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Effect of Flexing on the Barrier Properties of Metallized Films

Anjum Parkar

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Thesis

Effect of Flexing on the Barrier Properties of Metallized Films

By

Anjum Parkar

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M.S. DEGREE THESIS

The M.S. Degree thesis of Anjum Parkar
has been examined and approved
by the thesis committee as satisfactory
for the thesis requirements for the
Master of Science Degree

Fritz Yambrach

Thomas Voss

Christopher Donnelly

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Abstract

One of the major concerns with respect to metallized films is the effect of flexing on their barrier properties. Films encounter a series of mechanical stress situations during manufacturing, processing, handling, and distribution. These mechanical stresses often result in flexing of the packaging film, which is more prominent with metallized films. The first part of my study evaluates the effect of real stresses of flex by using packages already manufactured and that have been through the distribution cycle. Metallized film samples from these packages were tested to see the effect of real stress on their barrier properties. The results showed an increase in the oxygen transmission rates and water vapor transmission rates of the flexed samples indicating that flexing decreases the barrier properties of metallized films. Flexing leads to the initiation of pinholes that subsequently lead to a loss in barrier properties. The second part of my study evaluates whether the Gelbo flex tester simulates the actual distribution environment encountered by flexible packages. The metallized films were submitted to 10, 50 and 100 full flex cycles on a Gelbo flex tester and their permeation rates were evaluated comparatively. The results showed that for different films, different numbers of flex cycles are required to simulate mechanical stress during processing and distribution.

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Chapter I

Introduction

Flexible packaging is growing in popularity at the expense of rigid containers, both among food manufactures and consumers ("Flexible Future," 2002). Food packaging applications will be stimulated by the ability of converted flexible packaging to provide more improved and cost effective protection from contamination while enhancing shelf life and visuals (Weizer, 2004). The current trend is to move from rigid containers like can, drums and bottles into flexible packaging for reasons of both cost and convenience. This rise in flexible packaging applications is driving the need for improved packaging barriers, which in turn favors the selection of metallized films due to their high barrier properties (Mount, 2004).

Metallized films incorporate the advantages of both metal and plastic films, thus offering consumers much more versatility in application. Polymer films are metallized with aluminum to provide moisture, oxygen and light barrier properties for food packaging applications. One of the most significant barrier property of all metallized films is its light barrier. This plays an important role in preserving foodstuffs that contain unsaturated oils, which turn rancid by exposure to light (Mount, 2004). Metallized films for food packaging applications have seen a steady growth largely due to improved properties of metallized films, which in turn is a result of new metallizing process enhancements such as plasma pretreatment of metallized films (Mount, 2001). The aluminum coating is very thin compared to the polymer base. This very thin coating still has a profound influence on the gas permeability of the film.

One of the most challenging decisions in food packaging is choosing the most appropriate metallized film for a particular application. In order to make this decision, one should know the barrier-property profiles of the various metallized films and the product failure modes such as rancid, loss of nutritive value or loss of flavor (Mount, 2004). In some cases a metallized film alone will not provide the needed protection that is required and so multilayer structures are needed to provide both strength and barrier, where each layer provides a different structural barrier or adhesive function.

Gas permeability values of a particular film depend on a number of variables such as temperature, relative humidity, film thickness, time, grade of barrier plastic, packaging structure, and processing conditions. There exists a range of gas permeability values, which can vary even for the same resin (Soroka, 2003). Another factor having an impact on the barrier properties of metallized films is the storage conditions. Elevated temperatures in combination with moisture corrode the metal layer and thus increase gas permeation (Weiss, 1991). Most of the food products require barrier protection against oxygen and/or water vapor. In order to maintain a high shelf life for a given content a high barrier against oxygen and/or water vapor permeation is necessary. Water vapor and oxygen barrier are critical requirement for many food-packaging applications since discoloration, bacterial growth, rancidity, and other problems can affect the appearance, taste and freshness of a packaged product as well as reducing its customer appeal (Ashley, 1985).

The packaging materials are subjected to a series of mechanical stresses, which they generally encounter during processing operations and during distribution from the manufacturer to the end-user. During package forming, the film is subjected to stresses due to web tension as it passes through rollers through the webfed machine. The formed package encounters stresses during the distribution environment as a result of vibration in transit as well as the handling procedure. So the packaging material chosen should preserve its barrier properties to maintain the necessary protection. The mechanical stresses lead to flexing of the packaging film, which is more prominent with metallized films. Creases are created when plastic films are flexed. The intersection of creases results in stress concentration points and repeated flexing of these points eventually lead to the initiation of pinholes (Varughese, & Gyeszly, 1993). Plastic pouches encounter vibration during transit which result in repeated flexing and pinhole formation. Flexing is also a major issue with regards to medical product packaging. Pinholes in plastic films lead to loss in product sterility. (Hackett, Scholla, Rudys, & Bletsos, 2000)

There are various methods that have been used to simulate the mechanical stresses that flexible packages encounter during processing and distribution. The most widely used equipment is the Gelbo Flex Tester, which attempts to simulate conditions of stress using a twist and crush action. It flexes the film samples to simulate the stresses encountered during manufacturing and distribution. The test is designed to evaluate the performance of plastic films when they are subjected to mechanical stresses, which are reproducible. The advantage of these laboratory based stress simulation tests is to reduce both the cost and time necessary to conduct practical field tests.

A. Summary

The use of metallized films is growing in food applications due to their excellent barrier properties. Polymers can have their barrier performance improved by a factor of several hundreds by metallization. One of the major concerns is the effect of flexing on the barrier properties of metallized films. Films encounter a series of mechanical stress situations during manufacturing, processing, handling, and distribution. These mechanical stresses often result in flexing of the packaging film, which is more prominent with metallized films. Flexing leads to the initiation of pinholes and stress cracks that could subsequently lead to a loss in barrier properties.

B. Problem Statement

1) What is the effect of flexing on the barrier properties of metallized films?

The first part of the study looks into the effects of flexing on the oxygen and water vapor permeability of metallized films.

2) Does a Gelbo Flex Tester simulate the actual distribution environment encountered by flexible packages?

The second part of the study evaluates whether the Gelbo Flex Test method is an appropriate method to determine the levels of flexing that are generally encountered by metallized packages during processing and distribution.

Chapter II

Literature Review

A metallized polymeric film can be envisaged as composed of two layers, the polymeric substrate and the metal coating (Del Nobile, Mensitieri, Aldi, & Nicolais, 1999). The polymeric substrate is more or less permeable to gases and vapors and hence barrier properties depend on the ability of the metal coating to obstruct the gas molecules from passing through the layers. Gas molecules would be prevented from permeating through the metallized polymeric film if the deposited metal layer were composed of a uniform defect-free layer. However, this is normally not the case. Due to the presence of micro-defects in the metal layer and the disordered aggregation of the deposited metal atoms, the metal coating loses its ability to completely prevent gas permeation through it and consequently through the metallized polymeric film. Hence the metal coating is not able to prevent the gas molecules from permeating through but is only able to reduce the permeation of gas molecules through it. Nobile and his colleagues confirmed this theory (Del Nobile, Mensitieri, Aldi, & Nicolais, 1999). They conducted a study on the transport mechanism of gases through metallized films and concluded that gas molecules could permeate through the metallized films due to the permeable porous structure of the deposited aluminum layer and also due to the presence of pinholes uniformly dispersed on the metallized film surface

Defects such as scratches, crazing, shading and pinholes often have a negative impact on barrier properties by providing areas for permeation (Comer, 1995). The sources of these defects are as follows:

a) Scratches: The most common source of metallized film scratching is from particulates used as antiblocks in the film. Scratches also result from the presence of hard additives in the film surface against which the metallized surface winds and rough idler rolls. Idler rolls in high-speed processes do not always turn at web speeds and this produces web scratches on clear, smooth films.

b) Crazing: Crazing is defined as fine and random cracking extending throughout the metal surface. Crazing results in increase in oxygen and water vapor permeation rates. The most common cause of crazing is the flexing of metallized films. Crazing disrupts the crystalline packing of the metal coating and shortens the migration path of oxygen and water vapor molecules that permeate metal coatings by migration along a tortuous path of aluminum crystalline interfaces. Crazing also results in debonding of the metal from the film surface resulting in increased permeation.

c) Shading: Shading is a variation in the thickness of the metal coating. Shading is a common phenomenon in films metallized in supported web vacuum chambers. Common causes of uneven deposition of aluminum on the polymer film are the polymer film flatness and uneven coefficient of friction on the non-metallized side of the web causing variations in web speed during coating.

d) Pinholes: Pinholes are defined as an area where no metal deposition is present. These voids are formed by abrasion of thin metal layers over the substrate film surface or by flexing, which leads to stress and the subsequent initiation of pinholes. Also a common cause of pinholes is the presence of dust or other foreign particles on the substrate film surface at the point of metallization. Not all pinholes lead to a loss of barrier and there are some pinholes that exhibit good barrier. These could be due to the fact that the aluminum may be oxidized forming a spurious pinhole believed to be aluminum oxide (Comer, 1995).

