have been used for organic vapors and provide the advantage of not being affected by the presence of the carrier gas and water vapor (Zobel, 1982). When a complex mixture of organic permeants is involved in the test, a gas chromatograph can be interfaced with a FID to separate individual permeant first, before quantification (DeLassus, 1985). Other techniques, based on either a photoionization detector or atmospheric pressure ionization mass spectrometer, have been employed by Caldecourt et al. (1985). Both detection systems were found to be very sensitive and useful in the characterization of the permeability of barrier membranes to organic penetrants. In some commercially available isostatic permeability testers, IR sensors and coulumetric sensors are also used for detecting water vapor and oxygen, respectively (MOCON; Operating Manuals, 1982; 1989).

Quasi- isostatic Method

The quasi-isostatic method is also known as the accumulation method. This method involves measurement of accumulated gas or vapor, which has permeated through a material as a function of time. In this method, one of the two chambers adjacent to the film is closed to the external environment. The gas or vapor being tested is allowed to flow through the high concentration cell chamber at atmospheric pressure. At the same time, the gas permeates into the lower concentration cell and aliquots are withdrawn from the low concentration cell for quantification. Typically for organic penetrants, samples are taken and injected directly into a gas chromatograph (GC), where a flame ionization detector is used for quantification, at pre-determined time intervals (Baner et al., 1984).

Using this method, the quantity of permeant accumulated increases as a function of time. When the relationship between quantity accumulated per unit of time is constant, a steady-state rate of diffusion has been reached. By extrapolating the linear segment of the curve to the x-axis, the lag time (θ) can be calculated from the intersection of the projection of the steady state portion of the transmission rate profile curve (Hernandez, et al., 1986 and Wangwiwatsilp, 1993). The diffusion coefficient is expressed by equation N.

$$D = L^2 / 6\theta \qquad \text{(N)}$$

where : θ = lag time

L = film thickness

and the permeability coefficient at steady state can be described by equation O.

$$P = \text{slope} \times L / A \times \Delta p \qquad \text{(O)}$$

where : slope = straight line portion of the transmission rate curve (quantity / time)

L = film thickness

A = surface area

Δp = partial pressure.

Water Vapor Transmission Rate Measurement

The water vapor transmission rate (WVTR) is defined as the rate of water vapor flow (Q/t), normal to the two surfaces, under steady state conditions, through a unit area of a test film.

$$\text{WVTR} = Q/At$$

The WVTR does not take into account the thickness of the test material or the driving force of permeant across the polymer. Therefore it is not a constant for the test film, but is useful for comparative purposes. WVTR data are normally reported at 38°C for films tested at 95% relative humidity. There are several methods for measuring WVTR and water vapor permeability. Earlier methods (ASTM E-96) were based on a Gravimetric procedure and measured the weight increase by a desiccant sealed in an aluminum cup by the test film. In 1990, ASTM introduced a new test standard (ASTM F 1249) based on the isostatic method, which employed solid state electronics with pulse-modulated infra-red sensors, which can detect down to one ppm water vapor.

MOCON® (Modern Controls Inc. Minneapolis, MN) manufactures and markets an instrument, the Permatran-W 3/31, which meets the requirements of ASTM F 1249. Test temperatures can be controlled from 10 to 40°C (± 0.5°C) and relative humidity from 35% to 90% RH (± 3%). The instrument can test at 100% RH (± 3%) by inserting water saturated sponges in to the test cell.

Relative humidity is controlled by exposing pressurized dry nitrogen gas to pure water (HPLC grade) in an enclosed chamber, when the equilibrium relative humidity reaches 100%. The gas is then released to a lower pressure environment which results in a reduction in the percent relative humidity. This two-pressure method is used by the Permatran-W 3/31 to generate water vapor at the required percent relative humidity. Test gas relative humidity is measured by a solid state semi-conductor device, which is located in the outer chamber of both test cells.

Water vapor permeating across the film is transported by dry nitrogen gas to a pressure modulated infrared detection system, intended for operation over a 5 to 50°C temperature range. The detector consists of a pump, a sensing chamber, infrared source, a 2.6 micrometer infrared filter, a lead sulphide photo detector and an amplifier. The pump varies the pressure and density of the gas mixture in the sensing chamber, which consequently varies the absorption rate of infrared radiation by the water vapor present. The infrared photo detector produces a low-level electrical signal in response to the change in transmitted infrared radiation. The amplifier produces a filtered DC signal in direct proportion to the water vapor in the test cell and is therefore, proportional to the water vapor transmission rate of the test film. The instrument must be calibrated using reference films of known

WVTR and at specific flow rates, generally at 10 cm^3min^{-1} and 100 cm^3min^{-1}. The system must be operated using calibration flow rates, good barriers at the higher flow rate and poor barriers at the lower flow rate.

An efficient process for measuring water vapor transmission rate of barrier materials combines solid state electronics with patented pulse-modulated infra-red to detect down to one part per million (ppm) of water vapor (Modern Controls Inc. Minneapolis, MN). This instrumentation is capable of testing multiple samples quickly and accurately and after six years of comparison testing with E-96, became the basis for the newest ASTM water vapor transmission rate (WVTR) standards in the United States (Demorest and Mayer, 1996). When determining water vapor transmission rates of barrier materials, making direct measurements under precise testing conditions is the most reliable method. It is now recommended that the generated RH method can be employed to generate the precise humidity desired. WVTR tests can be performed on all types of barrier materials without factors such as salt inaccuracies, corrosion or assumed humidities being factors. The standard method of establishing a differential gradient across a film surface is still the fastest way to measure permeability (Demorest and Mayer, 1996). Modern test methods have been developed that quickly and reliably measure the permeability, diffusion and solubility coefficients for the various polymer/permeant combinations used in food and other packaging (Demorest and Mayer, 1998).

MAS Technologies, Inc. (Zumbrota, MN) is another manufacture of Permeability instruments. There products include the MAS 500 Isostatic Oxygen Diffusion System, the MAS 1000 Moisture Permeation System and the MAS 2000 Organic Permeation System. The principle of both Modern Controls and MAS Technologies permeability instruments is based on an isostatic procedure. Typically, a film sample is mounted between two cell chambers. One of the cell chambers holds the test gas to be used as the permeant, while the other chamber holds carrier gas that flows through the cell to the detector. When the permeant diffuses from the high concentration chamber into the low concentration chamber, it flows directly to the detector for measurement.

The MAS 1000^{TM} Moisture Permeation System is designed to test the levels at which moisture will permeate. Diffusibility and solubility coefficient values for the packaging material can also be determined. This system employs mass transport theory within a unique software package, which allows for early prediction of steady state permeation values. This highly sophisticated system incorporate precise temperature and flow rate control and sensitivity in the 0.001 grams/ m_2 /day region. The test RH level is fully controlled through software to assure consistent and realistic measurements without the requirements of salt solution preparation. The MAS 1000^{TM} also incorporates a multiple zone cell to provide the user with significant improvement in test flexibility. This allows the user to select the appropriate test sensitivity level. Measurements requiring high detector sensitivity may employ all zones, while low sensitivity measurements may be conducted using a single zone.

Confectionery Packaging

The packaging requirements for chocolate confectionery products are similar to other food products (Martin, 1987 and Anon, 1998) and are summarized below:

1- Protection: The product should be protected by the package from the time of manufacture to consumption. Water vapor, oxygen and undesirable environmental odors need to be excluded and the product flavor kept inside the package.

2- Function: The package should be functional to facilitate the manufacture, shipping, storage, display and use of the product.

3- Sales Appeal: The package must attract the shopper, appeal to emotions, inform and trigger the sale.

Chocolate enrobed candy bars require that packaging material provide excellent barrier, good print receptivity and ability to be sealed rapidly at temperatures low enough to avoid melting of the chocolate coating. The printed glassine was the most common packaging material used for confectionery packaging that did not meet all these requirements; it kept the product clean and identified the brand but provided little or no barrier; shelf life was less than three months (Jenkins and Harrington, 1991). PVDC-coated cellophane laminations replaced glassine, increased the shelf life and made attractive package (Jenkins and Harrington, 1991). The most widely used film construction currently in use is "Lacquer/ink/whiteOPP/PVDC//cold seal". This construction provides the oxygen and moisture barrier, and the cold seal pattern enables the package to be sealed at low temperatures below the melting point of chocolate (Jenkins and Harrington, 1991).

There are several common polymeric films/flexible materials used in confectionery packaging structures. These include cellulose, high density polyethylene (HDPE), polypropylene (PP), polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), aluminum foil, and paper / glassine. In addition, a number of newer materials with excellent barrier properties are suitable for confectionery packaging (Jenkins and Harrington, 1991).

Characteristics of Seal

Two major factors should be considered in the selection of adhesive systems for package sealing. First, is the chemical nature of the adhesive components, which acts as the binder. The second factor to consider is the way in which the bond is formed, by loss of water or solvent, by loss of heat or by chemical reaction. In practice, adhesives are widely used in forming multilayer structures involving the combination of polymeric films or other non-polymeric structures, as well as to seal fabricated package systems (Lazarus, 1990).

In general, the primary bonding associated with adhesives include three types: covalent bonds, ionic bonds and metallic bonds. Three mechanisms for adhesive bond formation (Lazarus, 1990) are summarized below:

Loss of carrier: The bond is formed when the carrier is lost through adsorption into the substrate or by evaporation. Water based adhesives are preferred from an environmental point of view, but removal of water requires more energy. Solvent based adhesive systems are more common. Solvent based adhesives are preferred, where two impermeable substrates are to be bonded such as lamination of plastic films. It is easier to achieve good adhesion to plastic films with solvent based types.

Loss of heat: The application of a molten adhesive, which solidifies on cooling, has some advantages. This type adhesive has application with porous and impermeable substrates and provides good adhesion. However, this molten adhesive can not be applied to heat-sensitive substrates.

Chemical reaction: A liquid material is applied to the substrate and then reacted chemically to create a solid. This technique is commonly used for structural adhesives, where high bond strengths are needed. In many packaging applications the substrates are relatively week and high strength adhesives are not required.

Heat Seal

The heat seal process requires is to reactivate a layer of thermoplastic material or adhesive to react with an adherend by heat, enabling it to form a bond with another adherend usually assisted by pressure (Booth, 1990).

Hot melt adhesives are thermoplastic and are amorphous, softening gradually over a wide range of temperature. Adhesive performance can be best understood by discussing the solid to liquid change in relation to adhesive application, and the liquid to solid change in relation to the formation of a good bond (Kettleborough, 1990). The speed of bond formation on modern high-speed machinery depends on several factors, such as the specific adhesive system, temperature, porosity and surface characteristics of substrates, as well as application conditions, and the time and extent of compression of the surfaces. It is essential to have a clear understanding of practical adhesive application technology if bonding problems are to be avoided and maximum production cost benefits obtained. If all factors are carefully considered, the relatively high price of 100% solids hot melts may be offset by various economic factors, including operational costs and performance (Kettleborough, 1990).

Hot melt adhesives can be based on a number of different chemical systems but those based on vinyl acetate-ethylene copolymers represent the largest class. These copolymers are readily available in different grades and have a high degree of versatility and potential to tailor the formulation of the adhesive systems for specific end use applications. These polymer systems offer excellent machineability, setting and adhesion characteristics, coupled with good low temperature flexibility, as well as very good compatibility with other formulating constituents used in the manufacture of hot melts or heat seal adhesives. Other types of polymers employed as hot melt adhesives include polyethylene, polyamides, polyurethanes, and thermoplastic block copolymers (Coggin, 1990).

