

# The Effect of High Pressure Processing on the Morphology of Polyethylene Films Tested by Differential Scanning Calorimetry and X-ray Diffraction and Its Influence on the Permeability of the Polymer

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**ABSTRACT:** This study investigated the influence of high-pressure processing on the morphology and permeability of low-density polyethylene (LDPE) films used for food packaging. This was done by monitoring the crystallinity, melting temperature ( $T_m$ ), and oxygen transmission rate (OTR) of the materials before and after the pressure treatments. A first set of pouches made from the LDPE films were filled with 95% ethanol then pressured at 200, 400, 600, and 800 MPa for 5 and 10 min at 25 and 75°C. The crystallinity and  $T_m$  of the films were measured using differential scanning calorimetry (DSC). X-ray diffraction (XRD) was also used to determine the crystallinity. A second set of LDPE pouches were similarly made but a half of them were filled with 95% ethanol and the other half filled with distilled water. These second set of pouches were pressured at 200, 600, and 800 MPa then

their OTR tested. Results of the DSC experiments showed that the  $T_m$  increased with increasing pressure intensity but the crystallinity changes were not detectible. The XRD method on the other hand, showed significant ( $P < 0.05$ ) crystallinity increases with increasing pressure treatments. The gas permeability analyses showed decreasing OTR's with increasing high-pressure intensity treatments. The OTR in the pouches filled with the 95% ethanol was slightly lower than that of the pouches filled with water. These findings allowed us to better anticipate the behavior of LDPE films used to package high-pressure processed foods. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 107–113, 2009

**Key words:** polyethylene films; morphology; high pressure processing; permeability

## INTRODUCTION

The high-pressure processing (HPP) of certain foods has grown significantly in recent years. This process denatures protein molecules, whereas many compounds responsible for sensory and nutritional quality are unaffected. The availability of flexible polymeric films has allowed the application of HPP to prepackaged foods. Most of these films are capable of withstanding the high pressure process without visible signs of integrity loss. However, HPP has the potential to produce undesirable effects in some polymeric films. Previous studies have shown that some flexible materials can lose significant barrier to oxygen, carbon dioxide, and water vapor when exposed to HPP.<sup>1–3</sup>

The morphology of a polymer refers to its percent crystals and their homogeneity when compared with the noncrystalline regions within the matrix of the material. It also refers to the arrangement of its poly-

meric chains. The higher the percent crystallinity of the polymer, the better is its barrier to permeating gases and vapors, the greater its stiffness, and the lower its transparency. These properties exist because the higher the percent crystallinity, the greater the orderliness of the polymeric chains and the lower the presence of void spaces within the material. When gases transverse the walls of a plastic material they do so mainly through the void spaces within the amorphous regions of the polymer. On the other hand, the orderliness and tightness of the polymeric chains in the crystalline regions of the polymer impedes the permeation of diffusing gases and thus increases the barrier of the material.

During the treatment of prepackaged food products, it is essential to estimate the impact of the processing technique on the properties of the packaging material. Significant changes to the material could impact the shelf life of the packaged product. For example, if a processing treatment results in crystallinity changes to a polymeric packaging material, this could affect the gas barrier, stiffness, and thermal properties of the plastic. Depending on the nature of the packaged product, this could result in a reduction of its shelf-life. Foods that are

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susceptible to oxidation can become rancid after exposure to high oxygen levels, for example. On the other hand, foods that are moisture sensitive can spoil quickly by either rapid water gain or loss during storage.<sup>4</sup>

HPP is a technique designed to kill bacteria in certain products without affecting the texture, natural taste, nutrient content, and color of the food, when compared with traditional processes such as steam treatment.<sup>5</sup> During the HPP, damage to the bacterial coat is achieved by the extremely high pressures generated within the system (as high as 800 MPa). To ensure that the advantages of this technique are not lost during the process, it is essential that the influence of the pressure on the morphology of the polymer used to prepackage the food is investigated. Because different polymers have different properties, it is thus imperative to gain a clear understanding of which materials can be affected by HPP and how these changes can be detected. This study provides important scientific information that can be used to better understand how HPP influences the properties of polyolefins used to package certain foods.