The barrier properties of metallized films are influenced by the surface properties of the polymer film and the characteristics of the deposited aluminum layer. Some of the parameters leading to aluminum layer damages are high web tension, metal abrasion and high aluminum thickness (Yializis, Ellwanger, & Harvey, 1997). The pulling of the web as it passes through the rollers on a webfed machine causes web tension. High web tension during the processing stages leads to aluminum metal micro cracking and creation of pinholes in the aluminum layer, subsequently leading to a loss of barrier properties. Metal abrasion takes place by the films contact with rollers in the processing stage as well as rubbing against each other during distribution, leading to pinholes. Most of the metallizing converters metallize packaging films to about the same optical density, favoring thicker coatings to assure better barrier properties. Yializis and his colleagues found out that as the aluminum thickness increases, the metallized aluminum layer becomes more brittle leading to pinhole formation on flexing and subsequent loss in barrier properties (Yializis, Ellwanger, & Harvey, 1997). Thin aluminum layers transmit gas and vapor through them and do not provide the required barrier protection. It seems there exists an optimum aluminum layer thickness that will maximize oxygen transmission rate and water vapor transmission rate values.

The major forms of mechanical abuse that flexible packages encounter are scuffing during package forming and crumpling during distribution of the flexible packages from the manufacturer to the end-user (Goddard, 1979). The British research association for the paper and board, printing and packaging industries (PIRA), arranged a cooperative research project to study the barrier performance of metallized films. In the study, barrier performance of metallized films were evaluated before and after subjecting them to mechanical abuse test. The metallized films were subjected to scuffing, flat creasing and Gelbo flexing in the laboratory. In the scuffing test, films were rubbed by pulling them in a reciprocating manner over two parallel polished stainless steel bars, placed 50 millimeters apart. The effect of 100 and 500 rubs on a range of materials was measured. Results showed that scuffing reduced the barrier property of unprotected metallized films but still even after 500 rubs, they were twice as good as the unmetallized material. They found that laminating and/or lacquering with LDPE dramatically decreased the effect of scuffing. Water vapor transmission was less affected by scuffing than oxygen transmission. The flat creasing test showed similar results to the scuffing test. A significant increase in the oxygen and water vapor transmission was observed in the unprotected metallized films, whereas the lacquered and/or laminated metallized films showed a much lower increase in oxygen and water vapor transmission. In the Gelbo Flex Test, the metallized films were subjected to severe stressing on a Gelbo Flex Tester. The oxygen and water vapor transmission rates were measured after subjecting the films to different flex cycles. The results showed a very significant increase in the barrier property of unprotected metallized films. The lacquered and/or laminated metallized films also showed significant increase in the oxygen and water vapor transmission but performed better than the unprotected metallized films. The overall results from these three mechanical abuse tests were:

- Protecting the metallic layer by lacquer and/or lamination decreased the effect of the abuse on the barrier properties of metallized films.

- The Gelbo Flex Test resulted in the greatest adverse effect on the barrier properties of metallized films. Sharp creasing was next, while the scuffing test had the least effect.
- The oxygen barrier was more affected to the mechanical abuse than the water vapor barrier.

The barrier properties of metallized films are controlled by the number and fractional area of pinholes, i.e. small spots without metal on them. One of the major causes of pinhole defects is the presence of dust particles on the polymer film surface during metallization. These dust particles subsequently become dislodged and leave an unmetallized shadow. (Jamieson & Windle, 1983). In order to identify the cause of pinholes in metallized films, Jamieson and Windle metallized a series of equivalent films in a small laboratory evaporator. They found out that if metallized films were handled properly, they appeared to be free from pinholes in the 1 to 10 μm range, although larger defects of 25 to 50 μm, which are associated with dust particles, were sometimes apparent. But on rubbing the metal surface with a camel-hair brush, 1 to 10 μm pinholes were observed. The camel-hair brush removed the loose aluminum deposits on the metal layer. The formation of pinholes was complete after two to three passes of the brush and subsequent rubbing did not produce any further pinholes. This indicated that the pinholes are due to specific weak-points in the metal layer and not the consequence of straightforward mechanical damage.

Summary

The packaging material chosen should maintain an adequate barrier over the required shelf life of the product. Metallized films are subjected to mechanical stresses during processing and distribution, which often result in flexing and subsequent initiation of pinholes and flex-cracks. Pinholes often have a negative impact on barrier properties by providing areas for permeation. The packaging materials should be tested to gauge the effects of mechanical stresses on their barrier properties. In order to gauge the effect of flexing on the barrier properties of metallized films, it is necessary to develop test methods that will simulate the effect of flexing on their barrier properties. The test methods should be able to reproduce the same results every time one runs an experiment with the same initial conditions, inputs and procedures.

A. Simulation Methods:

1. Vibration table and helical compression springs

A test method was developed that uses a vibration table and helical compression springs to determine the susceptibility of plastic films to pinhole formation under conditions of repeated flexing (Varughese, & Gyeszly, 1993). The Vibration Flex Test was designed to induce flexing in plastic film samples. Varughese & Gyeszly tested the resistance of five different film rolls of film samples. The specimens were visually inspected to determine that there were free of creases and attached to the sample holder of the spring-mass system. The spring-mass system was then placed on a vibration table and operated for one hour. Multiple flexing is produced throughout the film specimen due to the movement of the sample holder at natural frequency. The difference in natural frequencies of a matched pair of spring-mass systems force the top and bottom of the film specimen to flex at different times, causing multiple creases to form at different locations and intersections. This attempts to replicates the multiple flexing that is encountered by the walls of a flexible plastic pouch during transit, primarily when the vibrational frequency of the transit vehicle is at or near the critical frequency of a flexible package. The ability of the helical compression springs in flexing the film sample becomes hindered, if the film sample is thick and stiff. Hence the Vibration Flex Test method is only appropriate for thin film samples. Also the Vibration Flex Test is able to simulate only the vibration stresses during distribution. It fails to account for the processing stresses as well as the other distribution stresses like free-fall stresses and scuffing between packages in a unit case.

2. Gelbo Flex Tester

To help predict the impact of flex-cracks on packaging barrier films, Toedel and his associates from Milprint Inc. (1977), put together a three-pronged test combination.

1) A Gelbo Flex Tester

2) An OX-TRAN oxygen permeability tester

3) A Honeywell rapid water vapor transmission tester.

Toedel preferred the Gelbo Flex Test to the 180° crease test as he believed that the 180° crease test did not simulate the rough handling that occurs during warehousing and shipping. The oxygen and water vapor transmission test overcome the limitations of standard test method ASTM F392-93. The method involves measuring the pinholes formed in the structure to determine failures due to flexing and suggests gas transmission rates as an alternate criterion. However the failure of a barrier ply in a flex-durability test would not be detected by the pinhole formation test with staining techniques as the detector.

To stress the importance of testing for flex-crack resistance, Toedel composed three different structures and subjected each material to 200 flex cycles on a Gelbo Flex Tester. The results are tabulated below.

Material	WVTR grams/100^2 inch/24 hrs at 100°F, 90% RH	
	Unflexed	After 200 flex cycles
Paper/polyethylene/foil/polyethylene	0.02	0.08
Paper/ionomer/foil/polyethylene	0.02	0.25
Alternate construction of first material	0.02	0.28

The results showed a significant increase in the water vapor transmission rates after 200 flex cycles on a Gelbo Flex Tester indicating a loss in water vapor barrier in all the three films that were tested.

B) Summary

The Vibration Flex Test was designed to induce flexing in plastic film samples by using a vibration table and helical compression springs. The test method can be used to evaluate the performance of plastic films under conditions of flexing caused by vibration. The Gelbo Flex Tester uses a twisting and crushing motion to induce flexing in film samples.

The Vibration Flex Test is only appropriate for thin film samples since the ability of the helical compression springs in flexing the film samples becomes hindered, if the film sample is thick and stiff. Film thickness is not an issue with the Gelbo Flex Tester. Also the Vibration Flex Test only simulates the vibration stresses during distribution and does not account for the other stresses encountered by flexible packages during processing and distribution. In this study the Gelbo Flex Tester is used to induce flexing since it is widely accepted and also because by changing the number of cycles of the test, one is able to simulate any degree of handling, from very mild to very severe.

Chapter III

Hypothesis

H_1 – Flexible packages encounter mechanical stress during processing and distribution that leads to a change in the barrier properties of the material.

H_2 – The Gelbo Flex Tester produces different stress levels than actual flex-levels encountered during processing and distribution.