Hot melts are well known for their versatility and functionality, mainly in applications related to packaging. There rapid green-strength development, coupled with environmental durability, make them a highly cost effective product for high speed production lines in packaging operations. They have limitations which include: limited heat resistance due to the thermoplastic nature of the adhesive system, susceptibility to solvent and plasticizer attack and bond failure under high stress or load. A clean substrate surface is also a requirement for effective bonding. Hot melts based upon ethylene-vinyl acetate copolymers are dominant in this group with 50-55 % of the market volume. Polyolefins, such as low density polyethylene and amorphous polypropylene account for 30-40% of the market volume, while the remaining balance of 5-15% is made of "specialty" hot melts (Kuzma, 1990).

Cold Seal

The term "cold seal" is used to describe the creation of an effective seal without the use of heat. This technique requires two surfaces of cold seal adhesives being bonded together under pressure alone. Booth (1990) defined cold seal as "the ability of a non-tacky adhesive film to bond to itself under pressure at room temperature".

In the field of packaging, cold seal closures have been widely used for food product packaging as well as for other heat sensitive products. Early applications of this sealing technique were hindered, however, by the need to use organic solvents, which were not suitable for food contact, in applying the cold seal adhesive pattern. Now, with the development of new cold seal materials, which are water based and rubber latex stabilized with alkali, the use of cold seal adhesives has found considerable utility in the packaging of confectionery products (Jones, 1985).

Cold seal adhesives were first introduced in the 1960's for confectionery packaging. Since then, their usage has increased significantly, and a wide range of substrates have been evaluated (Stone, 1976, Anonymous, 1980 and Layfield, 1990). Cold seal adhesives are a blend of natural rubber latex and an acrylic resin to reduce the self adhesion so that pressure is needed to form the bond. Biscuits, chocolate and other heat sensitive foods are wrapped in films coated with cold seal adhesive. This technique allows packing at very high speed with pressure so that the contents remain unaffected (Lazarus, 1990). Natural rubber latex formulations have wide use in cold seal applications because they form films that exhibit auto adhesion and blocking resistance (Baetzold and Polance, 1998). Coextruded polyester films are ideal for cold seal applications. They offer good adhesion for metallizing or printing with either solvent-based or waterborne inks. Applications include use for candy wrappers and other cold seal packages (Anonymous, 1991). A metallized OPP film which uses a cost effective packaging material is suitable for preventing moisture loss in low fat soft cookies. The OPP film Torayfan PC-1 from Toray Plastics is easily converted in to a variety of laminated structures. One side of the film is highly corona treated, making it convertible with water-based inks, adhesives, cold seal coatings and the other side is designed to be metallized (Anonymous, 1993). A one side metallized heat-sealable OPP film designed specifically for packaging applications is now available from ICI and sold under the trade name Propafoil. It is already being used for the packaging of chocolate biscuits, confectionery and ice cream. Propafoil can be used for heat seal and cold seal coating applications (Tebbatt, 1983).

Cold seal adhesives are normally used on flexible film webs to replace a laminated or extruded polyethylene layer as the sealing medium. This improves the output and economy in the flexible packaging industry (Layfield, 1990). Cold seal adhesives are based on a mixture of natural and synthetic rubber latexes, combined with a number of lesser ingredients, such as antifoams, antifungicides, and filling agents. The natural latex confers the characteristics of self adhesion. Synthetic latexes are used to control the variable cohesive properties, to improve stability, to increase resistance to oxidation, or to improve adhesion to difficult substrates, and may also be used to reduce costs (Anonymous, 1980). From the printers viewpoint the most desirable properties of cold seal adhesives are long shelf life, low foaming, excellent printability, readily sealable and non blocking. The application of cold seal adhesives in the confectionery industry is recognized as revolutionary with respect to optimization of machine efficiency and reduction of running costs (Layfield, 1990). According to Levine (1976) and Jones (1985), the most important factors contributing to the dramatic growth in the use of cold seal coated materials are:

1. Elimination of heat damage to heat sensitive products, such as chocolate. Heat is not required in the bonding process, only contact pressure is required.
2. Less distortion and shrinkage of polypropylene packaging films.
3. Water based adhesive formulation eliminates solvent related concerns.
4. Elimination of temperature control equipment on the packaging line and lower power consumption.
5. Easy machine maintenance and non-sticking of the coating to the product.
6. Faster than heat sealing.

Compared to heat sealing techniques, machine speeds can be doubled with the use of a pattern cold seal. Cold seals are normally based on a type of natural rubber latex and are widely categorized into two types, which can be described by the nature of the dried film. "Hard" cold seals are essentially non pressure-sensitive and usually exhibit low bond strength. The nature of the dried film is less prone to blocking and stringing. "Soft" cold seals show a greater degree of pressure sensitivity and will seal more readily. This characteristic has lead too much higher seal strengths and in some cases to cause film tear. It has a higher probability of blocking and stringing. The softer varieties of cold seals are usually more tolerant to surface contamination. However, they exhibit a slight reduction in seal strength (Layfield, 1990). In recent years, the trend with respect to cold seal has been towards maximizing bond strength and obtaining 100% fiber tear on single web films, especially low density pearlized polypropylene. Some fragile products need an easy-open, peelable bond, this requirement necessitates a seal strength in the region of 100g/25mm (Layfield, 1990).

In addition to the well-established confectionery and biscuit markets, cold seal adhesives may find use in other applications, such as medical packaging, tea packaging or frozen food packaging. Also development of adhesive technology to maintain performance with new films and inks/lacquers will be critical to the industry (Stone, 1976 and Layfield, 1990). Advantages of cold seal films in biscuit and confectionery packaging include reduced product damage, reduction in packaging materials waste, ease of operation and start-up, reduced maintenance costs, plant safety and energy savings (Matthews, 1980). Cold seal provides better protection against moisture and costs are less when the packaging is made of laminated material, since only a single film web is used with a cold seal pattern application (Arnold, 1981).

Moisture Permeability Characteristics of Chocolate

The shelf life of a food product is determined by numerous, complex interactions between parameters related to the product itself and/or associated with the external environment. Among those factors, the interaction between moisture and the food is critical. Moisture transfer in finished food products frequently leads to deleterious changes in quality. Biquet and Labuza (1988) found that moisture transfer can occur between a food and its environment and with in a non homogeneous structured food system. In both cases, it results in a change of the water activity (a_w) and the moisture content of the product as a function of time. They also reported that chemical and enzymatic reactions in food, as well as the microbial stability of food products, are strongly influenced by the water activity. The use of adequate packaging material can control moisture exchange between a food product and its surrounding. A more challenging problem is to prevent or slow down moisture exchange within multi-component food products. The rate of moisture exchange may be reduced by appropriate manipulation of certain parameters.

In a study conducted by Biquet and Labuza, (1988) the moisture barrier properties of a semi sweet dark chocolate film were determined at variable film thicknesses, temperature and relative humidity in the intermediate moisture range. They concluded that the chocolate film 0.6 mm (24 mil) thick was a better moisture barrier than a 1 mil thick low density polyethylene film. The mathematical packaging model for non-edible packaging materials worked well for a typical outer barrier coated model system, while a new mathematical model predicted well the moisture transfer within a bi-component system of different initial a_w, with the barrier between them. In peanut butter or cookies enrobed with chocolate, the oil may migrate into the outer chocolate layer. This can cause the chocolate to become soft and sticky. The crystal structure of the chocolate to change causing "fat bloom," the enrobed material to become "dry," and the product to undergo a flavor change (Brake and Fennema, 1993). Lipid migration in chocolate enrobed cookies occurs rapidly during the early stages of storage and diminishes with further storage (Wooton et al., 1970). It is difficult to maintain low storage temperatures throughout the distribution system (Wacquez 1975). Brake and Fennema, (1993) found that the shelf life of products susceptible to fat migration can be extended by storing at low temperatures, using a thicker chocolate coating, adding stabilizers or reducing fat content of the filling. Dry films from cellulose derivatives are good lipid barriers, but films as thin as 0.005 mm have been detectable in the mouth (Nelson and Fennema, 1991). Sealing enrobed centers with confectioner's glaze or similar sealant has been suggested to inhibit fat transfer (Minson, 1990).

Designing a semi-solid, edible coating for use in confectionery products, must satisfy several requirements: (1) the coating should be an effective barrier to lipid migration; (2) it should not notably alter sensory properties; and (3) its water activity must be similar to that of major components, preferably without drying. Coatings containing hydrocolloids and sweetners were tested for lipid barrier and sensory properties, adhesion to chocolate, viscosity, and a_w. (Brake and Fennema, 1993).

For composite foods consisting of multilayers with different composition, such as jelly-filled cookies, pizza, pies, chocolate coated products, snacks, candies, etc. it is possible for moisture in one component to migrate to another (Cakebread, 1972) leading to deteriorating changes in product quality (Biquet and Labuza, 1988). The direction of moisture migration is not necessarily from the layer with the higher moisture content but is related to the gradient in water activity (a_w); i.e.

the transfer occurs from the phase with high a_w to the phase with low a_w (Salwin and Slawson, 1959). In the past decade several authors have reported on how to control moisture migration in composite products; mainly by separating the different product components with an edible moisture barrier (Biquet and Labuza, 1988; Kamper and Fennema, 1985). As recently reviewed by Biquet and Labuza (1988) plain chocolate has a low water activity (0.2-0.4 a_w) and also good moisture barrier properties. Because of these reasons many dry and semi-moist products, which are coated with chocolate, have a considerable shelf life at room temperature.

Larumbe et al (1991) studied the behavior of caramel jam-filled chocolate coated candy during storage at room temperature and reported, that due to transfer of moisture between components, the a_w of the chocolate coating increased during storage at 25°C. They also reported growth of fungi on the chocolate due to increased a_w and contamination of the chocolate surface. Debeaufort et al (1993) conducted a study on the polarity, homogeneity, structure and the water vapor permeability of model edible films, and reported an increase of water vapor transmission rate with hydrophilicity and heterogeneity.

Moisture Isotherm and Shelf life of Food Products

The shelf life of most foods is affected by critical parameters such as moisture content and water activity. Textural quality, chemical and biochemical reactions and microbial growth rates are greatly affected by these parameters. Water activity, which describes the availability of water to play a role in physical, chemical and biochemical reactions, has been used to explain the influence of moisture on reaction rates. Recently, the glass transition theory from polymer science, has been introduced to food preservation, particularly for intermediate and high moisture foods (Nelson and Labuza, 1994; Chirife and Pilar Buera, 1994). The relationship between glass transition temperature and food stability has been seen with increasing interest and is helping researchers to understand the influence of water on food deterioration reactions.

Food product moisture content and equilibrium water activity of a food product are related to each other by the food sorption isotherm. Several equations have been used to mathematically describe sorption data representative of different groups of food products. A review of the work devoted to the prediction of moisture sorption behavior of mixed or multi-component products from individual component's behavior is also presented .The control of moisture uptake or loss during storage is one of the major protection functions of the food package. Fast and reliable methods for shelf life prediction are of great interest as a tool for package development. Mathematical models correlating the characteristics of the product, the package properties, and the environmental conditions are less time consuming and have lower cost than other shelf life determination techniques.

Most food sorption isotherms show a hysteresis behavior, i.e., the moisture content is lower on equilibrium by adsorption than by desorption. This has important implications with respect to food stability, since foods adjusted to the desired a_w by desorption rather than by adsorption, may deteriorate more rapidly because of their higher moisture content. A number of equations or mathematical models have been proposed to describe the moisture sorption behavior of foods. Some are based on theoretical principles, while others are proposed due to their curve fitting capability to experimental data. Chirife and Iglesias (1978) reviewed the equations existing in the literature and compiled twenty-three equations, discussing their origin, range of applicability and use. Some of these equations were mathematically equivalent and some were limited to a specific range of a_w or type of foods. Boquet et al. (1978) and Boquet et al. (1979) evaluated equations with two and three parameters for fitting experimental data of moisture sorption by fruits, meats, milk products, proteins, starchy foods and vegetables.

