Effect of High Pressure Processing for Packaged Foods on the Mass Transfer and Mechanical Characteristics of the Flexible Packaging Materials.

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ABSTRACT

EFFECT OF HIGH PRESSURE PROCESSING of PLASTIC PACKAGED FOODS on THE MASS TRANSFERR AND MECHANICAL CHARACTERISTICS OF THE PACKAGE.

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High pressure processing (HPP) can be applied to either in bulk or prepackaged food in flexible or semi rigid packaging materials. Since the integrity of the package during and after processing is of paramount importance, this study investigated the effects of HPP on the barrier, mechanical, physical characteristics and sorption behavior of selected flexible structures.

In chapter 2 the “barrier properties” and in chapter 3 the “mechanical properties” were compared for high-pressure treated and non-treated pouches. After HPP, the permeability, tensile properties and sorption behavior of the materials were evaluated. Scanning electron microscopy (SEM), and scanning acoustic microscopy (C-SAM) measurements were also taken to investigate the presence of micro defects in the films. Films used in this study were PET/SiO_x/LDPE, PET/Al_2O_3/LDPE, PET/PVDC/nylon/HDPE/PE, PE/nylon/EVOH/PE, PE/nylon/PE, metallized PET/EVA/LLDPE, PP/nylon/PP, PET/EVA/PET and PP. Results showed that the permeability of metallized PET was most severely affected by HPP. Permeability changes in the other materials were small compared to metallized PET. Tensile properties

of the films were not affected. However, physical damage to the metallized-PET films was identified by SEM and C-SAM analyses.

In chapter 4 the sorption of d-limonene was evaluated in both the polymeric structures (PP, multilayer PE/nylon/EVOH/PE, and metallized PET/EVA/LLDPE) and the food simulants, in both the HPP and untreated pouches as a function of time. Results showed that d-limonene concentration, both in the polymers and in the food simulants for pouches made of PP and (PE/nylon/EVOH/PE), was not significantly affected by HPP. However, the metallized PET/EVA/LLDPE showed a significant difference in the amount of d-limonene between HPP and control pouches. As expected, changes in temperature significantly affected the sorption behavior of all polymers. While PP and PE/nylon/EVOH/PE films retained d-limonene amount, the metallized-PET did not.

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Introduction

Food preservation and protection is essential for delivering food to the consumer in its best possible quality. The main aim of food processing methods is to achieve desirable changes while preventing or retarding undesirable changes to the food. Food can be preserved by thermal and non-thermal processes.

Thermal processing methods are widely used in the food industry to increase shelf life and maintain food safety by employing heat to kill microorganisms (Palou et al, 1999). In traditional thermal methods, food is subjected to a temperature of 60 to 100°C for a few seconds to minutes (Barbosa-Canovas et al, 1996). During this time period, large amounts of energy are transferred to the food. This energy may trigger several unwanted reactions in the food, leading to undesirable results such as: vitamin loss, changes in sensory properties such as color and flavor, odor, nutrient destruction, and formation of undesirable substances, causing quality deterioration (Ohlsson, 1996; Kimura, 1992). In an attempt to eliminate these thermal processing disadvantages, a number of "non-thermal processing" techniques have been developed in the pursuit of producing better quality foods (Hayashi, 1989; Mertens, 1993; Nachmanson, 1995). The main driving force in the development of non-thermal processing methods for food preservation is that food is keep at lower temperatures. Thus, the heat induced quality deterioration is minimized (Campbell and Goddard, 1993; Hoover et al, 1989). Techniques include high intensity pulsed electric fields, hurdle technology, radiation, light pulses, ultrasonic, and high pressure techniques) (Knorr, 1994).

In the past few years there has been great interest in the use of non-thermal high pressure processing (HPP) as an industrial technique for food preservation. A great advantage of this technique is the minimal quality alteration compared to thermal treatment (Farkas and Hoover, 2000). Combining high pressure with high temperature can also inactivate spores. This process applies high pressure, 300 to 800 MPa, to the foodstuff to reduce or eliminate microorganisms and deactivate enzymes by pure mechanical action at relatively low temperature when compared with thermal processing techniques. HPP uses hydrostatic pressure which is evenly distributed throughout the product. As a result, the processing time does not depend on size and shape of the product (Pre, 1992). Hydrostatic pressure does not create shear forces to distort food particles. Today, high pressure processing of foods has become a commercial reality for processing of certain food products; however, increased use of HPP for food and packaged food should be discussed and considered (Mertens and Deplace, 1993; Palou et al, 1999). Examples of the applications are tenderization of beef, manufacture of food purees, jams and jellies, and of marmalade from oranges, and milk. Packaged foods subjected to HPP were found to retain most of their original texture, nutritional, and sensory quality (Cheftel, 1992; Mertens and Knorr, 1992). These positive attributes may lead to wider commercial applications of HPP for certain food products in the near future.

Liquid or solid food products can be high-pressure processed either in bulk or prepackaged in flexible or semi-rigid packaging materials. Although food can be processed in bulk followed by aseptic filling, the most efficient procedure is to package the products in sealed non-rigid containers before they are subjected to HPP, to prevent subsequent recontamination by microorganisms. In the latter case, the packaging material together with the food is subjected to the action of high-pressure treatment.

Since the integrity of the package during and after processing is of paramount important to secure the benefits of this technique, selecting a suitable package is crucial to the success of HPP. The package needs to withstand the compression forces generated during high-pressure processing. It must also be flexible and able to maintain its physical integrity to prevent subsequent recontamination of the food by microorganisms (Anon, 1996; Cano et al, 1997). Metal cans or glass bottles are not well suited for HPP because they deform irreversibly or tend to fracture, respectively. Similarly, paperboard-based packages have limited application in HPP due to their lack of cohesion and tendency to deform (Mertens, 1993).

Desirable characteristics of flexible plastics such as light weight, clarity, good processing and good sealing attributes, strength, barrier properties and low cost make them widely used as packaging materials (Hernandez, 1996). Moreover, they are typically used for the type of prepackaged foods that may be HPP treated (Nachmanson, 1995). Ideally, HPP should not affect to any degree the integrity of the packaging structures. Recent research has demonstrated however, that this may not be the case for some composite flexible structures (Hayahsi, 1989).

A reversible response to compression of the whole package is crucial for success in pressure treatment. Pressure causes the product to compress tri-dimensionally up to 12%, depending on the pressure level. The product must recover its initial volume after the pressure is released. For the prepackaged product, the high compression forces also act on the polymeric package reducing its volume. Packaging materials for HPP need to have sufficient flexibility to compensate for the compression and volume reduction and to prevent deformation (Sanchez et al, 1993). For these reasons, single or multilayer plastic flexible structures having significant resiliency and elasticity are the best-suited packaging materials for processing prepackaged foods by HPP (Knorr 1995). Although HPP is a non-thermal treatment, molecular friction during high pressure generates enough heat to increase the temperature of the food-package system. The temperature of compressed water increases in the range of 2-3 °C for every 100 MPa of the compression (Ting et al, 2002). The increase in temperature also affects the package's ability to adapt to withstand the combined effect of rising temperature and decreasing volume during the HPP treatment. Therefore, the package must be able to withstand pressure.

Lack of information on prepackaged high-pressure treatment has been a major issues in using this technology commercially for prepackaged food products. Effect of high pressure processing on packaging structures may impact the product quality, safety and shelf life. An understanding of the effect of HPP on the packaging structure should lead to improved packaging. Using unsuitable packaging structures may lead to undesirable outcomes, including flavor scalping by the package, migration of undesirable components from the packaging material to the product, and permeation of gases and vapors from the external environment into the package and subsequently into the product. The exchange between the package and its environment is dependent upon the integrity of the packaging structure and mass transfer characteristics of the packaging materials.

The mass transfer properties (sorption and permeability) of these materials should not be affected in such a manner that they may significantly affect product quality and shelf life. While many researchers have dealt with the specific effects of HPP on various food constituents, relatively few investigations have dealt with the effect of HPP on food packaging materials. Changes resulting in plastics due to HPP are of prime importance in food packaging applications, where such changes may directly affect the quality of packaged foodstuff. There exists limited data on permeability, physical and mechanical integrity, sorption and migration behavior of flexible packaging structures exposed to HPP.

These studies, therefore, focused on the permeability, mechanical properties and integrity at microscopic level, and also the sorption behavior of selected flexible packaging structures.

The protection of packaged foods from gas and vapor exchange with the environment depends on the integrity of packages, and on the permeability of packaging materials. Changes in permeation, migration, sorption, and package integrity after pressure treatment may negatively affect product safety, quality and shelf life. Sorption is directly related to food quality and has also been considered to be a main factor in degradation of flavor or food quality (Nielsen and Giacin, 1994; Fukamachi et al, 1996). Pressure-temperature induced changes in the materials should not significantly affect the barrier (permeability), mechanical, and mass transfer (sorption) properties of the packaging structures. Knowledge of any such effects would be of importance to the food industry and government food regulatory agencies. Present information is not sufficient for prepackaged high-pressure treatment of food. Thus, the food industry must take full responsibility for determining the suitable flexible packaging structures to keep food of good quality and safe. Quality loss may result from mass transfer. In addition to mass transfer properties, mechanical properties and sorption behavior may play key roles in quality loss of packaged food products. For successful development of safe and good quality HPP food products, a better understanding of mass transfer issues within the food/package system is important to ensure consumer confidence.

Previous researchers have shown that flexible packaging materials can be used in HPP of pre-packaged food, because they were able to withstand the process without visible signs of integrity loss (Mertens, 1993; Knorr, 1995). However, there is little published data that reports on the effects of such treatment on the mass transfer, mechanical and physical properties of HPP treated materials.

Based on these considerations the possible effects on the mechanical, barrier, and sorption properties of a series of high-barrier food packaging multilayer structures were evaluated under a variety of HPP conditions. The flexible plastic structures were tested for effects of pressure, process time, and temperature on their various mechanical, barrier (permeability) properties and sorption behavior.

The specific objectives of this research are:

a. To evaluate possible changes in the gas and vapor permeability of the package material after high pressure treatment.
b. To evaluate mechanical behavior of selected packaging structures exposed to high pressure treatment relative to the package material at atmospheric pressure.
c. To highlight the changes occurring at the microstructural level and visualize the microstructure of the selected structure after the package material was exposed to high pressure treatment
d. To evaluate the magnitude of sorbate (d-limonene) in both the selected flexible structures and the food simulant in selected high pressure treated and untreated

flexible structures.

Hypothesizes

I It is expected that high pressure will not affect the morphology of the polymer, and thus permeability of a treated single layer plastic material will not be affected significantly. Permeability of a treated multilayer plastic structure, on the contrary, may be affected since the interlayer bonding can be disrupted due to difference in coefficients of compressibility and the layer relaxation.

II The mechanical properties of a single layer plastic will not be affected since HPP will not affect polymer morphology. HPP may affect integrity of multilayer structure due to different compressibilities.

III The solubility coefficient of a single layer should remain unaffected by HPP because it will not affect the morphology of the single layer polymer. On the other hand, solubility coefficient of treated multilayer plastic structures may be affected depends on different compressibilities of multilayer structure.

The knowledge gained from this project will further the development of safe, high quality, value-added food products to meet consumer needs and preferences, and enhance the long term viability of food industry within the global economy.

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CHAPTER 1

Literature Review

Consumers are demanding today higher quality food with fresh-like attributes that provide convenience, safeties and have long shelf life.

Traditionally, thermal processing is used in the food industry to increase shelf life and maintain food safety by subjecting the food to temperature for several minutes (Barabosa-Canovas et al, 1998; Hayashi, 1989). This energy may result in unwanted reactions in the food, leading to undesirable changes or formation of by-products. Therefore, less damaging treatments with fewer additives are required to preserve food product quality without loss of "fresh" taste. Not only shelf life demands but also food quality requirements and sensory needs lead to a need for preserving food using nonthermal methods (Nachmanson, 1995; Palou et al, 1999). Nonthermal methods for food preservation are being developed to minimize the quality degradation and changes of foods that results from thermal processing (Gould, 2000; Qin et al, 1995).

New technologies are being explored as potential alternatives to thermal methods. New technologies include high pressure processing (HPP), oscillating magnetic fields, high intensity pulse electric fields, and irradiation (Barabosa-Canovas et al, 1998; Ohlsson, 1994).

Oscillating magnetic fields (OMF) is applied in the form of constant amplitude or decaying amplitude sinusoidal waves. Preservation of foods with OMF includes package food in a plastic bag and subjecting it to 1 to 100 pulses in an OMF with a frequency between 5 to 500 kHz at temperatures in the range of 0 to 50 °C. Inhibition of growth and reproduction of microorganism s may be explained based on breaking of covalent bonds, cell membranes and also alteration in molecules like DNA. Frequencies higher than 500 kHz are less effective for microbial inactivation and tend to heat the food material. OMF of frequency of 5 to 500 kHz was applied and reduced the number of microorganisms by at least 2-log cycles (Barbosa-Cánovas et all 1998; Barbosa-Cánovas and Swanson 1996).

High intensity pulse electric fields (PEF) processing involves of short pulses of high voltage (typically 20 - 80 kV/cm) to foods. In pulsed electric field technology, the generation of high electric field intensities, the design of chambers that impart uniform treatment to foods with minimum increase in temperature, and the design of electrodes that minimize the effect of electrolysis are critical aspects. The impact of electrical fields to biological cells in a medium causes disruption of cell membranes (Bolado-Rodriguez et all 2000).

Irradiation is the process of exposing product to a carefully controlled amount of ionising energy from either machine-generated electron beams or gamma rays from cobalt-60. The ionising radiation passes through the food generating large numbers of short-lived free radicals. These can changes to chromosomal DNA and membrane rsult in kill micro-organisms, The length of time the food is exposed to the ionising energy and the strength of the source determine the irradiation dose, measured in kiloGrays (kGy), the food receives (Farkas 1997).

1.1. High Pressure Processing (HPP)

High pressure processing (HPP) refers to the application of pressure uniformly throughout a product by compressing the water surrounding the food. HPP subjects liquid and solid foods, with or without packaging, to pressures between 300 and 800 MPa for several minutes.

Food packages are loaded into the vessel filled with a pressure-transmitting medium. The pressure medium, usually water mixed with a small percentage of soluble oil for lubrication, is pumped into the vessel from the bottom. Once the desired pressure is reached, pumping is discontinued, valves are closed, and the pressure maintained (Deplace and Martens, 1992; Knorr, 1995). The holding time depends on the food and processing temperature (Coles, 1997). The pressure is transmitted rapidly and uniformly throughout both the pressure medium and the food product (Zimmerman, 1996). A large headspace within the package slows down the HPP and can result in a lowering of efficiency of the system. Pressure is equal from all sides (Figure 1.1). Consequently the pressure experienced by the food is independent of its volume, shape or physical state during processing (Knorr, 1996; Mertens, 1993a). The volume decrease for water at 22°C is approximately 4% at 100 MPa and 11.5% at 400 MPa. The whole package must be able to return back to its original shape after pressure treatment. Pressure causes the product to compress up to 12% depending on the pressure level (Cheftel and Dumay, 1998). In practice, the pressure itself causes a slight rise in temperature. Adiabatic compression of water causes a temperature increase of 2-3 °C per 100 MPa depending on initial temperature and pressure increase, if high pressure chamber were not have temperature controlled (Cheftel and Dumay, 1998; Hayashi, 1989).

This technique has unique advantages over conventional thermal treatments, namely: it produces high quality products with minimum damage to the original properties, and it can be applied at low temperatures which improves food quality retention. Since HPP is independent of product size and geometry, its effect is uniform and instantaneous (Mertens, 1993a). Vegetative bacteria, yeast and molds in foods are killed by HPP at 400 - 600 MPa, whereas bacterial spores require very high pressure (Kalchayanand et al, 1998). Pressure treatment can also inactivate microbes at ambient temperature, without the use of preservatives (Mackey et al, 1994). Since high pressure has had promising results for its usefulness in inactivation of microorganisms and enzymes this technology could be used by itself or in combination with other techniques to develop shelf-stable products for consumers (Meyer et al, 2000; Gola et al, 1996).

The possibility of increase product shelf-life without subjecting it to excessive heat meets well with consumer demand (Swientek, 1992). HPP avoids several of the disadvantages of thermal methods that have been used successfully to extend the shelf life of high acid foods. There is an increasing interest in the use of HPP to extend the shelf life of low-acid foods. HPP can be used as an alternative to thermal preservation for the processing of food, but has not really reached the point of full commercial utilization at this point in time (Patterson and Kilpatrick, 1998; Mermelstein, 1997, 1998).

Food can be high pressure processed in two fundamentally different ways: batch HPP technology and semi-continuous HPP technology.

1.1.1. Batch HPP Technology

In the batch operation system, packaged food is loaded into the pressure vessel, the vessel is closed, and water is pumped into the vessel to displace any air. When the vessel is full, the pressure relief valve is closed, and water is pumped into the vessel until the desired pressure is reached. The compression rate is proportional to the horsepower of the pressure pump. When the process time is completed, the pressure relief valve is opened and the water used for compression is allowed to expand and return to atmospheric pressure. The package is then removed Figure 1.1 (Farkas and Hoover, 2000).

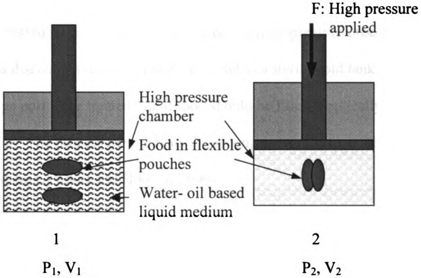

Figure 1.1 A typical schematic view of the batch high-pressure processing vessel for a packaged food product 1) before pressure 2) during pressure.

1.1.2. Semi-Continuous HPP Technology

Semi-continuous HPP uses a pressure vessel containing a free piston to compress liquid food. As the vessel is filled, the free piston is displaced. When filled, the inlet port is closed and high-pressure process water is introduced behind the free piston to compress the liquid food. After the appropriate process hold time, the system is decompressed by releasing the pressure on the high-pressure process water. The treated liquid is discharged from the pressure vessel to a sterile hold tank through a sterile discharge port. The treated liquid food should be filled aseptically into a pre-sterilized container. The process then repeats for as long as needed to meet production requirements (Farkas and Hoover, 2000).

1.2. Critical Process Factors

To ensure that a given product is sterilized, certain variables need to be measured (Farkas and Hoover, 2000; Meyer et al, 2000).

i type of microorganism
ii temperature, pressure magnitude, and holding time
iii ratio of pressurizing fluid to product in vessel chamber

1.2.1.1 Type of Microorganism

High pressure is capable of inactivating microorganisms through the effects of pressure do not mirror the effect of temperature. Gram-positive bacteria are usually more pressure resistant than gram-negative bacteria. The major cause of damage to microorganisms subjected to high pressure is due to modification of the molecules in the cell membranes leading to increase permeability (Hoover 1993). Applied at room temperatures, high pressure is likely to kill vegetative microorganisms although spores present are more resistant, but when combined with mild thermal treatment they too may be inactivated. The more developed the life form, the more sensitive it is to pressure. Composition, pH, and water activity of the food are also key factors for HPP (Meyer et al, 2000).

1.2.1.2 Temperature, Pressure Magnitude, and Holding Time

Increasing the pressure magnitude, time, or temperature of the pressure process will increase the number of microorganisms inactivated. Temperatures in the range of 50 °C appear to increase the inactivation rate of food pathogens and spoilage microbes during HPP treatment. Since products are compressed, there is the combined effect of increasing temperature and pressure. All compressible substances change temperature during compression. The magnitude of this change depends mainly on the compressibility of the substance (Farkas and Hoover, 2000).

1.2.1.3 Ratio of Pressurizing Fluid to Product in Vessel Chamber

Since specific heat of the pressurizing fluid differs from that of a food product, the ratio of the food product to pressurizing fluid must be kept the same to obtain a repeatable result (Meyer et al, 2000).

1.2.2.1 HPP Sterilization Production Cost:

An example of the production costs a per-pound cost is: Labor $ 0.009/lb, maintenance $0.018/lb, depreciation $0.0185/lb. The total cost is estimated to be 0.0455/lb. A cost of about $ 0.03/lb is possible with expected future improvements (Mayer et al, 2000). The cost of the vessel will decrease over time.

1.3. Food Packaging and High Pressure Processing

HPP is getting closer to becoming a commercial reality as a method to increase shelf life. HPP product is available in the Japanese market, and interest is increasing in the food industry in Europe and in the USA. In Japan, HPP is done commercially on a meaningful scale with fruit jams, jellies, salad dressing, yogurts, fruit mixes, fruit juice and concentrates. In the United States most of the activity has been still confined to research labs and pilot plants, where good results have been obtained. High pressure processing is already being used commercially for pasteurization of few products such as guacamole, meats, and seafood but not yet for sterilization (Meyer et al, 2000). A combination of vacuum packaging and high pressure is now being used by food processors. Unprocessed food in vacuum-packed containers may subjected to pressures (Anon, 1996). Commercially, the HPP system is being used for freshly squeezed citrus juice in flexible HDPE bottles (173 MPa, 10 min). Packaging, when under pressure, must be able to accommodate a 5-7% reduction in liquid volume (Ayshford, 1997). More attention is also being focused on the suitability of packaging technology with this method.

Foods can be processed in bulk followed by aseptic filling, such as individually prepackaged food in non-rigid containers. These are then sealed before being subjected to HPP. In this case, suitable packaging materials for high-pressure treatments are required. Packaging design and material properties are important challenges for the high pressure processing industry. Plastic packaging materials play a significant role in the HPP foods in order to prevent microbial recontamination after treatment. For HPP, some types of packaging will not stand up to the pressure without problems. Glass and metal containers are not likely to be suitable. Paperboard cartons will also suffer some degradation. Flexible packaging, using either laminated or monolayer films, is the most suitable and is widely used (Mertens, 1993b; Knorr, 1995). This is because rigid packaging such as metal cans or glass bottles tends to fracture or become distorted. Films, which contain metal foils or thin paper layers, may be used, but inner and outer layers should be plastic in order to achieve a good heat seal and good protection from the pressure medium (Mertens, 1993a; Mertens, 1993b; Nachmanson, 1995).

To ensure the development of safe and good quality food products using HPP technology, an understanding of mass transfer issues within the food/package system is an important safety consideration. Changes in permeability of the packaging materials, as well as the loss or gain of specific aroma constituents during storage or distribution, can result in product quality loss. Although packaging is a key factor to preserve food qualities, compatibility between packaging and high pressure treatment has been largely neglected (Mertens, 1993b).

One of the disadvantages of plastic packaging, for even high barrier materials, is its permeability to vapors and gases that reduce the shelf life of certain foods. After high pressure processing, the properties of these materials should not be affected in such a manner that their migration, sorption and permeability potentials to gases and flavors may significantly affect product shelf life and quality. While many researchers have dealt with the specific effects of HPP on various food constituents, relatively few investigations have dealt with the effect of HPP on food packaging materials. Changes in plastics due to HPP are of prime importance in a food packaging application, where such changes may directly affect the quality of a packaged foodstuff. There is not much research reported on the effect of HPP on packaging materials for food packages. None of the tested materials showed any significant changes in mechanical strength even though some showed surface deformation. Therefore, these changes seem to have small or no effect on the shelf life of packaged foods. The magnitude of these changes depends on the type of structures and the processing conditions. Even though some barrier properties may be affected by HPP, the author found no evidence that these changes have a negative impact on performance of the materials (Lambert et al, 2000).

Laminated plastic package structures were filled with water and then pressure treated at 400MPa, for 10 min. Oxygen and water permeability properties of the films did not change due to HPP. An extraction test on the films was carried out using 4% acetic acid, 20% ethyl alcohol, and n-heptane. The amounts of evaporation residue were at an acceptable level. Tensile strength properties of a PP/PVdC/PP structure were also measured. Pouches were made of this film and filled with water, sealed and pressurized at 400 MPa, for 10 min. The author reported that tensile properties did not change due to the high pressure treatment (Ochiai and Nakagawas, 1992).

Mertens (1993 c) investigated the mechanical properties of flexible packaging film after HPP (400 MPa and 60°C for 30 minutes). Flexible structures used in this study were LLDPE/EVA, EVOH/EVA /LLDPE, and PET/Al Foil/PP. Their mechanical properties, tensile strength, and elongation were compared with the corresponding values for non-treated film. Tensile strength and elongation properties of these structures were unchanged by the high-pressure treatment.

Masuda et al (1992) investigated the following flexible structures: PP/EVOH/PP, OPP/EVOH/PE, PVDC-coated OP/CPP and PET/Al/CPP. They measured the water permeability at 40 °C, 90 % and oxygen permeability at 23 °C, 90 % RH. Films were treated at 400 MPa and 600 MPa for 10 min at 20 °C. Pressure treatment did not change barrier properties against water and oxygen. They also measured the tensile strength and heat seal performance of these films. The author reported tensile and heat seal performance were not affected by the high pressure treatment.

Little is known about sorption and migration processes from pressurized materials. HP-treatment did not result in a significant increase of overall migration of the packaging materials tested (Mertens and Knorr, 1992). HPP did not affect migration from pressurized packaging films containing four solvents (water, 4% acetic acid, 20% ethyl-alcol and n-heptane) (Ochiai and Nakagawas, 1992).

In another detailed study, Lambert et al (2000) were investigated package properties after HPP. Pouches made of six different multilayer flexible films (15x15 cm) were filled with 25 cl of food simulants (distilled water, 15 % ethyl alcohol, 3% acetic acid, olive oil). Flexible structures were: 1) PA/70 µm PE (medium density), 2) PA/ 60 µm PE (linear), 3) PA/ 40 µm PE, 4) PET/PVdC/PE, 5) PA/PE surlyn, 6) PA/PP/PE. Pressurization processes were carried out at 200, 350, and 500 MPa for 30 min at ambient temperature. Oxygen permeability of treated packages 2, 4 and 6 were allowed a deviation of 12 %. However, the oxygen permeability of packages 1 was increased 25 %, and package 5 was decreased 16 %. Even though these exceeded levels of oxygen permeability, there were still within acceptable limits according to these authors. Changes in water permeability were higher than those packages for oxygen permeability. Values of water permeability were increased for packages 1, 4 and 6 more then a 12 %, but water permeability were decreased for packages 2 and 5. However, according to same authors reported that the water permeability properties of the packages stayed acceptable and compatible for the foodstuff. Modification in barrier properties did not seem to be very significant. Tensile properties of most of the plastic structures after HP treatment were within the allowable deviation of 25%, however, PA/ 40 µm PE was not within the allowable deviation after high pressure treatment. The global migrations of packages were also evaluated after HPP treatment (500 MPa for 30 min at 20 °C). Selected plastic packages were in contact with four simulants for 10 days at 40 C. All the values for global migration of the treated flexible plastic were the same before and after treatment. Global migration of the packages did not seem to be correlated with the film thickness, the materials nature, or the fabrication process (Lambert et al, 2000).