Chapter IV

Test Methodology

A) Objective

1) Evaluate real stresses of flexing by using packages already manufactured and that have been through the distribution cycle. Films from these packages were tested to see the effect of real stress on their barrier properties.
2) Evaluate the stresses encountered by the same material on a Gelbo Flex Tester. Films were subjected to stress on a Gelbo Flex Tester and tested to see the effect of simulated stress on their barrier properties.

B) Materials

Two different film samples were obtained from Polibak® Plastic America. The first film is a lamination of 12 micron thick metallized polyethylene terephthalate (PET) layer with a 50 micron thick low density polypropylene (LLDPE) layer. The second film is a gravure printed laminated film containing a 12 micron thick metallized polyethylene terephthalate (PET) layer plus a 50 micron thick low density polypropylene (LLDPE) layer. The second film is corona treated on the outside. Also packages formed from these films and distributed to retail stores were obtained and shipped via Federal Express to the test site.

C) Test Procedure

The barrier properties of two different metallized films were evaluated by calculating the oxygen transmission rates (OTR) and the water vapor transmission rates (WVTR) of the sample films. The oxygen transmission rates of the sample films were calculated using MOCON's OX-TRAN equipment in compliance with standard test method ASTM D3985-02. The water vapor transmission rates were determined using MOCON's PERMATRAN equipment in compliance with standard test method ASTM F1249-01.

In order to quantify the variability in the MOCON equipments, a Measurement System Analysis (MSA) was performed before testing the metallized films. One sample from a particular film was taken and run for 5 consecutive tests on both the MOCON equipments i.e. the OX-TRAN and the PERMATRAN. Then another sample from the same film was taken and run for 5 consecutive tests on both the MOCON equipments. The results were than analyzed to determine the variability in the equipments.

After qualifying the MOCON equipments for repeatability, the oxygen and water vapor transmission rates of the unflexed films were calculated using the MOCON equipment. Five film samples were cut from each film roll and tested for both oxygen and water vapor transmission rates. Test film samples were cut from film rolls using the MOCON sample cutter. The procedure to test the samples on the OX-TRAN and PERMATRAN is described later in detail.

Then packages made from the same metallized films, that were subjected to stress during processing operations and distribution where evaluated. The packages encountered both the distribution environments i.e. first the normal distribution environment from the manufacturer to the retail store and then the small parcel distribution environment via Federal Express. Film samples were cut from these formed and flexed packages. The oxygen and water vapor transmission rates were calculated to see the effect of flexing caused by real stress on the barrier properties of metallized films.

In order to stimulate the worst distribution environment for packages, an additional test was conducted. Some of the packages were put on a vibration table to stimulate the truck distribution environment. The vibration table was run for 1 hour in accordance with ASTM D4169. Film samples from these packages were then evaluated on the MOCON equipment to see the effect of real distribution stress on the barrier properties of metallized films.

For the second part of the study, samples of the unflexed films were flexed on a Gelbo Flex Tester. The samples were cut into 200 mm by 280 mm flat sheets and the 200 mm dimension was affixed in the test direction. The samples were flexed at a rate of 45 cycles per minute, using a motion that repeatedly twists and crushes the film. The samples were subjected to 10, 50 and 100 full flex cycles on the Gelbo Flex Tester in accordance with standard test method ASTM F392-93.

The Gelbo Flex Tester consists of a 90 mm diameter stationary mandrel and a 90 mm diameter moveable mandrel spaced at a distance of 180 mm apart from face to face at the starting position of the full stroke. The sample to be flexed is affixed between the two mandrels, which contain vents to prevent pressurization of the samples. The moveable mandrel is attached to a grooved shaft, which controls its movement. For the full flex test cycle the groove is designed to give a twisting motion of 440° in the first 90 mm of the stroke of the moveable mandrel, followed by a straight horizontal motion of 65 mm, so that at the closed position the mandrels are 25 mm apart. The motion of the Gelbo Flex Tester is reciprocal with a full cycle consisting of the forward and return strokes.

After flexing the samples on a Gelbo Flex Tester, the oxygen and water vapor transmission rates were calculated using the MOCON equipment. The results were then compared against the other sample groups to determine whether the flex levels that the films are subjected to on a Gelbo Flex Tester are true indication of the flex levels encountered during handling and distribution. Comparing sample groups will determine if the Gelbo Flex Test method is an appropriate method to determine the flex levels encountered during a processing operations and distribution.

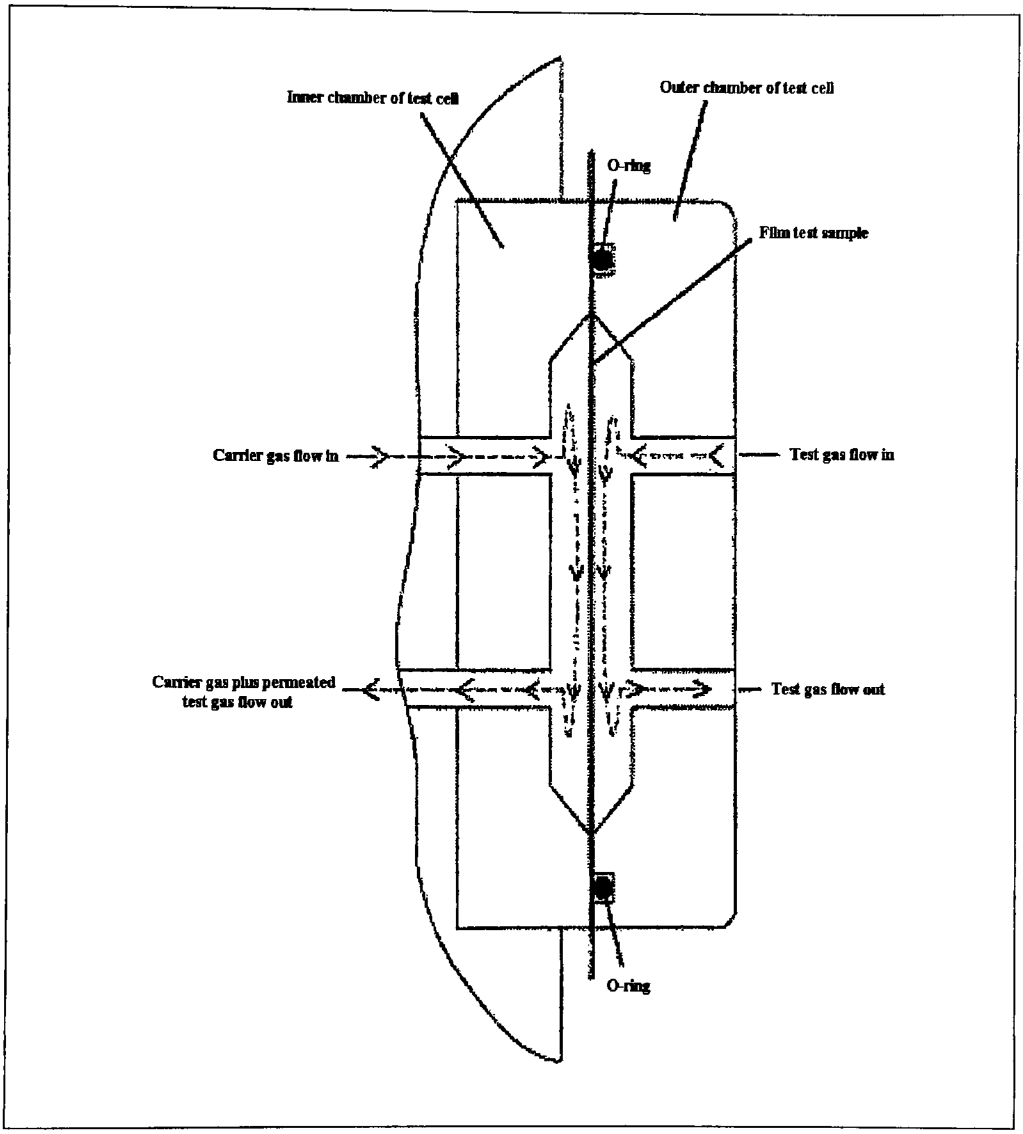
OX-TRAN Procedure

MOCON OX-TRAN Model 2/21 was used to measure the oxygen transmission rates of film samples. The module has two test cells enabling the testing of two samples at a time. Each test cell is divided into two halves by the film sample. Figure 1 shows a simplified view of the test cell.

The test cell was opened always making sure that the sensor was in standby. The sealing rim of the test cell was lightly greased with Apiezon T grease to ensure a tight seal. The film sample was placed in the cell and flattened to remove wrinkles or creases. After mounting both the film samples in the two test cells, the cells were closed and clamped. The cells were then purged of residual oxygen by the carrier gas. The carrier gas is a mixture of nitrogen (98%) and hydrogen (2%). Before entering the test cells, the carrier gas passes through a catalyst. The hydrogen reacts with any oxygen that may be present in the carrier gas to form water vapor. This helps ensure that the carrier gas does not contain any oxygen that might affect transmission rate data.