In an attempt to include interaction parameters Nieto and Toledo (1989) applied an empirical approach using a factorial design of 4 x 3 levels of combinations of NaCI, non-fat dry milk and lard added to minced fish to produce a fish sausage. Although good agreement was obtained between the experimental and predicted values, the regression equation was limited to the factors and respective levels used in the validation experiment.

Iglesias et al. (1979) assumed the additivity of the component's isotherms, in calculating a mixture isotherm from the weight percentage of each component multiplied by the amount of moisture it would sorb alone. The merit of this approach lies in the use of a non-linear isotherm. The BET equation is used with applicability in the range of a_w from 0.05 to 0.40. Interest in the development of shelf-life models for moisture sensitive products has been recognized for a long time. However, most studies have focused on packages of single products. Based on the concepts introduced by Heiss (1958), other studies on shelf-life modeling have followed, eliminating some of the assumptions originally made and increasing the complexity and applicability of the models.

Heiss (1958) discussed the relationship between moisture sorption properties of foods, packaging film permeability, and the shelf-life of the product, and developed a solution based on Fick's laws of diffusion. The model was modified by Karel (1967), who assumed a linear isotherm and later by Labuza, Mizrahi and Karel (1972) who introduced the non-linear isotherms. Clifford et al. (1977) reported a shelf-life model taking into consideration the moisture in the package head space, assuming a linear isotherm. Peppas and Khanna (1980) developed a model using the Nernst-Plank diffusion equation combined with the non-linear BET, Halsey, Oswin and Freundlich isotherm models. The model was further extended to packaging systems where the polymeric film is appreciably swollen by the diffusing water. Kim (1992) developed a model and a computer program for predicting the shelf-life of a packaged pharmaceutical tablet, based on the unsteady state mass transfer of water through the package and within the tablet and used the method of finite differences to solve the model. The influence of temperature on the system was introduced by Lee (1987), who considered its effect on the permeability coefficient and by Kirloskar (1991) who considered the effect of temperature on the sorption isotherm. Cardoso and Labuza (1983) developed a dynamic mathematical model to predict moisture transfer for packaged pasta under controlled, unsteady state conditions of temperature and relative humidity. Although moisture transfer in composite foods has been studied by several authors, very little work has been done for the case where the mixture is packaged in a moisture permeable package. In multi-component foods, it is assumed that the amount of water sorbed at any a_w is equal to a weighted average of the moisture each component would absorb alone. Hong et al. (1986) developed a computer-aided model using the finite element method to predict moisture transfer in a multi-component mixed system during storage.

Texture Profile Analysis

As described by Steffe (1996); " Texture refers to the human sensation of food derived from its rheological behavior during mastication and swallowing. Obtaining a quantitative description of texture using instrumental data is very complicated because no instrument can duplicate human capabilities. From an engineering perspective, the mouth can be considered to be an intricate mechanical system and chemical reactor that can crush, wet, enzymatically degrade, pressurize, heat or cool, pump, chemically sample for taste, and sense force and temperature. " According to Brandt et al. (1963), texture profile is defined as the organoleptic analysis of the texture complex of a food in terms of its mechanical, geometrical, fat, moisture content, the degree of each present, and the order in which they appear from first bite through complete mastication. Different texture profile methods offer a means to help the food researcher obtain descriptive and quantitative sensory data on the textural characteristics of food products.

Steffe (1996), in his review of texture profile analysis, described two methods to evaluate food texture, sensory and instrumental. The sensory method of developing a texture profile utilizes a human taste panel and provides the ultimate test, which cannot be completely duplicated by any instrumental procedure. Instrumental methods, however, are much less costly and time consuming than sensory tests. Moreover, they often can be correlated to critical sensory attributes, which allow some measure of consumer acceptability. It is, however, rare for them to stand alone as a complete test. Friedman et al. (1963) reported good correlation between the Texturometer and intensity of mechanical characteristics of texture as perceived in the mouth. Friedman et al. (1963) and Szczesesnaik et al. (1963) were poineers of Texture Profile Analysis using a General Food Texturometer. Breene (1975) said that Bourne in 1968 was the first to apply the Instron machine to objective texture profile analysis of a food. Steffe (1996) reported that Bourne in 1968 and 1974 adopted and extended, the technique to the Instron Universal Tensile Tester, where a food sample is compressed, two times, usually to 80 percent of its original height. Compression is achieved using parallel plates where one plate is fixed and the other plate moves with a reciprocating linear cyclical motion. Since this test is intended to reflect the human perception of texture, the first and second compression cycles are referred to as the first bite and second bite, respectively. Textural parameters such as fracturability, hardness, adhesiveness, stringiness, springiness, cohesiveness, gumminess and chewiness may be determined from the Texture Profile Curve using the Instron Universal Tensile Tester. Harris et. al (1992) used an Instron Universal Testing Machine for texture measurements of chocolate caramel rolls stored at 21°C and 38°C for 12 months. Guinot and Mathlouthi (1991), performed a study on the objective texture measurements of sponge cake using a Universal Instron Testing Machine Model 1121. The Instron Universal Testing Machine can also be used to measure hardness, fracturability, adhesiveness, cohesiveness, springiness, gumminess and chewiness (Bryant, 1993). Green et al. (1981) used a Instron Universal Testing Machine to measure the texture of cheddar cheese. Lee et al. (1985) studied the changes in instrumental and sensory rheological parameters of chewing gum during storage. They reported that texture was influenced to a great extent by the moisture content of chewing gum while processing conditions and storage temperature had little effect on texture change. Culioli and Sherman (1976) used an Instron Universal Testing Machine to study the influence of cheese maturity, test temperature, sample shape, sample height and surface area, on the force compression behavior of Gouda cheese. Bertola et al. (1992) analyzed rheological parameters during ripening of Tybo Argentino cheese. They applied the compression test in two successive cycles to determine hardness, adhesiveness and cohesiveness.

MATERIALS AND METHODS

Water Vapor Transmission Rates:

Packaging Materials:

Eight commercial barrier film structures were evaluated to determine their water vapor transmission rates. All packaging films were coated with a 0.5 inch wide pattern cold seal (PCS) on the non-printed side of the film. The eight film structures evaluated included:

A 0.75 mil OPP/ink/adhesive/0.35 mil met PET/PCS

B 0.75 mil OPP/ink/adhesive/1.2 mil white opaque PP/PCS

C Overlacquer/ink/1.2 mil white opaque PP/PCS

D Overlacquer/ink/1.2 mil white opaque PP/PCS

E Overlacquer/ink/1.2 mil white opaque PP/PCS

F Overlacquer/ink/primer/0.6 mil polyester/adhesive 0.35 mil PET/PCS

G Overlacquer/ink/1.2 mil CO-PET/white PP/ CO- PET/PCS

H Overlacquer/ink/primer/0.35 mil met PET/adhesive/1.2 mil white PP/PCS

Water Vapor Transmission Rate Measurement

Water vapor transmission rates and permeance of the film structures were determined on a MOCON Permatran-W 3/31 - Water Vapor Transmission System (Modern Controls, Inc. MN, USA).

A film sample, prepared using a special die, was placed within the test cell. A 50 cm^2 film surface separates the outer and inner cell chambers which are clamped together during testing to provide a gas tight seal. During the testing cycle, water vapor at a fixed and constant vapor pressure flowed through the outer cell chamber at a pre-determined flow rate and nitrogen carrier gas transported the water vapor permeated through the inner cell chamber to an infrared sensor which quantifies the amount of water vapor in the carrier stream. A re-zeroing operation is conducted at a pre-determined time interval between test runs to determine the zero baseline and provide a more accurate transmission rate result. The temperature controlled test cells can be operated between 5 and 50°C. Film samples were tested at 23 and 37.8°C, at relative humidities of 35, 80 and 90%. The test conditions are shown in Table 1.

Table 1. Test conditions for WVTR determination using the Mocon Permatran-W 3/31.

Test parameters	**Values**
Conditioning time (min)	00
Test cycle duration (min)	10
Re-zeroing cycle	05
Cell temperatures (°C)	23, 23, 37.8
Cell relative humidity (%)	35, 80, 90
Carrier gas flow rate (cm^3 min^{-1})	100

Water Vapor Transmission Rate Measurement using Gravimetric Method

This method was used to determine the water vapor transmission rates of all packaging film stocks at 23°C and 20 % RH. The standard ASTM E-96 method (ASTM, 1988), was followed for this determination, where aluminum dishes containing desiccant were covered with the packaging material, sealed with paraffin wax, weighed and placed in a constant temperature at 23°C and 20 % relative humidity chamber for a total of 27 days. The stored samples were weighed periodically, at specific time intervals, until a constant moisture gain rate was obtained. The net weight gain in grams (g) was plotted as a function of time (days). The slope of the straight line portion of the graph was taken as the water vapor transmission rate of the packaging film. From the water vapor transmission rate and the partial pressure gradient, permeance constants for the packaging films were determined.

Determination of Moisture Isotherm

Equilibrium sorption isotherms were determined at room temperature 23°C for both the chocolate and nougat component of the confectionery bar. The equilibrium moisture content (EMC) is usually expressed as percent moisture on a dry weight basis. The initial moisture content (IMC) of both the chocolate and nougat component were measured with a high degree of accuracy by the Karl Fischer titration method. In developing moisture sorption isotherm data, care was taken to insure the relative humidity chambers employed were maintained at constant temperature and relative humidity by monitoring periodically using a Hygrodynamics (Newport Scientific, Inc. Jessup, MD, USA) instrument equipped with temperature and RH sensors. The moisture sorption isotherms developed in this study were determined by placing chocolate bars of known initial moisture content in a series of eight relative humidity buckets maintained at constant room temperature at 23°C ± 2°C and determining the moisture content of chocolate and nougat component of the confectionery bar at pre-determined intervals. The relative humidity buckets were prepared and maintained from 8.6% to 75.3% RH at temperature of 23°C ± 2°C. The desired humidities in these buckets were obtained by placing appropriate salt solutions into tightly closed plastic buckets. The salt solutions employed and their corresponding relative humidities are summarized in Table 2.

Table 2. Equilibrium relative humidities for saturated salt solutions.

Saturated salt solution	**% RH at 23°C Expected**	**% RH at 23°C Experimental**
Lithium Chloride	12.0	8.6
Potassium Acetate	22.7	21.6
Magnesium Chloride	33.2	34.2
Potassium Nitrite	48.1	47.3
Sodium Nitrite	64.3	63.2
Sodium Chloride	75.8	71.2
Ammonium sulfate	80.3	75.3

Salt solutions were prepared by adding distilled water (slowly) to the chemically pure salt in a crystallization dish with constant stirring and heating slightly until about half the salt crystals were dissolved. The prepared salt solutions were placed within the tightly closed buckets and allowed to equilibrate. The relative humidity within each of these buckets was monitored periodically using Hygrodynamics instrument. This procedure was used to assure that constant relative humidity and temperature conditions were maintained. Three replicate determinations for % moisture were made at each relative humidity condition. The moisture content of the chocolate and nougat phase of the confectionery bar were determined using a Brinkmann 720 KFS Titrino: (Brinkmann Instruments, Inc. Westbury, NY, USA). Approximately 0.5 g of sample was added to the Brinkmann titration vessel in the presence of Methanol Solvent. The sample was then homogenized for 60 seconds with the attached homogenizer and titrated with Hydranal Composite 5 Reagent. The percent moisture content was recorded using a printer. The Instrument was calibrated prior to running the test samples, to obtain accurate moisture values. This procedure was repeated until no significant change in moisture content was observed.