Few studies have been published related to the sorption process. Kubel et al (1996) investigated sorption of aroma compounds p-cymene and acetophenone into flexible packaging film. The flexible structures were LDPE/HDPE/LDPE, PET/LDPE, and HDPE. Internal pouches (70x12 mm) and external pouches (105x15 mm) were prepared. The internal pouches were filled with a solution of H_2O/EtOH/p-cymene or H_2O/EtOH/acetophenone and then sealed. These pouches were placed into external ones which had been filled with H_2O/EtOH, then sealed. After pressure treatment in the range of 0.1- 450 MPa, diffusion rates were measured as function of pressure by UV spectroscopy. Under high hydrostatic pressure, the concentration of p-cymene and acetophenone was not significantly affected. Diffusion of food components into the packaging material during exposure to high pressure did not affect the aroma of high pressure sterilized food.

1.4. Packaging and Protection

The main purpose of packaging food is protect the packaged product from the environmental influence from the outside influence, through processing to final consumption (Robertson, 1993).

Product quality, or shelf life, is determined by the following parameters: a) the product's physical, chemical, and biological characteristics; b) processing conditions; c) package characteristics and effectiveness; and d) the environment to which the product is exposed during distribution and storage (Hernandez and Giacin, 1998).

While the package serves as a barrier between the product and environment to which the product/package system is exposed, the degree of protection varies. This variation is particularly important in connection with the transport of gases, vapors, or other low molecular weight compounds between the external environment and the internal package environment. These transports are controlled by the packaging material. The specific barrier requirement of the package system will be dependent upon the product's characteristics and the intended end –use application. For the purpose of package design and optimization, it is important to consider how the mass transfer characteristics of the packaging material determine the transport of low molecular weight compounds both into and through the package (Hernandez and Giacin, 1998).

1.4.1. Plastic Structures As Food Packaging Materials

Plastic structures are polymeric materials built up from long repeating chains of molecules and are commonly used as packaging materials for foods. These organic (carbon-containing) molecules can be formed into a variety of products. The length of the plastic's molecules and the specific monomers present determine the properties of the plastic. All plastics, whether made by addition or condensation polymerization, can be divided into two groups: thermoplastics and thermosetting plastics. These terms refer to the different ways these types of plastics respond to heat. Thermoplastics can be repeatedly softened by heating and hardened by cooling. Thermosetting plastics, on the other hand, harden permanently after being heated once. Almost all polymers used for food packaging purpose are thermoplastics (Rodriguez, 1984; Paine and Paine, 1983).

Plastics are widely used in the food packaging industry because of their relatively low weight, ability to color when manufacturing, extremely competitive cost, transparency, barrier properties and mechanical strength, and the ability to mold complex shapes relatively easily. Therefore, the usage of various plastics for food packaging has been in great demand as compared with other materials such as glass, metal, and paper (Matsui and others, 1992). Increasing use of plastics is sustained by the growth of the food packaging industry (Gnanasekharan and Floros, 1997). However, plastics can also interact with foodstuffs, and this interaction can affect the quality of the packaged food.

1.5. Mass Transport Phenomena and Food / Packaging Interactions

Interaction between food and packaging influences the overall product quality. One of the primary functions of packaging is to protect food from contamination and to preserve its safety and quality. Plastic structures are not absolute barriers against gases such as oxygen. Even glass and metal containers are not completely inert with respect to foods. However, the large increase in the use of plastics for packaging has increased the degree to which packaging directly affects food. The shift from absolute barrier type packages to semi-permeable polymeric packaging systems has created a need to develop a better understanding of the transport behavior through polymer films (Hernandez et al, 1986). This also requires better understanding of the factors that influence transport mechanisms and food package interaction (Gavara and others, 1996). Food-packaging interactions can be defined as chemical and/or physical reactions between a food, its package, and the environment which alter the composition, quality, or physical properties of the food and/or package (Hotchkiss, 1995; Giacin, 1995). This is mainly associated with the mass transport of gases, water vapor and low molecular mass organic compounds between product, packaging material and storage environment. In food packaging, mass transfer is often decisive factor in determining the applicability of plastic films as protective packaging structures (Hernandez, 1997).

Mass transfer processes in packaging systems normally encompass a number of phenomena referred to as either permeability, sorption, and migration (Giacin and Hernandez, 1997).

In general, food-package interactions can be divided into four types:

1. Egress permeation: Transfer of product components through the package to the

environment. Loss of aroma-flavor volatiles, CO_2, or H_2O can result in changes in food quality.

2. Ingress permeation: Transfer of environmental components through the package to the product. Ingress of O_2, H_2O or undesirable odors or toxicants can be detrimental. Packaging materials that interrupt this process (e.g., oxygen interceptors) can be beneficial.
3. Scalping, sorption: Transfer of product components to the package Transfer of desirable aromas from food to packaging can result in flavor alteration and/or loss of package performance. Sorption of undesirable flavors or reduction in O_2 content of a package could be beneficial.
4. Migration: Transfer of package components to the product. This can result in safety concerns and flavor degradation. Transfer of desirable functional components such as antimicrobial agents may be beneficial (Hotchkiss, 1995; Hernandez, 1997).

Mass transport in polymers is very complex and is discussed in the following sections: permeability, sorption and migration.

1.5.1. Permeability

Barrier properties are very crucial parameters in selecting packaging materials for food products. This is due to the fact that the barrier properties, including oxygen, water, and carbon dioxide barrier is among factors controlling shelf life and the quality of many packaged products. For each product, certain requirements must be met by the package, but these requirements may vary widely from one product to another. Barrier properties vary and are dependent on the individual polymer's chemical and physical properties. When a polymeric material is used to pack food, gases and water vapor may permeate from the surrounding environment into the package. The number of gas and vapor molecules that penetrate into a package depends on the characteristics of the polymer, the characteristics of the penetrating molecules, their interaction, temperature, the penetrant concentration, and the water content (Hertlein et al, 1995).

Permeability is a mass transfer process associated with a function of the partial pressure differential of a gas or vapor between the two sides of packaging structures, among other parameters. Permeation is the diffusional molecular exchange of gases, vapors or liquid permeants across a plastic structure, interaction between polymer films and food, allowing the contents of a package to interact with the environment and vice versa (DeLassus, 1986; Hernandez, 1996). Permeability is referred to as the product of the thermodynamic parameter of solubility and the kinetic parameter of diffusion. The diffusion coefficient describes how quickly the molecular species moves in the film and the solubility coefficient is a measure of the quantity of a substance that will be sorbed by the polymer. The rate of permeability is greatly influenced by the absorption and solubility of the molecules in the polymer (Hernandez, 1996; Giacin and Hernandez, 1997). The deterioration of packaged foodstuffs largely depends on transfers that may occur between the internal environment and the external environment (Giacin and Hernandez, 1997). The mechanism of permeation of gases and vapors though polymers can be summarized: a) Absorption and solution of penetrant at one surface of the polymer; b) Diffusion of the penetrant through the polymer matrix; c) Desorption of the penetrant from the other surface of the polymer (Rogers, 1985; Hernandez, 1997, DeLassus 1986).

The diffusion flow (F) of a permeant through a polymer film is related to the amount of permeant passing through a surface of unit area normal to the direction of flow during unit time, as described by the following equation:

$$F=Q/A\ t \qquad (1)$$

where F diffusion flow or flux, Q is the amount of permeant, A is area, and t is time.

If the permeation rate and the concentration gradient is one of direct proportionality, Fick's fist law of diffusion applies (Mohney et al, 1998; Hernandez, 1997).

$$F=-D\frac{\partial c}{\partial x} \qquad (2)$$

where F is the flux (rate of the transport) per unit area of permeant through the polymer, c is the permeant concentration in the polymer, and D is the diffusion coefficient. Therefore, $\delta c/\ \delta x$ is the concentration gradient of the permeant across a thickness x.

Permeation is described by the permeability coefficient (P), diffusion coefficient (D) and solubility coefficient (S):

$$P=D\ S \qquad (3)$$

The solubility coefficient is a measurement of the concentration of penetrant molecules sorbed in the polymer matrix. In an unsteady state flow case, from a mass balance standpoint, assuming that diffusion takes place only in the x direction, Fick's Second Law provides the relationship:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{4}$$

where t is time.

When a polymer is contacted on both sides with a penetrant at different concentration values, this expression can be integrated at the surface x=0, the penetrant concentration $c=c_2$ and at x=L, $c=c_2$; yielding equation (5).

$$F = \frac{D(c_1 - c_2)}{L} \tag{5}$$

At sufficiently low concentrations, Henry's law often applies and the above expression can be rewritten by substituting for c.

$$c=S\ p \tag{6}$$

$$F = DS = \frac{(p_2 - p_1)}{L} \tag{7}$$

Where D S is referred to as the permeability coefficient or constant and is represented by the symbol P. Converting the flow rate to a flow per unit area, F=q/At, combining the equation above, and rearranging equations yields equation (8):

$$P = DS = \frac{qL}{At\Delta p} \tag{8}$$

where the permeability coefficient or constant, P, equals the amount of permeant q (cc, g) that has passed through a material of known thickness L (m, cm, mil) per unit area A (m^2, 100 in^2), in a given time t (sec, hr, day), at a known partial pressure difference Δp (atm, Pa, mmHg).

The transmission rate refers to the quantity of permeant derived from the expression for permeability disregarding thickness and the partial pressure gradient of the permeant (Robertson, 1993).

The permeability through a barrier polymer is dependent on several internal and external factors. The internal factors include the chemical structure of the polymer and permeant, and the physical structure of polymer (Koros et al, 1988; Nemphos et al, 1986). The external factors include the nature of the permeant, and the environmental conditions such as temperature and relative humidity. Each variable must be known, specified and controlled in order to obtain reliable, repeatable test results.

Many experimental techniques have been employed for measuring permeability and can be categorized as follows (Gavara and Hernandez, 1999):

i Pressure variable methods
ii Isostatic method
iii Quasi-isostatic method

1.5.1.1. Pressure Variable Methods

The ASTM standard method D-1434 was adopted for measuring gas transmission rates and permeabilities of film. In this technique, the high-pressure chamber is filled with the permeant at relatively high pressure and the permeated gas diffused to the other side of the film. The permeant is collected in a constant-volume chamber (pressure – variable) or allowed to expand against a constant atmospheric pressure (volume-variable). In the pressure variable, the cell is totally evacuated. During the diffusion process, the pressure increase in the low –pressure chamber is measured by a pressure gauge as a function of time (Gavara and Hernandez, 1999; Robertson, 1993).

1.5.1.2. Isostatic Method:

In this procedure, the flow system is designed to maintain the total pressure on both sides of the polymer at atmospheric pressure. A constant permeant vapor pressure is continuously flowed through the high concentration cell chamber, while the permeated vapor is conveyed by N_2 to the detector. The transmission rate is measured continuously until a steady-state value is reached (Hernandez et al, 1986; Gavara and Hernandez, 1999).

The permeability coefficient can be calculated by Eq (9):

$$P = \left(\frac{F_{ss} L}{\Delta p}\right) \tag{9}$$

Where F_{ss} is the steady state flow, and the diffusion coefficient D by Eq (10):

$$D = \frac{L^2}{7.199.t_{0.5}} \tag{10}$$

where $t_{1/2}$ is the time required for F_t/F_{ss} to reach a value of 0.5.

At steady-state, the permeability coefficient can be determined using following equation (11) (Hernandez et al, 1986; Gavara and Hernandez ,1999).

$$P = \frac{a \times G \times L}{A \times b} \tag{11}$$

where: a is the calibration factor to convert detector response to unit of mass of permeant ((mass/volume)/signal unit), G is the response unit from the detector output at steady state (signal output), f is the flow rate of sweep gas conveying penetrant to detector (volume/time), A is the area to the penetrant (area unit), L is the film thickness, b is the driving force (the concentration or partial pressure gradient).

1.5.1.3. Quasi-Isostatic method

In the quasi-isostatic (pressure increase or accumulation) method, a test film separates two chambers where one side of the film is exposed to the test gas, and the other is in contact with an inert gas. Samples of penetrated permeant are withdrawn from the low concentration cell chamber. By plotting the total quantity of permeated vapor as a function of time, the diffusivity and permeability coefficients can be determined. Diffusivitys is calculated by:

$$D = \frac{L^2}{6T} \tag{12}$$

where L is the thickness, and T is the lag time (Pain and Pain, 1983).

The steady state permeability coefficient is obtained using equation (13).

$$P = \frac{yL}{Ab} \tag{13}$$

where: y is the slope of the steady state portion of the transmission rate profile curve; l is the film thickness; A is the area of the film exposed to the permeant, b is the driving force (the partial pressure gradient).

1.5.1.4. Water Vapor Transmission Rate Measurement

The water vapor transmission rate (WVTR) is defined as the rate of water vapor flow under steady state conditions through a unit area of a test film material.

The most commonly used method for determining water vapor permeability (WVP) is the standard test method for WVTR of materials (ASTM, 1990). This gravimetric method involves sealing a test film in a cup partially filled with water leaving an air gap beneath the film (Anker, 1996).

The Permatran – W 3/31 (Modern Controls, Inc. Mocon, Minneapolis, MN) is an instrument used for measuring the rate at which water vapor diffuses through a permeable barrier according to ASTM F1249. Test cells consist of two sections separated by the material being tested. The RH in the enclosed chamber reaches 100%. Water vapor permeating across the film is transported by the dry nitrogen gas to a pressure modulated infrared detection system which determines the moisture in dry purge air. The infrared photodetector produces low-level electrical signals in response to the change in transmitted infrared radiation. This signal is directly proportional to the WVTR of the test cell.

1.5.1.5. Oxygen Tansmission Rate Measurement

The oxygen transmission rate is defined as the rate of oxygen flow, normal to the two film surfaces, under steady state conditions through a unit area of a test film.

An instrument widely used for the measurement of oxygen permeability by this method is the Mocon OxTran (Modern Controls, Inc, Minneapolis, Minn). The OxTran consists of two chambers of measuring cells between which the test film is placed. A gas stream of known oxygen partial pressure flows through one of the chambers. Oxygen - free carrier gas is passed through the other chamber to a coulometric detector. A computer will perform the testing procedure and display the resultant transmission rate values for each specimen tested. This oxygen permeability tester operates according to ASTM Standard Method D 3985-81 (Anonymous, 1981).

1.5.1.6. Carbon Dioxide Transmission Rate Measurement

The Permatran C-IV measures the carbon dioxide transmission rate of film. Test film is clamped between the upper and lower half of the diffusion cell, then the upper half is flushed continuously with carbon dioxide gas. Permeated gas is carried to an infrared sensor by nitrogen gas where a response is generated proportional to the amount of carbon dioxide present (Mocon, 1983). The Permatran C-IV can vary in operation according to suit the barrier properties of the film.

Static Accumulation- This method is for testing transmission rates less than 50 cc / (m^2 d). Carbon dioxide permeated through the test film accumulates in a cell for a predetermined time (2-80 h). The amount of accumulated carbon dioxide is quantified using a sensor and compared with the signal produced when a known amount of carbon dioxide is injected into an identical volume.

Dynamic Accumulation- This method is used for testing transmission rates between 50 and 300 cc / (m^2 d). As carbon dioxide permeation through the film increases, the corresponding output voltage increases with time, producing a straight line until its slope is constant. The observed response is subsequently translated to carbon dioxide concentration by comparision with the signal produced when a known amount of carbon dioxide is injected into an identical volume.

Continous Flow- This method is used for testing high transmission rates greater than 300 cc / m^2 d. Unlike static and dynamic accumulation, continous flow is operated in an open loop. The carbon dioxide transmitted through the test film mixes with the nitrogen carrier gas, passes into the infrared sensor, and is exhausted. The test film is compared to a reference film of known transmission rate which is similar to the expected value of the test film.

1.5.2. Sorption

Sorption behavior results in dissolution or transfer of a substance from the food to the polymeric structure. Sorption is a process that results when a flavor component of a product is soluble in a packaging material. The volatile component dissolves into the polymer, leaving a lower concentration in the package headspace. An imbalance in the flavor profile results in a detectable reduction in the organoleptic quality of the product. As opposed to plastic structure's prevalence, a serious problem has been identified concerning deterioration of intrinsic food flavors by plastic films (Matsui et al, 1992, Moshonas and Shaw, 1989). This sorption behavior depends on the relative strengths of the interactions between the permeant molecules and the polymer. In food product-package systems, sorption behavior needs to be characterized for quality control and for predicting the change in product quality, as related to the loss of components associated with product shelf life (Hernandez and Giacin, 1998). Consumer rejection of food is commonly associated with the presence of unacceptable flavors. In general, packaging materials can alter the flavor profile of packaged foods by absorbing flavor components, chemically reacting with food components to produce off-flavors, and/or by releasing components that produce off-flavors into the food (Gnanasekharan and Flores, 1997; Mannheim et al, 1987). This phenomenon may be brought about by the sorption of flavors in the plastic layer because the film is in direct contact with foodstuffs over time (Matsui and others, 1992). The solubility of essential flavor in the polymer structure is of paramount importance in avoiding the effect of "flavor scalping" or loss due to sorption (Fayoux et al, 1997). In a food packaging structure, the package material should sorb a minimum amount of the critical food-flavorants. The amount of sorption is expressed by the solubility coefficient, which describes how many molecules are in the polymer matrix. Several models have been proposed to describe sorption behavior, the main models are Henry's, Langmuir, and Flory-Huggins types (Rogers, 1985; Hernandez, 1996; Stern and Trohalaki, 1990).

1.5.2.1. Henry's law sorption

Henry's law sorption is the simplest case of sorption, which applies to an ideal case and occurs when interactions between the polymer/permeant and permeant/permeant are weak compared with the stronger interaction between the polymer/polymer interaction. In this case, the solubility coefficient is independent of the sorbed permeant concentration and the sorption isotherm shows a linear relationship between sorbate amount and permeant pressure at a given temperature (Rogers, 1985).

1.5.2.2. Langmuir sorption isotherm

This type of sorption is characterized by a high level of sorption occurring at a relatively low pressure. This is a characteristic of initial sorption on specific sites or microvoids in the polymer structure. After saturation of the active site, the permeant starts to dissolve in to the polymer matrix (Hernandez, 1996). A region of higher concentration may try to overtake a region of lower concentration (Sheng and Smith, 1999).

1.5.2.3. Flory-Huggins sorption

This type of sorption is where the penetrant/penetrant forces are stronger then the polymer/permeant interactions. The solubility coefficient increases with vapor pressure (Fayoux et al, 1997; Rogers, 1985).

1.5.2.4. Dual-mode sorption

This type of sorption is based on the existence of two sorbed penetrant populations in the polymer. One population of the permeant molecules dissolves into the polymer by a mode which obeys Henry's law, while the other population is sorbed into voids of the polymer obeying Langmuir type sorption (Stern and Trohalaki, 1990). The resulting sorption is then due to a combination of Henry and Langmuir sorption.

For a low partial pressure of gases, or for dilute concentrations of organic vapors, the solubility follows Henry's law:

$$C=S\ p \tag{14}$$

Where C is the concentration of sorbate in the polymer, S is the solubility coefficient, and p is the vapor pressure of sorbate.

The type functional group is characteristic of the penetrant molecule and is of great importance in determining the extent of sorption by the packaging material.

An increase in the temperature directly affects the solubility and can be described by an Arrhenius equation (Gnanasekharan and Floros, 1997).

1.5.3. Migration

Migration is the transport of compounds from the packaging materials into a food product. These compounds include residual monomers or oligomers from the incomplete polymerization process, additives such as heat and light stabilizers, antioxidants, antistatic agents, stabilizers, and lubricants. Under certain conditions, these relatively low molecular weight compounds will migrate from the package to the food (Lox and Pascat, 1996).

The migration from polymeric packaging materials to food products can be viewed as a two-step process in which the migrants diffuse from the surface to the contact phase, and then dissolve in the food and are dispersed therein. The desorption of a migrant from a polymer can be considered a function of the polymer-migrant interaction affinity and diffusion. The affinity is determined by the equlibrium amount of migrant transferred to the food phase (Gnanasekharan and Flores, 1997).

The amount of contaminant migrating from a plastic film or sheet into a food contact phase can be adequately characterized by equations that are derived from Fick's first and second laws of diffusion (Lox and Pascat, 1996).

Fick's second law is related to non-steady state diffusion, where concentration of the diffusing substance is changing with time (15):

$$\frac{dC_p}{dt} = D_p\left(\frac{d^2C_p}{dx^2}\right) \tag{15}$$

where the subscript "p" indicates that parameters pertain to the polymer.

The boundary condition that describes the concentration at the interface between the polymer and the external phase is strongly influenced by the extent of agitation, composition, and the volume of the external phase. If the external phase is stagnant, the migrant that leaves the polymer must diffuse through the external phase. Thus, an expression similar to that in the above equation can be written (16):

$$\frac{dC_e}{dt} = D_e\left(\frac{d^2C_e}{dx^2}\right) \tag{16}$$

Where the subscript "e" refers to the external phase. The boundary condition at the interface with the polymer is then given and also quantitatively described by the partition coefficient (K) (Little, 1983):

$$K=\left(\frac{C_e}{C_p}\right) \tag{17}$$

The transport of a migrant is dependent on the nature of the polymer matrix, the chemical structure of both the contaminants and the food type, and the test condition (temperature and storage time) (Little, 1983).

1.6. Factors Affecting Permeation, Sorption, and Migration Processes in Package-Product Systems:

The mass transfer process provides the basis for further physicochemical activities within the package system. Such activities may induce physicochemical changes in the product (Giacin, 1995).

Sorption, or the uptake of volatile components by the polymeric packaging material from the food, may also result in increased permeability to other permeants, lower chemical and mechanical resistance of the packaging material, and may affect the kinetics of the migration process. The overall effect may result in the loss of aroma and flavor volatiles associated with product quality, as well as other volatile organic food components during package storage.

The permeation, sorption and migration processes are affected several factors. The variables affecting permeation, sorption and migration can be grouped as composition and environmental and geometrical variables (Giacin 1995, Giacin and Hernandez 1997, Hernandez and Giacin 1998):

Composition variables

i Nature of polymer

ii Nature of permeant

Environmental and geometric variables

i Temperature

ii Relative humidity

iii Packaging geometry

1.6.1. Composition variables

1.6.1.1. Nature of Polymer

The relationship between penetrant transfer characteristics and the basic molecular structure and chemical composition of a polymer is rather complex, and a number of factors contribute to the sorption and diffusion processess including structural regularity, conformational flexibility and intermolecular forces of attraction (Giacin, 1995).

Morphology in polymer refers to the physical state by which amorphous and semicrystalline regions coexist. It depends not only on its stereochemistry but also on whether the polymer has been oriented or not.

Crystalline polymers have high melting points, high density. Mass transfer is restricted to the amorphous regions of the polymer Increasing polymer crystallinity on the reduction in sorption, diffusion and permeability properties. (Rogers, 1985; Hernandez and Giacin, 1998). Crosslinking polymer chain restricts chain mobility and consequently reduces permeability. Functional and side groups have effect oxygen permeability properties such as benzene rings offer poor barrier to hydroxyl groups

Polymer free volume is also a function of structural regularity, orientation and cohesive energy density (Giacin, 1995; Hernandez and Giacin, 1998; Rogers, 1985). The solubility of vapors and gases in polymers is also strongly dependent on crystallinity, since solubility is usually confined to the amorphous regions (Giacin, 1995; Giacin and Hernandez, 1997).

1.6.1.2. Nature of Permeant

The molecular structure of the permeant can play an important part. Since larger molecules has higher cohesive force to substrate surface, increase in permeant size mostly lead to an increase in solubility coefficient values. But the decrease diffusion coefficient values. The observed concentration of the permeance values may be attributed to penetrant/polymer interaction (Giacin, 1995).

Organic vapors are capable of exhibiting concentration-dependent mass transport processes. The permeation of more condensable vapors through a polymer proceeds at greater rates than permeation of gases. Therefore, the type and/or mixture of organic vapors will determine the magnitude of sorption and permeation, as well as the effect of a co-permeant on penetrant permeability.

The polymer and the permeant have similar chemical composition or polarity, high permeability is expected. Polar compounds will tend to dissolve in polar solevent (Giacin, 1995; Hernandez and Giacin, 1998).

1.6.2. Environmental and geometric factors

1.6.2.1. Temperature

Permeability (P), diffusion (D), and solubility (S) coefficients are affected by temperature following the Arrhenius relationship. as given in the following equations:

$$D = D_0 \exp(\frac{-E_D}{RT})$$

$$S = S_0 \exp(\frac{\Delta H_s}{RT})$$

$$P = P_0 \exp(\frac{-E_p}{RT})$$

where D, S, P are coefficients; D_0, S_0, and P_0 are pre-exponential constants, E_d is the activation energy for diffusion, ΔH_s is the heat of solution, Ep is the activation energy for permeation, T is the absolute temperature, and R is the universal gas constant.

The above equations can be used to calculate the permeability coefficient at a desired temperature from a known value. However, the permeation behavior is generally quite different below and above the glass transition temperature (T_g). Above the T_g of the polymer, enough energy is provided to produce segmental mobility in polymer chains, which corresponds with an increase in permeability and diffusion. Below the T_g, the polymer chains are fixed in a specific conformation. In general, at temperatures above T_g, the permeability coefficient is more temperature dependent (Hernandez, 1996; Hernandez and Giacin, 1998; Frisch, 1980).

1.6.2.2. Relative Humidity

Barrier properties are mostly sensitive to the amount of moisture present in a polymer. If water swells or plasticizers the polymer chains, the gas permeation can increase. This effect is due to the greater ease of polymer chain segmental mobility (Crank and Park, 1968; Axelson-Larsson, 1992), which results in an increased gas diffusion rate and greater sorption capacity of the polymer matrix (Lim et al, 1998).

1.6.2.3. Package Geometry

The area of exposure and thickness, shapes, the total volume are critical (Brown, 1992). The volume or mass ratio of the food phase and packaging material is also required for quantification of the equilibrium concentration for a specific product/package/sorbate system (Giacin, 1995).

1.7.1. Mechanical Properties

Polymers are increasingly used for packaging application because of their unique properties. In many applications, the mechanical properties of the polymer are of prime importance. It is essential that the plastic structure retain its mechanical strength, stability, and integrity in order for it to continue to execute its function over a useful time without failure. Quantitative information on the mechanical parameters of films is also essential for designing packaging sytems. By understanding the mechanical behavior and the factors controling it, polymeric materials can be properly and efficiently utilized. The mechanical properties of the polymer are dependent on internal and external factors.

1.7.1. Effect of External and Internal Factors on Mechanical Properties

The external variables refer to factors that have an appreciable effect on mechanical properties but are not directly concerned with the structure and composition of the polymer. The main external factors are time, temperature, and pressure (Lawrence, 1994). When the ambient temperature increases in a material, there is a gradual expansion of the material, resulting in more free volume and weakening of the bonding forces that hold the material together. In polymers, this mainly results in a reduction in the van der Waals forces between molecules. As such, all materials have less internal strength with increasing temperature, which is reflected in reduced maximum strength. Elongation at break usually increases. As pressure is increased, the strength of the polymer invariably increases. This would be expected since increasing pressure decreases free volume and increases the strength of the van der Waals bonds along with the density of the material (Lawrence, 1994, Bucknall et al, 1972).