After mounting the films in the cells, the oxygen flow rate is set to 20 sccm (Standard Cubic Centimeters per Minute) using the flowmeter. The carrier gas flow rate is set to 10 sccm for each cell.

Figure 1: OX-TRAN Model 2/21 Test Cell*



*Reproduced from OX-TRAN Model 2/21 Modular System Operator's Manual. MOCON, Minneapolis, MN.

In the testing process, oxygen is continuously routed to the outer half of the test cell while carrier gas is routed through the inner half of the test cell. As oxygen permeates through the film sample, it is picked up by the carrier gas and carried through the coulometric sensor, which produces an electric current when exposed to oxygen. The current generated is directly proportional to the amount of oxygen passing through the sensor. Data from the sensor is transmitted to the computer that calculates a final value describing the oxygen transmission rate of the tested material.

An Individual Zero Operation was done at the start of each test to compensate for individual variations, such as edge leaks, in the test cells. The module determines the amount of oxygen that is getting into the carrier gas from factors other than actual transmission through the film for each individual cell. During Individual Zero Operation, nitrogen is routed through both halves of the test cell. Any oxygen that is picked up on the carrier gas side is thus due to factors other than permeation. The computer automatically subtracts the individual zero value from the oxygen transmission rate value to produce an accurate result.

The testing of all samples was carried out in accordance with standard test method ASTM D3985-02.

Operating Test Conditions:

- Module Temperature: 23 °C
- Carrier Gas (Nitrogen + Hydrogen) Relative Humidity: 0 % RH
- Test Gas (Oxygen) Relative Humidity: 0 % RH
- Test Mode: Convergence By Cycles
- Exam Minutes: 45 minutes
- Convergence Period: 4
- Conditioning Time: 1 hour
- Sample Type: Film
- Sample Area: 50 cm^2

Calibration

Calibration of the OX-TRAN module is required to ensure system accuracy in determining the oxygen transmission rates. The module was calibrated before testing the first sample and intermittently thereafter. MOCON certified films with known oxygen transmission rates were used for calibrating the module. The calibration procedure is as follows:

1. A certified film that closely approximates the transmission rate of the film samples to be tested was selected and mounted in any one cell of the module.
2. The test was run until the certified film reached equilibrium. The procedure for running the test is similar to running any other film sample. The only difference was that the test mode was set to continuous and the sample type was set to package when setting the test parameters.
3. Once the certified film had reached equilibrium, the test was advanced and the module was then calibrated by entering the expected transmission rate value.

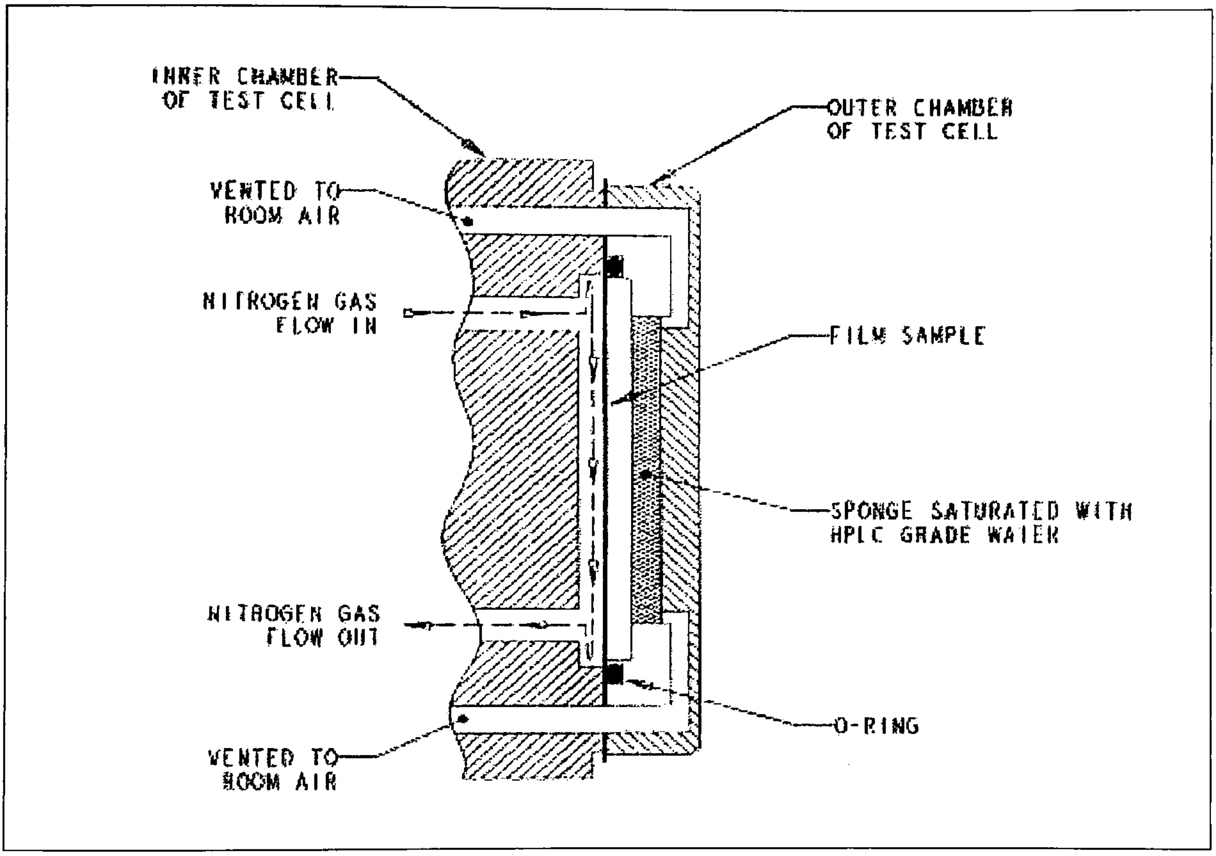
PERMATRAN Procedure

MOCON PERMATRAN Model 3/33 was used to measure the water vapor transmission rate of film samples. The module has two test cells enabling the testing of two samples at a time. Each test cell is divided into two halves by the film sample. Figure 2 shows a simplified view of the test cell.

The test cell was opened always making sure that the sensor was in standby. The sponges located in the outer cover of each test cell were saturated with HPCL grade water. The sealing rim of the test cell was lightly greased with high vacuum grease to ensure a tight seal. The film sample was then placed in the cell and flattened to remove wrinkles or creases. After mounting both the film samples in the two test cells, the cells were closed and clamped. The cells were then allowed to purge for 10 minutes by the carrier gas. Nitrogen is used as the carrier gas. Before entering the module, the carrier gas passes through an in-line molecular sieve desiccant. This ensures that the carrier gas does not contain any water vapor that might affect transmission rate data.

After mounting the films in the cells, the carrier gas flow rate was set to 100 sccm using the flowmeter.

Figure 2: PERMATRAN Model 3/33 Test Cell*



*Reproduced from PERMATRAN Model 3/33 Modular System Operator's Manual. MOCON, Minneapolis, MN.

In the testing process, water vapor is present in the outer half of the test cell while nitrogen is routed through the inner half of the test cell. Sponges saturated with HPCL grade water, located in the outer cover of the test cell are used as the source for water vapor when testing at 100% RH. As water vapor permeates through the film sample, it is picked up by the carrier gas and carried through a modulated infrared sensor. The sensor electronics generate a voltage that is directly proportional to the amount of water vapor passing through the sensor. Data from the sensor is transmitted to the computer that calculates a final value describing the water vapor transmission rate of the tested material.

An Individual Zero Operation was done at the start of each test to compensate for individual variations, such as edge leaks, in the test cells. The module determines the amount of water vapor that is getting into the carrier gas from factors other than actual transmission for each individual cell. During Individual Zero Processing, a blocking foil was placed in both the cells. Any water vapor that is picked up on the carrier gas side is thus due to factors other than permeation. When the individual zero part of the test was complete, the foil was replaced with the film sample and the test state was advanced. The computer automatically subtracts the individual zero value from the water vapor transmission rate value to produce an accurate result.

The testing of all samples was carried out in accordance with standard test method ASTM F1249-01.

Operating Test Conditions:

- Module Temperature: 37.8 °C
- Relative Humidity· 100 % RH
- Test Mode: Convergence By Cycles
- Exam Minutes: 45 minutes
- Convergence Period: 4
- Conditioning Time: 1 hour
- Sample Type: Film
- Sample Area: 50 cm^2

Calibration

Calibration of the PERMATRAN module is required to ensure system accuracy in determining the water vapor transmission rates. The module was calibrated before testing the first sample and intermittently thereafter. MOCON certified films with known water vapor transmission rates were used for calibrating the module. The calibration procedure is as follows:

1. A certified film that closely approximates the transmission rate of the film samples to be tested was selected and mounted in any one cell of the module.
2. The test was run until the certified film reached equilibrium. The procedure for running the test is similar to running any other film sample. The only difference was that the test mode was set to continuous and the sample type was set to package when setting the test parameters.
3. Once the certified film had reached equilibrium, the test was advanced and the module was then calibrated by entering the expected transmission rate value.