Determination of Equilibrium Moisture Contents

The equilibrium moisture content (EMC) at each relative humidity was calculated using the following equations:

$$W_m = \% \text{ moisture} / 100 = \text{g of water} / \text{g product}$$

$$EMC = (W_m / W_p - W_m)\, 100 = \text{g of water} / 100 \text{ g dry product.}$$

Where: W_m is weight of moisture

W_p is weight of product

The moisture sorption isotherm was obtained by plotting the average equilibrium moisture content of the three replicates versus relative humidity at room temperature (23°C ± 2°C).

Determination of Initial Moisture Contents

Initial moisture contents of the product were determined using a Brinkmann 720 KFS Titrino: automatic titration system (Brinkmann Instruments, Inc. Westbury, NY, USA). Approximately 0.5 g of sample was added to the Brinkmann titration vessel in the presence of methanol solvent. The sample was then homogenized for 60 seconds using a homogenizer and titrated with Hydranal Composite 5 Reagent. The percent moisture content was recorded using a printer. An average of seven samples was used to determine the moisture content of the chocolate phase, and fifteen samples for the nougat phase.

Determination of Moisture Content of a Packaged Confectionery Product with a Cold Seal Closure during Storage.

Samples of a chocolate type confectionery product packaged in the eight packaging structures were supplied by a commercial manufacturer. The confectionery products were manufactured in the dimension of 11cm x 3cm x 2cm (Length x Width x height). Sealing of the respective barrier structures was carried out with the same pattern cold seal adhesive and sealing conditions. For this study two product storage conditions were selected.

- 20 % relative humidity and 23°C ± 2°C
- 75 % relative humidity and 23° C ± 2°C

The product was stored for 115 days in both conditions and moisture determinations were performed at pre-determined time intervals of 0, 1, 2, 5, 10, 20, 30, 40, 55, 70, 85, 100 and 115 days, respectively. It should be noted that for the storage stability studies carried out at high relative humidity conditions, the environmental chamber was maintained at 75 % ± 3 % relative humidity and a temperature of 23°C ± 2°C over the 70 days storage period. Difficulty was experienced with the relative humidity control of the environmental chamber and highest relative humidity, which was to maintained at 60 %. Therefore, for the final seven weeks of storage, the conditions were 23°C ± 2°C and 60 % relative humidity. Because of this problem these studies will be referred to as the high relative humidity storage conditions, with an average relative humidity value of 67.5 %. Three samples for each wrapper type were selected randomly from the humidity chamber and the moisture content of the nougat phase was determined using the Brinkman's 720 KFS Titrino: (Brinkmann Instruments, Inc. Westbury, NY, USA). Each sample was discarded after use. The tests were performed at room temperature (23°C ± 2°C).

Determination of Texture of a Packaged Confectionery Product with a Cold Seal Closure during Storage.

To determine the effect of storage conditions on the texture of the nougat phase of the confectionery product, the packaged confectionery product was stored for 120 days at the above condition of temperature and relative humidity. Texture profile determinations (Hardness) were performed at pre-determined intervals of time 0, 20, 40, 60, 90 and 120 days. Three chocolate bars for each wrapper type were selected randomly from the humidity chamber. For this analysis, only the nougat phase of the bar was used. Measurements were made on an Instron Universal Testing Machine, model 1122 (Instron Corporation Canton, MA, USA). Each sample was discarded after use. The test was performed at room temperature (23°C ± 2°C).

Sample Preparation

The nougat sample was prepared by peeling away the chocolate layer of the candy bar after removing the packaging film wrapper at room temperature (23°C ± 2°C). The nougat phase was cut into cubes of 15 mm (height) x 25 mm (width) x

25 mm (length), just prior to the test. A sharp knife was used for peeling away the chocolate layer from the candy bar and for sample cutting. The test was performed at a constant temperature of 23°C ± 2°C.

Setting of the Instron

An Instron compression load cell (500 kg), fixed to the crosshead, was used to perform the compression tests. Determination of the hardness was based on force-displacement measurements using a plunger. The plunger, (0.5 inch diameter), was attached to the moving crosshead, which was set to cycle mode at a constant speed of 20 mm/min in both upward and downward directions. A flat holding plate was used to hold the nougat sample on the stationary horizontal bed plate of the machine, thus avoiding sticking of the nougat onto the plunger in its upward movement. The penetration of the plunger into the nougat sample was set at 11.25 mm, which corresponded to 75% of the height of the sample.

A bite was considered as a complete cycle of a downward plus upward movement of the plunger, which penetrated and then removed from the sample. To perform the tests, two bites were taken. The chart speed was set to 50 mm/min. A typical texture profile analysis (TPA) curve from the Instron universal testing machine is shown in Figure 1.

Textural Measurements of Nougat Phase of Confectionery Bar

The nougat phase of the candy bars was analyzed for texture properties by the Instron Universal Testing Machine, model 1122: (Instron Corporation Canton, MA, USA) following the procedure described by Friedman, et al. (1963), with related modifications as described below. The textural parameter; namely hardness was defined as the maximum force exerted on the sample, and was measured from the texture profile analysis (TPA) curve as the height of the first bite.

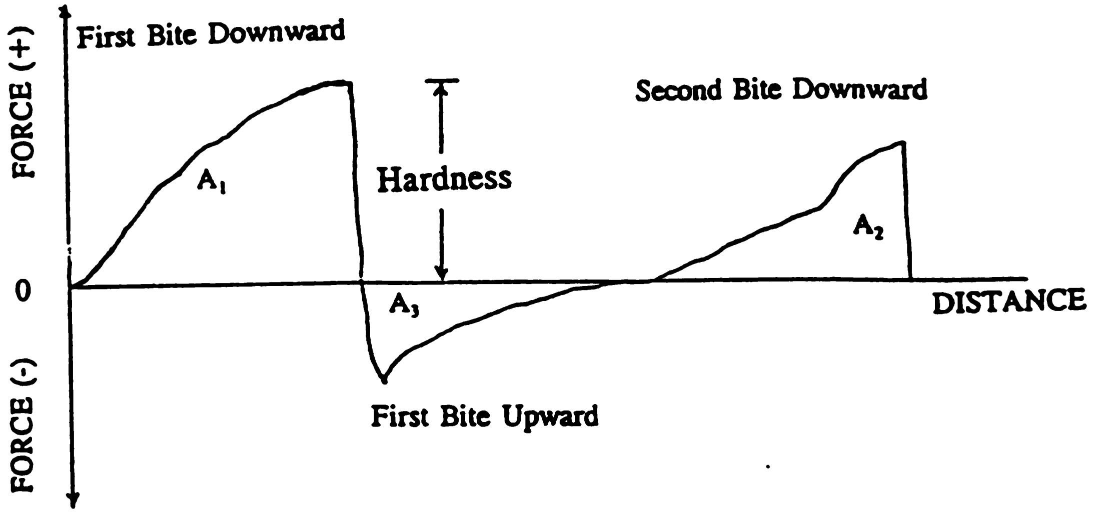

Figure 1 Typical Texture Profile Analysis (TPA) Curve Using The Instron Universal Testing Machine.

RESULTS AND DISCUSSION

Water Vapor Transmission Rates:

The water vapor transmission rates (WVTR) of the sample films were determined at a temperature of 37.8°C, and 90 % relative humidity, and at 23°C and relative humidities of 80%, 35%, and 20% respectively for all eight barrier film structures. The WVTR of the film structures were determined using a MOCON Permatran-W 3/31, for all conditions except for 23°C and 20 % relative humidity. A gravimetric method was used for WVTR determinations at the above mentioned conditions, since the Permatran -W 3/31 can not measure water vapor transmission below 35 % relative humidity. The WVTR values were converted into permeance values and are summarized in Tables 3-4, respectively. The packaging structures used in this study are listed as follows.

A 0.75 mil OPP/ink/adhesive/0.35 mil met PET/PCS
B 0.75 mil OPP/ink/adhesive/1.2 mil white opaque PP/PCS
C Overlacquer/ink/1.2 mil white opaque PP/PCS
D Overlacquer/ink/1.2 mil white opaque PP/PCS
E Overlacquer/ink/1.2 mil white opaque PP/PCS
F Overlacquer/ink/primer/0.6 mil polyester/adhesive 0.35 mil PET/PCS
G Overlacquer/ink/1.2 mil CO-PET/white PP/ CO- PET/PCS
H Overlacquer/ink/primer/0.35 mil met PET/adhesive/1.2 mil white PP/PCS

As shown in Table 4, packaging structure H was found to have the lowest permeance values and packaging structure F showed the highest permeance values as compared to the other film structures. Temperature was found to have a significant effect on the permeance values of all packaging structures, which is expected from the Arrhenius relationship. At constant temperature (23°C) the permeance values were similar over the relative humidity range evaluated (i.e. 20-80 %). Since the respective film structures were not highly hydrophilic, they were not expected to experience morphological changes as result of sorbed water. Thus, these results were expected. From this study, the film structure, H (Overlacquer/ink/primer/0.35 mil met PET/adhesive/1.2 mil white PP/PCS) was found to have the best moisture barrier properties among the eight polymer structures evaluated. The order of barrier properties for the packaging structures evaluated, in order of decreasing moisture barrier performance, is as follows: H, A, B, G, C, D, E and F.

To determine the statistical differences in the water vapor transmission rate values data was analyzed using a one factor randomized complete block design (MSTAT, Version 4.0, 1987) microcomputer statistical program. Analysis of variance (ANOVA) showed, that there was a significant difference ($p< 0.05$) between water vapor transmission rates of all film structures at all above mentioned conditions. A detailed description of the statistical analysis is presented in Appendix I-III.

Based on the statistical analysis, it was concluded that the film structures had significantly different water vapor transmission rates from each other for all conditions of relative humidity.

Table 3: Water vapor transmission rate of film structures at different temperature and relative humidity conditions.

SAMPLE ID	37.8°C 90%RH gm/ 100in^{2}day	23°C 80%RH gm/ 100in^2 day	23°C 35%RH gm/ 100in^2 day	23°C 20%RH gm/ 100 in^2 day
A	0.0531 (0.0015)	0.01082 (0.002)	0.002517 (0.0005)	0.0021 (0.0004)
B	0.1071 (0.0007)	0.01816 (0.0009)	0.006843 (0.0004)	0.0042 (0.0010)
C	0.1957 (0.0094)	0.02989 (0.0001)	0.010590 (0.0004)	0.0047 (0.0003)
D	0.2102 (0.0033)	0.04027 (0.0006)	0.014880 (0.0003)	0.0088 (0.0004)
E	0.2511 (0.0025)	0.05433 (0.0002)	0.021560 (0.0011)	0.0146 (0.0021)
F	0.7174 (0.0079)	0.17850 (0.0090)	0.084800 (0.0025)	0.0452 (0.0022)
G	0.1864 (0.0043)	0.02926 (0.0002)	0.011520 (0.0009)	0.0083 (0.0003)
H (Control)	0.0131 (0.0010)	0.00382 (0.0009)	0.001047 (0.0006)	0.0010 (0.0002)

(1) The results reported are the average of 4 replicates.
(2) The values in parentheses are standard deviation.

Table 4: The Permeance values of film structures at different temperature and relative humidity conditions.