The internal factors, on the other hand, are those that produce changes in mechanical properties by directly producing changes in morphological, chemical and physical structures of the polymer. The main internal factors are the following (Rubin 1982; Paul and Bucknall, 1999):

i chemical structure and composition,

ii degree of crystallinity

iii molecular weight

iv the presence of low molecular weight diluent (plasticizer, filler etc)

v orientation and other consequences of the processing history (thermal).

Thermal properties are also important factors in determining the brittleness and the ductility of a polymer. T_g relates to segmental mobility of the molecular chains, and it also determines whether chain-straightening and/or molecular slippage will occur. The chain-straightening refers to the elongation of the molecular chain from the equilibrium position to the new dimension under stress, while molecular slippage refers to the molecular movement past adjacent molecules due to the application of stress (Paul and Bucknall, 1999). As polymers are placed under stress, they may exhibit both phenomena, depending on their morphological structure. Besides the effect of thermal expansion, increase in temperature brings about changes in the state of the amorphous polymer. At a temperature below T_g, those phenomena do not occur appreciably. Therefore, the polymers are hard. At a temperature above T_g, polymers exhibit chain-straightening and molecular slippage. Therefore, the polymers are soft and flexible. In conjunction with these changes of state are changes in the mechanical behavior of the polymer (Rubin, 1982; Brucknall et al, 1972).

1.7.2. Tensile Properties

One of the most informative mechanical tests for any material is the determination of its stress-strain curve in tension. The stress-strain curve for plastic serves to define several useful quantities, including strength, yield strength, elongation at break, and modulus of elasticity. Different materials exhibit different tensile properties. The mechanical properties are measured by deformation of a sample and monitoring the stress and deformation until it breaks (Anker, 1996).

Stress (σ) and strain (γ) are calculated from the recorded force F and deformation.

$$\sigma = F/A$$

$$\varepsilon = L/L_0$$

Where, A is original crossectional area, L_0 original length and L the length change during extension.

A typical shape of the stress-strain curve for plastic material is shown in Figure 1.2. A great deal of information about a material can be obtained from the shape of its stress/strain curve (Figure 1.2 and Figure 1.3). That plot of stress versus strain can give us another very valuable piece of information including tensile strength, yield strength, percent elongation, modulus of elasticity, and toughness.

1.7.2.1. Tensile Strength

Tensile strength at break is the maximum stress that a polymer can withstand prior to failure, divided by the original cross-sectional area supporting the load. The static weighing test according to ASTM method D-882 is used to determine this property. The applied force and amount of grip separation are measured. The stress and strain of the sample are measured continuously and recorded on a chart. For determination of tensile strength, the stress is plotted against the strain; the load against the elongation.

1.7.2.2. Yield Strength

The yield strength is the tensile stress at which the material exhibits a first sign of non-elastic deformation occurs To determine this parameter the load at this point (yield point) divided by the original cross sectional area of the specimen.

1.7.2.3. Percent Elongation

The percent elongation is the extent to which a material can extend during tension testing and is usually taken at the point of break. Elongation is expressed as the change in length to initial length. Deformation is simply a change in shape that anything undergoes under stress. Usually percent elongation, which is just the length the polymer sample is after it is stretched (L), divided by the original length of the sample (L_0), and then multiplied by 100 according to ASTM D882:

$\%$ elongation $= \Delta L / L_0$

It is used as a measure of the film's ability to stretch, which indicates that the material may absorb a large amount of energy before breaking (Roberson, 1993).

1.7.2.4. Modulus of Elasticity

Modulus of elasticity is measured by calculating stress and dividing by elongation and would be measured in units of stress divided by units of elongation. It is a measure of the force that is required to deform the film by a given amount and so it is also a measure of intrinsic stiffness of the film.

1.7.2.5. Toughness

Toughness is really a measure of the energy a sample can absorb before it breaks.

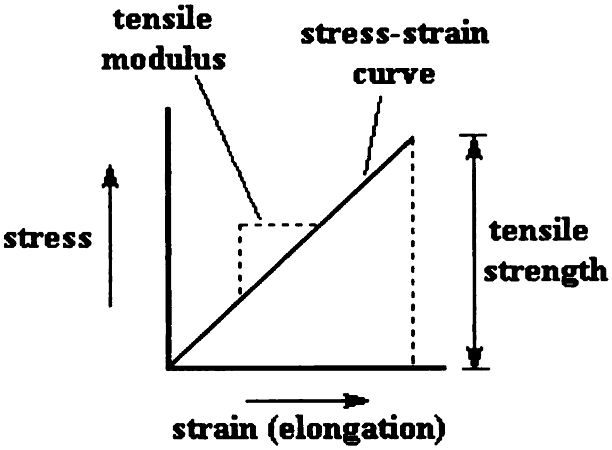

Figure 1. 2. A typical stress/strain curve for thermoplastic polymers.

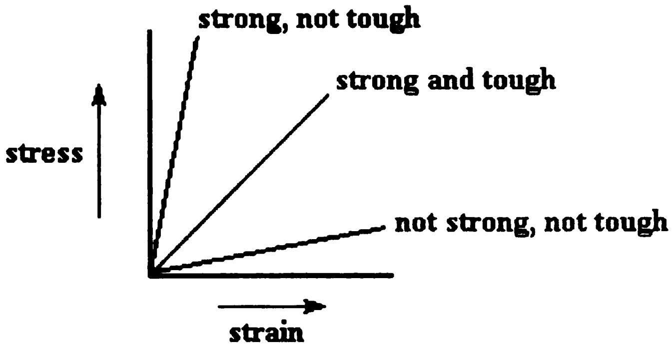

Figure 1.3. Typical stress/strain curves may obtain with plastic polymers.

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CHAPTER 2

Effect of High Pressure Processing on Permeance of Selected High-Barrier Laminated Films.

ABSTRACT

This study investigated the effects of high pressure processing (HPP) on the barrier properties of 8 multilayer films. Pouches made from the laminated films were filled with distilled water, heat sealed and then high pressure processed at 600 and 800 MPa for 5, 10 and 20 minutes at 45°C. Controls were similarly prepared but exposed to atmospheric pressure. After processing, all pouches were emptied, dried, and their oxygen, carbon dioxide, and water vapor permeance determined. All samples were tested in quadruplicate. Films used in this study were PET/SiO_x/LDPE, PET/Al_2O_3/LDPE, PET/PVDC/nylon/HDPE/PE, PE/nylon/EVOH/PE, PE/nylon/PE, metallized PET/EVA/LLDPE, PP/nylon/PP and PET/EVA/PET. Results showed that metallized PET was most severely affected by HPP. For this material, permeance values for oxygen, carbon dioxide, and water vapor showed increases as much as 150 %. Permeance changes in the other materials were small when compared to metallized PET.

2.1 INTRODUCTION

New food processing methods are continually being developed to produce better quality foods to meet consumers' demands. These demands include less severely processed, more natural, nutritionally healthier, and with food additives. One of these new process is high pressure processing (HPP) (Palou et. al., 1999; Pre, 1992). HPP of prepackaged foodstuff is steadily gaining ground as a method of food preservation, worldwide. Current HPP technology applied to liquid and paste foods uses high hydrostatic pressure in the range of 100-600 MPa for 2 to 10 min, to eliminate microorganisms and deactivate some enzymes, depending on the food type and process temperature (Mertens and Deplace, 1993; Palou et. al., 1999).

Although this treatment has been known as a potential food preservation technique for over a century, only in the last few years there has been rapid development in the engineering aspects of high-pressure technology. Thus, HPP provides the food industry an alternative method to produce foods of high nutritional and sensory quality, with more desirable texture and longer shelf life (Hayasi, 1995; Ledward, 1995). Foods can be processed in bulk followed by aseptic filling, or as individual prepackaged portions. High pressure processed foods have been marketed in Japan since the late 1980s. Since then, interest has also developed in the United States and Europe. High pressure processed foods have recently been introduced into these markets. During the high pressure process, pressures are transferred instantly and uniformly throughout the food system, even with air pockets within the package. Air pockets, however, should be avoided due to the high compressibility of gases compared to liquids. As a result, HPP will not be affected by the sample size and/or its geometry.

Previous research has shown that flexible packaging is more suited to HPP than rigid packaging (Mertens, 1993; Knorr, 1995). This is so because rigid packaging such as metal cans or glass bottles tend to fracture or become distorted. Even though flexible packaging such as polymeric films have been used to package foods processed by high pressure, there is little published research on the effects of such pressures on their chemical, mechanical and physical properties. Knowledge of any such effects would be of importance to the food industry and government food regulatory agencies. Changes in the permeation, migration, sorption, and package integrity, could affect negatively the product shelf life and quality. Specific changes that may occur due to HPP within the multilayer flexible structures will depend on the film composition and the HPP conditions. Based on these considerations, we have evaluated the permeation, migration and sorption of a series of high-barrier food packaging multilayer structures under a variety of HPP conditions. In this study we report and compare results for the permeability properties of the selected films.

2.2. Materials and Methods

The flexible structures investigated during this study are shown in Table 2.1. Pouches measuring 10 cm x 10 cm were fabricated from roll-stock of these materials and sealed using a Sencorp System, Inc. (Hyannis, MA) impulse heat sealer. For each structure, the best conditions for sealing were obtained by adaptation of sealing methods suggested by Lin et al. (1998). All pouches were filled with 150 mL of distilled water, then sealed with no headspace. For each test condition, two sets of pouches were prepared, one set was maintained at 1atm and 23°C, and the other one was processed at high pressures. This procedure was repeated twice (two blocks) for a total of four repetitions for each data point. The HPP conditions were 600 and 800 MPa for 5, 10 and 20 min at 45°C. Each test pouch was placed in a 10.5 cm x 10.5 cm 25.4-micron outer polyethylene envelope to protect the test pouches from direct contact with the HP liquid. The envelope containing the test pouch was vacuum-sealed using a Multivac 021-336 impulse sealer (Busch, Switzerland). After processing the test pouches were removed from the envelope. Control pouches were subjected to the same treatment except that pressure was 1 atm. Pouches were then emptied, opened, and dried before measuring the gas transmission rate. As indicated, four replicates were tested for each treatment.

Table 2.1. The composition of the test films used in this study.

Test film structures	Thickness (mil)	Manufacturer
PP/ 30 μm nylon-6/PP	4.6	Rexham Inc.
PET 12 μm /Al_2O_3 300Å /LDPE	2.5	GL-AE Toppan Co.
PET 12 μm/ SiO_x 300Å / LDPE	2.5	GL-AE Toppan Co.
Met-PET 12 μm /30%VA EVA/LLDP	2.0	Cello-Foil Pro. Inc.
PET/PVDC/nylon/HDPE/PE	4.1	Rexham Inc.
PE/nylon/EVOH/PE	2.5	Cryovac
PE/nylon/PE	2.0	Cryovac
PET/4%EVA	2.0	Cello-Foil Pro. Inc.
PP (single layer for comparison)	1.0	Tredegar Inc.

PP – Polypropylene

PET – Polyethylene terephthalate

Met-PET – Metallized polyethylene terephthalate

PE – Polyethylene

EVOH – Ethylene-vinyl alcohol

LLDPE – Linear low density polyethylene

HDPE – High density polyethylene

EVA – Ethylene-vinyl acetate

PVDC – Polyvinylidene chloride .

SiO_x – Silicon oxide

Al_2O_3 – Aluminum oxide

2.2.1. High-pressure apparatus

High pressure processing was done using a QFP-6 Tetra-Laval Quintal high pressure processor (ABB Autoclave System, Columbus, OH). This was located at the NCFST/FDA facilities in Summit-Argo, Illinois. This equipment had a 1 L pilot scale-processing vessel with an internal diameter of 6.0 cm by 18.8 cm in height, which allowed processing of two pouches each time. It was designed for a maximum pressure of 890 MPa and an operational temperature range of 5-70 °C. During analysis of the samples used in this study, the average time to attain the desired pressure was 2.3 ±0.25 min. The temperature at processing peaked to a maximum of 50°C but was maintained at 45 °C for the major part of each test run. The high-pressure transmission fluid used in this equipment was Houghto-Safe 620-TY (Houghton International, Valley Forge, PA), a glycol/water mixture. Processing conditions were as follows: two enveloped pouches were placed within the vessel filled with transmission fluid, clamped within the high-pressure chamber and then pressure processed.

2.2.2. Permeance

The outputs of the permeation apparatus were obtained either as steady state transmission flow rate F_V for oxygen and carbon dioxide, or steady state mass transmission rate F_M for water vapor. Units of F_V are $cm^3/m^2 \cdot d$ for oxygen and carbon dioxide, and $g/m^2 \cdot d$ for F_M of water vapor. The permeance (R) instead of the permeability coefficient is reported in this work for the multilayer films because of the non-polymeric nature of the metallized, aluminum oxide, and silica oxide coated layers in some of the films studied. Permeance was calculated as (Hernandez and Gavara, 1999):

$$R = \frac{F}{\Delta p} \quad (1)$$

Where F represents F_V or F_M and Δp is the partial pressure difference across the test film.

Because the area of each pouch was smaller than the required Permatran cell area, each film sample was mounted on a self-adhesive supporting 12 x 12cm paper/aluminum foil mask with a central circular opening of 5.00 cm^2. The mounted film was placed between the two half-cells of the respective permeation apparatus for testing. This procedure was followed for all measurements. Prior to running the test, both half-cells and the sample films were pre-conditioned for at least 2 h in a dry stream of nitrogen gas.

2.2.3. Water vapor transmission rate

The water vapor transmission rate (WVTR) of the test films was determined using a Permatran-W 3/31 Tester (Modern Controls, Inc., Minneapolis, MN), according to ASTM F 1249-90. Measurements were carried out at $37.8 \pm 0.5\,^{\circ}C$. The permeant high-pressure side of the cell was flushed with a nitrogen gas stream of about 10 mL/min humidified at 85% ±1% relative humidity (RH). The vapor was generated by flowing nitrogen gas into dionized water at 1.177 atm within the instrument. When this stream contacted the film it was at 1 atm of pressure. The permeant low pressure side of the cell was flushed with nitrogen carrier gas at 100 mL/min and 0% RH and also at 1 on of pressure. Therefore, the test was performed under a total pressure of 1 atm at both sides of the film. An infrared detector quantified the permeated water vapor molecules. The

apparatus was connected to a desktop computer. Output values were expressed as the steady state water vapor transmission rate (WVTR), calculated using Permw® - Windows® computer software. Polyethylene terephthalate (PET) film of standard WVTR was used to verify the operation of the Permatran W3/31.

2.2.4. Oxygen transmission rate

The oxygen transmission rate of the test film was determined in a 2-station Mocon Ox-TRAN® 200 (Modern Controls Inc., Minneapolis, MN), according to ASTM D 3985-81. The tester was equipped with a coulometric oxygen sensor sensitive to the 0.01 $cm^3/m^2 \cdot d$. Throughout the test, the permeant high-pressure side of the cell was swept with air at 20 cc/min at 1 atm. The partial pressure of oxygen was 0.21 atm. The low-pressure side of the cell was swept with pure nitrogen gas containing 1% hydrogen at atmospheric pressure at 30 cc/min, which conveyed the oxygen permeated to the detector. Measurements were carried out at $25 \pm 1^{o}C$. The Ox –TRAN 200 was connected to a desktop computer. Output values were expressed as the steady state oxygen transmission rate in $g/m^2 \cdot d$ using DOS computer software. Polyethylene terephthalate (PET) film of standard oxygen permeability was used to verify the machine conditions.

2.2.5. Carbon dioxide transmission rate

Carbon dioxide permeance was measured using a Mocon Permatran C-IV® carbon dioxide permeability tester (Modern Controls, Inc., Minneapolis, MN), using the static accumulation method which is recommended for high barrier films. Pure carbon dioxide gas of a flow rate of 80 cc/min was swept through the high-pressure permeant side of the cell. Permeated carbon dioxide was carried to the detector by nitrogen carrier gas at a flow rate of 200 cc/min. An infrared sensor interfaced with a strip-chart recorder measured the CO_2 concentration. Tests were conducted at 23 ± 1°C. The carbon dioxide transmission rate F_V was obtained as follows:

$$F_V = \frac{V \cdot H}{S \cdot A \cdot t} \tag{2}$$

where V is a constant calibration volume of 0.0248 mL, S is the infrared response peak corresponding to V, H is the infrared response peak of the permeated CO_2 accumulated in the detecting cell, A is the 5.00 cm^2 area of the film, and t is the accumulation time.

2.2.6. Statistical analysis

Experiments were planned to evaluate the combined effects of the pressure (600 and 800 MPa) and time (5, 10, and 20 min) factors on the barrier behavior of selected films. Permeance values were obtained in 2 trials consisting of 2 replicates each. A randomized complete block design was applied to the control samples (1 atm, 0 time) and samples processed at conditions determined by the arrangements of 600-5, 600-10, 600-20, 800-5, 800-10, and 800-20. Data collected were analyzed using a least squares mean generalized linear model (LSM-PROC GLM) in the statistical analysis software program (SAS Institute, Inc., 1990). The model assumes a fixed relationship between factors, differences between factors, and pair-wise differences between all combinations of factors. Statistical significance was defined as $p<0.01$.

2.3. RESULTS and DISCUSSION

2.3.1.Oxygen permeance

Figures 2.1 and 2.2 show the oxygen permeance for each film at 600 MPa and 800 MPa and at 5, 10, and 20 min respectively. It can be seen that PET/SiO_x, PET/Al_2O_3/PE, PET/EVA, PP/nylon/PP, and especially Met-PET showed differences in permeance after treatment by HPP when compared with their untreated counterparts. These differences are confirmed by the statistical analyses at a 99% confidence level.

The results obtained for Met-PET showed significant differences ($p<0.01$) in oxygen permeance between the HPP treated and untreated films. There were also significant differences between the films treated at 600 MPa for 5 and 10 minutes and those films treated at 800 MPa for 5, 10 and 20 minutes. Differences in permeance between Met-PET films treated at 600 MPa for 20 minutes and those treated at 800 MPa for 5 and 10 minutes, was not significant. There were also no significant differences in oxygen permeance between the metallized PET films treated for 5 min when compared to those treated for 10 minutes at both 600 and 800 MPa. Changes in permeance over the untreated samples are presented in Figures 2.3 and 2.4. These figures show that the largest increase in permeance (90%) was observed in Met-PET films treated at 800 MPa for 20 minutes.

Results for PP/nylon/PP show that there were significance differences in oxygen permeance between materials treated at 800 MPa for 10 and 20 minutes when compared to the untreated materials. Changes in permeance caused by HPP at 600 MPa and 800 MPa for 5 minutes, were not significant when compared to the untreated controls. Figure 2. 4 also shows the change in permeance for HPP treated PP/nylon/PP.

Although small in percent change, the statistical analyses showed significant increases in oxygen permeance for PET/SiO_x, PET/Al_2O_3/PE and PET/EVA. Maximum percent change in permeance for these materials shown in Figures 2.3 and 2.4 were at 800 MPa for 20 minutes. The respective percent increase were 10, 7 and 9%.

The oxygen permeance for PET/PVDC/nylon/HDPE/PE, PE/nylon/EVOH/PE, PE/nylon/PE, and PP was statistically unaffected by the HPP treatment. Comparing all 9 films, PE/nylon/PE showed the highest oxygen permeance value, which was significantly different from the other films. As expected, the lowest permeance values were seen in films with SiO_x, PVDC, Al_2O_3 and EVOH, since these components are high barrier materials. Although there were small changes in permeance between the untreated and treated PET/SiO_x, PET/Al_2O_3/PE films (less than 10%), they are nevertheless higher than, PE/nylon/EVOH/PE and PET/PVDC/nylon/HDPE/PE which are exclusively polymeric materials. This may indicate that inorganic base high barrier films are more susceptible to high-pressure treatment than polymeric films. This observation is further supported by the unaffected values of single-layer PP film.

In the case of Met-PET, permeance increased as a result of the HPP treatment, indicating that possible stretching of PET did not correspond to the metallized layer. The oxygen permeance changes observed in PP/nylon/PP were surprisingly high considering that no change was observed in PE/nylon/PE. Possible reasons for this result may be differences in material morphology and processing conditions. The PP/nylon/PP film was approximately twice as thick as the other films.

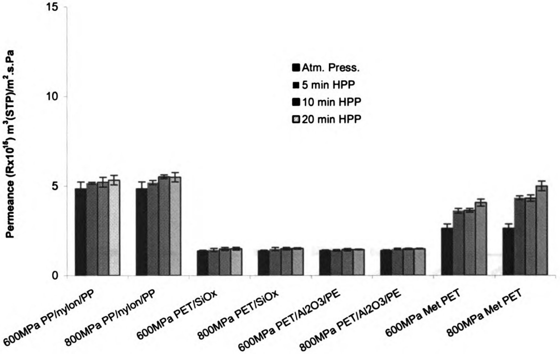

Figure 2.1. Oxygen permeance of multilayer films before and after HPP, at 23°C

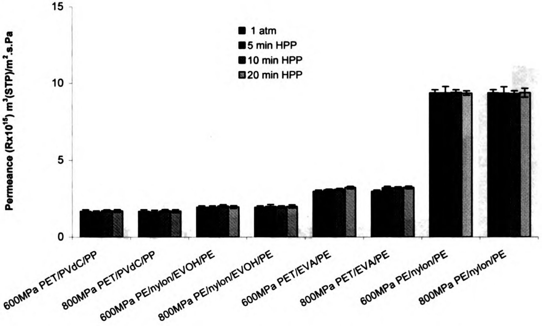

Figure 2.2. Oxygen permeance of multilayer films before and after HPP, at 23°C.

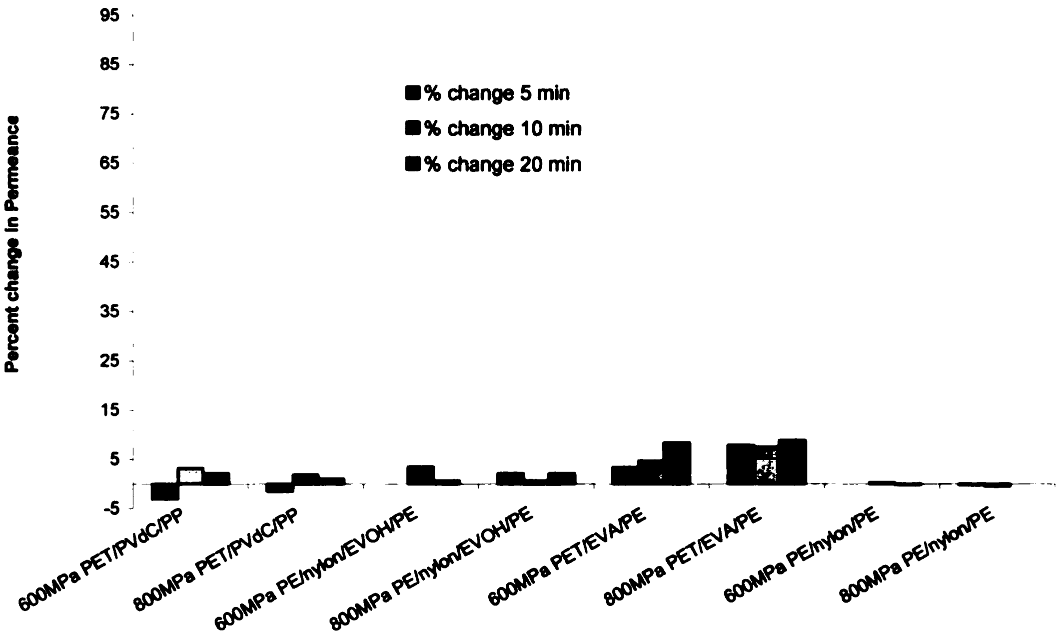

Figure 2.3. Percent change in oxygen permeance of multilayer films before and after HPP, at 23°C.

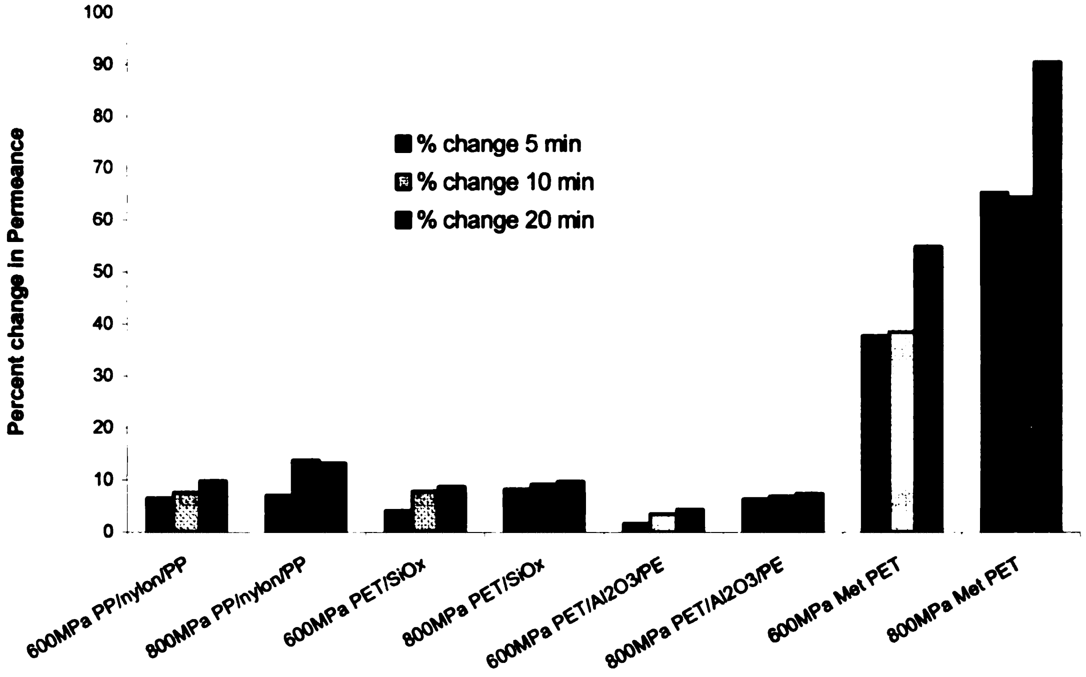

Figure 2.4. Percent change in oxygen permeance of multilayer films before and after HPP, at 23°C.

2.3.2. Water vapor permeance

The high-pressure process affected the water vapor permeance of PET/SiO_x, PET/Al_2O_3/PE, PET/PVDC/EVA, PP/nylon/PP and metallized PET (Figures 2.5 and 2.6). The statistical analyses showed that there were significant differences between the control films and the films treated at 600 and 800 MPa. The effects of HPP treatment on the water vapor permeance of the other films were insignificant. The percent changes in water vapor permeance for these HPP treated films are shown in Figures 2.7 and 2.8.