Chapter V

Controls for validity and reliability

The variables that affect transmission rate values like temperature, pressure, film thickness, carrier gas flow are kept constant for all the sample films. As a result the variations in the transmission rates due to change in variables can be safely neglected. Administering accurate measurement techniques in a consistent manner and drawing correct inferences from the data obtained are two major factors in this analysis.

One of the major concerns in experimental studies is equipment variability. When experimental runs are repeated without changing the settings of the variables, the response tends to vary rather than remaining constant. It is never possible to exactly repeat anything, although this is the goal. This is caused by the small effects of changes in many uncontrolled factors that exist in any experiment (Freund, 1984). In order to quantify such variability in the MOCON equipment, a Measurement System Analysis (MSA) was done. MSA is an experimental and statistical method of determining how much variation within the measurement process contributes to overall process variability. (http://www.isixsigma.com/dictionary/Measurement_System_Analysis_-_MSA-277.htm)

A) Measurement System Analysis

In order to qualify the MOCON equipment for repeatability, two different samples were taken and run on both the OX-TRAN and PERMATRAN. In order to replicate the experiments, the same samples were run five times on both the MOCON equipments. The results are summarized in tables 1 and 2.

There is only one parameter that varies since the operator is same for all the tests conducted, hence one-way analysis of variance (ANOVA) method to determine repeatability of the equipments was used. Repeatability is used to describe measurement variation obtained when one person measures the same characteristics several times with the same test equipment.

One-way ANOVA is a method used to compare the means (μ) of several groups of data (Freund, 1984). Assuming that there are 'r' samples. μ_1 is the mean of the first sample and μ_2 is the mean of the second sample. Then the null hypothesis of no difference is

$$H_o: \mu_1 = \mu_2 = \dots \mu_r$$

Minitab Software was used to generate the one-way analysis of variance table for the OX-TRAN and PERMATRAN equipments. The output is displayed in Tables 3 and 4.

An F-test is used to test the null hypothesis that the means of both the film samples are equal i.e. ($\mu_1 = \mu_2$) against the alternative hypothesis that the film sample means are not equal.

Assuming a confidence level of 95 % for the MOCON equipments. The value of $F_{0.05} = 5.32$, for 1 and 8 degrees of freedom (Obtained from Appendix A). From tables 3 and 4 it can see that the F value of both the MOCON equipments is less than $F_{0.05}$, it can be concluded that the MOCON equipments run at a 95 % confidence level.

Table 1: OX-TRAN variability test

Sample No	Sample 1 Transmission Rate [cc/(m2-day)]	Sample 2 Transmission Rate [cc/(m2-day)]
1	3.476179	3.471981
2	3.475754	3.485284
3	3.466313	3.478823
4	3.464463	3.464560
5	3.491780	3.477685

Table 2: PERMATRAN variability test

Sample No	Sample 1 Transmission Rate [cc/(m2-day)]	Sample 2 Transmission Rate [cc/(m2-day)]
1	1.585747	1.576210
2	1.598879	1.585840
3	1.610449	1.604114
4	1.601976	1.608993
5	1.596913	1.595520

Table 3: One-Way ANOVA for OX-TRAN Equipment

Source	Degrees of Freedom (DF)	Sum of Squares (SS)	Mean Square (MS)	F
Sample No.	1	0.0001428	0.0001428	1.99000
Repeatability	8	0.0005743	0.0000718	
Total	9	0.0007171		

Table 4: One-Way ANOVA Table for PERMATRAN Equipment

Source	Degrees of Freedom (DF)	Sum of Squares (SS)	Mean Square (MS)	F
Sample No.	1	0.0000542	0.0000542	0.420333
Repeatability	8	0.0010321	0.0001290	
Total	9	0.0010863		

Chapter VI

Results and Discussion

The water vapor and oxygen transmission rates of both the sample films under different conditions of stress are tabulated below. Also included are the unflexed water vapor and oxygen transmission rates of the sample films. The charts that follow offer a convenient comparative analysis between the real and simulated stresses for each film.

From Tables 5a and 6a it can be seen that water vapor transmission rates of both the films increase significantly once they are flexed. It can also be seen that the water vapor transmission rates of film 1 (Metallized PET + LLDPE) are more affected by flexing as compared to film 2 (Printed Metallized PET + LLDPE + Corona Treatment). With regards to Gelbo flexing, it can be seen from Tables 5b and 6b that the water vapor transmission rates increased as the number of full flex cycles increased from 1 to 100.

For film 1, from Tables 5a and 5b it can be seen that Gelbo full flex cycles somewhere between 50 to 100 cycles are sufficient to simulate the real stress that film 1 is subjected to during processing and distribution. For film 2, from Tables 6a and 6b it can be seen that Gelbo full flex cycles somewhere between 10 to 50 cycles are sufficient to simulate the real stress.

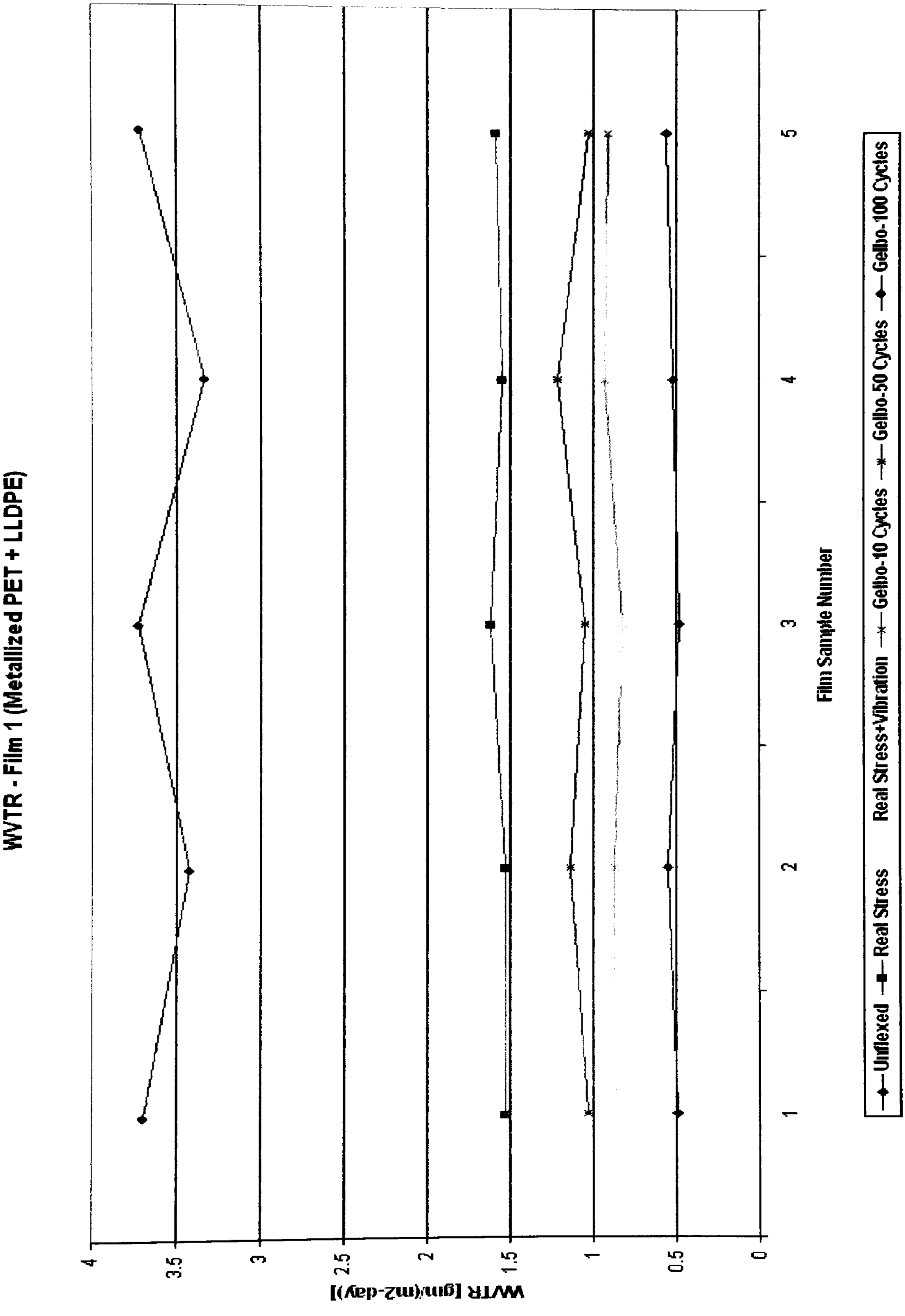
WVTR –FILM 1 (Metallized PET + LLDPE)