SAMPLE ID	37.8°C 90%RH gm/ 100 in^2 day mmHg	23°C 80%RH gm/ 100 in^2 day mmHg	23°C 35%RH gm/ 100 in^2 day mmHg	23°C 20%RH gm/ 100 in^2 day mmHg
A	0.0012	0.0006	0.00040	0.00024
B	0.0024	0.0011	0.00108	0.00098
C	0.0044	0.0018	0.00168	0.00110
D	0.0048	0.0024	0.00235	0.00209
E	0.0057	0.0032	0.00341	0.00345
F	0.0162	0.0146	0.01342	0.01073
G	0.0042	0.0017	0.00182	0.00167
H (Control)	0.0003	0.0002	0.00017	0.00025

The permeance constants reported are the average of 4 replicates.

Equilibrium Sorption Isotherm of the product

Initial Moisture content

Equilibrium sorption isotherms were plotted at room temperature 23°C for both the chocolate and nougat component of the confectionery bar. The initial moisture content (IMC) of both the chocolate and nougat component were measured with a high degree of accuracy by the Karl Fischer titration method. The data obtained for initial moisture content of the chocolate phase and nougat phase are given below.

Sample	% Moisture	Std. Dev.
Chocolate Phase	2.11	± 0.132
Nougat Phase	8.29	± 0.169

The chocolate phase values are averages of seven replicates and nougat phase values are average of 15 replicates. The initial moisture content values obtained, agreed well with the values reported by the manufacture of this product, as a part of their quality control tests.

Equilibrium Moisture Isotherm

The moisture sorption isotherms developed in this study were determined by placing chocolate bars of known initial moisture content in to a series of eight relative humidity buckets maintained at a constant temperature of 23°C ± 2°C. The moisture content of the chocolate and nougat components of the confectionery bars were determined at pre-determined intervals. The relative humidity buckets had humidities which ranged from 8.6% to 75.3%. In developing moisture sorption isotherm data, care was taken to insure the relative humidity chambers employed were maintained at constant temperature and relative humidity by monitoring periodically with Hygrometer sensors: (Newport Scientific, Inc. Jessup, MD, USA) containing both temperature and RH sensing capacity. The numerical data for the equilibrium moisture content and the associated relative humidity values for both phases of the product are summarized in the Tables 5 and 6 respectively. The accumulated data of product moisture content as a function of time is summarized in Appendix VI-VII. For better illustration, the equilibrium moisture content data are presented graphically in Figures 2 and 3 respectively, where the average equilibrium moisture content is plotted as a function of relative humidity. The equilibrium moisture isotherm data showed that at low relative humidity, the product looses moisture and at high relative humidity, the product gains moisture, in both phases of the product. As indicated from the results presented in Appendix VI-VII the product required a storage period of 90 days to reach equilibrium. The very slow process of moisture transfer into the nougat phase is attributed to the barrier characteristics of the chocolate phase of the product. Similar results have been reported by Labuza and Biquet (1988) in studies on chocolate. When only the nougat phase of the product was exposed to the relative humidity conditions, equilibrium was attained within a three week period, further supporting the moisture barrier role played by the enrobed chocolate layer. The data obtained for these studies is summarized in Appendix VIII.

Table 5: Equilibrium Moisture Content of the Chocolate Phase of the Confectionery Product as a Function of Relative Humidity (RH).

RH %	EMC[a] of Chocolate Phase* g water /100 g dry wt.
8.6	1.456 (0.070)
21.6	1.549 (0.089)
34.2	1.711 (0.179)
47.3	1.780 (0.075)
63.2	2.195 (0.053)
71.2	2.839 (0.058)
75.3	3.940 (0.068)

* Values are the average of 3 replicates analysis.

[a] Equilibrium moisture content

The values in parenthesis are standard deviation of % moisture.

Table 6: Equilibrium Moisture Content of the Nougat Phase of the Confectionery Product as a Function of Relative Humidity (RH).

RH %	EMC [a] of Nougat Phase* g water /100 g dry wt.
8.6	9.478 (0.087)
21.6	9.476 (0.176)
34.2	9.478 (0.209)
47.3	9.592 (0.202)
63.2	9.791 (0.308)
71.2	10.07 (0.259)
75.3	10.293 (0.094)

* Values are the average of 3 replicates analysis

[a] Equilibrium moisture content

The values in parenthesis are standard deviation of % moisture.

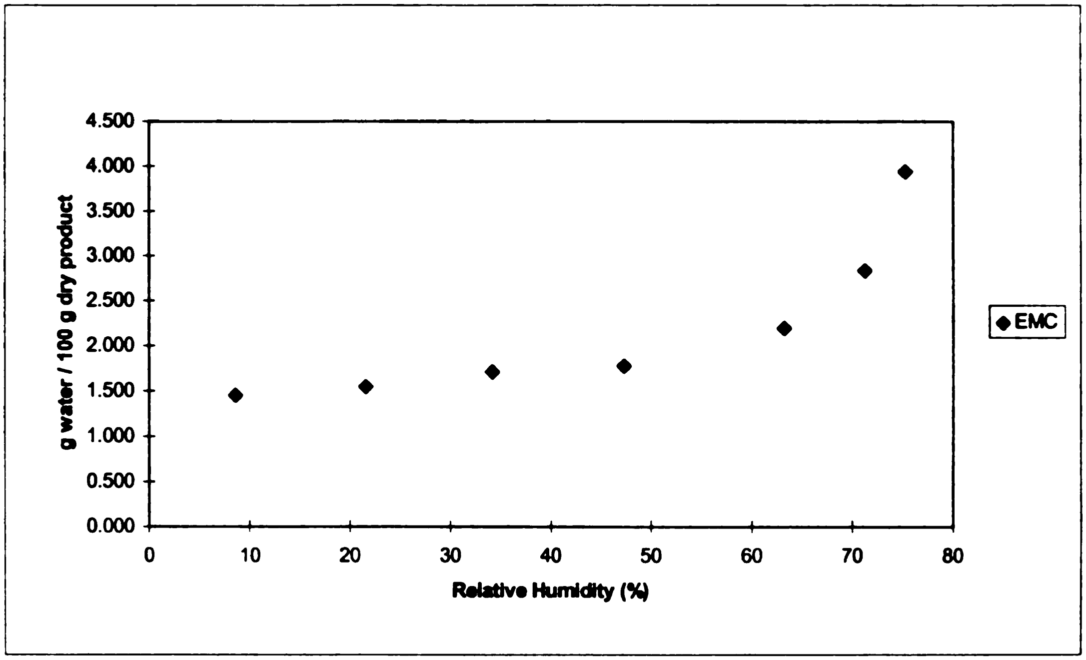

Figure 2: Equilibrium Moisture Content of Chocolate Phase of the Confectionery Product at 23°C.

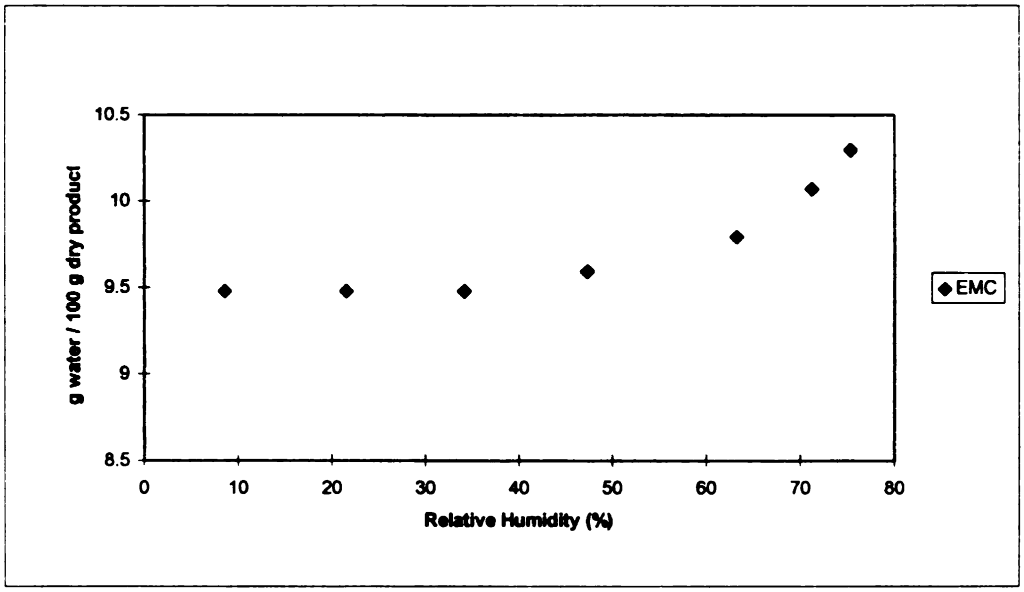

Figure 3: Equilibrium Moisture Content of Nougat Phase of the Confectionery Product at 23°C.

The Effect of Relative Humidity on Moisture Content of the Packaged Confectionery Product, Packaged with Cold Seal Closures

Based on the water vapor transmission rate and permenace values of the respective packaging film structures, the following assumptions were made for moisture uptake by the product/package system;

- The seals were hermetic.
- Moisture permeation occurs through the packaging film structures.

Samples of the chocolate confectionery product were packaged in the eight material structures, and stored under two conditions, (I) 20 % ±3 % relative humidity and 23°C ± 2°C; and (II) 75% ±3 % relative humidity and 23°C ± 2°C, for 115 days. It is noted that for the storage stability studies carried out at high relative humidity conditions, the environmental chamber was maintained at 75 % ± 3 % relative humidity and a temperature of 23°C ± 2°C over the initial 70 days storage period. At this time, difficulty was experienced with the relative humidity controls of the environmental chamber and the highest relative humidity, which could be maintained was 60 %. Therefore, for the final seven weeks of storage, the storage conditions were at 23°C ± 2°C and 60 % relative humidity. Because of this problem, these studies are referred to as the high relative humidity storage conditions, with an average relative humidity value of 67.5 %. The moisture content of the nougat phase was determined at time intervals of 0, 1, 2, 5, 10, 20, 30, 40, 55, 70, 85, 100 and 115 days, respectively. Three package samples for each wrapper type were selected randomly from the humidity chamber and the moisture content of the nougat phase was determined using the Brinkman 720 KFS Titrino, automatic titration system. The tests were performed at room temperature (23°C ± 2°C). The average values of % moisture, with a standard deviation, in the nougat phase are summarized in Tables 7-8, respectively, for each packaging structure, The change in moisture content at different time intervals during storage is presented graphically in Figures 4-5 for better illustration. As shown in Figures 4 and 5 an increase in moisture content over a storage period of 115 days was observed for product packaged in all of the treatment structures stored at high relative humidity conditions, while a decrease in moisture content over a storage period of 115 days was observed at 20 % relative humidity and 23 °C, for all packaged product.

Statistical analysis of the change in moisture content of confectionery packaged product with time, was based on a three way factorial design, using three way analysis of variance (ANOVA). The SAS (version 6.12, 1989) microcomputer statistical program was used for this analysis. The statistical analysis revealed that there was a significant effect of relative humidity and time on moisture uptake for respective product package systems. The statistical analysis also showed that the effect of relative humidity and time were not independent of each other. Packaging film structures had no statistically significant effect ($p< 0.05$) on moisture gain or loss, However a significant interaction ($p< 0.05$) between relative humidity and packaging film structure was observed. Analysis of variance (ANOVA) for moisture uptake for the respective product/package systems are presented in Appendix IV.