Significant increases ($p<0.01$) in water vapor permeance for PP/nylon/PP were seen in films treated at 600 MPa for 10 and 20 minutes and at 800 MPa for 20 minutes when compared to the control in each case. For PET/SiO_x, significant changes between the control and the treated film were observed for films pressured at 600 MPa for 20 minutes and at 800 MPa for 10 and 20 minutes. Significant increase in permeance caused by the increase in treatment times from 5 to 10 minutes at 600 MPa and from 5 to 20 minutes at 800 MPa were also observed for the PET/SiO_x, Similar results were also obtained for the PET/Al_2O_3/PE and PET/EVA materials. However, for PET/EVA, significant differences in permeance were also seen between the control and the films treated at 600 MPa for 5 and 10 minutes.

As in the case of oxygen, the largest changes in water vapor permeance for all the materials were seen in the metallized PET. Figure 2.7 shows a change of approximately 150% for that material treated at 800 MPa for 20 minutes. This large change in permeance resulted from the high-pressure treatment were much higher than change in the permeance for oxygen and carbon dioxide. For the other materials, changes in water vapor permeance were generally lower than those obtained for oxygen and carbon dioxide.

Relatively high permeance values were obtained for PE/nylon/EVOH/PE. Both EVOH and nylon are hydrophilic and we should expect relatively high water permeance values even though they have relatively low permeability to oxygen at dry conditions. When exposed to moisture, EVOH and nylon materials can show increased oxygen permeance (Hernandez, 1994).

The water vapor permeance of PP/nylon/PP compared to PE/nylon/PE is probably due to differences in sample themselves or the individual layers and overall thickness. As expected, structures containing PVDC, SiO_x, and Al_2O_3 had low water permeance values compared to nylon, PET and EVA based films.

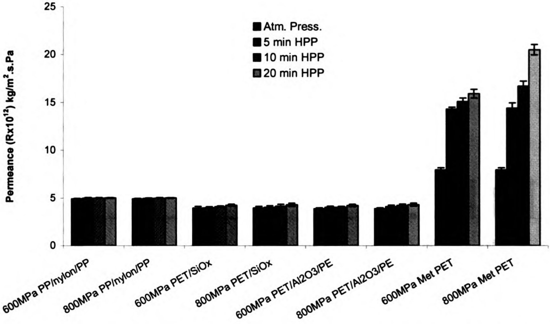

Figure 2.5. Water vapor permeance of multilayer films before and after HPP, at 37.8°C.

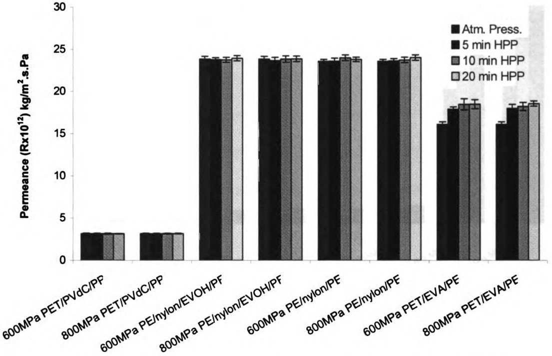

Figure 2.6. Water vapor permeance of multilayer films before and after HPP, 37.8°C.

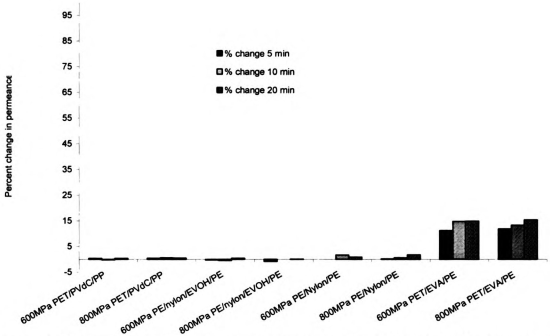

Figure 2.7. Percent change in water vapor permeance of multilayer films before and after HPP, at 37.8°C.

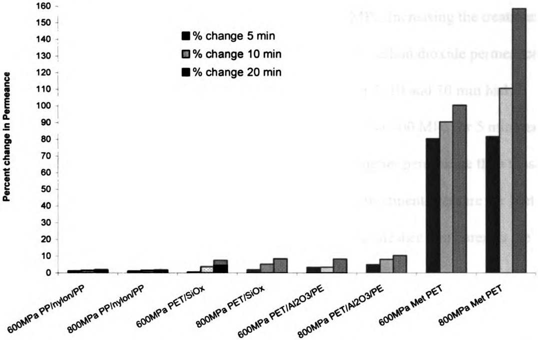

Figure 2.8. Percent change in water vapor permeance of multilayer films before and after HPP, at 37.8°C.

2.3.3. Carbon dioxide permeance

Permeance values of carbon dioxide through films (except PP/Nylon/PP) were from 2 to 5 times higher than for the respective oxygen permeance (Figures 2.1, 2. 2, 2. 9, and 2.10). The CO_2/O_2 permeance ratio was 3.8 for the single-layer polypropylene. These values are in very good agreement with the ratio of CO_2/O_2 permeability coefficients for single layer polymers (Hernandez, 1997). The CO_2/O_2 permeance ratio of PP/Nylon/PP, however, was 0.4 which is much lower than expected. The statistical analysis showed that there were significant differences ($p<0.01$) between all the Met-PET films treated by HPP for 600 and 800 MPa compared to their untreated counterparts. For those films treated at 600 MPa, increasing the treatment time from 5 to 20 min resulted in significantly increased carbon dioxide permeance. At 800 MPa, increasing the treatment times from 5 to 10 or 20 minutes had no significant effect on carbon dioxide permeance. However, the Met-PET pressure treated films at 800 MPa for 5, 10 and 20 min had significantly higher permeance than the same material treated at 600 MPa for 5 minutes. Films treated for 800 MPa for 20 minutes had significantly higher permeance than those treated at 600 MPa for 10 and 20 minutes. Thus, increasing treatment pressure for Met-PET resulted in more significant change in carbon dioxide permeance compared to the effect of changing pressure times.

The results obtained for PP/nylon/PP showed that the carbon dioxide permeance for this material was significantly increased only pressure treated film for both 600 and 800 MPa at 20 minutes when compared to the controls. Both treatment pressures at 20 minutes had the same effect on permeance for PP/nylon/PP because there was no significant difference ($p<0.01$) in permeance for carbon dioxide at 600 when compared to 800 MPa for 20 minutes. Thus, increasing the pressure from 600 to 800 MPa had no significant effect on permeance for 20 minutes of treatment. Similar results were obtained for PET/EVA and PET/Al_2O_3/PE. PET/EVA and PET/Al_2O_3/PE were significantly different between 600 and 800 MPa for 20 minutes and control

The results obtained for PET/SiO_x showed that both increase in treatment pressure and in processing times produced significant increase in carbon dioxide permeance. Significant differences in permeance were seen after the material was treated at 600 MPa for 20 minutes and at 800 MPa for 10 and 20 minutes when compared to the control.

Even though significant differences in carbon dioxide permeance were observed in all materials treated by high pressure, these changes were small when compared to metallized PET (Figures 2. 11 and 2. 12).

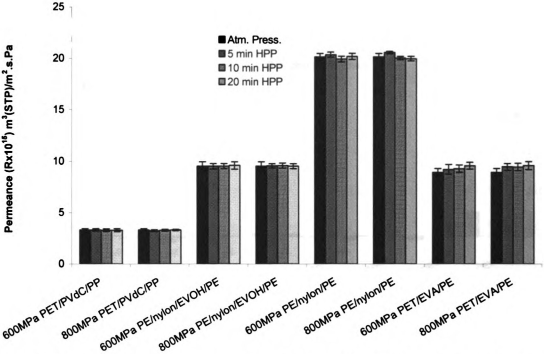

Figure 2.9. Carbon dioxide permeance of multilayer films before and after HPP, at 23°C.

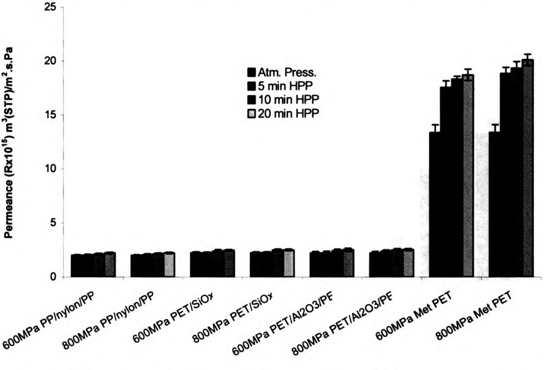

Figure 2.10. Carbon dioxide permeance of multilayer films before and after HPP, at 23°C.

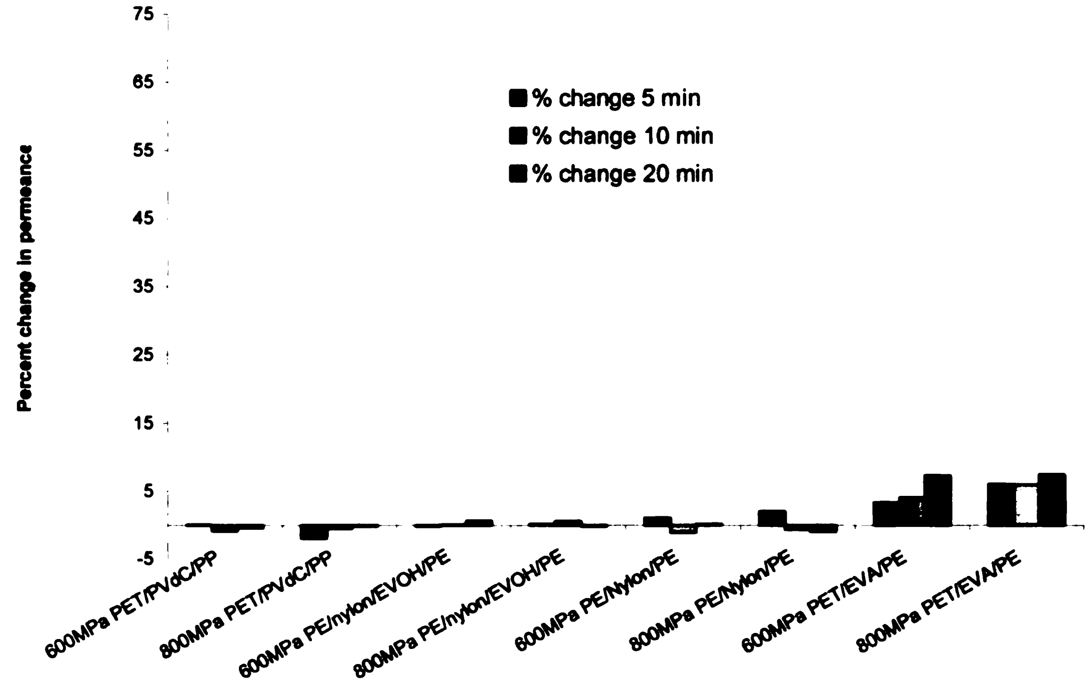

Figure 2.11. Percent change in carbon dioxide permeance of multilayer films before and after HPP, at 23°C.

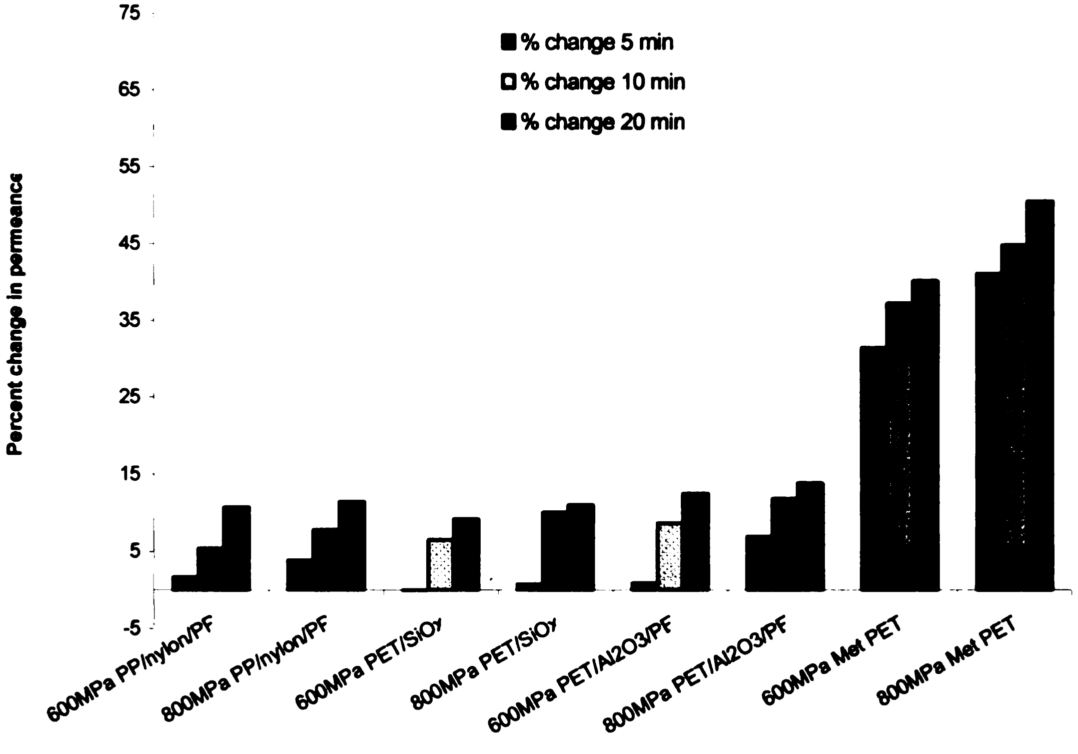

Figure 2.12. Percent change in carbon dioxide permeance of multilayer films before and after HPP, at 23°C.

2.4. CONCLUSION

From the results obtained during this study, it can be concluded that 1) for the inorganic-coated structures, 800 MPa and longer processing times seem to have a more pronounced effect on permeance change than 600 MPa and shorter exposure times. 2) The metallized PET was most severely affected by the high pressure processing. 3) The most severe effects were seen in changes to the water vapor transmission rate because of the smaller molecule size when compared to oxygen and carbon dioxide. 4) Apart from metallized PET, changes in permeance occurring in the other materials were fairly small, even though statistically significant in some cases. 5) Increases in permeance in structures other than Met-PET were less than 12%. Therefore, these changes may have small or no impact on the shelf life of the packaged foods. This, the structures used in this study may be well suited for high pressure processing. This was indeed the case as reported by Masuda et al. (1992) and Barnes (1992) who studied the effects of HPP at 400 and 600 MPa respectively, and found that the barrier materials investigated were not severely affected by those pressures.

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CHAPTER 3

Study of High Pressure Processing Effects on Flexible Food Packaging Structures by Mechanical Analysis, Scanning Electron Microscopy, and Ultrasonic Imaging

ABSTRACT

The effects of high pressure processing (HPP) on the mechanical and physical characteristics of 8 high-barrier multilayer films were investigated. This study also investigated the presence of micro defects in the films. These defects may have been caused by HPP. The films tested during this study were PET/SiO_x/LDPE, PET/Al_2O_3/LDPE, PET/PVDC/nylon/HDPE/PP, PE/nylon/EVOH/PE, PE/nylon/PE, metallized-PET/EVA/LLDPE, PP/nylon/PP, and PET/PVDC/EVA. In addition, PP was evaluated for comparison purposes. Pouches made from the films were filled with distilled water, sealed, then pressure processed at 600 and 800 MPa for 5, 10, and 20 minutes at 45°C. Pouches kept at atmospheric pressure were used as control. Prior to and after HPP, tensile strength, percent elongation, modulus of elasticity, scanning electron microscopy (SEM), and scanning acoustic microscopy (C-SAM) measurements were taken for each film. Results showed that no significant changes in tensile strength, elongation and modulus of elasticity of the films were detected. However, physical damage to the metallized-PET films was identified by SEM and C-SAM analyses.

3.1. INTRODUCTION

High pressure processing (HPP) is now used in conjunction with other novel, non-thermal food processing techniques such as pulsed electric fields, irradiation (including pulse light, electron beam, ultra violet light, gamma and x-rays) ultrasound and ozone treatment for food preservation (Cherry, 1999; Liangi, 1999; Sizer and Balasubramaniam, 1999; Thayer and Rajkowski, 1999). Interest in these technologies has been gaining ground within the United States because of consumers' demand for higher quality foods with more homestyle taste and appearance(Karel, 2000; Sloan, 1999). Applied to foods HPP in the range of 400 to 850 MPa has been shown to deactivate enzymes and reduce bacterial load (Aleman et al. 1998; Anathy et al. 1998). Since it requires less heat than traditional thermal techniques such as retorting and pasteurization, HPP leaves the food with little textural change and less vitamin and flavor loss. HPP technology offers the food industry the opportunity to develop food with more convenience, safety and extended shelf life (MacDonald et al. 2000). The recent introduction of continuous HPP systems in the United States has made it possible for processors to treat pumpable foods at commercial machine speeds followed by aseptic packaging. However, batch HPP systems are also available and can be used to treat non-pumpable foods and other prepackaged liquid and semi-solid foods in small portions. HPP has also shown to be an environmentally friendly alternative process because it uses less energy compared to thermal processing techniques (Denys and Hendrickx, 1999; Prestamo and Arroyo, 1998). The use of plastic-based flexible packaging films has allowed the application of high-pressure processing to pre-packaged foods. These materials have been shown to withstand the process without visible signs of integrity loss (Barnes, 1992). However, there is limited published data on the effects of HPP on the physical, mechanical, and package integrity characteristics of packaging materials. HPP treatment of prepackaged foods may cause defects in certain plastic packaging structures, which could result in loss of package integrity or at least compromise its barrier and safety characteristics.

Rigid packaging is not suitable for HPP since it has been shown to be susceptible to fracturing or distortion when exposed to high pressures (Barnes, 1992).

One of the most important factors that has contributed to the success of plastic films and sheets for food packaging is the availability of multilayer structures produced either by lamination or coextrusion. A flexible multilayer structure used for pre-packaged food HPP must have sufficient flexibility and resilience, and must resist delamination between layers during the compression process. Flexible structures in which HPP produces the formation of micro pockets in some of the layers may eventually compromise the safety of the package. In the converting industry, different materials are used to produce laminated structures. These include polymers such as PVDC, metals such as aluminum used for vapor deposition on plastic films like PET, and inorganic coatings such as silicon and aluminum oxides also used to coat plastic films. If the components of a multilayer structure show widely differing compressibility and resilience behavior under HPP, the film may exhibit a loss of integrity. For food products with extended shelf-life, these changes may be precursors to major food safety and quality issues.

Changes in the integrity of a multilayer film may be very small and difficult to detect. One way to study them is by using molecular probes such as permeation to gases and vapors. Other methods include acoustic imaging and electron microscopy. Scanning electron microscopy (SEM) has been used successfully to visualize evidence of mechanical deformation on the surface of various plastics (Choudry et al. 1998). However SEM gives information about the surface rather than inside of a multilayer materia.

C-mode scanning acoustic microscope (C-SAM) uses sound waves instead of light to produce images, and has the documented ability to detect, classify, and accurately reproduce the integral structure of opaque materials or components using high frequency ultrasound in the range of 5 to 500 MHz. C-SAM allows scanning and imaging of heterogeneous materials such as multilayer structures samples based on the intensity of acoustic waves reflected by the various constituents of the sample. This is done at variable depth and without destroying the test specimen. Since reflection intensity is based on impedance contrast, a change in the elastic properties between two constituents or within one constituent can be easily detected. Ultrasound is extremely sensitive to air gaps and gaps as small as 10^{-7}m can be detected. C-SAM uses pulse-echo technology in which a focused beam of ultrasound is pulsed into a sample. Reflections of the ultrasound beam are then received from the sample and processed by the electronics according to their phase amplitude. Ultrasound techniques have been used for detecting and visualizing hidden defects such as voids, cracks, folds, lamination, delamination and porosity in solid samples (Chen et al. 1991; Hafsteinsson et al. 1989; Ozguler et al. 1998; Povey and McClements 1988; Safvi et al. 1997).

In the present work we report the results of the effects of HPP on mechanical behavior by measuring the tensile properties, and use of SEM and C-SAM techniques to visualize the microstructure of the flexible films. These results are compared to the permeability results on the same structures from chapter 2.

3.2. MATERIALS & METHODS

Table 3.1 shows the multilayer films investigated during this study. These films were used to prepare 10 x 10 cm pouches using a Sencorp System, Inc. (Hyannis, MA) impulse heat sealer. The pouches were fabricated, sealed, filled with distilled water and high pressure processed as described in chapter 2. For each test condition, two sets of pouches were evaluated, one set was maintained at 1 atm and 23 ±1°C (control), and the other processed at high pressures. Four replicates were run for each material and each replicate was analyzed twice. The HPP conditions were 600 and 800 MPa for 5, 10 and 20 min at 45°C. After HPP, all pouches were emptied, opened, and dried before analysis for mechanical strength and electron microscopy. Control pouches were immersed in distilled water at 50°C for 20 minutes but maintained at 1 atm prior to testing.

3.2.1. High-pressure apparatus

High pressure processing was carried out using a QFP-6 Tetra-Laval Quintal high pressure processor (ABB Autoclave System, Columbus, OH) located at the National Center for Food Safety and Technology (NCFST) facilities in Summit-Argo, Illinois. This equipment had a 1 L pilot-scale processing vessel with an internal diameter of 6.0 cm by 18.8 cm in height. It was designed for a maximum pressure of 890 MPa and an operational temperature range of 5-70°C. During analysis of the samples used in this study, the average time to attain the desired pressures was 2.3 ± 0.25 min. The temperature at processing peaked to a maximum of 50°C but was maintained at 45 °C

($\pm 0.5\,^{o}C$) for the major part of each test run. The high-pressure transmission fluid used in this equipment was Houghto-Safe 620-TY (Houghton International, Valley Forge, PA), a glycol/water compound. For each run the following procedure was applied: 1) the pouch sample was immersed in the transmission fluid, 2) the pressure chamber was secured by a built-in locking device, and 3) the high pressure was activated.

3.2.2. Scanning Electron Microscopy

For this study, environmental scanning electron microscopy (ESEM) was used because of its ability to reveal sharp surface topography images of a specimen. The equipment used was an Electro Scan 2020 scanning electron microscope (Electroscan, Boston, MA). The test films were prepared by cutting 2 cm x 3 cm strips from each material treated by HPP and from the controls. Each strip was mounted onto the microscope specimen chamber by attaching it on a sample holder and positioning it along the electron beam pathway according the manufacturer's instructions. The pressure of the specimen chamber was maintained at 380 Pa while the electron gun chamber was kept at 1.33×10^{-5} Pa. The acceleration voltage was set at 12 kV for a working distance of 8 mm. During adjustment of the magnification the acceleration voltage was kept constant.

3.2.3. Scanning Acoustic Microscope

Scanning acoustic microscopy images were obtained on a Sonoscan D9000 C-mode Scanning Acoustic Microscope (C-SAM) (Sonoscan Inc. Bensenville U.S.A). The C-SAM uses "pulse-echo" technology, which includes a 100-230 MHz ultrasound beam, and allows for detection of internal damage and/or delamination in the multilayer structures. C-SAM in-depth information supplements the SEM superficial images. Samples were placed in the sample holder under the acoustic beam. Reflections of the sound were captured by a pulser-receiver and digitally processed according to their phase and amplitude. The images were constructed by making each pixel correspond to a data point in the sample and the phase/amplitude information from the reflections was assigned a pixel value. The number of pixels per image was 1024 x 920.

Images of both HPP treated and control (untreated) film samples were obtained using a 230 MHz ultrasound beam. The resolution of the transducer was 0.11 mm and the field of view for the images was 10.4 x 7.9 mm. Voids and delaminations block the transmission of ultrasound and appear in the images as bright white areas.

3.2.4. Tensile stress, strain, and modulus of elasticity

Tensile strength (TS), percent elongation at break (E), and modulus of elasticity (MOE) for each material (treated and controls) were measured using a Model 4201 Instron® (Instron, Canton, MA). From each material, two sets of 2.5 cm x 10.0 cm sample strips were prepared. One set was taken along the machine direction and the other along the cross directional orientation of each film. Film thickness (see Table 1) was measured using a micrometer model 549 TMI (Micrometer Testing Machines, Inc., Amityville, NY). The Instron tester was fitted with a 1 kN tension load cell. The jaws were set at 5 cm apart and the crosshead speed adjusted to 50 cm/min. All measurements were carried out at 23 °C (± 1 °C), and at 50% relative humidity. All samples were pre-conditioned by exposing them to these conditions for 24 hours prior to testing. Tensile strength was calculated by dividing the maximum load by the cross-sectional area. Strain at break was calculated by dividing the increased length at the moment of rapture by the initial length of the specimen. Modulus of elasticity was calculated from the slope of the elastic portion of the tensile stress versus strain curve.

3.2.5. Statistical analysis

This research investigated the effect of pressures (600 and 800 MPa) and processing times (5, 10, and 20 min) on the mechanical properties of the selected flexible materials. Mechanical properties were evaluated by analyzing 4 replicates of each film sample. Each test was repeated once. Each sample was analyzed for the effect of pressure and time on tensile strength, percent elongation and modulus of elasticity. The results obtained from these analyses were compared with the outputs obtained from the electron microscopy imaging of the sample materials. A completely randomized block design was applied to the controls and the samples processed at 600 MPa for 5 minutes (600-5), 600 MPa for 10 minutes (600-10), 600 MPa for 20 minutes (600-20), 800 MPa for 5 minutes (800-5), 800 MPa for 10 minutes (800-10), and 800 MPa for 20 minutes (800-20). The data collected were analyzed using a least square means generalized linear model (LSM-PROC GLM) of the statistical analysis software program (SAS, 1990). The model assumed a fixed relationship between factors, differences between factors, and pair-wise differences between all combinations of factors. Statistical significance was defined at $p < 0.01$.

Table 3.1. Composition of the test films used in this study.

Test film structures	Thickness (μm)	Manufacturer
PP/ 30 μm nylon-6/PP	115	Rexham Inc.
PET 12 μm /Al_2O_3 300Å /LDPE	62.5	GL-AE Toppan Co.
PET 12 μm/ SiO_x 300Å / LDPE	62.5	GL-AE Toppan Co.
Met-PET 12 μm /30%VA EVA/LLDPE	50	Cello-Foil Pro. Inc.
PET/PVDC/nylon/HDPE/PP	102.5	Rexam Inc.
PE/nylon/EVOH/PE	62.5	Cryovac
PE/nylon/PE	50	Cryovac
PET/PVDC/4%EVA	50	Cello-Foil Pro. Inc.