Table 5a: Real stress values

Sample No.	Unflexed Transmission Rate [gm/(m2-day)]	Real Stress Transmission Rate [gm/(m2-day)]	Real Stress + Vibration Transmission Rate [gm/(m2-day)]
1	0.492431	1.533177	1.608511
2	0.549055	1.529743	1.634877
3	0.481405	1.621955	1.687525
4	0.518190	1.545511	1.811839
5	0.558188	1.586267	1.745480

Table 5b: Gelbo flex values

Sample No.	Gelbo Transmission Rate [gm/(m2-day)]		
	10 Cycles	50 Cycles	100 Cycles
1	0.860888	1.028430	3.694176
2	0.872453	1.137431	3.419967
3	0.820593	1.049590	3.722677
4	0.935868	1.219568	3.334306
5	0.912033	1.026737	3.716057


WVTR - Film 1 (Metallized PET + LLDPE)
WVTR [gm/(m2-day)]
4
3.5
3
2.5
2
1.5
1
0.5
0
1
2
3
4
5
Film Sample Number
Unflexed
Real Stress
Real Stress+Vibration
Gelbo-10 Cycles
Gelbo-50 Cycles
Gelbo-100 Cycles

WVTR FILM 2 (Printed Metallized PET + LLDPE + Corona Treatment)

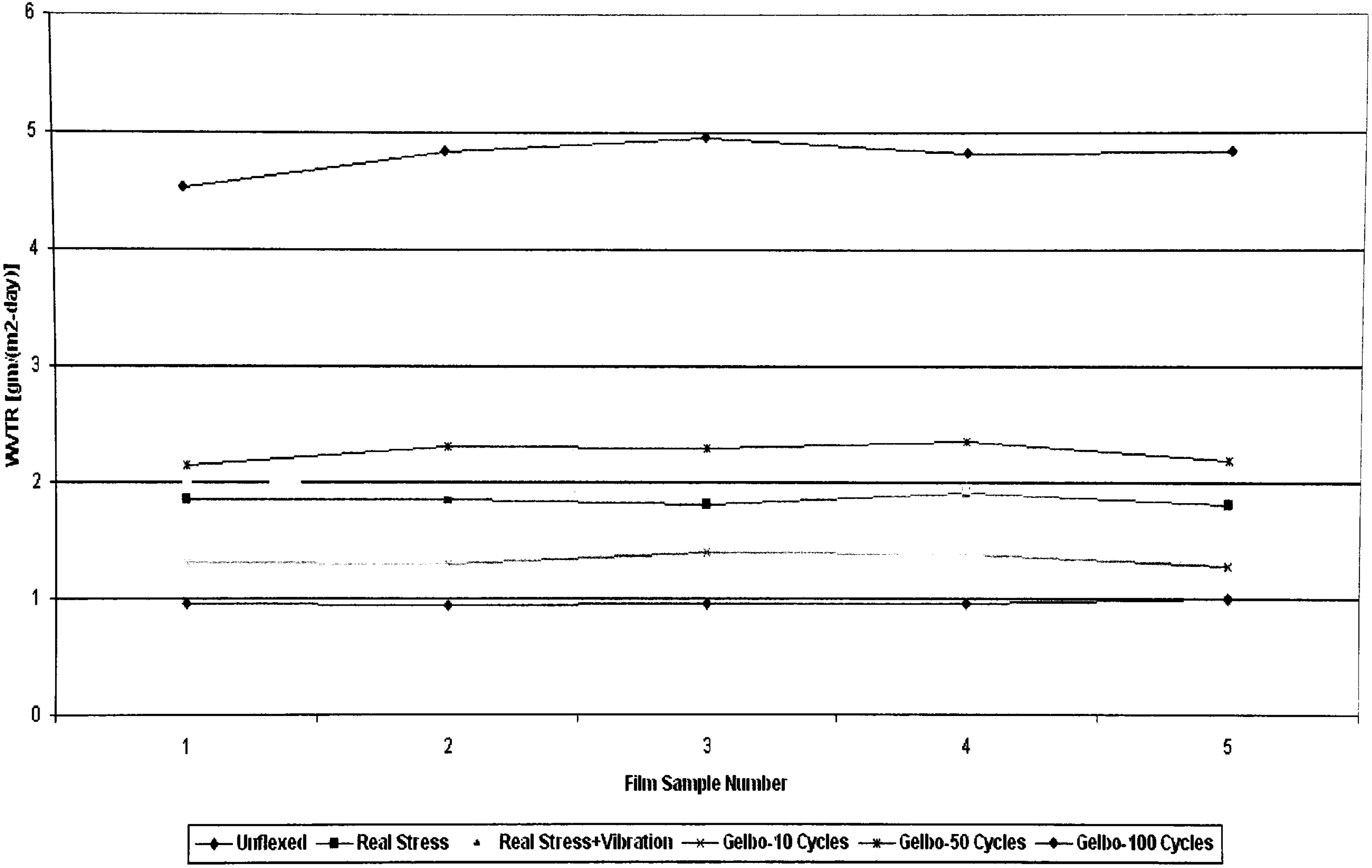
Table 6a: Real stress values

Sample No.	Unflexed Transmission Rate [gm/(m2-day)]	Real Stress Transmission Rate [gm/(m2-day)]	Real Stress + Vibration Transmission Rate [gm/(m2-day)]
1	0.950333	1.851277	2.046786
2	0.942993	1.850383	1.920442
3	0.957708	1.812071	1.907805
4	0.960372	1.905811	1.961854
5	0.993983	1.814362	1.955943

Table 6b: Gelbo flex values

Sample No.	Gelbo Transmission Rate [gm/(m2-day)]		
	10 Cycles	50 Cycles	100 Cycles
1	1.306164	2.153008	4.522452
2	1.291215	2.312260	4.843118
3	1.397040	2.289711	4.953165
4	1.384107	2.355167	4.827377
5	1.273639	2.195689	4.843280

WVTR - Film 2 (Printed Metallized PET + LLDPE + Corona Treatment)



With regards to oxygen transmission rates, from Tables 7a and 8a it can be seen that the oxygen transmission rates of both the films increase significantly once they are flexed. It can also be seen that the oxygen transmission rates of film 1 (Metallized PET + LLDPE) are more affected by flexing as compared to film 2 (Printed Metallized PET + LLDPE + Corona Treatment). With regards to Gelbo flexing, it can be seen from Tables 7b and 8b that the oxygen transmission rates increased as the number of full flex cycles increased form 1 to 100.

For film 1, from Tables 7a and 7b it can be seen that Gelbo full flex cycles somewhere between 50 to 100 cycles are sufficient to simulate the real stress that film 1 is subjected to during processing and distribution. For film 2, from Tables 8a and 8b it can be seen that Gelbo full flex cycles somewhere between 0 to 10 cycles are sufficient to simulate the real stress.