Thus, the objectives of this study are as follows: (1) to investigate the influence of HPP on the crystallinity and melting temperature ( $T_m$ ) of low-density polyethylene (LDPE) films used for food packaging; and (2) to determine the effect of HPP on the oxygen permeability of the LDPE films.

## MATERIALS AND METHODS

### Test material

Duplicate sample pouches measuring 10 cm × 10 cm were made from the LDPE films. The films (50 μm thick) were obtained from Ciba Specialty Chemicals Corp. (Tarrytown, NY). These films were divided into two sets. One set was filled with 95% ethanol as a food simulant, then sealed without headspace using a Sipromac vacuum sealer (St-Germain, Quebec) set at 70 KPa, zero gas pressure, and 0.8 s dwell time. The sealed samples were then high pressure processed. The second set of LDPE pouches were similarly prepared and high pressure processed. However, these pouches were filled with distilled water.

### High pressure processing

The HPP was performed in a QFP-6 Quintus high pressure food processor manufactured by Flow Autoclave System (Columbus, OH). The HPP conditions for the first set of pouches were 200, 400, 600, and 800 MPa for 5 and 10 min at 25 and 75°C. Control samples were similarly prepared but not high pressure processed. For the second set of pouches,

the HPP conditions were 200, 600, and 800 MPa for 5 min at 75°C. A half of these second set of pouches were filled with 95% ethanol and the other half filled with distilled water as a control. The HPP system generated the pressure via a hydraulic arrangement as described in previous studies.<sup>1,3</sup> The pressure transmission fluid used was 1,2 propanediol.

### Differential scanning calorimetry

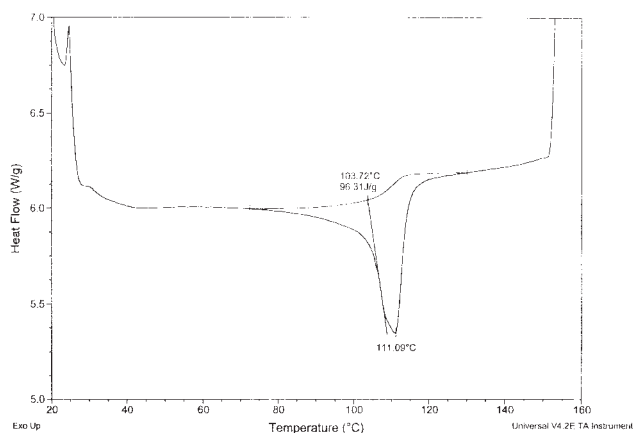
A Model 2920 TA Instruments Modulated Differential Scanning Calorimeter (DSC) (New Castle, DE) was used to investigate how HPP affected the thermal transition of the LDPE films. This was done at a heating rate of 5°C/min from 25 to 150°C. The weight of each sample was 0.9 mg. Thermal parameters such as melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H$ ) were determined from transitions in the DSC thermograms. The peak temperatures ( $T_m$ , °C) and heat of fusions (J/g) corresponding to the major endothermic peaks in the thermograms were determined by integrating the temperature versus the heat flow curve using the software provided by the instrument manufacturer. The crystallinity was calculated from the ratio of the heat of fusion ( $\Delta H$ ) to 293 J/g ( $\Delta H$  for 100% crystalline LDPE). This value for the 100% crystalline LDPE was obtained from studies reported by Brzezinska.<sup>6</sup>

### X-ray diffraction

X-ray diffraction (XRD) patterns for the LDPE films were obtained using an X-ray diffractometer DMS 2000 Scintag Series (Cupertino, CA). The sample size was 30 mm × 30 mm and the scanning range was 8 to 32θ at a wavelength of 1.54 Å. Prior to testing the samples, a quartz crystal was scanned and the values obtained were used as background subtraction for the test samples. The copper target tube of the X-ray diffractometer was set at 40 kV and 30 mA. During the test, the X-rays were allowed to pass through a 1° divergence slit onto samples of the films placed in the specimen chamber. Diffracted radiation from the samples was then allowed to pass through a 0.1° scatter slit before reaching the monochromator. Examination of the diffraction patterns was carried out at room temperature and under constant operation conditions. From the diffraction peaks obtained, the percent crystallinity,  $d$ -spacing, and crystallite thickness were estimated. The peak intensities were used to estimate the percent crystallinity. The  $d$ -spacing ( $d$ ) was calculated from the Bragg Equation:

$$n\lambda = 2d \cdot \sin \theta \quad (1)$$

where  $n$  is an integer,  $\lambda$  is the wavelength (1.54 Å), and  $\theta$  is the angle between the incident rays. The