PP – Polypropylene
PET – Polyethylene terephthalate
Met-PET – Metallized polyethylene terephthalate
PE – Polyethylene
EVOH – Ethylene-vinyl alcohol
LLDPE – Linear low density polyethylene
HDPE – High density polyethylene
EVA – Ethylene-vinyl acetate
PVDC – Polyvinylidene chloride
SiO_x – Silicon oxide
Al_2O_3 – Aluminum oxide

3.3. RESULTS AND DISCUSSION

Untreated (control) and HPP-treated polymeric sample films cut from the pouches were analyzed for mechanical performance in both the machine and cross directions. Machine direction (MD) refers to the parallel to which the film is wound by the uptake spool. In general, polymeric molecules are preferentially aligned in the MD as a result of the applied stress during the spooling and extrusion processes. Cross direction (CD) is the orientation perpendicular to the machine direction and the polymeric chains tend to be less aligned with respect to it. Since the results of the mechanical analyses of most polymeric films depend on whether the mechanical forces are applied in the MD or CD, both directions were evaluated.

The tensile strength, percent elongation, and modulus of elasticity values, both in MD and CD, for each material are shown in Figures 3.1 to 3. 6. These figures show little difference between the results obtained for the controls (non HPP treated) and the films treated at 600 and 800 MPa for 5, 10, and 20 minutes at 45°C. The statistical analyses shows that there were no significant differences ($p<0.01$) between the controls and the treated samples, both in the MD and CD, and within the treated samples at different time and pressure conditions. Similar results were reported by Masuda et al. (1992). These authors found no significant changes in the tensile strength and percent elongation of LLDPE/EVA/EVOH/EVA/LLDPE and PET/Al Foil/PP structures before and after pressure treatment at 400 MPa for 30 minutes at 60°C. Similarly, Mertens (1993) reported no significant effects caused by HPP on the tensile strength of PP/EVOH/PP, OPP/PVOH/PE, PVDC-coated-OP/CPP and PET/Al/CPP films treated at 400 MPa and 600 MPa for 10 min at 20°C. Also, no significant changes were found in to the tensile strength or percent elongation of pouches made of PP/PVDC/PP and high pressure processed at 400 MPa.

The superficial SEM micrographs for the control and treated films except the metallized-PET, at the 10-micrometer scale are shown in Figure 3. 7. The images show the food-contact side of the films. Processing values were 800 MPa and 20 minutes, which represents the more severe conditions. Monolayer polypropylene film was also included for reference purposes since it is a homogeneous plastic film with good resilience, and therefore is able to absorb the high-pressure impact without mechanical deformation, as confirmed by the images. Overall, no micro cracks or fissures were shown on any structure (Figure 3.7) that could weak the films; this corroborates the mechanical measurements. However, it appears that for PET/Al_2O_3/LDPE , PET/SiO_x/LDPE, and PET/PVDC EVA some superficial small wrinkles were created during HPP at the food-contact side of the films. From the SEM images we cannot deduct how these wrinkles were created, but again they did not affect the mechanical performance.

Figure 3. 8 shows the micrographs for the controls, and the 600 and 800 MPa treated metallized PET samples at 10-micrometer scale. These micrographs also confirm the absence of cracks or fissures in the structures after the HPP treatments. However, numerous and more pronounced wrinkles are seen on the food-contact layer. It appears that the extent of these deformations tends to increase with increasing exposure times at both 600 and 800 MPa pressures for the metallized PET. As with the other structures of figure 3. 7, the presence of wrinkles does not affect the mechanical performance of this film.

Because coating layers are normally very thin compared with the thickness of the polymeric layers (for example, 3 x 10^{-8}m of coating versus 5 x 10^{-5} m for the polymer), they do not significantly contribute to the material's mechanical strength. This means that we cannot detect any damage in the barrier layer by the measuring the mechanical properties, or by observing the external layer such as in SEM analysis. However one practical consequence of the rupture in the continuity of a barrier layer in a multilayer structure is an increase in the permeability to gases. Lambert et.al. (2000) suggested that only changes in barrier properties exceeding 25% are of industrial significance. Using this criterion, only metallized -PET would be unsuitable for high pressure processing at conditions similar to those used in this study. In order to confirm that metallized PET films could have been damaged at the metal barrier layer we carried out C-SAM studies. C-SAM micrograph images of the metallized-PET were obtained for untreated and HPP treated film pouches (Figure 3.9). Micrographs consist of black and white images that are composed of gray levels. The white areas correspond to the highest amplitude of reflected acoustic signal, i.e. highly reflecting areas. In Figure 3.9, the white areas are seen in the samples that were HPP treated, which indicate micro defects in the metallized structure. According to C-SAM theory, the white areas are considered to be the result of micro voids in the middle of the polymer film. Differences between treated and control films are also well apparent in Figure 3.9. The heterogeneous acoustic reflectivity was due to partly to an uneven surface. In these regions, the plastic structure could be interpreted as ruptured in the continuity of the atomic aluminum coating deposited on the PET layer. This unequivocally confirms the weakening of the barrier property of the metallized-PET structure while maintaining its mechanical performance. This study has clearly demonstrated that C-SAM can be useful to identify the existence of defects and properties, at the resolution of micro- and nanometer range. It is a very effective and precise way to image defects in certain food packaging structures. Even though some of structures have potential problems after high pressure treatment, flexible multi-material structures are the most suitable materials for prepackaged food products processed using high pressure (Mertens, 1993; Mertens, 1995; Lambert et al. 2000). Packaging design is still one of the important challenges for the high pressure processing industry (Knor, 1996).

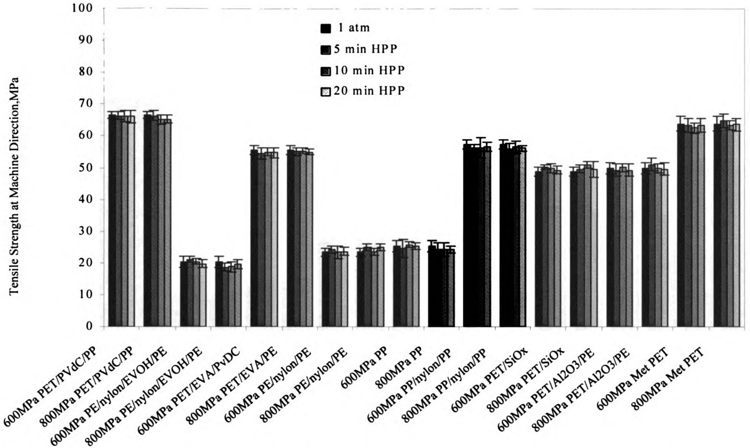


Figure 3.1. Tensile Strength (MPa) of plastic films at machine direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

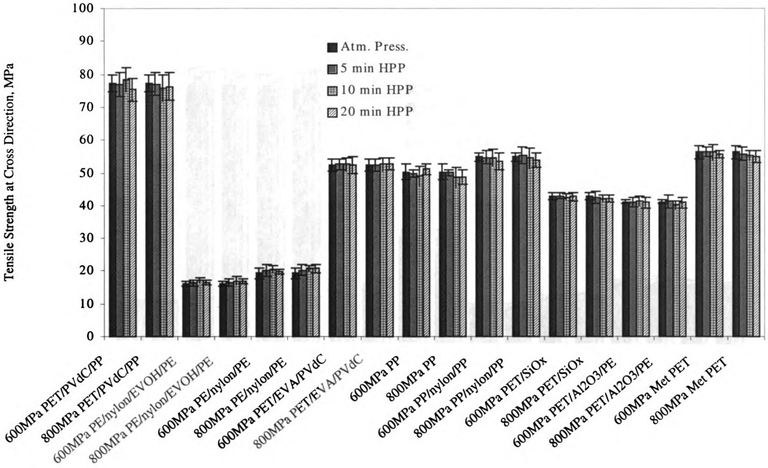


Figure 3.2. Tensile Strength (MPa) of flexible structure at cross direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

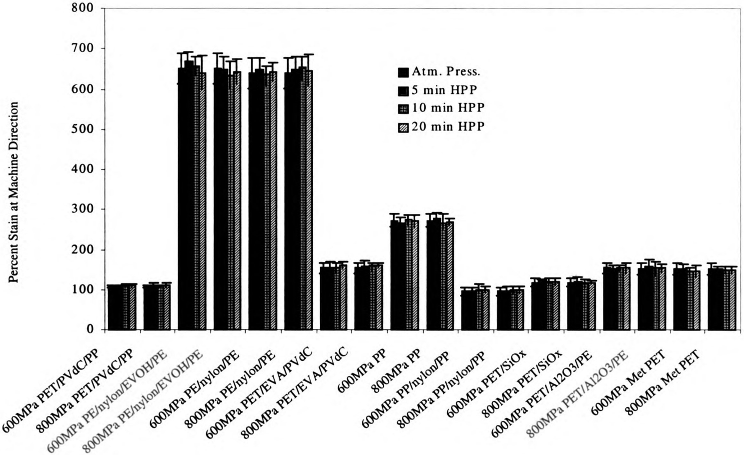


Figure 3.3. Percent Stain of flexible structure at machine direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

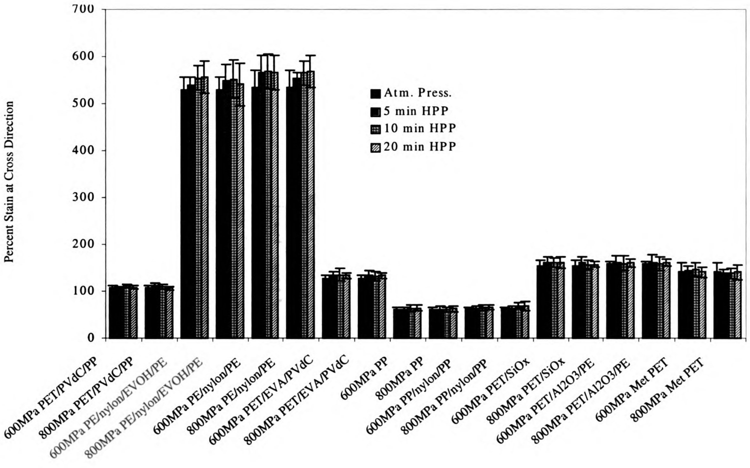


Figure 3.4. Percent Stain of flexible structure at cross direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

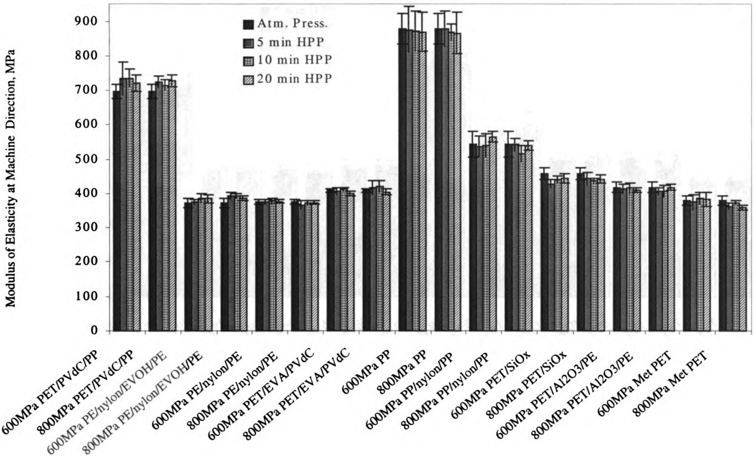


Figure 3.5. Modulus of Elasticity (MPa) of flexible structure at machine direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

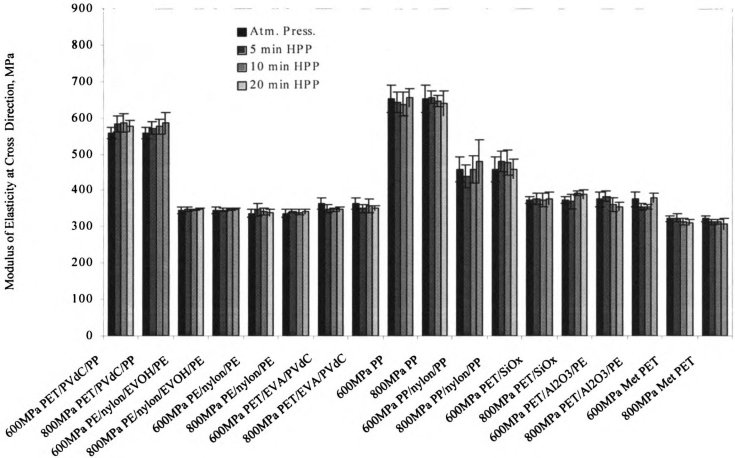
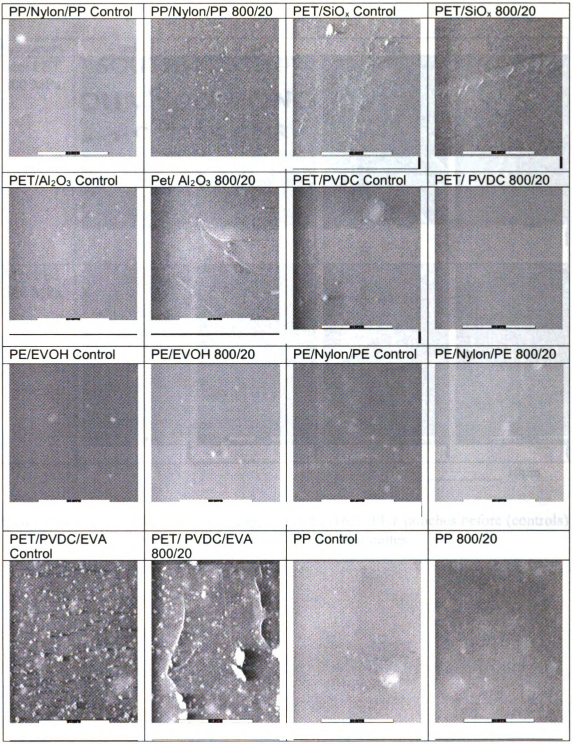


Figure 3.6. Modulus of Elasticity (MPa) of flexible structure at cross direction before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.



800/20=800 MPa at 20 min

10μm

Figure 3. 7. Scanning electron micrographs of PP/ Nylon-6/ PP, PET / Al$_2$O$_3$/ LDPE, PET /SiOx/ LDPE, PET/PVDC/Nylon/HDPE/PP, PP/EVOH/Nylon/PP, PE/Nylon/PP, PET/PVDC/EVA and PP films before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

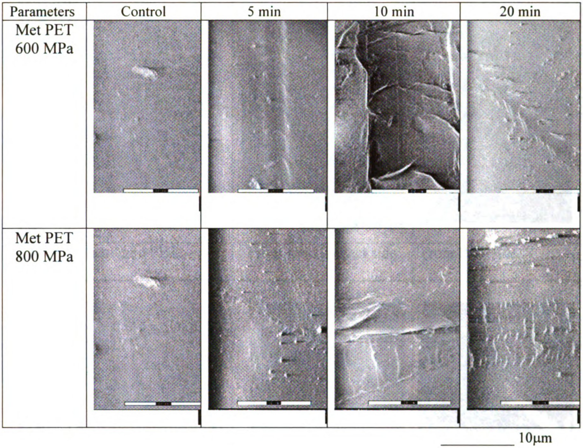


Figure 3. 8. Scanning electron micrographs of metallized -PET pouches before (controls) and after HPP treatment at 45°C for 5, 10 and 20 minutes.

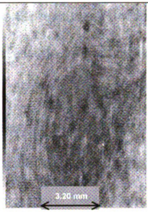
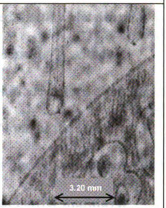
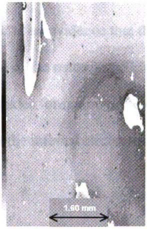
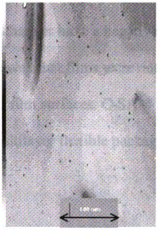
MET -PET	Metallized PET	From food contact side	From PET Side
Control Untreated10 min 45 °C			
MET -PET	Metallized PET	From food contact side	From PET side
Treated 800 MPa 10 min 45 °C			

Figure 9. Scanning acoustic micrograph of metallized -PET pouches before (controls) and after HPP treatment at 800MPa and 45°C for 10 minutes.

3.4. CONCLUSION

From the results obtained in this study, it can be concluded that: 1) Metallized-PET showed the most structural damage after high pressure processing. 2) Although PET/Al_2O_3, PET/SiO_x and PET/PVDC/EVA also showed some surface deformation, it was to a lesser extent than what was seen in metallized-PET. 3) None of the tested materials showed significant changes in mechanical strength even though some showed surface deformation. This research demonstrated that certain high barrier multilayer films can be affected by HPP. The magnitude of these changes depends on the type of structure and the processing conditions. Even though some materials can be affected by HPP, we found no evidence that these changes have a negative impact on the performance of the materials. SEM showed that films were not perforated or cracked but showed wrinkles formation on selected film surfaces. C-SAM analyses are useful tools in the study of the internal structure of multilayer flexible packaging materials.

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CHAPTER 4

The Effect of High-Pressure Food Processing on the Sorption Behavior of Flexible Packaging Polymeric Films

ABSTRACT

The sorption behavior, or flavor scalping, of selected, flexible polymeric films filled with food simulant liquids based on ethanol and acetic acid aqueous solution was evaluated after high pressure processing (HPP). Films used were single layer polypropylene (PP), multilayer PE/nylon/EVOH/PE, and metallized PET/EVA/LLDPE. The sorbate d-limonene, a component of the liquid simulant, was evaluated in both the polymeric structures and the food simulants, at the HPP conditions (800 MPa, 10 min, 60 °C) and in an untreated control (1atm, 60°C, 40°C) as a function of time. Analysis was performed using a purge/trap and extraction technique and also gas chromatography (GC). Results showed that d-limonene concentration, both in the polymers and in the food simulants (in pouches) made of PP and PE/nylon/EVOH/PE was not significantly affected by HPP. However, the metallized PET/EVA/LLDPE showed a significant difference in d-limonene amount with respect to the control pouches. These results also correlate with those obtained in previous studies. As expected, changes in temperature significantly affected the sorption behavior of all polymers. While PP and PE/nylon/EVOH/PE films retained their d-limoenene amount, the metallized-PET clearly did not.

4.1 INTRODUCTION

With increasing consumer demand for fresh-like and high quality foods with more home style taste, there has been growing interest in development of new food processing methods such as pulse electrical fields, irradiation, and high pressure processing (HPP). Interest in HPP is steadily gaining important ground as a food preservation method that maintains natural sensory and nutritional attributes (Gould, 2000). HPP can kill microorganisms and inactivate enzymes by the physical action of very high pressures, which are in the order of 100 to 800 MPa. In addition, HPP is a technique that can produce uniform effects throughout the product, at low application temperature ranges (0°C to 60 °C), causing effective preservation, and safe and comparatively easy operation (Farkas and Hoover, 2000; Lambert et al., 1999). Today HPP is commercially used in the Europe and Japan for processing products like fruit juice, guacamole paste, and tomato-based salsa production (Neil, 1999). Liquid or solid foods can be high-pressure processed with or without packaging (Farkas and Hoover, 2000). Flexible packaging structures allow prepackaged foods to be processed by HPP, and therefore, prevents subsequent recontamination by microorganisms. Flexible packaging structures are made from single or multilayer, coated or uncoated, polymeric materials. Ideally, HPP should not affect to any degree the integrity of the packaging structure.

Besides mechanical considerations, another important issue is that HPP may affect plastic behavior regarding molecular mass transport between food and packaging such as sorption and migration (Mitsui et al., 1992). This could affect the organoleptic and nutritional quality attributes of the packaged product (Hernandez and Gavara, 1999;

Gavara and Hernandez, 1996). Three main types of interactions between food and packaging materials are defined i) permeation; ii) sorption and iii) migration (Olafsson and Hildingsson, 1995). The effect of HPP on permeation has been described in chapter (Mertens, 1993, Mertens, 1995).

The effect of HPP on the sorption behavior of plastics has not been sufficiently researched, and is the focus of this work. Sorption refers to the uptake of volatile components from the food product by polymeric packaging materials. Sorption, or flavor scalping, occurs readily in many types of foods, including juices, fruit-flavored cereals, and beverages. Sorption may eventually unbalance the product's original flavor profile, resulting in loss of food quality. This can lead to reduction of the shelf life of the packaged food (Kwapon and Hotchkiss, 1987; Arora et al., 1991; Fayoux et al., 1997; Gnanasekkharan and Floros, 1997). Sorption has been considered a main contributing factor in degradation of flavor or food quality during storage for some products (Nielsen and Giacin, 1994; Fukamachi et al., 1996). Sorbed aromas may permeate through the material, and evaporate outside the package, at a rate that depends both on their diffusivity and on their solubility in the polymer (Lebosse, et al., 1997). Potentially, any volatile food component could be lost by sorption to the packaging materials. Different types of polymer materials have been shown to have various affinities for aroma compounds. Chemical composition (polarity), polymer morphology, temperature, and pH of polymers are important factors that influence migration and sorption properties (Nielsen et al., 1992; Nielsen et al., 1994; Leufven and Hermansson, 1994; Johansson and Leufven, 1994).

Generally, the polyolefins, i.e. LDPE, LLDPE and PP, absorb larger quantities of aroma compounds than do polar polymers, such as PET and PA (Nielsen et al., 1992). Matsui et al. (1992) also indicated that sorption greatly depends on the polarity of the volatile compound.

The solubility parameter (δ) was developed to describe the enthalpy of mixing of simple liquids (nonpolar) but has been extended to polar solvents and polymers from knowledge of the properties of the components (Grulke, 1999). For sorption, if the polymer and sorbate have equivalent solubility parameters they should be mutually soluble. In other words, substances with similar chemical structures should be quite likely to dissolve in each other and exhibit a high propensity for sorbate/polymer interactions (Hernandez and Giacin, 1998).

The solubility parameter, δ, of a substance measures the strength of attraction between molecules within the material and is given by the square root of its molar cohesive energy density. The value of δ arises from the contribution of three inter-molecular forces: dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h): $\delta^2=\delta^2_d+\delta^2_p+\delta^2_h$. Values of δ can be obtained experimentally, or more commonly calculated by group contribution methods. To determine whether a polymer favors the sorption of a particular sorbate, the solubility parameter of both the polymer (δ_P) and compound (δ_L) need to be compared. A large difference between the solubility parameters of the substances (when ($\delta_P - \delta_L$) is > 5 $(J/cm^3)^{1/2}$) occur, lower solubility values are expected. However, good solubility is obtained when (δ_P-δ_L) is < 5 $(J/cm^3)^{1/2}$.

The difference of solubility parameter values of the limonene and polymers were calculated using the group contribution method $(\delta_P-\delta_L)=[(\delta_{d,P}-\delta_{d,L})^2+(\delta_{p,P}-\delta_{p,L})^2+(\delta_{h,P}$

$-\delta_{h,L})^2]^{1/2}$, where the subscripts d, p, and h refer to the type of molecular force as indicated above, and P and L refers to polymer and d-limonene respectively (Grulke, 1999). Calculating the difference in the solubility parameters can help to interpret sorption results.

During HPP, an isostatic pressure is applied to the packaged product via a pressure medium. This causes the product to compress uniformly up to 12 %, depending on the final pressure. The product returns to its initial volume after the pressure is released. The compression forces also act on the polymer, reducing its volume.

HPP also increases the temperature of the food-package system according to $dt/dp=\forall T/pc_p$, where T is temperature, $\forall$ is the thermal expansion coefficient, and c_p, is the heat capacity. Compressed water will rise 3.0 C per 100 MPa.

Therefore, there is a combined effect of increasing temperature and decreasing polymer volume during the HP treatment. These effects are reversible and the polymers are expected to recover their initial condition after the treatment. In principle, the volume decrease and temperature increase may affect the sorption behavior of the polymer during HPP by decreasing the amount of sorbed. Once the pressure stops acting on the system, it should be expected that polymers would revert to their initial state. While substantial research has dealt with the specific effects of HPP on various food constituents, relatively little is known about the effect on HPP on sorption behavior of flexible food packaging materials (Kubel et al., 1996; Imai et al., 1990).

Since better understanding is needed regarding sorption behavior of polymer materials after HPP treatment, this study aimed to quantify change in the sorption behavior of selected plastic structures when the food/package system is subjected to high pressure. The objectives of this study were: a) to evaluate effect of HPP on the sorption process in selected plastic structures; b) to determine the effect of temperature at 1 atm, on sorption, and c) to predict the sorption behaviors of sorbate for polymers on the basis of the affinity concept by calculating the solubility parameter. For this purpose d-limonene was selected as the sorbate and pouches made with the packaging structures were filled with acid and low-acid food simulant liquids (FSL). D-limonene is a natural terpene commonly found in citrus juices (Kutty et al., 1994). D-limonene can be easily absorbed by many packaging materials because of its hydrophobicity (Mannheim et al., 1987; Nielsen et al., 1992; Nielsen and Giacin, 1994). Its availability, prominence in orange flavor, and ease of analysis make it the most extensively studied compound with respect to its sorption by polymers (Fayoux et al., 1997; Imai et al., 1990; Olafsson and Hildingsson, 1995).

4.2 MATERIALS and METHODS

4.2.1 Materials

D-limonene ($C_{10}H_{16}$) 98% pure (Aldrich Chemical Com. Milwaukee, WI) was used as the sorbate. The food packaging flexible structures (films) selected were the following (Table 4.1).

a) Single layer PP

b) PE/nylon/EVOH/PE

c) Metallized PET/EVA/LLDPE as an inorganic coated multilayer

Table 4.1. The composition of the test films used in this study.

Test film structures	Thickness (μm)	Manufacturer
Met-PET 12 μm /30%VA EVA/LLDPE	50	Cello-Foil Pro. Inc.
PE/nylon/EVOH/PE	62.5	Cryovac
PP (single layer for comparison)	25	Tredegar Inc.

PP – Polypropylene
PET – Polyethylene terephthalate
Met-PET – Metallized polyethylene terephthalate
PE – Polyethylene
EVOH – Ethylene-vinyl alcohol
LLDPE – Linear low density polyethylene
EVA – Ethylene-vinyl acetate

4.2.2. Equipment

4.2.2.1. High-pressure processor.

High-pressure processing was carried out using a pilot scale QFP-6 Tetra-Laval Quintal high-pressure processor (ABB Autoclave System, Columbus, OH). This equipment contained a cylindrical 1 L -processing vessel with an internal diameter of 6.0 cm by 18.8 cm in height. It was designed for a maximum pressure of 890 MPa at an operational temperature range of 5-70 °C. The processing temperature was maintained at 60 °C ±2 °C for each test run. Three pouches were loaded into the pressure vessel that was preheated to around 30 °C, then clamped within the high-pressure chamber, and finally pressurized for 10 min (holding time) up to 800 MPa at 60 °C, pressure processed. A cooling system maintained the temperature of the chamber during the pressurization time.

The desired pressure was reached in 2.3 ±0.25 min. The high-pressure transmission fluid used in this equipment was Houghton-Safe 620-TY a glycol/water compound from Houghton International (Valley Forge, PA).