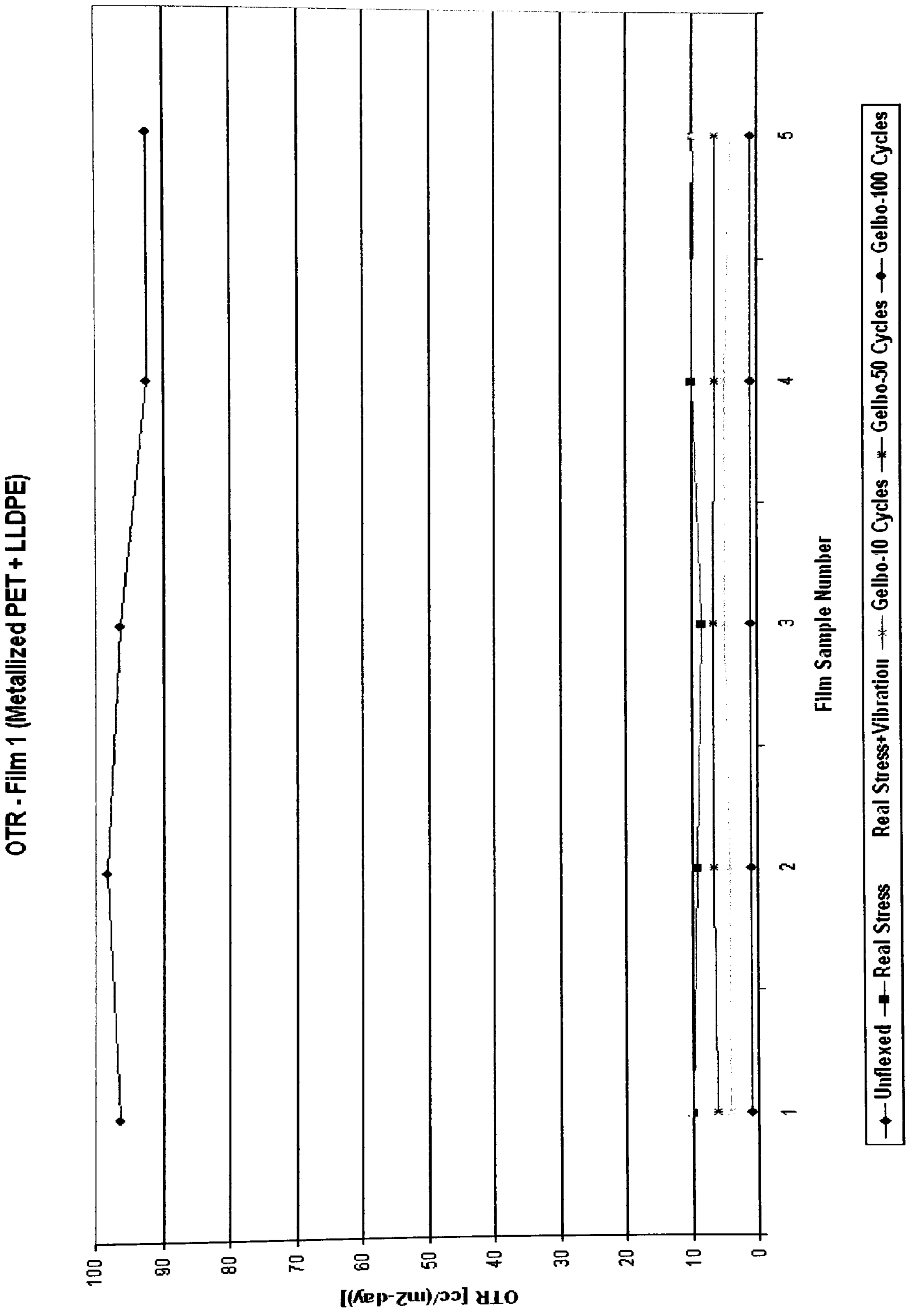
OTR –FILM 1 (Metallized PET + LLDPE)

Table 7a: Real stress values

Sample No.	Unflexed Transmission Rate [gm/(m2-day)]	Real Stress Transmission Rate [gm/(m2-day)]	Real Stress + Vibration Transmission Rate [gm/(m2-day)]
1	1.030156	9.963076	10.97997
2	1.001114	9.179478	11.08105
3	1.048027	8.382612	11.49721
4	1.006217	9.799760	11.51061
5	1.036140	9.558182	9.624363

Table 7b: Gelbo flex values

Sample No.	Gelbo Transmission Rate [gm/(m2-day)]		
	10 Cycles	50 Cycles	100 Cycles
1	4.116830	6.224154	96.23741
2	4.113942	6.681870	98.23164
3	4.885408	6.729946	96.41483
4	4.946768	6.390831	92.29630
5	3.997638	6.327703	92.27210


OTR - Film 1 (Metallized PET + LLDPE)
OTR [cc/(m2-day)]
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
Film Sample Number
Unflexed
Real Stress
Real Stress+Vibration
Gelbo-10 Cycles
Gelbo-50 Cycles
Gelbo-100 Cycles

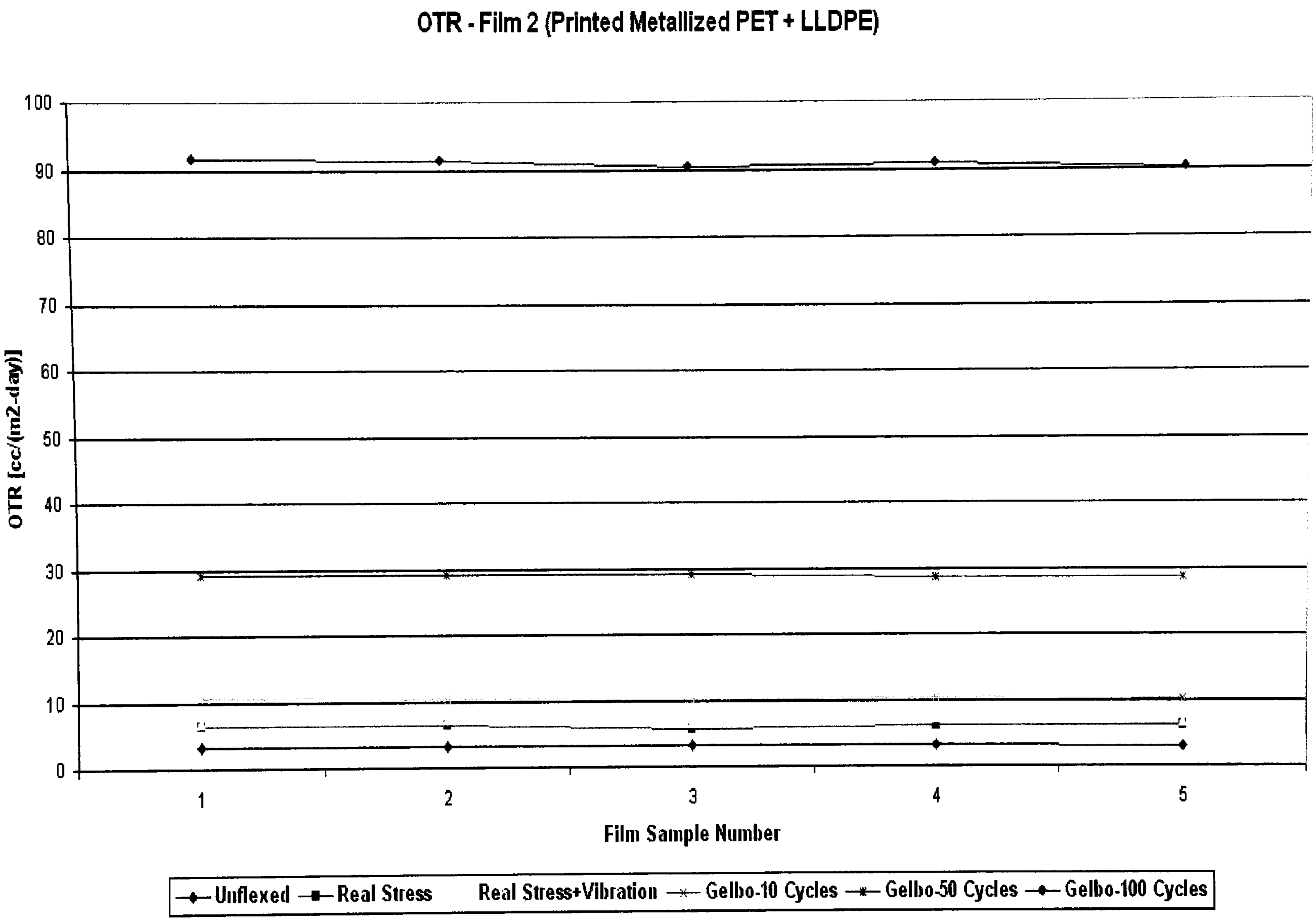
WVTR FILM 2 (Printed Metallized PET + LLDPE + Corona Treatment)

Table 8a: Real stress values

Sample No.	Unflexed Transmission Rate [gm/(m2-day)]	Real Stress Transmission Rate [gm/(m2-day)]	Real Stress + Vibration Transmission Rate [gm/(m2-day)]
1	3.178048	6.542932	6.891797
2	3.238272	6.399051	7.332980
3	3.157463	5.578464	6.728310
4	3.206849	6.062238	7.382991
5	3.009870	6.190353	6.745780

Table 8b: Gelbo flex values

Sample No.	Gelbo Transmission Rate [gm/(m2-day)]		
	10 Cycles	50 Cycles	100 Cycles
1	10.50112	29.22296	91.51017
2	10.35970	29.04974	91.31435
3	10.19157	29.02026	90.41506
4	10.40223	28.74082	90.89006
5	10.02814	28.75393	90.19617


OTR - Film 2 (Printed Metallized PET + LLDPE)
OTR [cc/(m2-day)]
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
Film Sample Number
Unflexed
Real Stress
Real Stress+Vibration
Gelbo-10 Cycles
Gelbo-50 Cycles
Gelbo-100 Cycles

The results show a significant increase in the oxygen and water vapor transmission rates of the flexed samples indicating that flexing decreases the barrier properties of metallized films. This proves that mechanical stresses caused by processing operations as well as distribution produce significant alteration in the barrier properties of metallized films. The processing stresses i.e. package forming stresses that the films encounter are generally caused due to high web tension as the film passes through rollers on the webfed machine as well as due to abrasion as the film slides over the rollers of the webfed machine. The distribution stresses are generally caused due to the vibration caused as the flexible packages are transported mostly via road or rail from the manufactures to the retail stores. The handling procedures at the manufacture, distribution center as well as the retail store too add to the stresses that the flexible package encounters. The flexible packages also encounter crumpling stresses as the customers pick them up in the retail store.