**Figure 1** An example of a DSC thermogram showing the baseline and the heat flow curves used to determine the heat of fusion and the melting temperature.

crystalline thickness ( $D$ ) was determined from the Scherrer Equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where  $\beta$  is the full-width at half maximum. Both  $\beta$  and  $\theta$  were obtained from the peaks generated from the X-ray scans. The peak fitting program in the computer attached to the instrument was used to edit the initial profiles and refine them for more accurate computation.

### Oxygen transmission rate

This test was done on the LDPE films exposed to HPP at 200, 400, 600, and 800 MPa at 25 and 75°C. Films not high pressure processed were also tested as controls. The oxygen transmission rate (OTR) analyses were conducted in triplicate on a Mocon Ox-Tran 2/21 ML permeability tester (Minneapolis, MN). The test conditions were 50% RH, 1 atm, and 23°C. This equipment was fitted with a coulometric detector and the test was done according to the ASTM F 1927-98 Method.<sup>7</sup>

### Statistical analysis

The DSC, XRD, and OTR analytical data were plotted for samples before and after HPP treatments. These plots were the averages of three replicates for each treatment. These responses were treated independently and analyzed statistically using ANOVA with an  $\alpha$ -level of 0.05. The statistical analyses were conducted separately for each analytical method to determine the effect of HPP on the DSC, XRD, and OTR analytical data of the samples with those of the controls. To determine the effect of the high pressures, processing times, and temperatures on the

DSC, XRD, and OTR analytical data, the effects of the processing parameters were analyzed using a general linear model (GLM). All analyses were done using Minitab 14 (State College, PA).

## RESULTS AND DISCUSSIONS

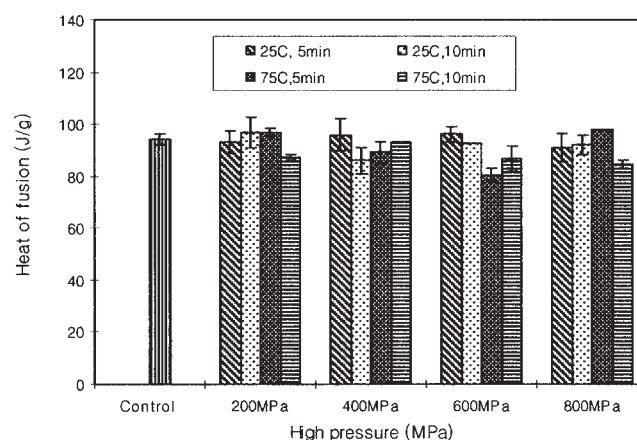
For the DSC analysis, the area under the curve (heat of fusion,  $\Delta H$ ) and melting temperature ( $T_m$ ) were selected to determine the crystallinity for all samples. Figure 1 shows an example of a thermogram obtained in this study. The curved baseline, taking into account the variation in heat capacity before and after the heat transitions at two designated points (72.5 and 130°C) on the thermogram, was used to calculate the heat of fusion ( $\Delta H$ ). The asymmetric and broad shape of the transition in Figure 1 indicates that the LDPE films tested in this study were complex structures. This is consistent with published reports that polyethylene is composed of crystalline and amorphous regions.<sup>8</sup>

The effect of HPP on the crystallinity and melting temperature ( $T_m$ ) of the LDPE samples using the DSC analysis are shown in Figures 2 and 3, respectively. Figure 2 shows that HPP did not significantly ( $P > 0.05$ ) affect the crystallinity of the samples. However, HPP significantly ( $P < 0.05$ ) increased the  $T_m$  when compared with the results obtained for the controls. These controls were not high pressure treated (Fig. 3).