4.2.2.2. Dynamic thermal stripper (DTS)/thermal desorption (TD)/gas chromatograph (GC) system.

The extraction and quantification of d-limonene from the films was carried out using:

a) A dynamic thermal desorption unit Model 890 from Dynamic Analytical Instrument, Inc., (Kelton, PA);

b) b) 6 mm O.D x 4 mm I.D. x 11.5 cm length Carbotrap® multi-bed thermal desorption tubes (Supelco Inc., Bellefonte, PA).

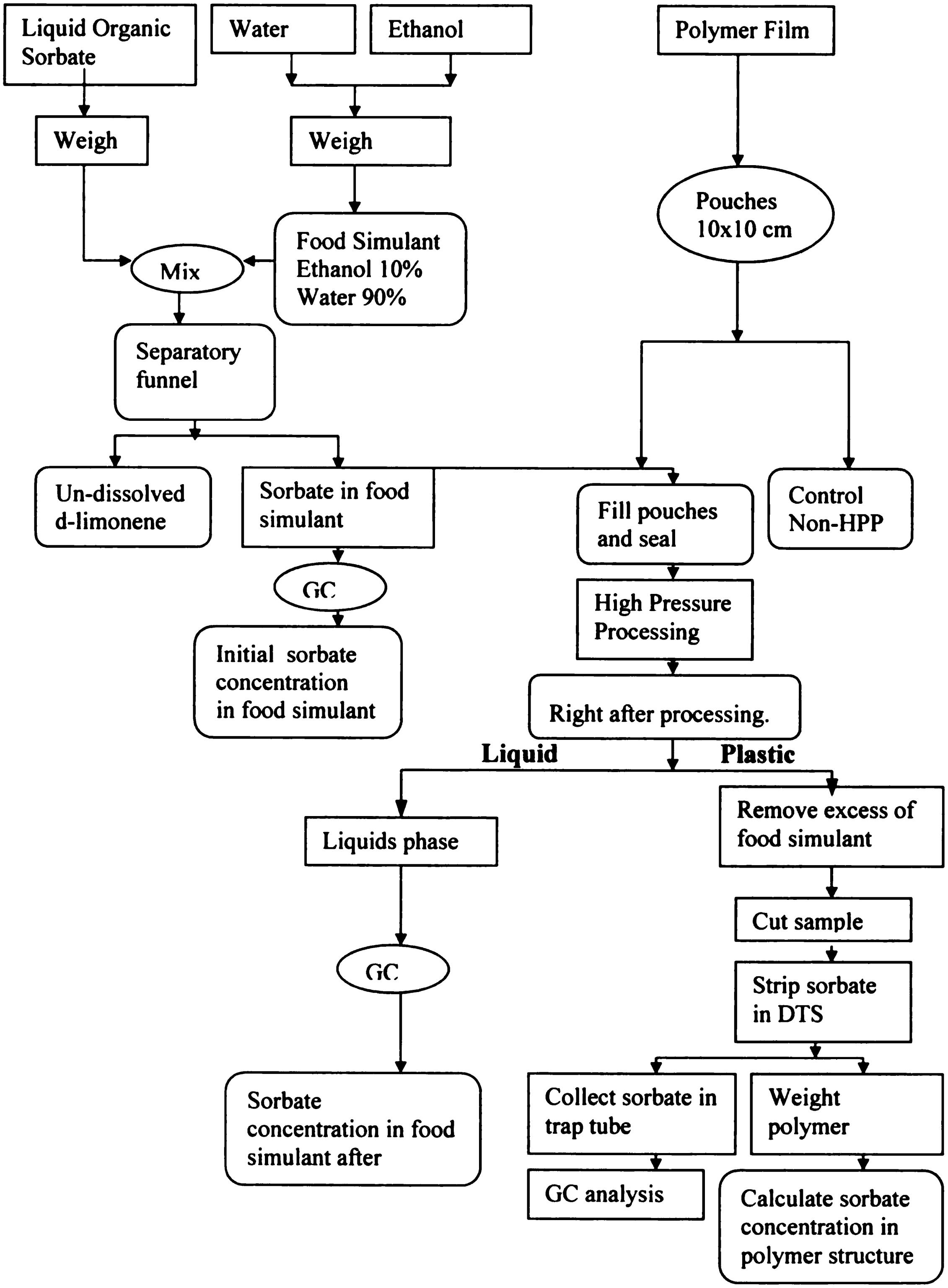
c) Hewlett Packard 5890-A gas chromatograph equipped with a gas flame ionization detector (Avondale, PA, USA) and capillary column.

4.2.3. Methods

A flow-sheet diagram indicating the main steps for preparing and analyzing the samples is shown in Figure 4. 1.

Food simulants were selected to represent both acid and low-acid food simulant liquids (FSL). Aqueous solutions of 165 ppm (165 mg/L) of d-limonene in either 10% ethanol (Reagent HPLC grade, Sigma Chemical, St Louis MO) or 3% acetic acid (Spectrum quality products, Inc, Gerdena CA) were prepared. The FSL were obtained by mixing either 10% ethanol or 3% acetic acid with distilled water. The FSL was mixed with d-limonene in a separatory funnel. After settling, the undissolved d-limonene upper phase was separated from the FSL containing dissolved d-limonene.

Figure 4.1: Flow sheet diagram indicating main steps of general sample preparation.



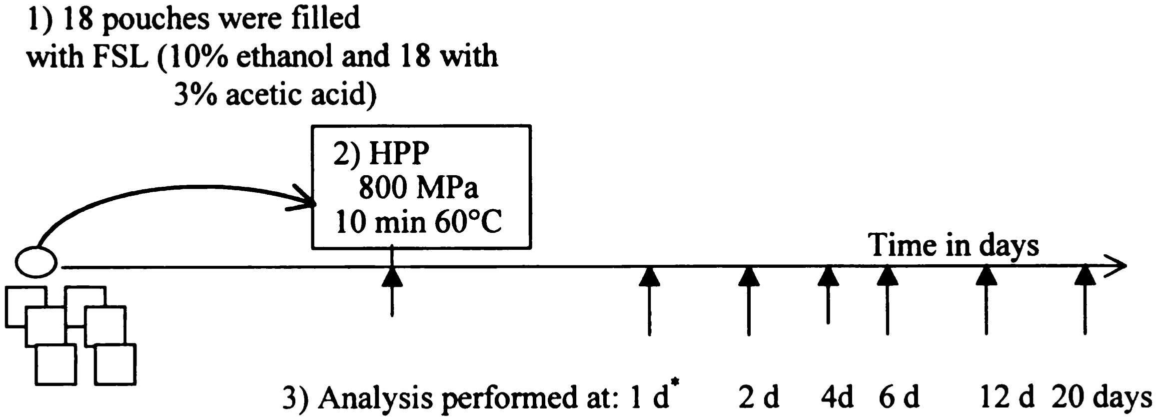
The 10.0 x 10.0 cm pouches were fabricated from the films, filled with FSL. Filled pouches were heat-sealed with as little headspace as possible using a Sencorp heat-sealer (Sencorp Systems, Inc., Hyannis MA). Samples were divided into two sets: one to be kept at atmospheric pressure as control (23°C), and the other to be processed at high pressure. Control pouches were exposed to atmospheric pressure (1 atm) at 60 °C for 10 min in an electric oven. In addition some control pouches were left at 40°C for 10 min. For the treated sample, HPP was conducted at 800 MPa for 10 min at 60°C.

Sorbate levels in the films were determined by DTS-TD and GC on aliquot strips cut from the treated pouches. Three replicates of each pouch were analyzed for sorbate content.

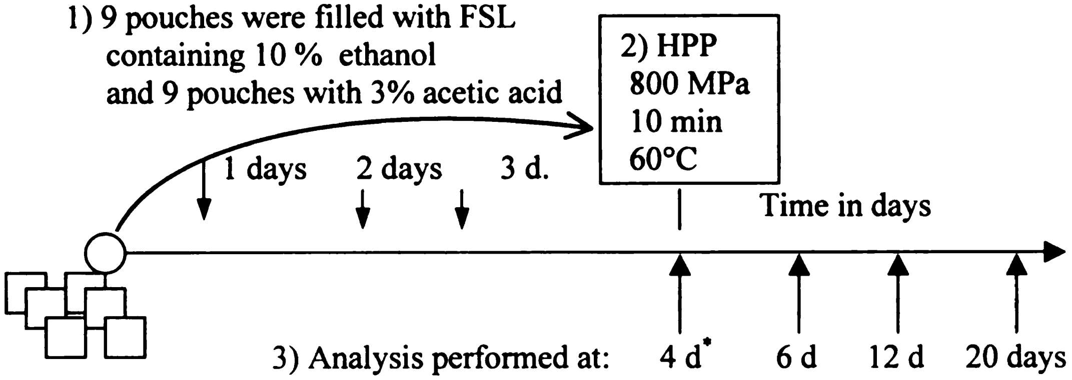
Two procedures were followed to describe the sorption behavior of d-limonene as indicated in Figure 4.2. One procedure (A) was selected to evaluate whether the high pressure would affect the unsteady state sorption process as compared to sorption at one atmosphere. The second procedure (B) was for determining whether HP had any effect on the sorption capacity of the films once they were equilibrated with d-limonene at one atmosphere. For procedure (A) the pouches were filled with FSL immediately before HPP and then analyzed. In procedure (B) pouches were first filled with FSL, then allowed to equilibrate, and then HPP; analysis of pouches was performed before and after HPP. Following HPP, pouches were kept at 23°C.

Figure 4.2: Diagram indicating the two procedures followed to evaluating the sorption behavior.

a) Procedure A (Filled before HPP). Pouches were1) filled with FSL, 2) were pressure treated and maintained at 23°C, and 3) aliquot of pouches and FSL were analyzed according to the following schedule:



b) Procedure B (At equlibrium HPP). Pouches were 1) filled with FSL and kept at 23°C to equilibrate for several days, 2) pouches were pressure treated, and 3) aliquot of pouches and FSL were analyzed according to the following schedule.



* days

4.2.3.1. Dynamic thermal stripping.

A Dynamic thermal stripper-thermal desorption (DTS-TD) unit was used to extract the sorbate from the polymer sample. Polymer strips of about 20x25 mm were cut from pouches and immediately transferred into the 20 ml sparging tube housed in the 20x20 x20 cm oven of the DTS instrument and connected to the sorption tubes containing Carbotrap 300 multi-bed materials mounted outside the oven. The conditions used for the thermal stripper unit and thermal desorption are summarized in Table 4.2.

Table 4.2. Thermal and flow rate conditions used for the thermal stripper.

	Preheat	Purge	Dry
He Flow rate, mL/min	50	100	50
Time, min	3	15	1
	Block	Oven	Tube
Temperature °C	110	100	75

After stripping, the Carbotrap sorption tube containing the trapped sorbate was transferred to the tube chamber of the thermal desorption unit. A transfer line connected the thermal desorption unit to GC. Sorbate collected in the traps was thermally desorbed from the carbotrap tube by heating into GC using the conditions shown in Table 4.3. A stream of helium (7 mL/min, 275 kPa) quantitatively carried the sorbate directly into to the GC for separation and detection. The quantities of sorbed compounds were obtained the and used to evaluate the effect of high pressure on the sorption behavior.

Table 4.3. Conditions used for thermal desorption unit.

Tube desorption chamber temperature, (°C)	370
Valve compartment temperature, (°C)	250
Transfer line temperature, (°C)	250
Tube preparation chamber temperature, (°C)	350
Tube preparation chamber temperature, (°C)	350
Desorption time, min	5
Preparation time, min	20

4.2.3.2. Gas chromatography.

Quantification of d-limonene was carried out on a Hewlett Packard 5890-A GC equipped with gas flame ionization detector and interfaced with a Hewlett-Packard 3395 integrator for separation and quantification of the sorbate compound. The GC conditions were as follows: H_e carrier gas at 7.0 ml/min, H_2 at 40 ml/min, air at 400 ml/min, N_2 at 30 ml/min, the initial oven temperature was 50°C for 2 min, and the temperature was raised at a rate of 7 °C /min to 200 °C and kept for10 min.

The d-limonene concentration in the FSL, in g/L, was determined by direct injection of 1.0×10^{-6} L of solution into the GC. The amount of sorbate in the plastic was calculated as $C = \frac{C_F \times A_U}{W}$, where C is the concentration in microgram of d-limonene/g of polymer, A_U is the GC area response, C_F is the calibration factor, and W is the polymer sample weight.

4.2.3.3. Determining d-limonene from plastic film using a liquid extraction method.

Since the HPP equipment was housed 300 km from the lab where the analysis was performed, a liquid-solid extraction procedure was used to extract the d-limonene sorbed by the plastic films immediately after HPP. The procedure was follows: Pouch samples were cut into pieces of approximately 200 mg and dipped into 16 mL glass extraction vials (Supelco Inc., Bellefonte, PA) containing 10 ml of solvent. The solvent was either toluene for PP or a mixture of 70% toluene and 30% m-cresol for Met-PET and EVOH based structures. The vials were tightly closed with screw caps lined with PTFE/silicone septa (Supelco Inc., Bellefonte, PA) and kept for 24 hours at 40 °C in an oven for better extraction conditions. Aliquots of the solutions were then injected into Carbotrap® tubes and thermally desorbed directly into the GC port. The d-limonene concentration in the pouch material was determined by $C = \frac{C_F \times A_U \times V_T}{V_I \times W}$, where C is the concentration in :g of d-limonene/g of polymer, A_U is the GC area response, C_F is the GC calibration factor, W is the polymer sample weight, V_T is total volume of solvent in the glass vials, and V_I is injected volume of solvent in the Carbotrap® tube. Sampling times were different for procedures (A) and (B). For procedure (A) the film and FSL were evaluated right after pressure treatment and at1, 2, 4, 6, 12, and 20 days for multilayer structures 1, 2, and 3 days for the single layer structure (Figure 4. 2). For procedure (B), the film and FSL were evaluated at after reaching equilibrium which are 4, 6, 12, and 20 days for multilayer structure; 1, 2,and 3 for single layer structure (Figure 4. 2). Because multilayer structures need longer time than single layer to reach equilibrium, sampling time for the single and multilayer were different.

4.2.3.4. Statistical analysis

A completely randomized experimental design was applied to evaluate the effect of high pressure processing on the sorption of d-limonene by polymers. The quantity of d-limonene sorbed by the packaging structures was measured on samples HPP treated and samples maintained at 1 atmosphere (referred to as controls). Statistical analysis of data was carried out by using the Statistical Analysis Systems PROC MIXED procedure (SAS Institute, Inc., NC.(32) statistical software. Least Square Mean (LSMEANS) differences adjusted by the Tukey adjustment factor were also used to determine differences between factor levels.

4.3. RESULTS AND DISCUSSION

The quantity of sorbed -d-limonene both in polymer structures and in the food simulants were determined for each structure as according to Figure 4. 2.

4.3.1. Polypropylene (PP)

Figure 4.3 compares the sorption of d-limonene by PP structure in contact with d-limonene in 10% ethanol at 800 MPa, for 10 min at 60 °C. Figure 4.2 compares the sorption of d-limonene by PP in contact with 3% acetic acid at 800 MPa, for 10 min at 60 °C. For comparison of temperature effect on sorption we also compared 40 °C control (1atm). These figures show a rapid increase in the sorbed amount of d-limonene to reach a maximum value that tends to approach a pseudo equilibrium point. After that there is a decrease in concentration created by loss of d limonene by permeation with simultaneous decrease in concentration in the liquid phase. The sorbed amount of d limonene was not significantly (P<0.01) affected by pressure treatment. D limonene shows a rapid sorption increase (2228 ±51) in about 6 hours to reach a maximum value of 2300 ± 49 micrograms per gram PP in 10 % ethanol and about 800±36 micrograms per gram of PP in 3 % acetic acid (Figure 4.3 and Figure 4.4).

Losses of d-limonene in the food simulant liquid are shown in Figure 4.5 and 4.6. As shown, the liquids lose 0.047 ±0.004 g/L for ethanol and 0.003±0.0005 g/L for 3% acetic acid) in about 24 hours due to permeability of the d-limonene through the film. Similar behavior in terms of sorption of limonene was shown in both HP processed and non-HPP films. No significant (p<0.01) differences were found.

Absorption of D-limonene in an acetic acid food simulant was much lower than an ethanol food simulant.

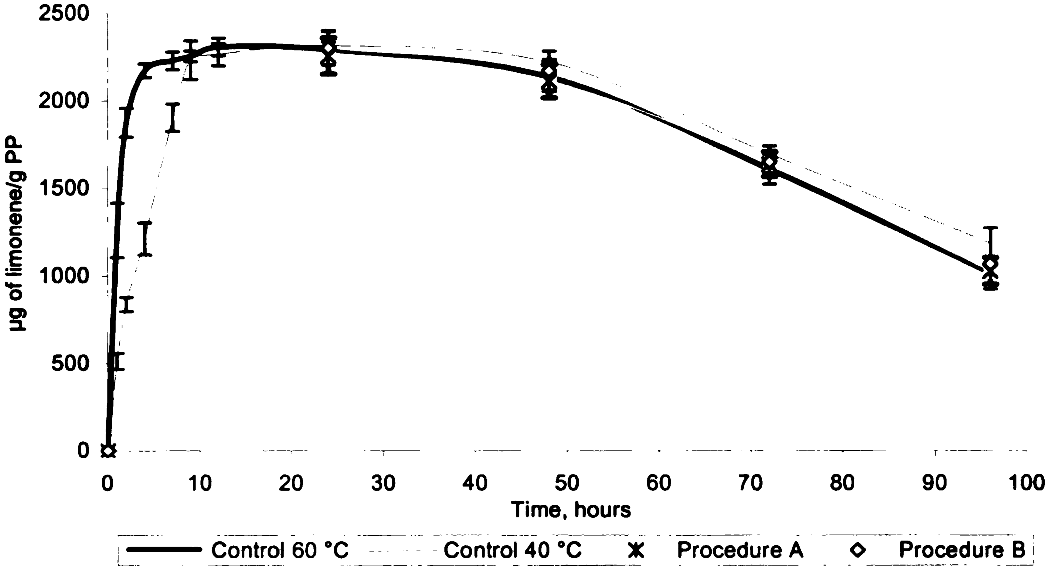


Figure 4.3: Concentration of d-limonene in PP film contacting 10% ethanol FSL treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

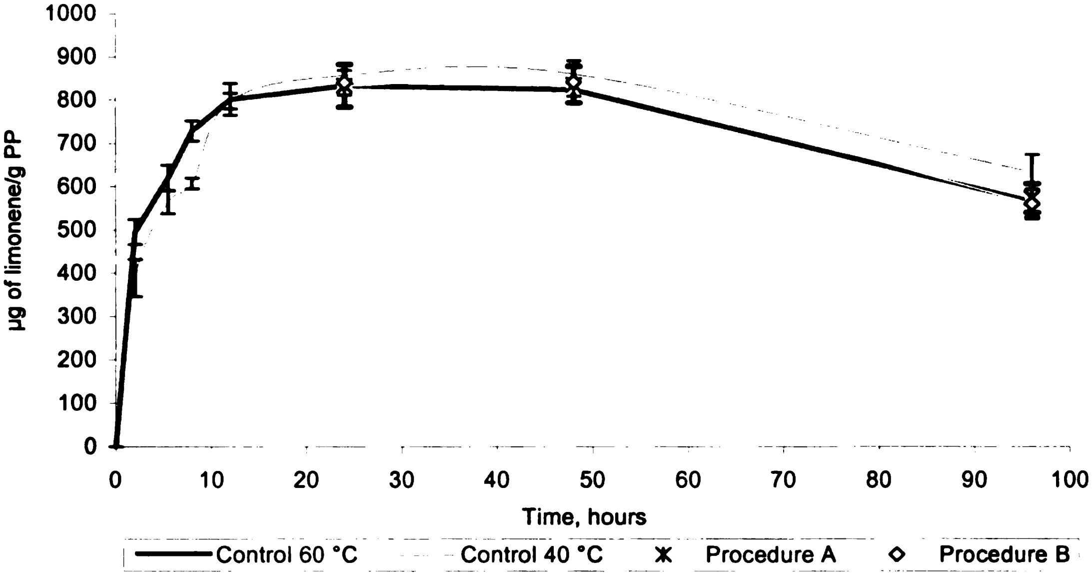


Figure 4.4: Concentration of d-limonene in PP film contacting with 3% acetic acid FSL treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

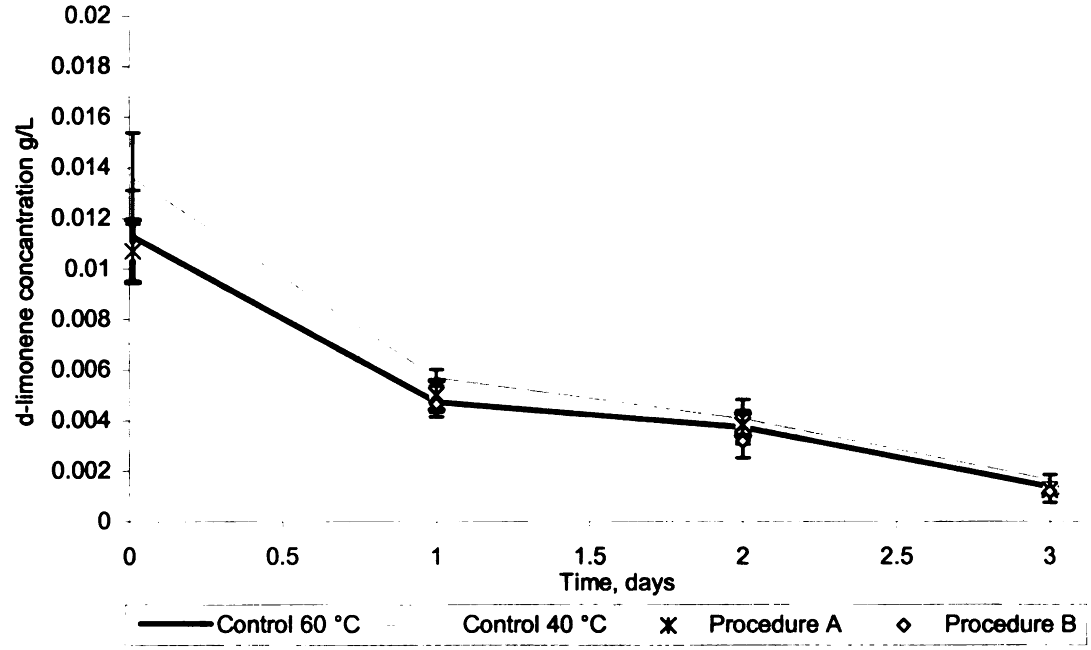


Figure 4.5: Concentration of d-limonene in FSL (10% ethanol) in PP film treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

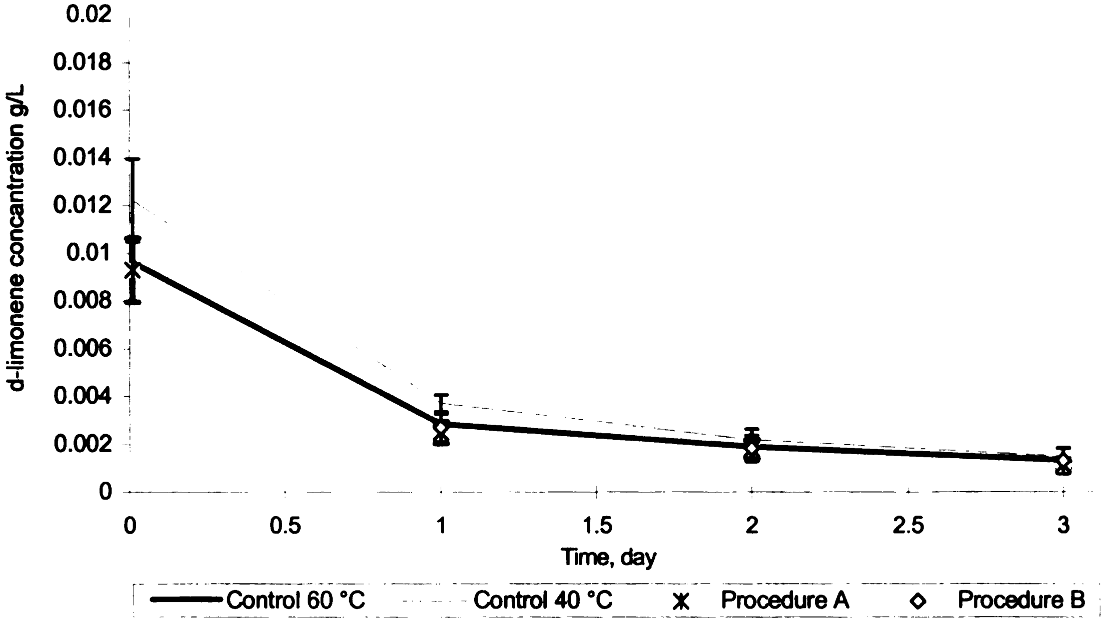


Figure 4.6: Concentration of d-limonene in FSL (3 % acetic acid) in PP film FSL treated at 800 MPa and 60 °C according to procedures (Filled before HPP) and B (At equlibrium HPP).

4.3.2. PE/nylon/EVOH/PE

A similar pattern was observed for the PE/nylon/EVOH/PE structure. Figure 4.7, 4.8, 4.9 and 4.10 summarize the results obtained with this film. The amount of d-limonene concentration was not significantly ($P<0.01$) affected by HPP. D-limonene values are the same before and after treatment (800 MPa, 10 min, 60 C). D-Limonene concentration increases slowly for EVOH, and in about 2 days reaches at with a value of 600±15 micrograms per gram EVOH in 10% ethanol and about 50±2.5 micrograms per gram of EVOH in 3% acetic acid (Figure 4.7 and 4.8). Losses of d limonene are shown in Figure 4.9 and 4.10. The liquid d-limonene contents about 0.018±0.0012 g/L in about one week for the 10% ethanol (Figure 4.9). D-Limonene concentration was about 0.017±0.001 g/L in about one week for the 3% acetic acid solution (Figure 4.10). The liquid d-limonene concentrations were lost half of its-d limonene in about one week. The amount of d limonene (0.014±0.0015 g/L for 10% ethanol and 0.013±0.0012 g/L for the acetic acid) was the same before and after HPP after 20 days (Figure 4. 9 and 4. 10). No significant differences ($p<0.01$) were found between the HPP treated and non-treated pouches.

As expected, pouches made of the EVOH multilayer structure took a much longer time to lose the limonene compared to pouches of single layer PP.

Since single layer structures may not be able to meet all the demands for many packaged products, combinations of polymers are used as laminates, to achieve the intended shelf life.

