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IOP Conf. Series: Materials Science and Engineering **485** (2019) 012007 doi:10.1088/1757-899X/485/1/012007

Study on the changes induced by the Pressure-Assisted Thermal Processing (PATP) in polymer films used as packaging by the meat industry

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Abstract. The purpose of this study was to assess the changes induced by pressure-assisted thermal processing (PATP) treatment in two multilayer polymer films used as packaging material by the meat industry. The changes induced by the treatment at 600 MPa, 70 ºC for 10 minutes on the structural, mechanical and thermal properties of two multilayer polymer films (Pev-70 coextruded high barrier multilayer film with the structure PA / EVOH / PA / PE and Pob-60 combination of biaxially oriented polyamide with a co-extruded barrier film of the polyethylene / EVOH / m-polyethylene structure) were studied. Numerous changes induced by the PATP treatment on the structural, mechanical and thermal properties of the two multi-layered polymer films used as packaging materials in the meat industry have been identified. The choice of a packaging material according to the PATP treatment requires a better understanding of all the changes induced by this treatment. So, this study has preliminarily identified a part of those changes that occurs and could irreversible affect the quality of foods.

1. Introduction

Pressure assisted thermal processing (PATP) is a combined technique designed to prolong food shelf-life. Very limited information is available on impact of combined pressure-heat treatment on packaging material during PATP treatment [1-6].

The integrity maintenance of flexible polymeric films used for packaging during PATP treatment has a particular importance for the food safety and food shelf-life [2-4, 6]. Prior to PATP treatment, the packaged products should be preheated to a target temperature. The preheating efficiency depends on the polymeric film used. The results have shown that multilayer films require a shorter preheating time than thin polymeric materials. In addition, it has been observed that multilayer polymer films represent a viable option for the packaging materials used in the PATP treatment process in terms of the strength and the overall appearance [7]. Lately, various kind of packaging materials are thermally processed ensuring pre-packed food quality during the shelf-life [8]. The main goal of this study is to select the most suitable packaging material able to withstand the PATP treatment.

2. Materials and methods

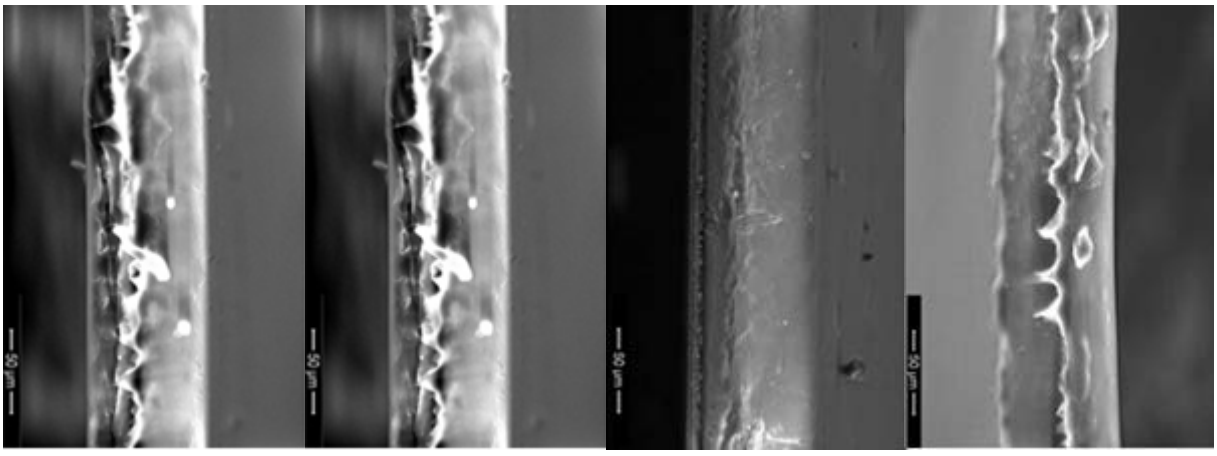
To achieve this objective, the analysis of structural, thermal and mechanical properties induced by PATP (pressure-assisted thermal processing) were performed on two multilayer polymeric materials: Pev-70 (coextruded high barrier multilayer film with the structure PA/EVOH/PA/PE) and Pob-60 (combination of biaxially oriented polyamide with a coextruded barrier film of the structure polyethylene/EVOH/m-polyethylene), used in the meat industry.

These materials were used to obtain the bags for pork packed under vacuum-conditions. The bags containing pork were pressurized at 600 MPa for 10 min at 70 °C (PATP treatment) and at 600 MPa for 10 min at 20 °C (HPP treatment) in a Resato HPP equipment with water-glycol mixture as a pressure transmission medium. The high pressure processing treatment (HPP) at 600 MPa for 10 min at 20 °C, was applied to evaluate only for the effect of high pressure on the system, and it was considered an equivalent to the pasteurization treatment. The PATP treatment applied is equivalent to the thermal sterilization. The conditions chosen in this case are above the limits currently applied by the industry but in line with the further expected developments while the purpose of this study was to identify the limits imposed by PATP for the polymeric films used as packaging material. The structural and thermal behaviour of polymeric materials were evaluated using SEM (Scanning Electron Microscopy) and DSC (Differential Scanning Calorimetry), respectively. For the SEM analysis, the packaging films were analyzed using Quanta 200 microscope at various magnification levels and a low voltage (20 kV). Mechanical tests were performed to determine Young's modulus of elasticity, breaking strength and elongation, using an universal test machine, Testometric M350-5AT. The mechanical parameters were calculated according to ASTM D882-02 (ASTM 2002). Differential scanning calorimetry was used to evaluate the effect of PATP on the thermal behaviour of polymeric materials. Also, the changes of thermodynamic parameters can be attributed to the thermal damage that occurs during preheating [7].