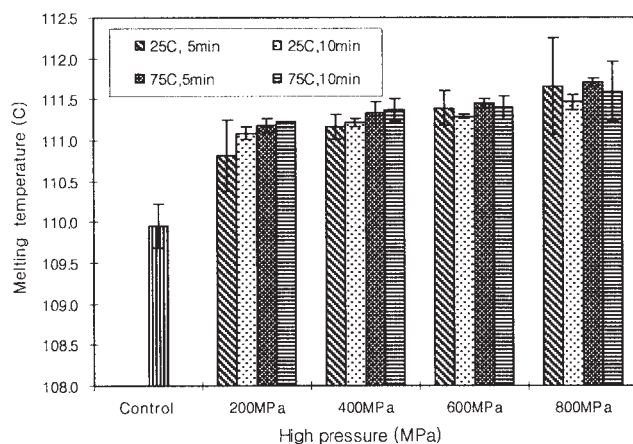
The statistical analysis of the crystallinity and  $T_m$  began by finding an appropriate ANOVA model to describe the data. The following model was chosen:

$$P_{ijkl} = \mu + \rho_i + \tau_j + \theta_k + (\rho\tau)_{ij} + (\tau\theta)_{jk} + (\rho\theta)_{ik} + (\rho\tau\theta)_{ijk} + \varepsilon_{ijkl} \quad (3)$$

where  $P_{ijkl}$  is the observed crystallinity measurement at pressure level  $i$ , temperature level  $j$ , time  $k$ , pouch number  $l$ ;  $\mu$  is an overall mean parameter,  $\rho_i$  is the



**Figure 2** The effect of different HPP conditions on the crystallinity of LDPE films tested by DSC.



**Figure 3** The effect of different HPP conditions on the melting temperature of LDPE films tested by DSC.

effect of pressure; the effect of temperature  $\tau_j$ ; the effect of time  $\theta_k$ ; and  $\varepsilon_{ijkl}$  is a random error term (independent and identically distributed according to a normal distribution). The indices were as follows:

- $i = 200, 400, 600, 800$  pressure levels
- $j = 25, 75$  temperature levels
- $k = 5, 10$  time levels
- $l = 1, 2$  pouch number

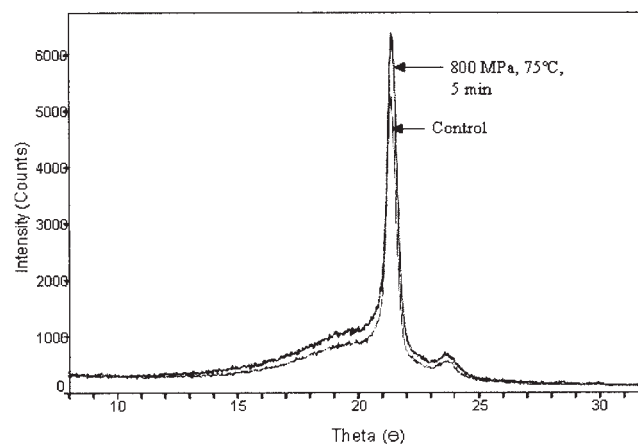
Fitting the model yielded an ANOVA table which showed that there was no evidence that the individual effect of pressure, temperature, or time significantly ( $P > 0.05$ ) influenced the crystallinity of the LDPE films. A similar behavior was observed when DSC studies were done on high pressure treated (690 MPa) ethylene vinyl alcohol (EVOH) copolymers used to package a food simulant.<sup>3</sup> Those findings suggested that the effect of the interaction of these HPP-based treatments on changes to the peak sizes in the DSC thermogram were generally marginal.

For the  $T_m$  analysis, the ANOVA table showed that the HPP conditions on a whole, had a significant ( $P < 0.05$ ) effect when compared with the control samples. Although the effect between the HPP conditions by themselves was not significant ( $P > 0.05$ ), we found a slightly increasing trend in the  $T_m$  of the films exposed to increasing pressure treatments. We believed that this increase in  $T_m$  was caused by an increasing crystallization of the HPP treated materials when compared with the films exposed to lower pressures. Similar findings were also reported by Badr et al., who found changes to the melting point and crystallinity of LDPE films exposed to increasing irradiation treatments.<sup>9</sup> Because the DSC analysis in our study did not show that the HPP conditions had a significant impact on crystallinity, we decided to investigate this issue fur-