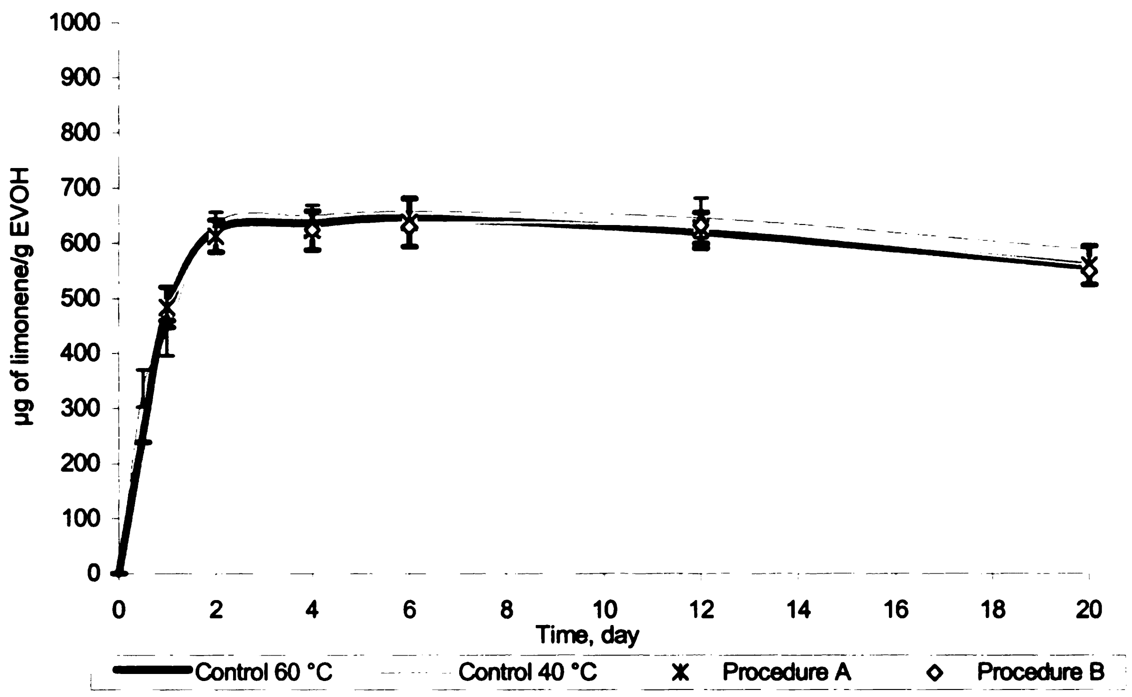


Figure 4.7: Concentration of d-limonene in PE/nylon/EVOH/PE film contacting with 10% ethanol FSL treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

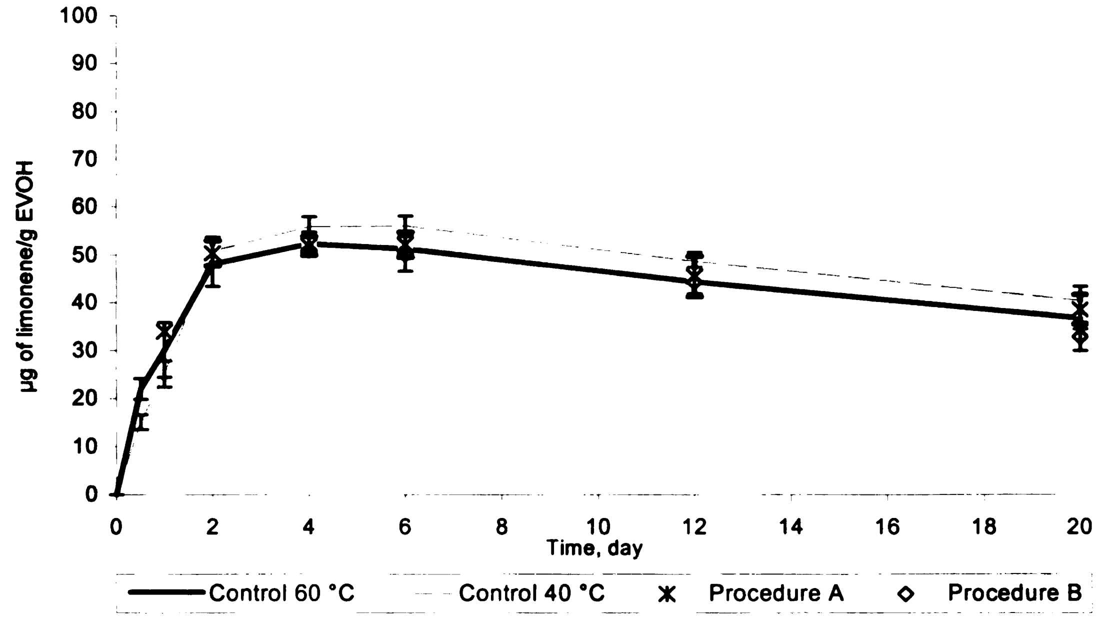


Figure 4.8: Concentration of d-limonene in PE/nylon/EVOH/PE film contacting with 3% acetic acid FSL treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

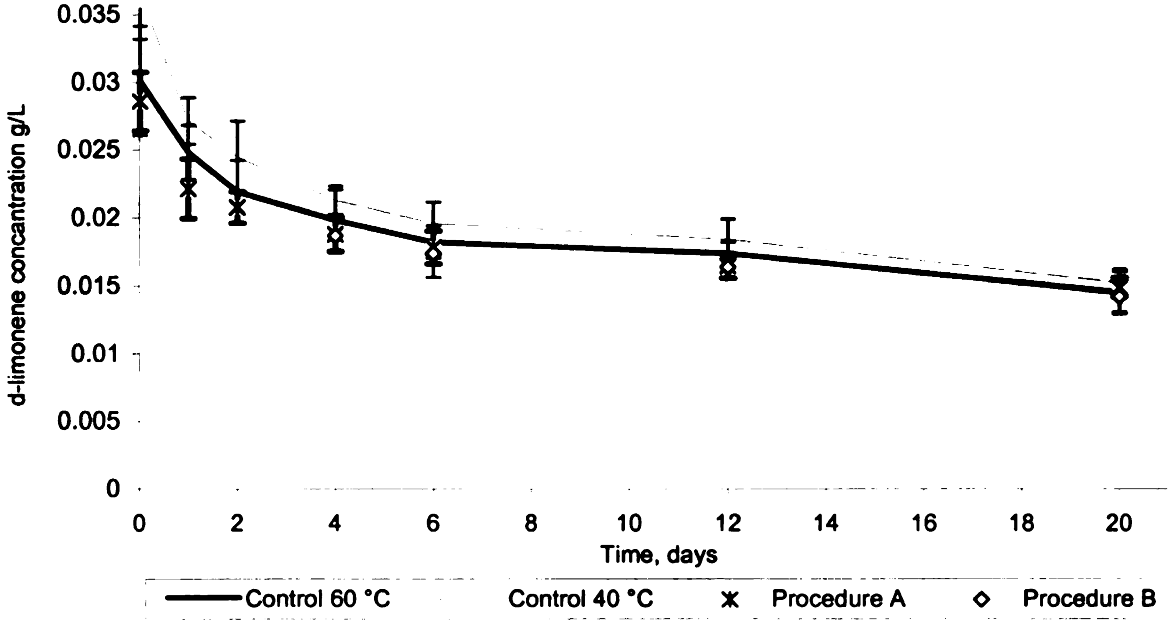


Figure 4.9: Concentration of d-limonene in FSL (10% ethanol) in PE/nylon/EVOH/PE film treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

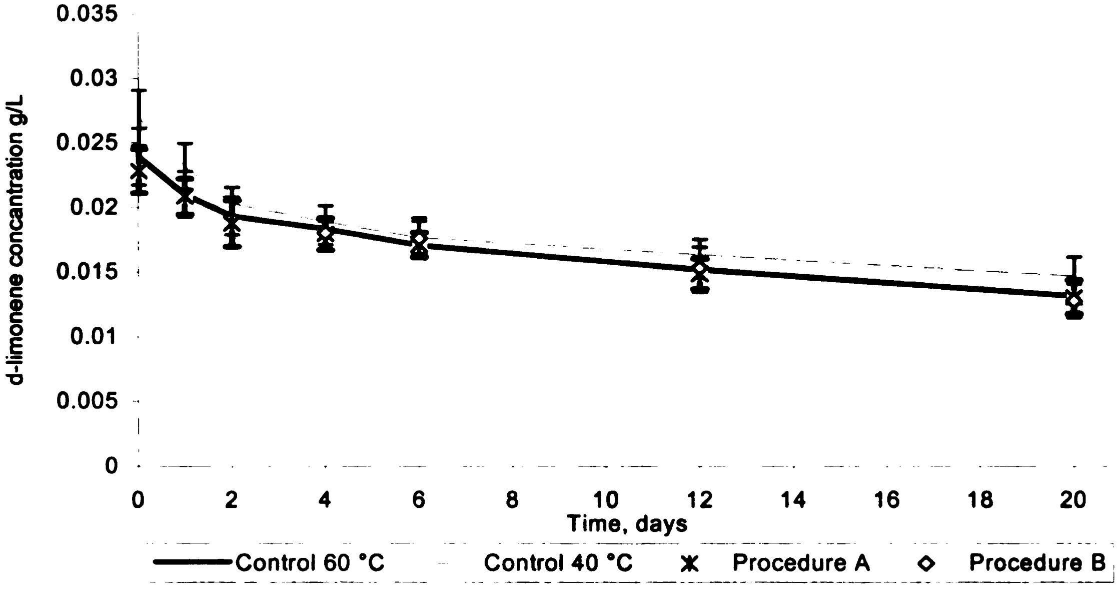


Figure 4.10:Concentration of d-limonene in FSL (3% acetic acid) in PE/nylon/EVOH/PE film treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

4.3.3. Met-PET 12 μm /30%VA EVA/LLDPE (coated multilayer structure)

Figures 4.11, 4.12, 4.13 and 4.14 summarize the results for the met-PET polymer structure for both the polymer and food simulant. The d-limonene concentrations in the treated pouches were significantly lower than in the non-HPP ones. The amount of d-limonene continuously decreased during the 20-day period of observation. The control met-PET showed a relatively slow sorption process reaching a maximum in about 4 days at a value of 1300 ±55 micrograms per gram of polymer in 10% ethanol and about 85±7.5 micrograms per gram of polymer in 3% acetic acid (Figure 4. 11 and 4. 12, respectively). It can be seen that d-limonene in the HPP treated met-PET was significantly ($p<0.01$) different from the non-HPP treated met–PET. The amount of d-limonene in 10% ethanol FSL was 0.0026±0.00058 g/L limonene for right after HPP (procedure A; Figures 4.2) at 4 days (Figure 4.13). The amount of d-limonene in 3% acetic acid FSL was 0.00339±0.000486 g/L for HPP at equlibrium (procedure B; Figure 4.2) at 4 days (Figure 4.14). Similarly, the result of PROC MIXED SAS analysis among overall (20 days storage time) the d limonene concentration of FSL in the HPP treated met-PET for the 10% ethanol and 3% acetic acid solution are significantly ($P<0.01$) different from the non HPP treated met-PET (Figure 4.13 and 4.14). The values of the d-limonene in the food simulant were found to be significantly ($p<0.01$) lower in HPP processed pouches as compared to the non-HPP pouches, both in 10% ethanol and 3% acetic acid (Figure 4.13 and 4.14, respectively). Sorption-permeation behavior of the met-PET was profoundly affected by the HPP treatment.

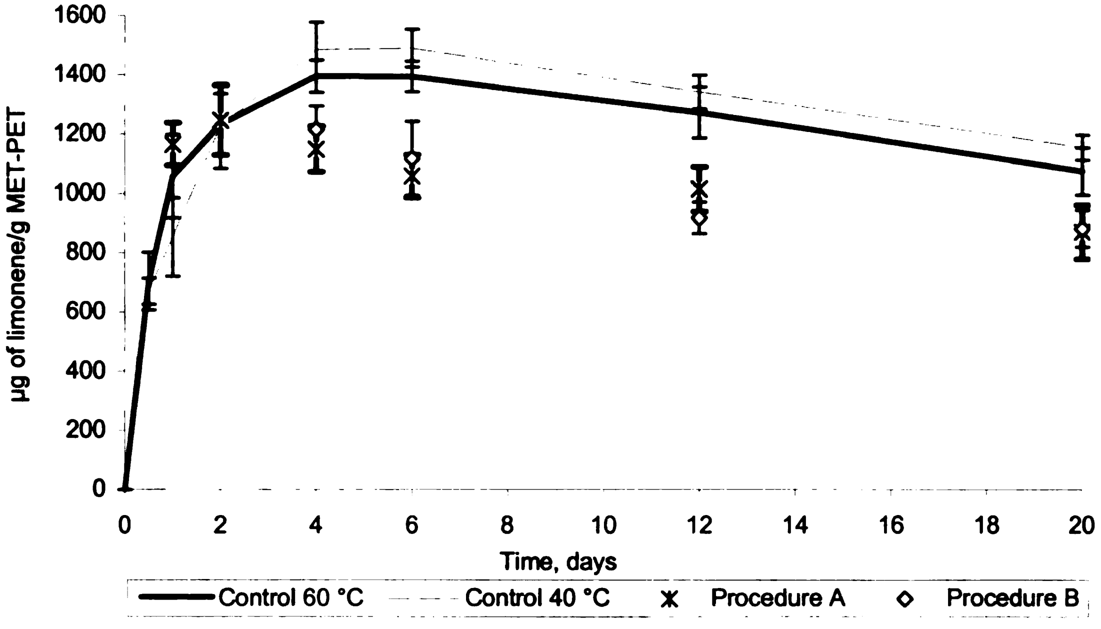


Figure 4.11: Concentration of d-limonene in Met-PET/EVA/LLDPE film contacting with 10% ethanol FSL treated at 800 MPa and 60 °C according to procedures (Filled before HPP) and B (At equlibrium HPP).

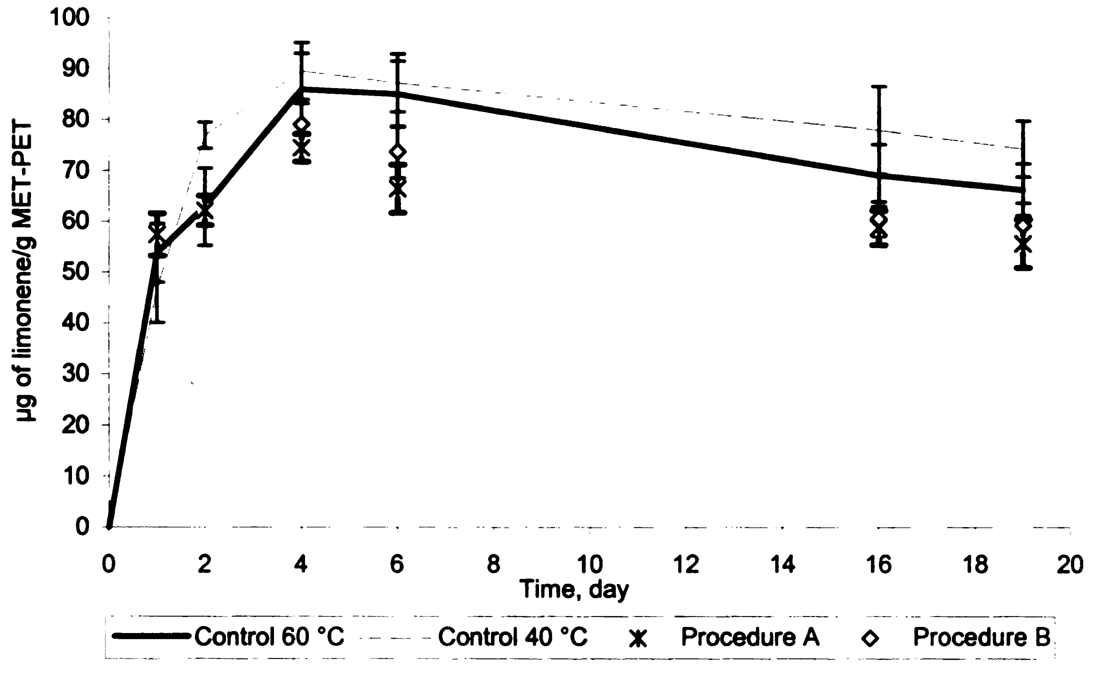


Figure 4.12: Concentration of d-limonene in Met-PET/ EVA/LLDPE film contacting with 3 % A.A FSL treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

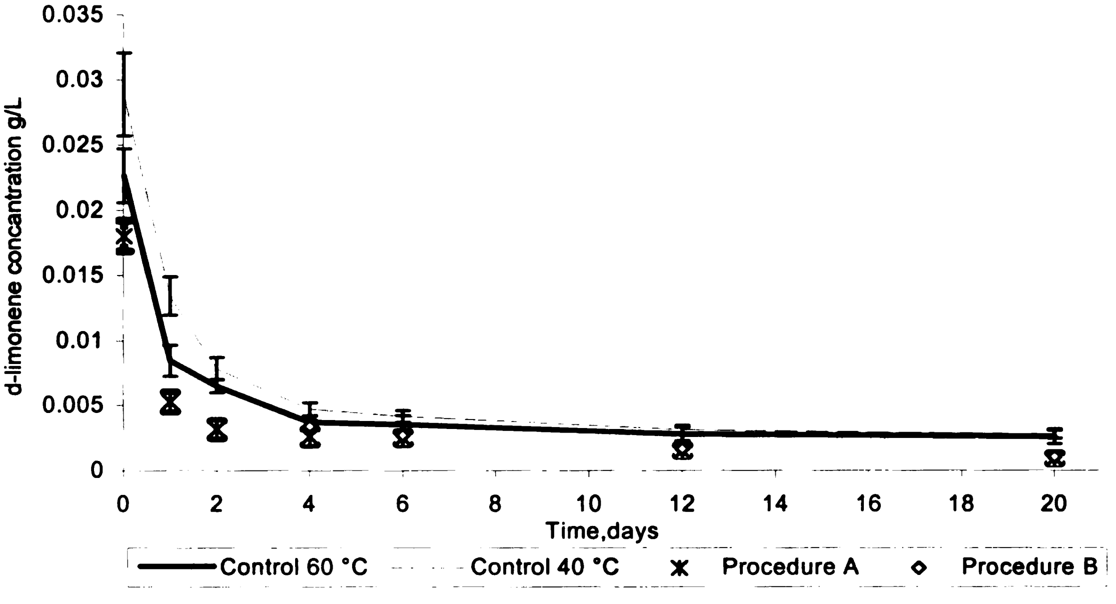


Figure 4.13: Concentration of d-limonene in 10 % ethanol FSL in Met-PET/EVA/LLDPE film treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

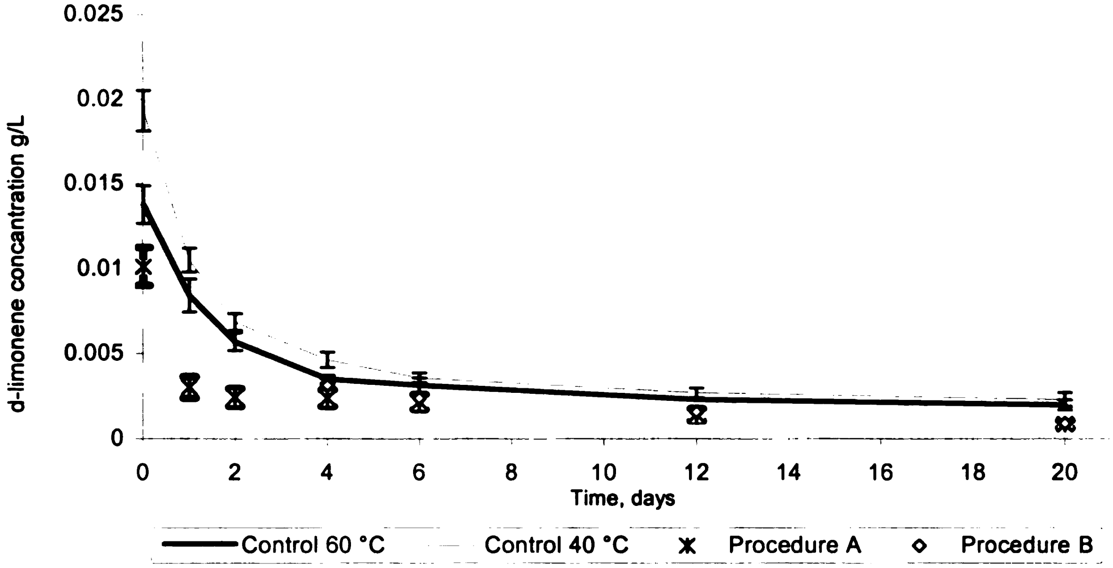


Figure 4.14: Concentration of d-limonene in FSL (3% acetic acid) in Met-PET 12 μm /30% VA EVA/LLDPE film treated at 800 MPa and 60 °C according to procedures A (Filled before HPP) and B (At equlibrium HPP).

For the PP and EVOH structures, the d-limonene content of pressure-processed pouches was similar to non-treated ones. However, for the met-PET this was not the case. D-limonene concentration decreased in the polymer with time after reaching a maximum value, due to permeation. The pH of the FSL was found to influence the amounts of aroma component sorbed in the polymer. The equlibrium values achieved for 10% ethanol were 2300±49 microgram/g for PP, 600±15 microgram/g for EVOH and 1300 ±55 microgram/g. for met-PET. The equlibrium values achieved for 3% acetic acid was 800±36 microgram/g for PP, 50±2.5 microgram/g for EVOH and 85±7.5 microgram/g for met-PET. These results were in agreement with Leufven and Hermansson.

Process temperature was shown to have an impact on the degree of sorption of d-limonene by the polymer. As expected, significantly ($P<0.01$) lower amounts of d-limonene were sorbed at higher temperature (60EC) as compared to the lower temperature (40EC) for all structures (Figures 4. 3- 4. 14). Also, temperature accelerated the sorption process and the time to reach the maximum was shorter at higher temperature (60C). This is in agreement with Nielsen et al. (1992) and (1994); Fayoux et al. (1997). The reason for the increasing values at higher temperature might be due to the greater mobility of molecules, or that the polymer may have been affected in some way, such as swelling.

Temperature rise due to compression heating depends on the pressure, product compressibility, and initial temperature. The pressure media also great influences the apparent product temperature rise in a process vessel. Water (3°C per 100 MPa) is the lowest compression heating increment during the pressure treatment. Change in product temperature as a result of compression heating and subsequent heat transfer should be considered during HPP. Foods are composed mostly of water and water has very low compressibility. There is no heat transfer during HPP. However, depending on the food, a slight temperature change may occur with compression. This is reversed during decompression. The effect of changing pressure has significant effects on the volume temperature relationship due to the compressible nature of the polymer. An increase in pressure decreases the specific volume at given temperature. It is remarkable that the compression response of the polymers is so similar. This may occur if molecules are very tightly bound so that displacements around the minimum are equally difficult in compression or dilation. For organic compounds, with weak attractive van der Waals forces, it was expected that a much less symmetric internal energy (compression more difficult than dilation) would be found.

In Table 4.4 are summarized the ∂ values of the limonene compounds and contact polymers used in this study. The solubility behavior of an unknown substance often gives us a clue to its identification, and the change in solubility of a known material can provide essential information about its aging characteristics. The solubility parameters of the d-limonene and polymer indicate chemical similarity between the polymer and d-limonene (Table 4.4). The smaller the differences between the ∂ values of two substances the greater the solubility (Grulke, 1999). Consequently, a comparison of ∂ values of a polymer and an aroma compound gives an indication of their solubility behavior. Differences of solubility parameters values of d-limonene and PP, PE and LDPE (d-limonene-polymer) were lower than 5 ($\partial\partial$ =0.5 (J/cm^3)$^{1/2}$ <5 (J/cm^3).$^{1/2}$).

Therefore a high degree of compatibility was expected between limonene and PP, PE and LDPE. Since the solubility parameters are similar, completely miscibility is expected to occur. The difference of solubility parameters values between d-limonene and PET (12.8), Nylon (13.4), EVA (15.39) and EVOH (5.36), indicating that all of the limonene-the polymer (δ_P-δ_L) greater than 5 $(J/cm^3)^{1/2}$ ($\partial\partial$ =0.5 $(J/cm^3)^{1/2}$ >5 $(J/cm^3)^{1/2}$ poor solubility is expected). Therefore, a low degree of compatibility was expected between limonene and PET, Nylon, EVA and EVOH. The solubility parameter (∂) is a useful measure to qualitatively estimate the solubility of a solvent in a polymer, and is a good indicator of the chemical compatibility between a sorbate and a polymer.

D-limonene, which is a non-polar compound and, has a small dipole moment, had the greatest affinity for the plastic phases. As seen from these results there were major differences between the amounts of d- limonene absorbed by the different polymers. Generally poyolefins, i.e. PP, absorb larger quantities of aroma than more polar polymers, such as PET (Nielsen et al., 1992).

Table 4.4. The solubility parameters, δ (J/cm^3) and δ_P-δ_L

Substance	δ^a (J/cm^3)	δ_d $(J/cm^3)^{1/2}$	δ_p $(J/cm^3)^{1/2}$	δ_h $J/cm^3)^{1/2}$	δ_P-δ_L $(J/cm^3)^{1/2}$
Limonene	16.84	0	0	0	
PP	17.28	17.28	0	0	0.19
PE	17.31	17.31	0	0	0.22
LLDPE	17.31	17.31	0	0	0.22
PET	22	17.9	7.3	10.5	12.8
Nylon	22.87	18.62	5.11	12.28	13.4
EVA	25.66	20.93	11.27	9.66	15.39
EVOH	22.2	--	-	-	5.36 *
Water	48	13.3	31.3	34.2	45.2

Source of δ, δ_d, δ_p, δ_h were Grulke, 1999.Table 10. * Calculated based on solubility parameters

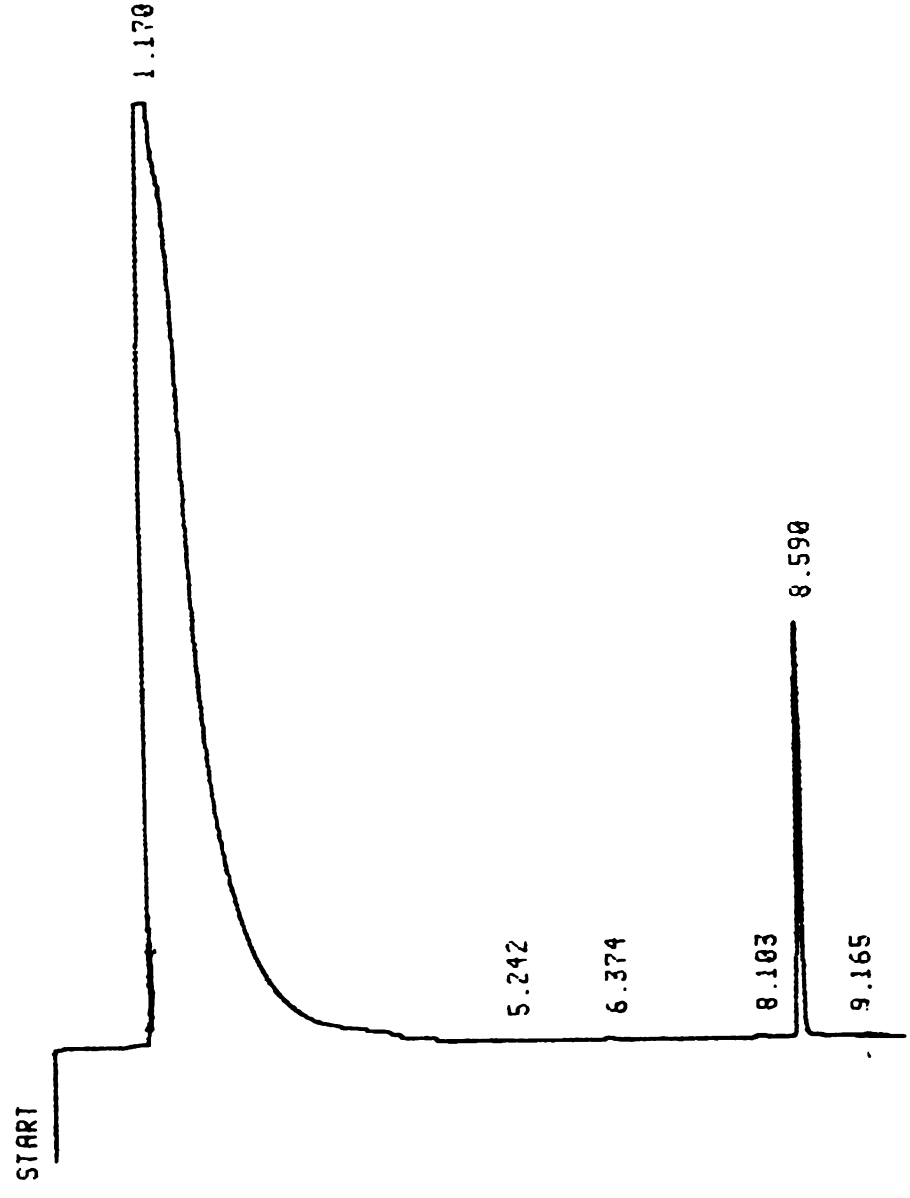


Figure 4.15. Coming up time for d-limonene using GC.