Based on the statistical analysis of the data for change in moisture content of confectionery packaged product in all eight packaging structures and the data for water vapor transmission rates of all eight film structures in sheet form, it can be concluded that the moisture gain or loss by the product is through micro-voids in the cold seal closure, rather than through permeation through the film structures. This conclusion is based on the fact that there is a statistically significant difference between the water vapor transmission rates of the respective film structures used. There was no statistically significant difference between the moisture content of the confectionery product packaged in the test packaging structures. These results are similar to the results reported by Lin (1995) on the permeability of organic vapors through a packaged confectionery product with a cold seal closure. The assumption initially made was that the product package system is hermetically sealed and that diffusion through the package structure, as described by Fick's First and second laws, is the principle mechanism resulting in moisture ingression. Based on statistical analysis of the water vapor transmission rates of the test film structures and the moisture uptake of the packaged confectionery product, the assumption that moisture uptake through the film structure appears not to be valid. Thus, as indicated above, mass transfer through micro-voids in the cold seal closure area is the principle mechanism of moisture ingression and not the result of diffusion through the package film structure.

Table 7: The change in moisture content of the nougat phase of the confectionery product at room temperature (23°C) and 20 % relative humidity during 115 days storage period.

SAMPLE ID	0 day	1 day	2 days	5 days	10 days	20 days	30 days	40 days	55 days	70 days	85 days	100 days	115 days
A	8.77 (0.35)	8.68 (0.07)	8.84 (0.44)	8.88 (0.12)	8.72 (0.49)	9.22 (0.01)	8.82 (0.36)	8.96 (0.39)	9.22 (0.13)	8.84 (0.20)	8.66 (0.39)	8.25 (0.61)	8.32 (0.10)
B	8.75 (0.06)	8.64 (0.22)	8.82 (0.21)	9.08 (0.16)	8.91 (0.17)	9.00 (0.11)	9.05 (0.92)	9.15 (0.09)	8.93 (0.17)	9.08 (0.73)	8.34 (0.22)	8.07 (0.06)	8.22 (0.25)
C	8.80 (0.08)	8.84 (0.07)	8.91 (0.32)	8.78 (0.42)	8.88 (0.14)	9.01 (0.61)	8.80 (0.18)	8.78 (0.28)	8.96 (0.37)	8.28 (0.17)	8.34 (0.03)	7.96 (0.30)	8.30 (0.13)
D	8.88 (0.10)	8.85 (0.25)	8.73 (0.79)	8.83 (0.08)	8.73 (0.06)	8.89 (0.32)	8.89 (0.13)	8.96 (0.17)	9.03 (0.18)	8.50 (0.17)	8.30 (0.13)	7.89 (0.03)	7.90 (0.56)
E	8.88 (0.06)	8.67 (0.12)	9.03 (0.20)	8.93 (0.16)	8.75 (0.05)	9.13 (0.30)	8.76 (0.13)	9.18 (0.14)	8.92 (0.30)	8.47 (0.14)	8.46 (0.37)	8.36 (0.19)	8.47 (0.49)
F	8.81 (0.05)	8.81 0.30)	8.70 (0.50)	8.94 (0.59)	8.76 (0.11)	8.62 (0.21)	8.93 (0.50)	9.16 (0.60)	9.12 (0.36)	8.69 (0.24)	8.76 (0.31)	7.65 (0.32)	7.98 (0.86)
G	8.82 (0.05)	8.97 (0.07)	8.76 (0.16)	8.66 (0.22)	8.72 (0.06)	8.92 (0.02)	8.65 (0.14)	8.82 (0.17)	8.90 (0.09)	9.23 (0.45)	8.39 (0.32)	8.09 (0.35)	8.03 (0.78)
H (Control)	8.74 (0.03)	8.74 (0.12)	8.83 (0.18)	8.92 (0.20)	8.84 (.03)	9.13 (0.01)	9.16 ((0.65)	9.34 (0.30)	9.09 (0.11)	8.59 (0.36)	8.63 (0.37)	8.45 (0.11)	8.34 (0.35)

(1) The results reported are average of 3 replicates.
(2) The values in parentheses are standard deviation.

Table 8: The change in moisture content of the nougat phase of the confectionery product at room temperature (23°C) and high relative humidity during 115 days storage period.

SAMPLE ID	0 day	1 day	2 days	5 days	10 days	20 days	30 days	40 days	55 days	70 days	85 days	100 days	115 days
A	8.77 (0.35)	8.68 (0.05)	8.84 (0.07)	8.71 (0.16)	8.92 (0.10)	8.75 (0.38)	9.20 (0.22)	8.67 (0.13)	9.23 (0.15)	9.44 (0.38)	8.94 (0.13)	9.09 (0.05)	8.87 (0.24)
B	8.75 (0.06)	8.74 (0.11)	8.89 (0.14)	8.90 (0.07)	8.74 (0.45)	8.74 (0.14)	8.97 (0.16)	9.06 (0.09)	9.47 (0.12)	9.22 (0.56)	8.92 (0.03)	8.77 (0.05)	9.04 (0.56)
C	8.80 (0.08)	8.82 (0.13)	8.47 (0.48)	8.83 (0.16)	8.81 (0.50)	9.01 (0.08)	9.31 (0.11)	9.27 (0.23)	9.25 (0.19)	9.31 (0.65)	8.92 (0.53)	8.63 (0.20)	8.86 (0.55)
D	8.88 (0.10)	8.74 (0.06)	8.68 (0.60)	8.98 (0.32)	9.12 (0.27)	8.77 (0.19)	9.12 (0.13)	8.96 (0.08)	9.40 (0.48)	9.52 (0.21)	8.94 (0.69)	8.74 (0.11)	9.02 (0.24)
E	8.88 (0.06)	8.64 (0.04)	8.85 (0.18)	8.89 (0.14)	9.12 (0.17)	8.77 (0.58)	9.30 (0.21)	9.23 (012)	9.55 (0.19)	9.79 (0.13)	8.97 (0.05))	8.91 (0.16)	9.54 (0.75)
F	8.81 (0.05)	8.76 (0.12)	8.95 (0.18)	9.03 (0.35)	8.91 (0.66)	9.29 (0.14)	8.83 (0.24)	9.38 (0.31)	9.54 (0.24)	9.86 (0.10)	8.94 (0.15)	8.99 (0.07)	9.18 (0.31)
G	8.82 (0.05)	8.70 (0.04)	8.80 (0.43)	8.88 (0.13)	8.73 (0.39)	8.81 (0.10)	9.05 (0.32)	9.12 (0.10)	9.35 (0.12)	9.23 (0.65)	9.23 (0.36)	8.86 (0.16)	9.16 (0.31)
H (Control)	8.74 (0.03)	8.69 (0.16)	8.78 (0.02)	8.78 (0.21)	8.75 (0.08)	9.00 (0.35)	8.72 (0.41)	8.85 (0.30)	9.05 (0.04)	9.23 (0.31)	8.87 (0.14)	8.64 (0.09)	8.85 (0.27)

(1) The results reported are average of 3 replicates.
(2) The values in parentheses are standard deviation.

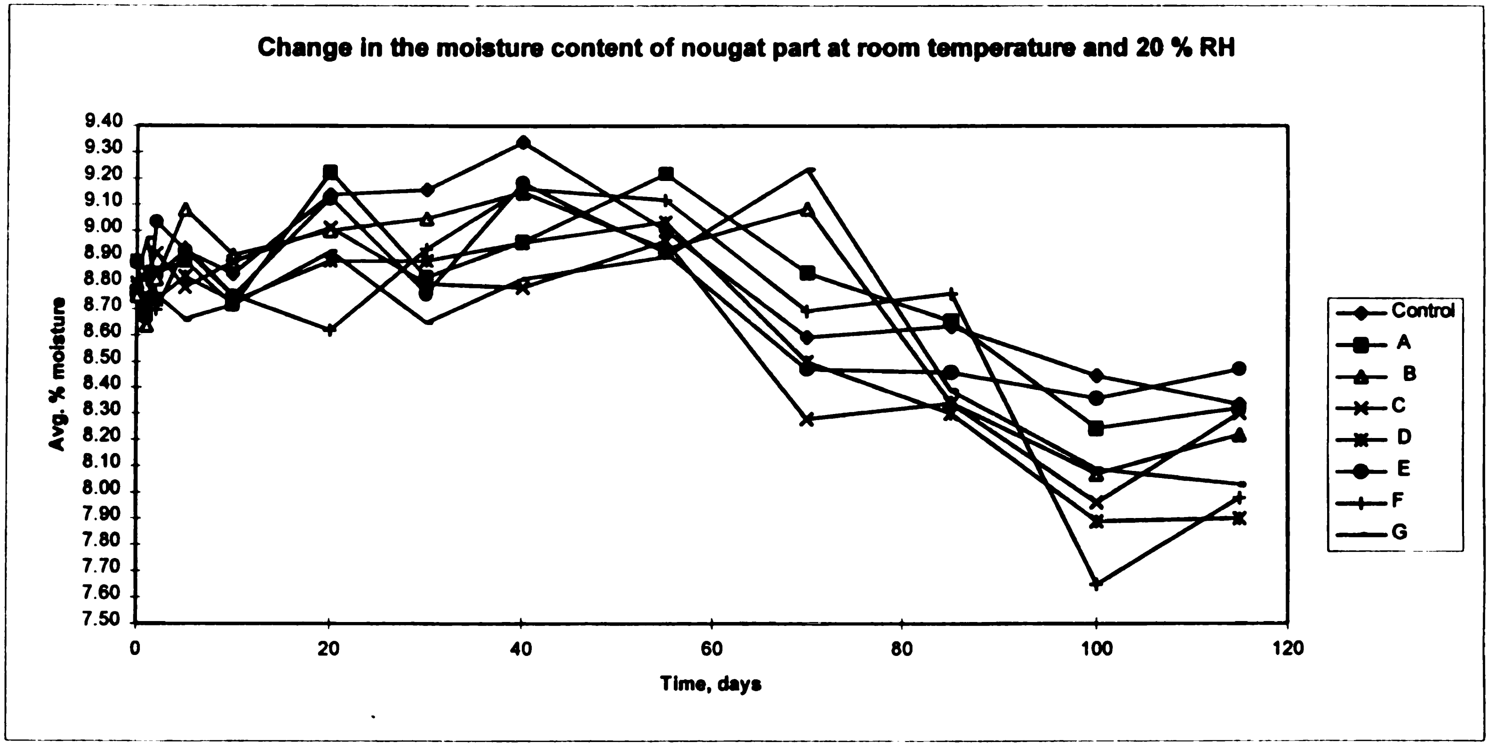

Figure. 4: The change in moisture content of the nougat phase of the confectionery product stored at room temperature (23°C) and 20% relative humidity, during 115 days storage period.