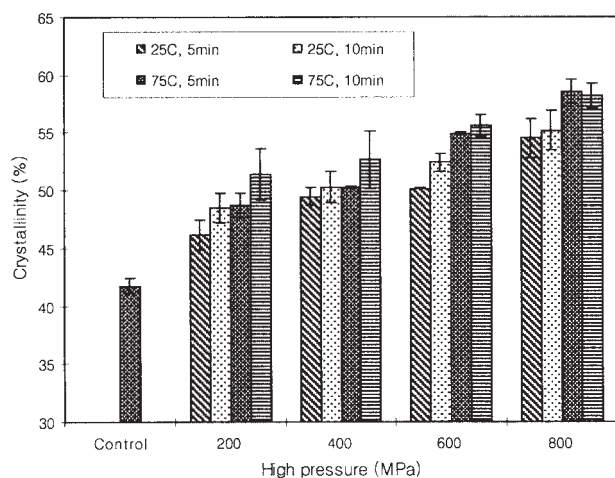
ther. As a result, the XRD analysis was done on the samples to determine if the DSC method had limitations in correlating the HPP conditions with the crystallinity of the LDPE films.

Figure 4 shows an example of the XRD patterns obtained in this study. The percent crystallinities of the treated and untreated samples were obtained from patterns like this for all films tested by XRD. Figure 4 shows an overlay of the pattern for a sample treated at 800 MPa when compared with the control. The figure shows that the 800 MPa sample has a peak with a larger area and greater intensity. These patterns also show that the 800 MPa pattern is slightly broader than that of the control sample. All diffractograms show peaks at approximately  $21.35^\circ$  and  $23.65^\circ$ . The amorphous region is located at  $19.8^\circ$ . These peaks correspond to the 110 and the 200 lattice planes of the orthorhombic crystalline form of polyethylene.<sup>10</sup> The differences in the breadth of the patterns may indicate that there might have been a broader distribution in the size of the crystals or that there were distortions in their long range order when compared with the control samples, as examples. Combinations of these changes could have also occurred. As was done in this study, Liu et al. also used the breadth of the diffraction peak to estimate the crystallite size from the Scherrer Equation.<sup>11</sup>

Figure 5 shows the results from the XRD analyses for crystallinity changes in the LDPE films. These results show that all HPP conditions increased the crystallinity of the treated samples when compared with the controls. Figure 5 also shows that the crystallinity increased with increasing pressure from 200 to 600 MPa and also with increasing temperatures. As was the case with the data obtained from the DSC analyses, the primary tool used to analyze the XRD data was the ANOVA. An examination of



**Figure 4** XRD pattern showing the increase crystallinity count of the 800 MPa treated samples when compared with the controls. This is an example of the raw data that were collected during this part of the study.



**Figure 5** The effect of different HPP conditions on the crystallinity of LDPE films tested by XRD.

the  $P$ -values showed that only the main effects (pressure, temperature, and time) were significant ( $P < 0.05$ ). This finding reinforces the results seen in Figure 5. These results also showed that, for the samples treated for 5 min, those exposed to 75°C temperatures were significantly ( $P < 0.05$ ) higher in crystallinity when compared with the samples exposed to 25°C. This result was also consistently similar at all HPP treatments. For the samples treated for 10 min, the percent crystallinity was significantly higher ( $P < 0.05$ ) at the 600 and 800 MPa pressure levels. The results show that the processing time (5 and 10 min) did not produce significant changes ( $P > 0.05$ ) in the crystallinity of the LDPE samples.

The results for the crystallinity obtained from the XRD analyses were not corroborated with those from the DSC analysis. This is a matter that needs further study. However, we could speculate that this may have occurred because DSC measures the quan-