4.4. CONCLUSION

When pouches made of the selected polymers (PP, EVOH, metallized-PET) are submitted to a pressure treatment at 800 MPa for 10 min; no significant changes in the sorption behavior are observed compared to unprocessed structures from in PP and EVOH. D-limonene concentration in both FSL 10% ethanol and FSL 3% acetic acid were not significantly changed after high pressure treatment. On the contrary, Metallized-PET was significantly ($P<0.01$) affected by HPP. D-limonene amount in pressure treated both Metallized-PET and also FSL (10% ethanol and 3% acetic acid) were significantly lower than non-high pressure treated ones .

In terms of d-limonene retention, EVOH appeared to be the best of the three polymers. Sorption by MET-PET and EVOH was significantly less than for PP. Furthermore, sorption of d-limonene amount was lower in the multilayer structure. Temperature affected the amount of sorbed d-limonene and the time it took to reach the maximum value. Sorption is also affected by the pH of the FLS. Using acetic acid to lower the pH altered the solubility of d-limonene in the polymer. Factors that affected absorbed amount of d-limonene depended on polarity and solubility properties of the polymers and on the type of food simulant. Solubility parameters can be used to predict sorption behavior of plastic and polymer-solvent interaction. It may also possible to estimate the order of solubility behavior based on compression of ∂ values of a polymer and an aroma compound.

The above d-limoenene values indicate that existing single layer and multilayer plastic packaging structures can be used in combination with HPP.

4.5. REFERENCES

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Chapter 5

Conclusion and Future Work

The permeability, mechanical behavior by measuring the tensile properties, and use of SEM and C-SAM techniques and sorption behavior were studied. Results from these studies showed that permeance of the most of the multilayer structures tested were unaffected and suitable to high pressure treatment, even though some of them were statistically significant. However, the metallized PET inorganic coated multilayer was most severely affected by the high pressure processing. Higher (800 MPa) pressure and longer processing times (20 min) seem to have a more pronounced effect on permeance values when we compare the change lower (600 MPa) pressure and shorter exposure times (5 min). The water vapor permeance were more than 100% higher in most cases and had more changes when we compare to oxygen and carbon dioxide.

Images obtained using SEM and C-SAM confirm that metallized-PET showed the most structural damage after high pressure processing. SEM showed mettalized-PET had numerous folds and wrinkle formation on the film surfaces. C-SAM analyses showed that delamination occurred in random locations at the interlayer of met-PET.

None of the tested materials showed significant changes in mechanical strength even though some showed surface deformation.

Sorption behavior was tested to determine sorbate amount (d-limonene) in the polymer and in the food simulant liquid. D-limonene concentration in both PP and PE/Nylon/EVOH/PE was not significantly changed after high pressure treatment. D-limonene concentration in both FSL 10% ethanol and FSL 3% acetic acid were not significantly changed after high pressure treatment. On the contrary, d-limonene concentration in pressure treated metallized-PET and also in FSL (10% ethanol and 3% acetic acid) was significantly lower than non-high pressure treated.

This research demonstrated that certain high barrier multilayer films can be affected by HPP. The magnitude of these changes depends on the type of polymer structure and the processing conditions. Even though metallized-PET can be affected by HPP, we found that the rest of the structures tested not have any negative impact on the properties of the materials. The materials (except metallized-MET) are suitable for batch high pressure processed food packaging.

Understanding of changes in inorganic coated multilayer structures such as metallized-PET is crucial. Although detailed research has been done in this study in terms of the effect of HPP on plastic structures much remains to be done to conduct additional modeling research, using different metallized inorganic multilayer structures. Investigating the influence of pressure on permeability, mechanical and mass transport properties using proper experimental design (collection of data at different pressures and control of temperature) on different metallized inorganic coated structure can be helpful.

It is also recommended that further studies on bottles and other flexible containers be carried with high-pressure treatment.

In this way, critical process factors can be evaluated for polymer structures. Also, more stability studies are needed to identify the main diminishing plastic properties, which affect food quality and safety during storage of pressure-processed foods.

There is no doubt that HPP has a promising future as a prepackaged preservation method. Research is particularly needed to set critical limits of the process and extent to which this might ensure appropriate treatment of prepackaged food products. The possible commercialization of HPP also depends on its economic viability. Therefore, detailed economic analyses of HPP need to be done by comparing process costs with commercial methods.

Appendix A

Statistical analysis

The analysis of variance (ANOVA) was performed using LSM-PROC GLM in SAS program.

Table A1: Analysis of LSMEANS of the oxygen permeability ($Rx10^{15}$) $m^3(STP)/m^2.s.Pa$ of the flexible structures.

Oxygen permeability		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err
PET/PVdC/PP	600MPa	1.668	0.113	1.618	0.0921	1.722	0.0638	1.704	0.083
PET/PVdC/PP	800MPa	1.668	0.113	1.645	0.1029	1.699	0.0928	1.686	0.0942
PE/nylon/EVOH /PE	600MPa	1.944	0.0815	1.944	0.0928	2.012	0.099	1.958	0.0882
PE/nylon/EVOH /PE	800MPa	1.944	0.0815	1.985	0.129	1.958	0.0779	1.985	0.1041
PET/EVA/PE	600MPa	2.961	0.097	3.064	0.056	3.101	0.063	3.209	0.086
PET/EVA/PE	800MPa	2.961	0.097	3.195	0.093	3.185	0.082	3.222	0.089
PE/nylon/PE	600MPa	9.369	0.2018	9.373	0.4082	9.396	0.1851	9.355	0.1404
PE/nylon/PE	800MPa	9.369	0.2018	9.356	0.409	9.328	0.1661	9.376	0.2881
PP	600MPa	220.3	3.38	218.1	2.47	221.7	6.78	225.2	3.26
PP	800MPa	220.3	3.38	222.3	2.96	226.3	3.93	223.7	6.93
PP/nylon/PP	600MPa	4.852	0.381	5.167	0.054	5.222	0.269	5.331	0.269
PP/nylon/PP	800MPa	4.852	0.381	5.195	0.115	5.521	0.115	5.494	0.259
PET/SiO_x	600MPa	1.375	0.045	1.432	0.084	1.482	0.083	1.495	0.0803
PET/SiO_x	800MPa	1.375	0.045	1.489	0.0838	1.502	0.0702	1.509	0.0415
PET/Al_2O_3/PE	600MPa	1.387	0.039	1.41	0.0351	1.436	0.0649	1.448	0.026
PET/Al_2O_3/PE	800MPa	1.387	0.039	1.475	0.0342	1.482	0.0351	1.489	0.026
Met PET	600MPa	2.621	0.253	3.608	0.127	3.63	0.1029	4.06	0.2013
Met PET	800MPa	2.621	0.253	4.333	0.1012	4.31	0.179	4.991	0.271

Table A2: Analysis of LSMEANS of the water permeability ($Rx10^{12}$) $kg/m^2.s.Pa$ of the flexible structures.

Water vapor permeability		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN $Rx10^{12}$	Std Err	LMSEAN $Rx10^{12}$	Std Err	LMSEAN $Rx10^{12}$	Std Err	LMSEAN $Rx10^{12}$	Std Err
PET/PVdC/PP	600MPa	3.151	0.0654	3.161	0.0501	3.145	0.0607	3.161	0.0317
PET/PVdC/PP	800MPa	3.151	0.0654	3.164	0.0391	3.171	0.0461	3.167	0.0327
PE/nylon/EVOH /PE	600MPa	23.84	0.334	23.77	0.252	23.74	0.294	23.94	0.314
PE/nylon/EVOH /PE	800MPa	23.84	0.334	23.65	0.392	23.85	0.385	23.86	0.324
PE/nylon/PE	600MPa	23.59	0.221	23.6	0.349	24	0.341	23.81	0.264
PE/nylon/PE	800MPa	23.59	0.221	23.63	0.278	23.73	0.341	24.02	0.333
PET/EVA/PE	600MPa	16.08	0.305	17.89	0.273	18.46	0.653	18.48	0.537
PET/EVA/PE	800MPa	16.08	0.305	17.99	0.464	18.22	0.473	18.55	0.297
PP	600MPa	13.61	0.155	13.6	0.155	13.4	0.325	13.54	0.289
PP	800MPa	13.61	0.155	13.74	0.325	13.81	0.278	13.58	0.222
PP/nylon/PP	600MPa	4.92	0.0541	4.982	0.0696	4.998	0.0565	5.02	0.0425
PP/nylon/PP	800MPa	4.92	0.0541	4.977	0.0387	5.01	0.0535	5.014	0.0392
PET/SiO_x	600MPa	3.952	0.166	3.971	0.123	4.101	0.0733	4.252	0.1108
PET/SiO_x	800MPa	3.952	0.166	4.03	0.1702	4.156	0.1921	4.288	0.164
PET/Al_2O_3/PE	600MPa	3.898	0.0856	4.024	0.129	4.033	0.087	4.221	0.126
PET/Al_2O_3/PE	800MPa	3.898	0.0856	4.091	0.156	4.211	0.154	4.305	0.154
Met PET	600MPa	7.93	0.228	14.3	0.188	15.1	0.3602	15.9	0.459
Met PET	800MPa	7.93	0.228	14.4	0.5445	16.7	0.5183	20.5	0.5401

Table A3: Analysis of LSMEANS of the carbon dioxide permeability ($Rx10^{15}$) m^3(STP)/m^2.s.Pa of the flexible structures.

Carbondioxide permeability		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err	LMSEAN $Rx10^{15}$	Std Err
PET/PVdC/PP	600MPa	3.316	0.131	3.319	0.1285	3.289	0.1409	3.301	0.1547
PET/PVdC/PP	800MPa	3.316	0.131	3.251	0.0901	3.299	0.0808	3.311	0.0748
PE/nylon/EVOH /PE	600MPa	9.532	0.411	9.521	0.276	9.537	0.2509	9.591	0.3603
PE/nylon/EVOH /PE	800MPa	9.532	0.411	9.554	0.206	9.581	0.261	9.521	0.244
PE/nylon/PE	600MPa	20.14	0.309	20.35	0.239	19.93	0.276	20.18	0.295
PE/nylon/PE	800MPa	20.14	0.309	20.54	0.133	20.01	0.165	19.95	0.225
PET/EVA/PE	600MPa	8.92	0.371	9.217	0.484	9.282	0.356	9.566	0.332
PET/EVA/PE	800MPa	8.92	0.371	9.457	0.334	9.45	0.359	9.578	0.395
PP	600MPa	8.335	0.201	8.383	0.121	8.341	0.19	8.381	0.1211
PP	800MPa	8.335	0.201	8.311	0.0963	8.34	0.1304	8.338	0.1311
PP/nylon/PP	600MPa	2.006	0.0667	2.04	0.087	2.114	0.104	2.221	0.0811
PP/nylon/PP	800MPa	2.006	0.0667	2.083	0.0728	2.163	0.0621	2.236	0.0677
PET/SiO_x	600MPa	2.263	0.087	2.261	0.066	2.41	0.145	2.471	0.0825
PET/SiO_x	800MPa	2.263	0.087	2.281	0.0683	2.491	0.0918	2.511	0.0711
PET/Al_2O_3/PE	600MPa	2.236	0.121	2.256	0.1321	2.429	0.14	2.515	0.15
PET/Al_2O_3/PE	800MPa	2.236	0.121	2.392	0.112	2.501	0.116	2.546	0.102
Met PET	600MPa	13.36	0.73	17.55	0.612	18.33	0.279	18.72	0.526
Met PET	800MPa	13.36	0.73	18.85	0.555	19.34	0.6	20.1	0.524

Table A4: Analysis of LSMEANS of tensile strength (MPa) machine direction of the flexible structures.

Tensile Strength Machine Direction		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEANMPa	Std Err	LMSEAN MPa	Std Err	LMSEAN MPa	Std Err	LMSEAN MPa	Std Err
PET/PVdC/PP	600MPa	66.484	1.14	66.241	1.23	66.167	1.8	66.059	1.9
PET/PVdC/PP	800MPa	66.484	1.14	66.339	1.56	65.143	1.33	65.261	1.22
PE/nylon/EVOH/PE	600MPa	20.416	1.8	21.009	0.9	20.353	0.95	19.699	1.3
PE/nylon/EVOH/PE	800MPa	20.416	1.8	18.575	1.3	18.769	1.6	19.599	1.5
PET/EVA/PvDC	600MPa	55.529	1.5	54.349	1.8	54.934	1.3	54.703	1.7
PET/EVA/PE	800MPa	55.529	1.5	55.073	1.2	55.193	0.9	54.915	0.92
PE/nylon/PE	600MPa	23.347	1.3	24.163	1.02	23.36	1.88	23.664	1.34
PE/nylon/PE	800MPa	23.347	1.3	24.869	1.17	23.482	0.9	24.839	1.07
PP	600MPa	25.365	1.84	24.554	2.74	25.751	0.8	25.318	1.19
PP	800MPa	25.365	1.84	24.278	1.92	24.178	2.24	24.289	1.07
PP/nylon/PP	600MPa	57.238	1.31	56.053	1.07	56.276	3.15	56.723	1.41
PP/nylon/PP	800MPa	57.238	1.31	55.749	1.74	56.426	1.96	56.053	0.97
PET/SiO_x	600MPa	48.83	1.41	50.166	0.67	49.703	1.41	49.269	1.31
PET/SiO_x	800MPa	48.83	1.41	49.628	1.21	50.851	0.96	49.434	2.51
PET/Al_2O_3/PE	600MPa	49.678	1.81	49.267	1.93	50.032	1.34	49.253	2.06
PET/Al_2O_3/PE	800MPa	49.678	1.81	50.964	1.93	49.833	1.34	49.63	2.06
Met PET	600MPa	63.819	2.25	63.428	2.1	62.483	1.5	63.37	2
Met PET	800MPa	63.819	2.25	64.798	2.1	63.196	1.4	63.621	1.9

Table A5: Analysis of LSMEANS of tensile strength (MPa) cross direction of the flexible structures.

Tensile Strenght Cross Direction		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN MPa	Std Err	LMSEAN MPa	Std Err	LMSEAN MPa	Std Err	LMSEAN MPa	Std Err
PET/PVdC/PP	600MPa	77.264	2.56	76.938	3.7	78.425	3.8	75.425	3.5
PET/PVdC/PP	800MPa	77.264	2.56	76.99	3.5	75.845	4.1	76.371	4.3
PE/nylon/EVOH/PE	600MPa	16.213	0.78	16.365	1.01	17.3	0.78	16.411	0.76
PE/nylon/EVOH/PE	800MPa	16.213	0.78	16.464	0.95	16.897	1.3	16.822	0.86
PE/nylon/PE	600MPa	19.322	1.7	20.246	1.83	20.459	1.13	19.678	0.67
PE/nylon/PE	800MPa	19.322	1.7	20.317	1.5	20.72	1.07	20.782	1.2
PET/EVA/PVdC	600MPa	52.388	1.9	52.649	1.67	52.698	2.02	52.318	2.56
PET/EVA/PVdC	800MPa	52.388	1.9	52.278	1.78	52.569	1.89	52.641	1.9
PP	600MPa	50.227	2.4	49.711	1.1	48.967	2.9	51.1	1.5
PP	800MPa	50.227	2.4	50.118	0.98	48.584	3	48.78	2.2
PP/nylon/PP	600MPa	54.925	1.3	54.746	2.06	54.55	2.54	53.447	2.6
PP/nylon/PP	800MPa	54.925	1.3	55.301	2.6	54.477	3.04	53.924	2.1
PET/SiO$_x$	600MPa	42.827	1.1	42.954	0.99	42.662	1.06	42.687	1.3
PET/SiO$_x$	800MPa	42.827	1.1	42.581	1.9	42.199	1.05	42.136	1.04
PET/Al_2O_3/PE	600MPa	41.196	0.6	41.056	1.6	41.359	1.5	40.856	1.6
PET/Al_2O_3/PE	800MPa	41.196	0.6	41.27	2.05	40.242	1.3	40.917	1.6
Met PET	600MPa	56.35	2	56.37	1.4	56.303	2.4	55.604	1
Met PET	800MPa	56.35	2	55.713	2	55.256	1.5	54.946	1.8

Table A6: Analysis of LSMEANS of % elongation machine direction of the flexible structures.

% Elongation Machine Direction		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err
PET/PVdC/PP	600MPa	107.04	3.1	107.21	4.42	111.39	3.5	110.24	4.15
PET/PVdC/PP	800MPa	107.04	3.1	111.12	5.23	109	3.17	111.05	6.8
PE/nylon/EVOH/PE	600MPa	651.2	37.4	669.66	23.7	658	23	640.4	41.5
PE/nylon/EVOH/PE	800MPa	651.2	37.4	647.08	32.6	634.97	34.5	643.37	30.7
PE/nylon/PE	600MPa	639.93	37.8	648.08	28	636.13	21	642.18	22.7
PE/nylon/PE	800MPa	639.93	37.8	646.85	33	654.7	26.5	645.62	39.4
PET/EVA/PVdC	600MPa	153.8	13.6	153.56	15.2	155.6	11.5	160.1	8.9
PET/EVA/PVdC	800MPa	153.8	13.6	157.1	15.7	160.33	6.9	160.23	5
PP	600MPa	272.53	15.9	264.73	15.15	274.7	12.4	271.25	15.8
PP	800MPa	272.53	15.9	276.79	14.01	265.71	24.5	268.5	8.07
PP/nylon/PP	600MPa	95.47	9.7	97.35	6.3	98.74	13.9	99.96	7.2
PP/nylon/PP	800MPa	95.47	9.7	97.38	9.2	100.18	6.4	99.67	7.9
PET/SiO_x	600MPa	117.7	10.64	121.8	4.9	119.2	10.6	119.9	8.6
PET/SiO_x	800MPa	117.7	10.64	119.1	12.3	118.06	8.51	117.8	4.75
PET/Al_2O_3/PE	600MPa	153.6	14.1	152.9	6.8	153.7	6.25	153.78	12.7
PET/Al_2O_3/PE	800MPa	152.6	14.1	156.5	19.1	154.7	13.9	154.3	10.4
Met PET	600MPa	151.5	14.4	150.42	11.7	147.18	8.16	147.2	14.72
Met PET	800MPa	151.5	14.4	151.9	6.78	147.6	8.65	148.8	8.07

Table A7: Analysis of LSMEANS of % elongation cross direction of the flexible structures.

% Elongation Cross Direction		1 atm		5 min HPP		10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err
PET/PVdC/PP	600MPa	106.6	6.8	106.2	3.2	111.6	4.03	107.7	3.5
PET/PVdC/PP	800MPa	106.6	6.8	111.6	4.8	110.6	4.89	106.7	4.2
PE/nylon/EVOH/PE	600MPa	529.56	27	540	17.06	554.8	25.4	556.9	34
PE/nylon/EVOH/PE	800MPa	529.56	27	547.6	35	552	41	540.6	45
PE/nylon/PE	600MPa	535	34.75	565	37	568.18	36.9	565.9	36.1
PE/nylon/PE	800MPa	535	34.76	553.87	12.3	565.08	25.4	567.3	34.2
PET/EVA/PVdC	600MPa	126.2	7.8	133.4	8.5	135.2	12.65	133.3	6.4
PET/EVA/PVdC	800MPa	126.2	7.8	134.1	9.9	131.5	10.14	133.4	6.7
PP	600MPa	60.2	6.58	61.8	4.8	62.5	7.5	63.96	5.6
PP	800MPa	60.2	6.58	61.13	6.06	60.91	4.6	62.52	6.9
PP/nylon/PP	600MPa	63	2.6	64.32	4.1	64.75	5.4	66.43	5.3
PP/nylon/PP	800MPa	63	2.6	62.55	6.4	68.5	5.9	68	10.3
PET/SiO_x	600MPa	153.92	10.8	160.2	12.3	161.3	10.2	161	11
PET/SiO_x	800MPa	153.92	10.8	161.6	12.7	155.9	10.5	157.3	6.8
PET/Al_2O_3/PE	600MPa	157.5	6.24	161.93	13.6	159.5	15.8	159.8	9.4
PET/Al_2O_3/PE	800MPa	157.5	6.24	159.9	17.9	158.2	13.9	161.7	6.9
Met PET	600MPa	140.9	18.87	143.9	9.5	146.3	14.21	140.5	11.5
Met PET	800MPa	140.9	18.87	139.1	7.8	137.9	9.9	140.9	15.8

Table A8: Analysis of LSMEANS of % modulus of elongation machine direction of the flexible structures.

%Modulus of Elongation Machine Direction		Atm. Press.		5 min HPP		10 min HPP	std error	20 min HPP	
Structure	Pressure	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err
PET/PVdC/PP	600MPa	697	19.1	734	47.1	735.48	25.3	720.41	23.1
PET/PVdC/PP	800MPa	697	19.1	724.7	15.7	714.5	15.4	728.9	16.5
PE/nylon/EVOH/PE	600MPa	373.11	12.8	376.9	6.8	385.9	12.6	384.5	13.01
PE/nylon/EVOH/PE	800MPa	373.11	12.8	392.33	9.9	392.37	6.7	387.71	6.8
PE/nylon/PE	600MPa	375.9	6.8	375.73	6.1	377.62	9.8	376.26	5.34
PE/nylon/PE	800MPa	375.9	6.8	366	12.3	372.46	5.3	373.4	5.1
PET/EVA/PVdC	600MPa	408.57	4.4	406.54	8.8	412	5.7	399.9	5.3
PET/EVA/PVdC	800MPa	408.57	4.4	415.7	20.2	420.06	17.1	404.6	9.5
PP	600MPa	879.42	44.5	876.51	65.3	871.11	59.3	869.42	57.4
PP	800MPa	879.42	44.4	877.72	50.3	868.4	24	865.63	60.4
PP/nylon/PP	600MPa	544.25	37.3	536.6	30	539.58	34.4	564.62	15.9
PP/nylon/PP	800MPa	544.25	37.3	542.57	19	516.01	24.5	539.4	14
PET/SiO$_x$	600MPa	458.77	16.5	428.47	11	441.15	9.5	444.71	14
PET/SiO$_x$	800MPa	458.77	16.5	442.61	17.9	437.64	8.3	442.35	10.8
PET/Al$_2$O$_3$/PE	600MPa	418.2	16	413.52	13	415.29	15	410.43	7.3
PET/Al$_2$O$_3$/PE	800MPa	418.2	16	406.8	8.7	406.9	16.7	418.44	8.9
Met PET	600MPa	379.34	13.4	374.52	22.1	387	17.9	384	20.8
Met PET	800MPa	379.34	13.4	363.43	8.2	373.69	6.1	359	7.8

Table A9: Analysis of LSMEANS of % modulus of elongation cross direction of the flexible structures.

% Modulus of Elongation Cross Direction		Atm. Press.		5 min HPP	std error	10 min HPP		20 min HPP	
Structure	Pressure	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err	LMSEAN	Std Err
PET/PVdC/PP	600MPa	557.99	15.13	584.15	21.4	586.3	25.17	576.3	16.36
PET/PVdC/PP	800MPa	557.99	15.13	571.81	16.25	576.12	20.4	585.15	29.13
PE/nylon/EVOH /PE	600MPa	344.39	8.8	348.13	7.6	346.84	2.6	346.97	3.4
PE/nylon/EVOH /PE	800MPa	344.39	8.8	346.5	4.5	348.6	3.5	348.03	3.2
PE/nylon/PE	600MPa	336.52	11.3	347.51	17.8	342.22	9.4	338.46	8.3
PE/nylon/PE	800MPa	336.52	11.3	342.7	4	340.24	6.7	341.26	5.5
PET/EVA/PVdC	600MPa	364	15.9	348.94	10.5	346.78	4	348.4	7.2
PET/EVA/PVdC	800MPa	364	15.9	350.37	10.3	356.95	19.4	351.38	7.6
PP	600MPa	652.09	38.6	642.566	27.3	638	32.02	656.43	25.07
PP	800MPa	652.09	38.6	656.86	18.3	647.4	15.6	639	34.6
PP/nylon/PP	600MPa	457.45	35.4	438.8	32.3	456.9	38	479	59
PP/nylon/PP	800MPa	457.45	35.4	479.8	27	477.41	34	458.9	27
PET/SiO_x	600MPa	373.365	9.8	375.11	15.5	372.23	19.15	377.67	17.3
PET/SiO_x	800MPa	373.65	9.8	368.86	20.1	391.44	6	389.79	12.8
PET/Al_2O_3/PE	600MPa	374.76	19.07	383.44	14.09	360.51	17.9	355.52	11.9
PET/Al_2O_3/PE	800MPa	374.76	19.07	354.56	9.5	354.98	6	379.9	12.9
Met PET	600MPa	322.12	8.5	324.12	11	312.65	9.3	311.6	8.6
Met PET	800MPa	322.12	8.5	312.7	8	313.9	6.2	307.3	15.9