The results also show that on flexing the oxygen transmission rates increase more significantly than the water vapor transmission rates. This shows that the oxygen barrier property was more severely affected by flexing than the water vapor barrier property. This is probably due to the excellent water vapor barrier properties of PET and LLDPE. Also LLDPE is considerably less sensitive to flex cracking than the metallized PET and thus is efficient in hindering the passage of water vapor through the entire film structure. The oxygen barrier is provided by metallized PET since LLDPE has poor oxygen barrier properties. The flex resistance of LLDPE is of little benefit as the films depends on metallized PET layer for the oxygen barrier, which is damaged on flexing. Flexing leads to the initiation of pinholes in the metallized PET layer and that subsequently leads to a loss in oxygen barrier properties of the films.

From the results, it can be seen that the oxygen transmission rates as well as the water vapor transmission rates of film 1 (Metallized PET + LLDPE) show a significant increase on flexing caused by real stress as compared to film 2 (Printed Metallized PET +LLDPE + Corona Treated). This shows that film 1 was more affected by flexing than film 2. This could be due to the corona treatment that film 2 was subjected too. Corona treatment is generally used to increase the surface energy of plastic substrates in order to make them more receptive to printing inks and coatings. It involves applying electrical charge to the substrates in order to restructure the bonds on the plastic surface (Mount, 2001). It leads to an improvement in the aluminum layer quality and this is most likely the reason for improved barrier properties of film 2 when subjected to stress.

With regards to the second part of the study i.e. Gelbo flexing, the oxygen and water vapor transmission rates increased as the number of full flex cycles increased from 0 to 100. This again proves that flexing decreases the barrier properties of metallized films. For film 1, the results suggest that Gelbo full flex cycles somewhere between 50 to 100 cycles are sufficient to simulate the mechanical stress to which flexible packaging materials are subjected during processing and distribution. For film 2, the real stress water vapor transmission rate values lie between 10 to 50 full flex Gelbo cycles whereas the real stress oxygen transmission rate values lie between 0 to 10 full flex Gelbo cycles. This study looks at the loss of total barrier properties due to flexing and not the loss in individual oxygen or water vapor barrier properties. Hence, for film 2 the results signify that Gelbo full flex cycles somewhere between 10 to 50 cycles are sufficient to simulate the real flexing stress. Since both the films require different flex cycles to simulate the real stress, it implies that for different films, different numbers of flex cycles are required to simulate the mechanical stress that films encounter during processing and distribution.

Chapter VII
Conclusion

The study showed that the barrier properties of metallized films are affected by the mechanical stresses that the films encounter during processing stages as well as during distribution from the manufacture to the end-user. Metallized films have a tendency to flex-crack and this leads to the initiation of pinholes and subsequent loss in barrier properties. The study showed that flexing leads to an increase in the oxygen and water vapor transmission rates of the sample films implying that flexing decreases the barrier properties of metallized films.

The study demonstrated that different films have different responses to flex-crack and require different number of flex cycles on a Gelbo Flex Tester to simulate the mechanical stress that they encounter during processing operations and distribution. The advantage of using the Gelbo Flex Tester to simulate mechanical stress is the reduction in cost and time needed to conduct practical field test. But it is necessary to conduct practical field test in order to know the number of flex cycles for each particular film that are required in order to simulate the real stresses. Once the number of flex cycles is known for a particular film, the Gelbo Flex Tester is a useful tool that helps to evaluate the performance of plastic films when they are subjected to mechanical stresses.

This study can be used by manufactures as well as end-users of metallized films to gauge the effect of flexing on the barrier properties of metallized films. It is not uncommon for a metallized film intended for barrier applications to have no measurable permeability in the flat form but to have significant permeability when formed, folded and creased into a package. Manufactures should evaluate metallized films for their barrier properties on the finished package after all machining is complete and preferably after a real or simulated shipping cycle.

It is impossible to keep the barrier properties of metallized films intact. But one could certainly reduce the loss in barrier properties by laminating the metallized films with polymeric materials. In general, laminations provide higher flex resistance than plain metallized films. With heavy laminations, the effect of pinholes is almost negligible. The transmission rate through pinholes in metallized films can be reduced considerably if a second layer consisting of a plastic film is laminated to the metallized layer. The chance that pinholes in the two layers would be located on top of one another is very small. Thus, there would be a layer of film on top of practically every pinhole.

How much effect laminations have on the barrier properties of metallized films should be tested in future research. Metallized film laminations containing different polymeric substrates should be tested in future and analyzed to determine the impact of different laminations on the barrier properties of metallized films.

APPENDIX: VALUES OF $F_{0.05}$

Degrees of freedom for numerator

Degrees of freedom for denominator	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	161	200	216	225	230	234	237	239	241	242	244	246	248	249	250	251	252	253	254
2	18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5	19.5	19.5	19.5	19.5
3	10.1	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.70	8.66	8.64	8.62	8.59	8.57	8.55	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.77	5.75	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.53	4.50	4.46	4.43	4.40	4.37
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44	3.41	3.38	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.90	2.86	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.61	2.57	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.42	2.38	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.29	2.25	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.29	2.15	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.11	2.07	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.18	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.50	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

*Reproduced from John E. Freund, "Modern Elementary Statistics", 6th Ed.

Bibliography

Ashley, R.J. (1985). Permeability and Plastics Packaging. In J. Comyn (Ed.), Polymer Permeability (pp. 269-308). New York: Elsevier Applied Science.

Del Nobile, M.A., Mensitieri, G., Aldi, A., & Nicolais, L. (1999). The Transport Mechanisms of Gases through Metallized Films Intended for Food Packaging Applications. *Packaging Technology and Science, 12,* 261-269.

Freund, J.E. (1984). *Modern Elementary Statistics.* (6th Ed.). New Jersey: Prentice-Hall, Inc.

Hackett, E.T., Scholla, M.H., Rudys, S. & Bletsos, J. (2000. March). How Small is Small: The Effects of Pinholes on Medical Packaging. *Medical Device & Diagnostic Industry, 22*(8), 52-66.

Mount III, E.M. (2004, March). Metallized Films for Food Packaging. *Converting Magazine, 22*(3), 28.

Mount III, E.M. (2001, March). Plasma Pretreatment for Metallizing Packaging Film. *Converting Magazine, 19*(3), 124-131.

Rao, P. V (2003, August 29). *Six Sigma.* Retrieved April 19, 2005, from http://www.isixsigma.com/dictionary/Measurement_System_Analysis_-_MSA-277.htm.

Staff Writer (2002, May) Flexible future: the growing popularity of flexible packaging for food applications spurs on further industry research. *Canadian Packaging, 55*(5), 44.

Soroka, W (1995) *Fundamentals of Packaging Technology* (pp.313-328). Virginia: Institute of Packaging Professionals.

Soroka, W. (2003, February). The bare facts about barrier materials. *Machine Design,* 20-26.

Sundell, H.A., Holen, B., Nicolaysen, F., Hilton, C., & Lokkeberg, O. (1992). Bag-in-box Packaging for Wine: Analysis of Transport Stress in Barrier Films. *Packaging Technology and Science, 5,* 321-329.

Troedel, M.L. (1977, March). Tests Reveal Flex Cracks Hidden Impact on Films. *Package Engineering, 22*(3), 34-35.

Varughese, J.V., & Gyeszly, S.W. (1993, May). The Vibration-Flex Test Method to Determine the Susceptibility of Plastic Films to Pinhole Formation Due to Flexing. *Journal of Testing and Evaluation*, *21*(3), 188-191.

Yializis, A., Ellwanger, R.E., & Harvey, J. (1997). Barrier Degradation in Aluminum Metallized Polypropylene Films. *Proceedings of the 40th Annual Technical Conference-Society of Vacuum Coaters*, (pp. 371-376), New Orleans, LA

Weizer, W (2000, August). Converted Flexible Packaging: Trends to Watch. Paper, Film and Foil Converter, 74(8), 42-43

ASTM D3985-02. Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using a Coulometric Sensor. *Annual Book of ASTM Standards*, Philadelphia, PA: American Society for Testing and Materials, Vol. 15.09, pp. 458-463.

ASTM F392-93 (Reapproved 1999). Standard Test Method for Flex Durability of Flexible Barrier Materials. *Annual Book of ASTM Standards*, Philadelphia, PA: American Society for Testing and Materials, Vol. 15.09, pp. 1120-1123.

ASTM F1249-01. Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor. *Annual Book of ASTM Standards*, Philadelphia, PA: American Society for Testing and Materials, Vol. 15.09, pp. 1281-1285.

OX-TRAN Model 2/21 Modular System Operator's Manual. Mocon, Minneapolis, MN.

PERMATRAN Model 3/33 Modular System Operator's Manual. Mocon, Minneapolis, MN.