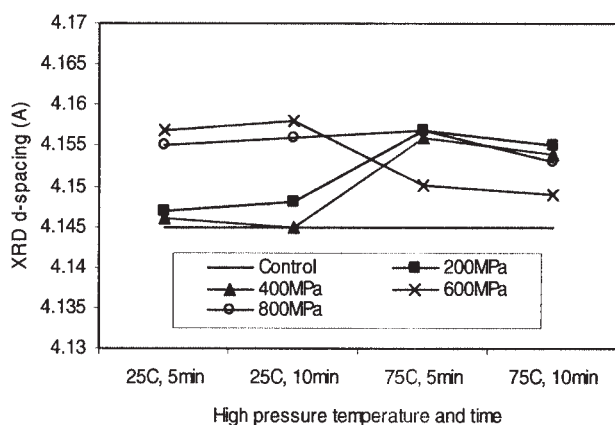
tity of heat required per unit mass of a compound to increase its temperature when compared with a reference analyzed under similar conditions. XRD on the other hand, measures crystallinity based on volume ( $d$ -spacing and crystallite size  $[D]$ ). Thus, if HPP reduces the volume of the polymer by compressing its amorphous regions, DSC would be less sensitive to these changes because it depends on the mass of the polymer. XRD on the other hand, would be more sensitive to these volume changes. The increase in the  $d$ -spacing and crystallite sizes as shown in Figures 6 and 7 support this assumption. The influence of HPP to produce changes in the volume of polymers is documented in studies reported by Schauwecher et al. and Masson.<sup>3,12</sup> It should be noted that the pressures used in our study were relatively high ones and the correlation between these pressures and changes to the morphology of polymers used in food packaging is a topic of ongoing research by the authors. Little is reported in the literature on this topic.

Figure 8 shows the OTR results for the LDPE controls and films treated by HPP. The results show that HPP significantly decreased ( $P < 0.05$ ) the oxygen permeability of the test films.

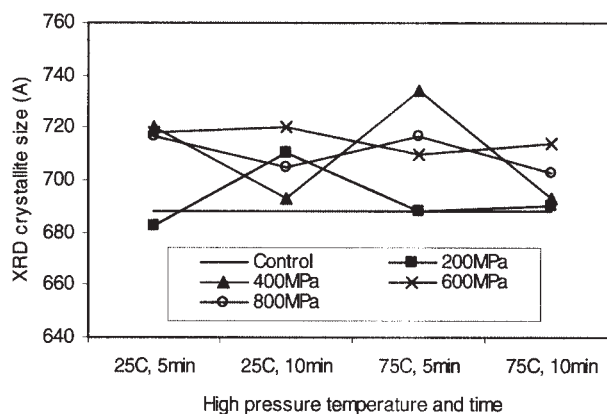
The statistical model used to analyze the OTR data sought to determine whether the different combinations of treatments changed the permeation of the LDPE films. The ANOVA model used to determine this was:

$$P_{ijkl} = \mu + \rho_i + \tau_j + \theta_k + \varepsilon_{ijkl} \quad (4)$$

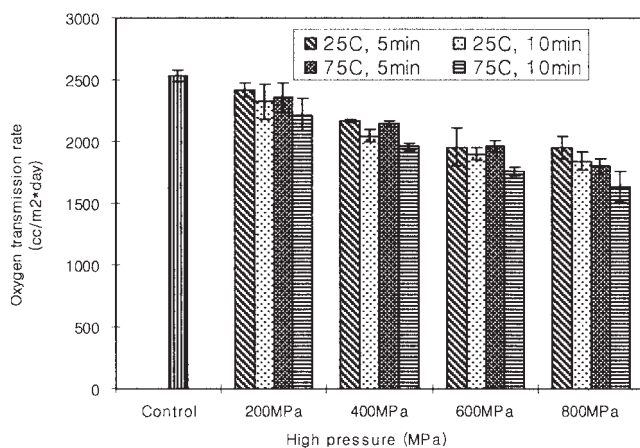
where  $P_{ijkl}$  is the observed average permeability measurement from two repeated measures at pressure level  $i$ , temperature level  $j$ , time level  $k$ , and pouch number  $l$ ;  $\mu$  is an overall mean parameter,  $\rho_i$  is the effect of pressure;  $\tau_j$  is the effect of temperature;  $\theta_k$  is the effect of time; and  $\varepsilon_{ijkl}$  is a random error term (independent and identically distributed



**Figure 6** The effect of different HPP conditions on  $d$ -spacing measurement of the crystals in the LDPE films tested by XRD.