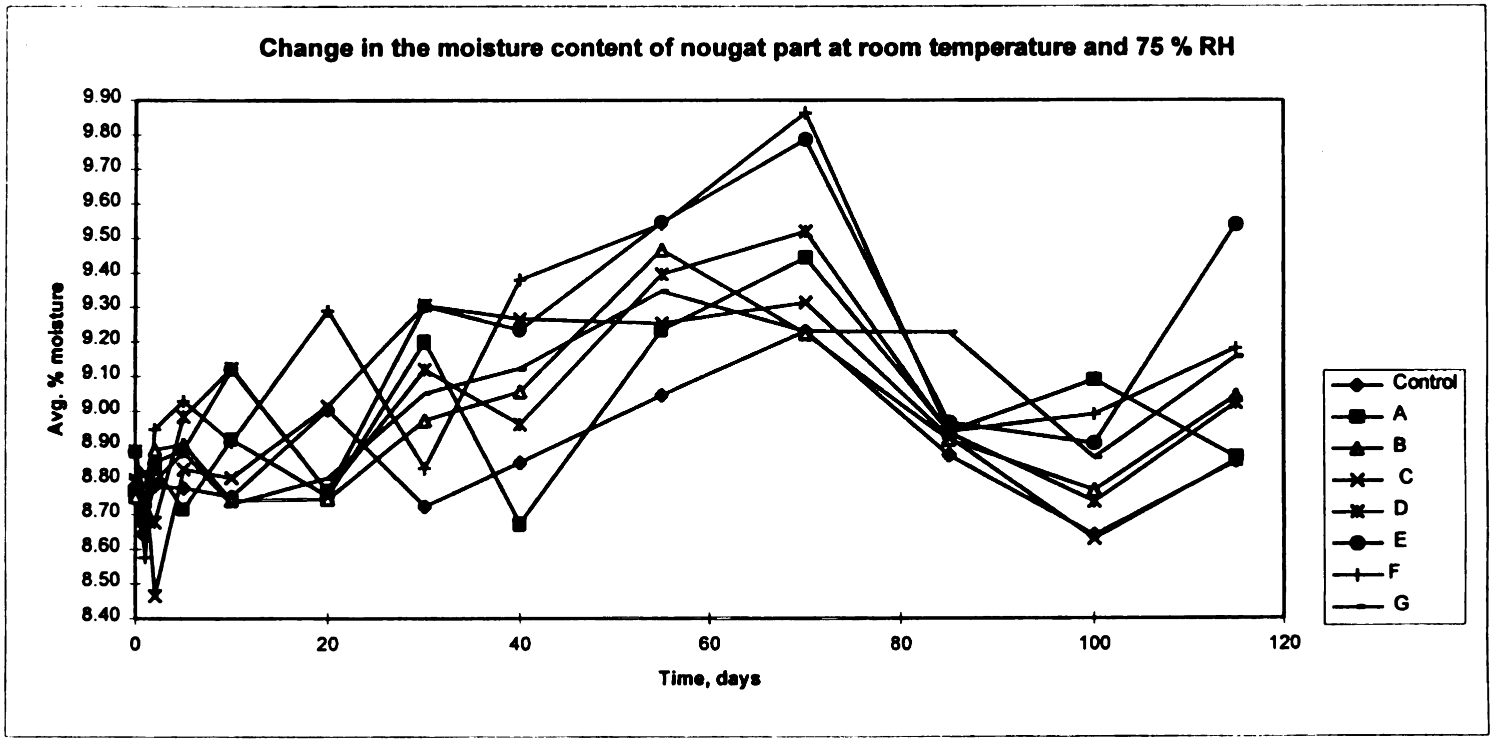

Figure. 5: The change in moisture content of the nougat phase of the confectionery product stored at room temperature (23°C) and high relative humidity, during 115 days storage period.

The Effect of Relative Humidity on Texture of the Packaged Confectionery Product, Packaged with Cold Seal Closures

To determine the effect of storage conditions on the texture of the nougat phase of the confectionery product, the packaged confectionery product was stored for 120 days at two conditions of temperature and relative humidity, and texture characteristics were determined by obtaining a texture profile curve on an Instron Universal Testing Machine, model 1122. The nougat phase of the candy bars was analyzed for its texture properties. The textural characteristics; namely hardness was determined from the texture profile curve at pre-determined time intervals of 0, 20, 40, 60, 90 and 120 days respectively.

Hardness of Nougat Phase

Hardness is defined as the maximum force exerted on the sample, and was measured from the texture profile analysis (TPA) curve as the height of the first bite (Friedman et al 1963). The complete data for hardness during the storage period is listed in Tables 9-10 and a plot of hardness, as a function of time presented in Figures 6-7, for comparison between packaging structures. A slight increase in hardness over a storage period of 120 days in all packaging structures was observed at 20 % relative humidity and 23°C, while a slightly decrease in moisture content over a storage period of 120 days in all packaging structures was observed at high relative humidity storage conditions and 23°C. The change in hardness values at different time intervals during storage is presented graphically in Figures 6-7 for better illustration.

Statistical analysis showed that relative humidity and time had a significant effect ($p < 0.05$) on the hardness of the packaged product. However the packaging structure had no statistically significant effect on hardness. Statistical analysis indicated that relative humidity and packaging structure have a ($p < 0.05$) significant interaction. Similarly, packaging structure and time were dependent upon each other. Relative humidity and time had significant interaction at ($p < 0.05$). Analysis of variance (ANOVA) for hardness of the nougat phase of product is given in appendix V.

Table 9: **The change in hardness (Newton) of the nougat phase of the confectionery product at room temperature (23°C) and 20% relative humidity during 120 days storage period.**

SAMPLE ID	0 DAY	20 DAYS	40 DAYS	60 DAYS	90 DAYS	120 DAYS
A	14.37 (1.13)	12.08 (1.50)	13.39 (0.55)	16.00 ((2.96)	16.98 (2.08)	23.51 (6.79)
B	11.10 (0.57)	16.00 (4.83)	17.96 (2.71)	15.02 (0.57)	16.00 (0.57)	24.49 (0.98)
C	12.08 (2.26)	12.74 (0.98)	19.27 (2.47)	16.00 (2.04)	15.67 (0.98)	22.53 (1.70)
D	12.08 (1.50)	15.35 ((4.63)	19.59 (1.92)	16.97 (2.07)	16.98 (1.13)	25.47 (8.98)
E	16.65 (0.98)	13.39 (2.04)	13.72 (2.41)	14.37 (1.13)	15.68 (0.00)	35.27 (3.92)
F	13.39 (2.83)	16.98 (2.02)	18.94 ((1.92)	20.25 (1.13)	18.29 (2.26)	24.17 (2.99)
G	14.04 (0.57)	16.33 (2.99)	17.63 (0.00)	14.37 (1.13)	17.64 (0.00)	18.29 (1.13)
H (Control)	16.98 (1.13)	14.04 (2.83)	20.57 (1.96)	16.00 (0.57)	19.59 (2.18)	19.92 (2.47)

(1) The results reported are average of 3 replicates.
(2) The values in parentheses are standard deviation.

Table 10: The change in hardness (Newton) of the nougat phase of the confectionery product at room temperature (23°C) and high relative humidity during 120 days storage period.

SAMPLE ID	0 DAY	20 DAYS	40 DAYS	60 DAYS	90 DAYS	120 DAYS
A	14.37 (1.13)	12.74 (0.00)	16.00 (3.96)	11.10 (1.13)	12.41 (1.13)	11.10 (1.13)
B	11.10 (0.57)	9.80 (0.00)	15.68 (1.96)	12.41 (1.51)	11.77 (1.98)	9.14 (1.13)
C	12.08 (2.26)	10.12 (2.04)	15.68 (5.96)	13.39 (2.26)	11.43 (1.98)	11.10 (2.26)
D	12.08 (1.50)	10.12 (0.57)	12.74 ((2.94)	12.41 (3.71)	11.43 (1.50)	9.80 (1.13)
E	16.65 (0.98)	10.78 (0.98)	13.72 (3.39)	12.41 (1.13)	10.45 (0.57)	10.45 (1.96)
F	13.39 (2.83)	10.78 (0.00)	15.67 (3.39)	11.43 (0.57)	10.12 (2.47)	7.84 (1.96)
G	14.04 (0.57)	12.08 (0.57)	16.33 (1.13)	10.78 (0.98)	11.76 (0.00)	8.49 (1.13)
H	16.98 (1.13)	11.10 (0.57)	16.98 (2.26)	14.70 (0.98)	14.04 (0.57)	11.10 (2.99)

(1) The results reported are average of 3 replicates.
(2) The values in parentheses are standard deviation.

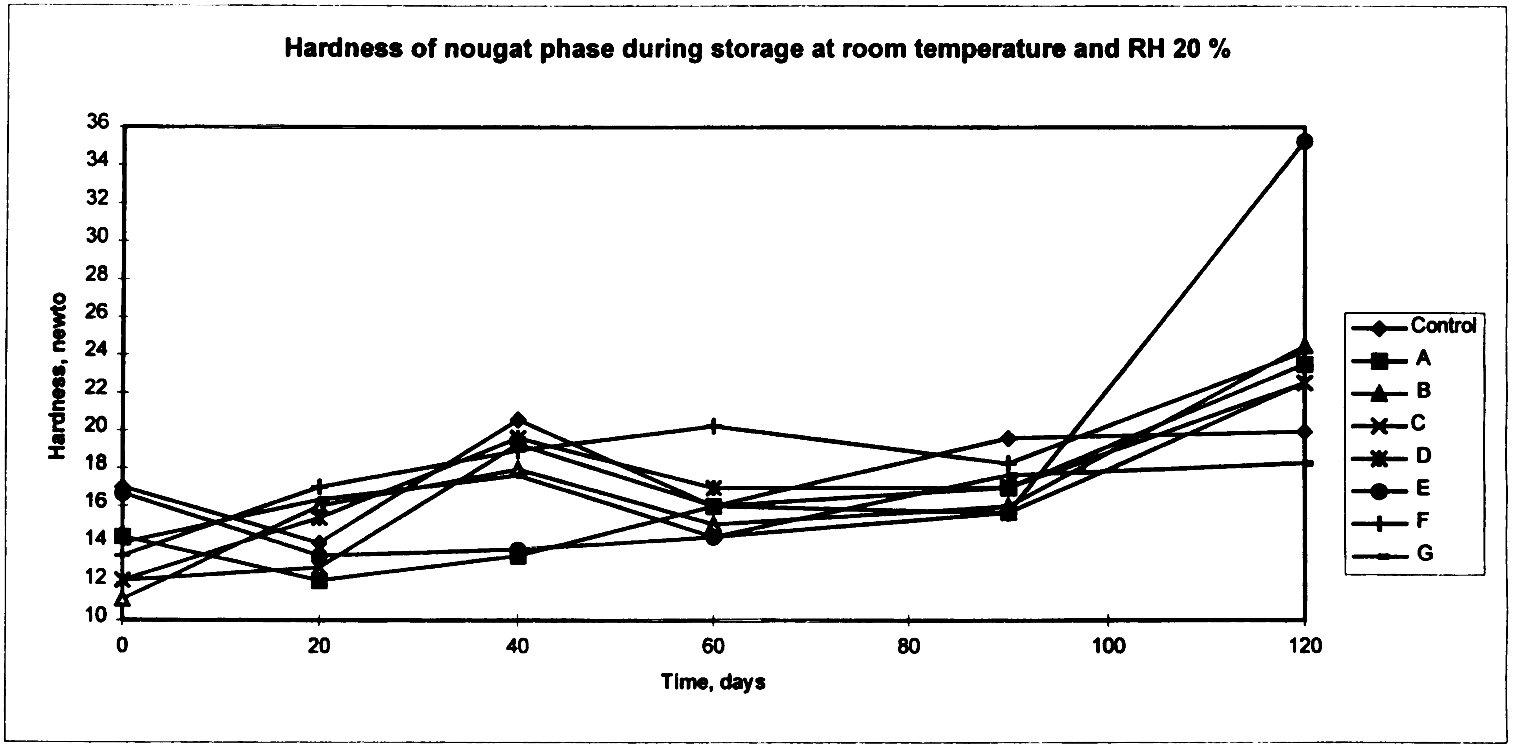

Figure 6: The change in hardness of the nougat phase of the confectionery product stored at room temperature (23°C) and 20% relative humidity, during 120 days storage period.