**Figure 7** The effect of different HPP conditions on crystallite size of LDPE films tested by XRD.



**Figure 8** The influence of HPP on the OTR of the LDPE samples.

according to a normal distribution). The indices are as follows:

- $i = 200, 400, 600, 800$  pressure levels
- $j = 25, 75$  temperature levels
- $k = 5, 10$  time levels
- $l = 1, 2$  pouch number

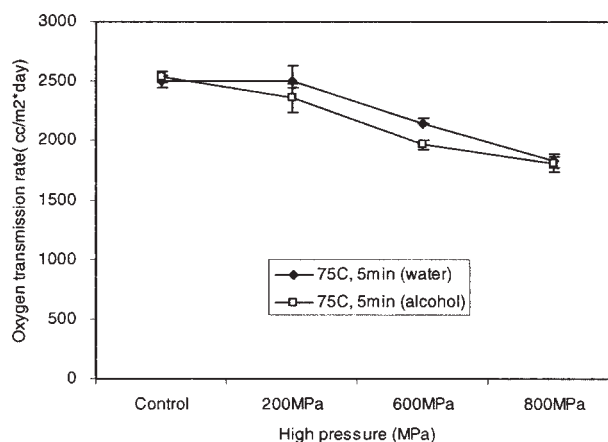
This model is saying that the observed measurement is an additive function of the effects of pressure, temperature, and time. Results from the ANOVA showed that increasing the pressure during the HPP treatment significantly decreased the OTR of the samples. The effect of temperature and time was marginal. The ANOVA on the relationship between HPP and the OTR specifically showed that, on average, pouches treated with 800 and 600 MPa of pressure were not significantly different in their effect on the permeability of the samples. Those treated with 400 MPa and 600 MPa of pressure were not significantly different. Those treated with 400 MPa of pressure had a permeability value that was 398.30 higher (95% confidence interval: 150.6–646.0) on average than those treated with 200 MPa when adjusting for all other effects. Those treated with 400 MPa of pressure had a permeability value that was 436.2 higher (95% confidence interval: 176.5–696.0) than those treated with 800 MPa on average when adjusting for all other effects. In determining the combination that would produce the lowest permeability, we found that there were no statistically significant differences ( $P > 0.05$ ) resulting from different combinations of time and temperature.

Results similar to what was obtained in this study for the impact of HPP on the crystallinity of the LDPE films are also reported by Lima et al.<sup>13</sup> In that study, Lima et al. showed that HPP influenced crystallinity changes in the test polymers. Because the permeability of a plastic material is influenced by the morphology of its chemical structure and the ratio between its

crystals and the void spaces, the increase in crystallinity of the LDPE films in this study resulted in an increase in its barrier properties.

Figure 9 shows the results of HPP on LDPE pouches filled with 95% ethanol when compared with distilled water. This comparison was done to investigate the influence of the alcohol on the results obtained in this study. This result shows that the OTR of the films exposed to the alcohol was slightly lower than those filled with the water. Polyolefins are hydrophobic in nature and are good barriers to moisture. However, if sorption of the 95% alcohol occurred during the pressure treatment, this could act synergistically with the HPP to influence the OTR of the polymer. When sorption of a compound occurs, the permeant occupies the void spaces within the matrix of the polymer. However, in real life situations, the packaged food that the 95% ethanol represents, remains in contact with the packaging material until the package is opened by a consumer and the contents wholly or partially consumed. Thus, the total absence of the food simulant from the polymer does not represent a real world situation. This matter is the subject of ongoing investigations.

All OTR analyses of the samples exposed to HPP were conducted 7 days after the treatment. The samples were also stored at 25°C prior to the analysis. This was done to allow drying of the samples and the loss of temporary memory caused by the high pressure treatment. This loss of memory is what is expected in real life situation because in most instances, packaged products are consumed several days after they are processed. Previous studies have shown that the retorting of EVOH induced a temporary loss of oxygen barrier, but a significant recovery occurred after allowing the material time to recover.<sup>8</sup> Although the authors recognized that HPP lowered the OTR of the material when compared with retorting (which increased OTR), that study showed that



**Figure 9** The influence of HPP on the OTR of the LDPE samples exposed to water compared with 95% ethanol.

certain polymers are capable of recovery after exposure to the stresses caused by certain food processing techniques.

### CONCLUSIONS

From the results obtained in this study, it could be concluded that HPP caused significant changes to the crystallinity of LDPE films. These changes were caused in films exposed to increasing pressures from atm to 800 MPa. The DSC analysis was only able to detect significant changes in melting temperature in the LDPE films caused by the HPP. HPP significantly decreased the oxygen permeability of the treated LDPE films. This increase in barrier was caused by the increasing pressures and temperatures (25–75°C) of the process.

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