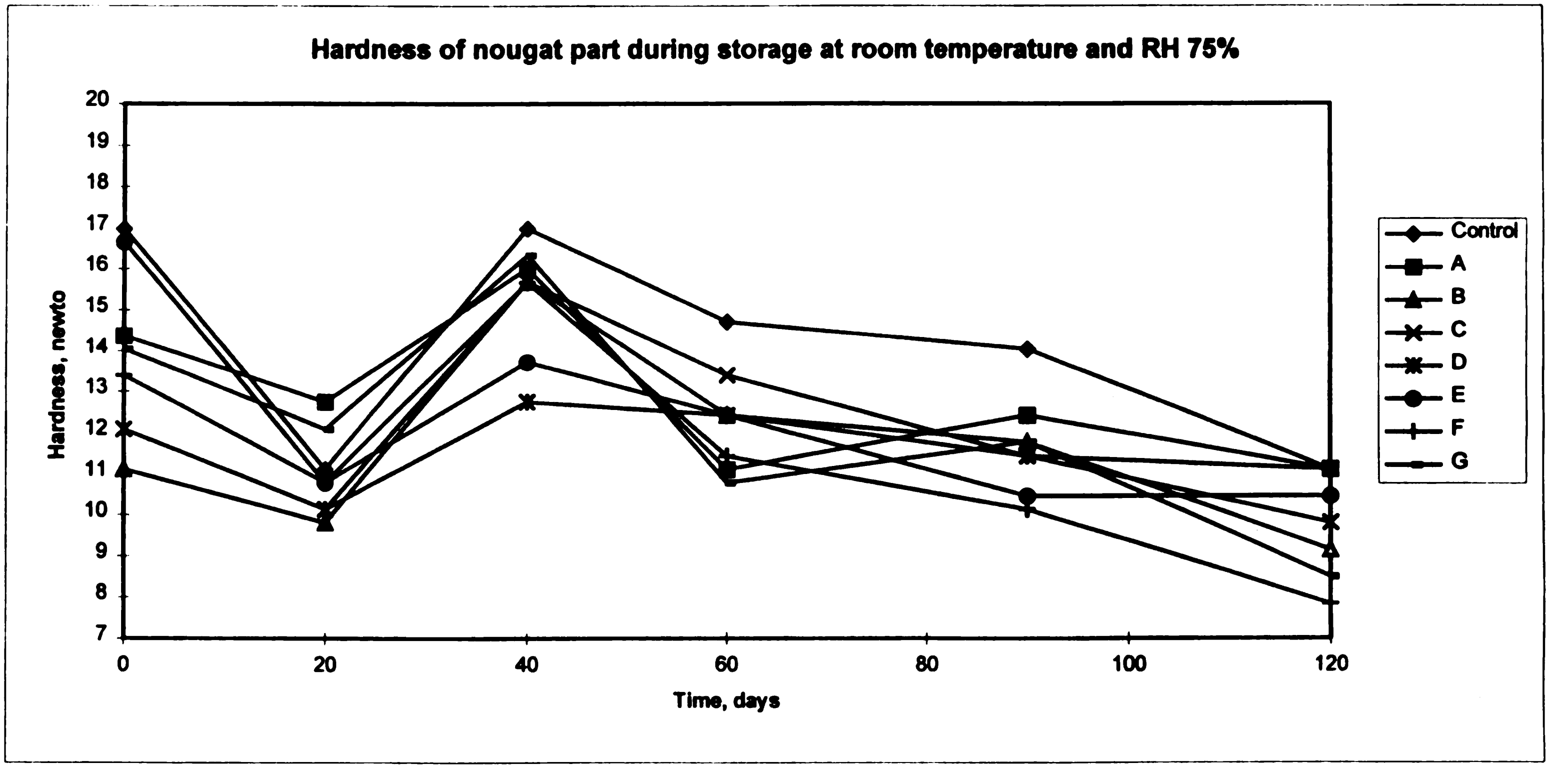

Figure 7: The change in hardness of the nougat phase of the confectionery product stored at room temperature (23°C) and high relative humidity, during 120 days storage period.

SUMMAY AND CONCLUSION

For a series of commodity film structures, permeance values were obtained from permeability studies based on an isostatic procedure utilizing the Mocon' s Permatran W 3/31 WVTR. Permeability studies were carried out at two temperatures to allow evaluation of the Arrehenius relationship. In addition, the respective commodity film structures were used to package a confectionery product with a cold seal closure technology. To evaluate the integrity of the cold seal closure, with respect to water vapor ingression, storage stability studies were carried out for a 115 day storage period at two relative humidity conditions. Moisture isotherm of the confectionery product was developed at 23°C. A textural parameter (Hardness) was measured to evaluate the effect of relative humidity and moisture content in the nougat phase of the confectionery packaged product in several packaging structures.

The temperature dependency of the transport process associated with the respective barrier membranes, over the temperature range studied was found to follow well the Arrehenius relationship.

The packaging film structure, "Overlacquer/ink/primer/0.35mil met PET/adhesive/1.2 mil white PP/PCS" was found to exhibit the best water vapor barrier properties among the eight polymer membranes evaluated, when tested in film form. There were statistically significant differences between the water vapor barrier properties of the respective polymer structures, in flat sheet form.

There was no statistically significant difference between the performance of the product package system with regards moisture uptake. These findings indicate that the barrier performance of the film structures showed significant differences, when evaluated as flat film stock. This suggests that moisture uptake by the packaged product is a result of moisture ingression through the seal area as the predominant mechanism and not the result of diffusion through the package structure. Statistical analysis showed that there is no significant difference between the performance of the product package system for texture (Hardness) of the nougat phase of the confectionery packaged product over a storage period of 120 days within the same storage conditions. However, relative humidity and time had a significant effect on hardness of the confectionery packaged product.

Appendix I

Analysis of Variance (ANOVA) for Water Vapor Transmission Rate of Packaging Film Structures at 37.8°C and 90 % Relative humidity.

Source of variance	Degree of freedom df	Sum of Square	Mean Square	F Value (1)
Film Structure	7	1.3340	0.1910	9179.043*
Replication	3	0.000	0.000	2.2653
Error	21	0.000	0.0001	
Total	31	1.335		

(1) F Table Value : $F_{0.05\,(3,\,21)} = 3.07$; $F_{0.05\,(7,\,21)} = 2.49$.

* = Significant difference at $p \leq 0.05$

Appendix II

Analysis of Variance (ANOVA) for Water Vapor Transmission Rate of Packaging Film Structures at 23°C and 80 % Relative humidity.

Source of variance	Degree of freedom df	Sum of Square	Mean Square	F Value (1)
Film Structure	7	0.088	0.013	1200.1340*
Replication	3	0.000	0.000	0.9788
Error	21	0.000	0.0001	
Total	31	0.088		

(1) F Table Value : $F_{0.05\,(3,\,21)} = 3.07$; $F_{0.05\,(7,\,21)} = 2.49$.

* = Significant difference at $p \leq 0.05$

Appendix III

Analysis of Variance (ANOVA) for Water Vapor Transmission Rate of Packaging Film Structures at 23°C and 30 % Relative humidity.

Source of variance	Degree of freedom df	Sum of Square	Mean Square	F Value (1)
Film Structure	7	0.021	0.003	35.9234*
Replication	3	0.000	0.000	0.6580
Error	21	0.002	0.0001	
Total	31			

(1) F Table Value :$F_{0.05\,(3,\,21)} = 3.07$; $F_{0.05\,(7,\,21)} = 2.49$.

* = Significant difference at $p \leq 0.05$

Appendix IV

Analysis of Variance (ANOVA) for Moisture Content for Product Package Systems

Source of variance	Degree of freedom (df)	Sum of Square	Mean Square	F Value (1)
RH	1	9.29	9.29	91.73*
Film	7	0.88	0.13	1.24
RH x Film	7	2.25	0.32	3.18*
Time	12	20.63	1.72	16.98*
RH x Time	12	16.30	1.36	13.42*
Film x Time	84	5.35	0.06	0.63
RH x Film x Time	84	8.73	0.10	1.03
Error	416	42.13	0.10	
Total	623	105.58		

(1) F Table Value :$F_{0.05\,(1,416)} = 3.84$; $F_{0.05\,(7,416)} = 2.01$; $F_{0.05\,(12,416)} = 1.75$; $F_{0.05\,(84,416)}=1.26$

* = Significant difference at $p \leq 0.05$

Appendix V

Analysis of Variance (ANOVA) for Hardness of Product Package Systems.

Source of variance	Degree of freedom (df)	Sum of Square	Mean Square	F Value [(1)]
RH	1	1731.37	1731.37	238.81*
Film	7	95.62	13.66	1.88
RH x Film	7	121.71	17.39	2.40*
Time	5	633.91	126.78	17.49*
RH x Time	5	1453.51	290.70	40.10*
Film x Time	35	627.92	17.94	2.47*
RH x Film x Time	35	342.41	9.78	1.35
Error	192	1392.00	7.25	
Total	287	6398.45		

(1) F Table Value :$F_{0.05\,(1,192)} = 3.84$; $F_{0.05\,(7,192)} = 2.01$; $F_{0.05\,(5,192)} = 2.21$; $F_{0.05\,(35,192)} = 1.43$

* = Significant difference at $p \leq 0.05$

Appendix: VI

The data for Moisture Isotherm of Chocolate Phase of the Confectionery Product.

RH %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %
	3/12/97	3/22/97	3/31/97	4/11/97	4/26/97	5/15/97	6/1/97
8.6	1.916	1.650	1.506	1.620	1.506	1.386	1.486
21.6	1.940	1.820	1.646	1.676	1.506	1.590	1.463
34.2	1.823	1.800	1.853	1.770	1.683	1.556	1.810
47.3	1.726	1.750	1.710	1.793	1.730	1.696	1.803
63.2	2.090	2.010	1.970	1.960	2.053	2.110	2.186
71.2	2.173	2.310	2.450	2.370	2.490	2.720	2.803
75.3	2.313	2.820	3.033	3.353	3.456	3.743	3.840

RH %	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±
8.6	0.023	0.070	0.166	0.113	0.040	0.055	0.106
21.6	0.026	0.080	0.090	0.049	0.089	0.026	0.421
34.2	0.125	0.113	0.113	0.105	0.023	0.049	0.145
47.3	0.119	0.087	0.088	0.104	0.036	0.037	0.064
63.2	0.225	0.165	0.045	0.030	0.057	0.079	0.045
71.2	0.235	0.131	0.026	0.060	0.262	0.135	0.135
75.3	0.140	0.180	0.332	0.101	0.176	0.301	0.190

Appendix: VII

The data for Moisture Isotherm of Nougat Phase of the Confectionery Product.

RH %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %	Moisture %
	3/12/97	3/22/97	3/31/97	4/11/97	4/26/97	5/15/97	6/1/97
8.6	8.586	8.520	8.550	8.563	8.580	8.596	8.720
21.6	8.426	8.676	8.420	8.486	8.463	8.530	8.780
34.2	8.240	8.716	8.810	8.383	8.586	8.510	8.806
47.3	8.076	8.830	8.730	8.276	8.610	8.270	8.896
63.2	8.440	8.610	8.460	8.463	8.700	8.483	9.136
71.2	8.006	8.886	8.590	8.573	8.740	8.966	9.333
75.3	8.410	8.796	8.590	8.470	8.920	9.266	9.400

RH %	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±	Std.Dev. ±
8.6	0.084	0.245	0.156	0.097	0.095	0.055	0.026
21.6	0.282	0.145	0.087	0.020	0.085	0.131	0.023
34.2	0.305	0.188	0.122	0.263	0.020	0.080	8.806
47.3	0.512	0.043	0.150	0.107	0.168	0.085	0.136
63.2	0.173	0.350	0.050	0.115	0.101	0.150	0.050
71.2	0.075	0.045	0.170	0.239	0.105	0.037	0.051
75.3	0.281	0.144	0.110	0.113	0.138	0.385	0.060

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