The data were statistical analyzed using MINITAB 16 software (Tukey analysis and single-factor analysis). These experimental data were obtained from mechanical tests.

3. Results and discussion

From the micrographs of all cross sections of the treated films it can be seen that processing at 600 MPa, 70 °C, during 10 minutes induces structural defects (Figure 1).



a b c d

Figure 1. Micrographs of all cross sections of the treated films
a) Untreated Pob-60, b) PATP Pob-60, c) Untreated Pev-60, d) PATP Pev-70

Compared to the untreated film, the boundary limit between the layers of the Pob-60 treated PATP film is not clear, even if the layers are parallel. Obviously, there are some areas of low separation between the layers. A clear film-air interface can be observed in the PATP-60 film that occurred most probably

during decompression. In case of the Pev-70 treated PATP film, the layers are not well defined, compared to the untreated film. Unclear film layers could give less vapor permeability and/or weaker mechanical properties, confirmed by tear resistance analysis.
In order to obtain more in-depth results, the treated HPP (PM) and PATP (PTM) films from Pob-60 and Pev-70 packaging materials were mechanically tested. In addition, comparative studies of the bands obtained from films treated at 70 ºC (T1) were performed. The influence of the treatment on the value of three parameters of multilayered polymer films (Young's modulus of elasticity, breaking stress and elongation) was analyzed.
The effect of the treatments applied on the breaking elongation (%) of the studied polymeric films is shown in Figure 2. Statistically, the treatment effect on the breaking elongation has a significant influence ($p < 0.05$), but it does not depend on the type of the polymer film studied, all the samples being influenced equally by the applied treatment (Figure 2).

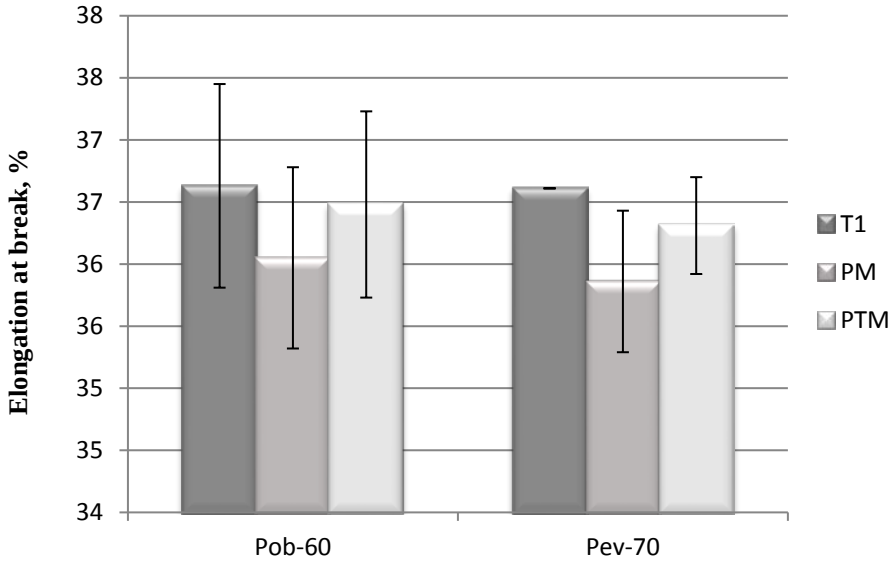


Figure 2. The influence of the treatment on the value of the breaking elongation of multilayer polymer films

The breaking elongation of the Pob-60 films has a very small reduction (Figure 2), regardless of the treatment applied (HPP or PATP), this behavior revealing the formation of a rigid structure [9], confirmed by the SEM analysis. The high resistance of these films can indicate that no breaks occurred between the polymer layers, and did not hindered the film elongation. In the case of the Pev-70 film, the breaking elongation is practically constant (Figure 2). Actually, the applied treatment has induced changes on the breaking elongation of the treated samples, being 2 % for the sample treated with HPP (PM) and 0.8 % for the PATP treated sample (PTM) and proving good mobility of the polymer chain.

The elasticity modulus is significantly influenced ($p < 0.05$) by the type of the polymer film used as packaging material in case of the HPP and PATP treatments. As shown by the graph, the elasticity modulus of Pob-60 and Pev-70 polymer films is influenced by high pressure treatments in the same way (Figure 3). This behavior is similar with the one reported for polymeric structure containing PE and EVOH of these multilayer films [7]. The strongest influence of HPP and PATP treatments on the elasticity modulus can be seen in the Pob-60 film in case of the PM sample. The elasticity of the Pob-60 film decreases by 64 % for the treated PM sample and 48 % for the PTM sample, compared to the blank sample (T1), which showed the highest elastic modulus value (1247.15 MPa). The rigid behavior of this highly elastic polymeric film can be explained by the intra- and interstructural changes induced by high-pressure treatment. The overall tendency of the elasticity modulus for the analyzed films is to decrease more under the influence of HPP treatment than under the influence of PATP.

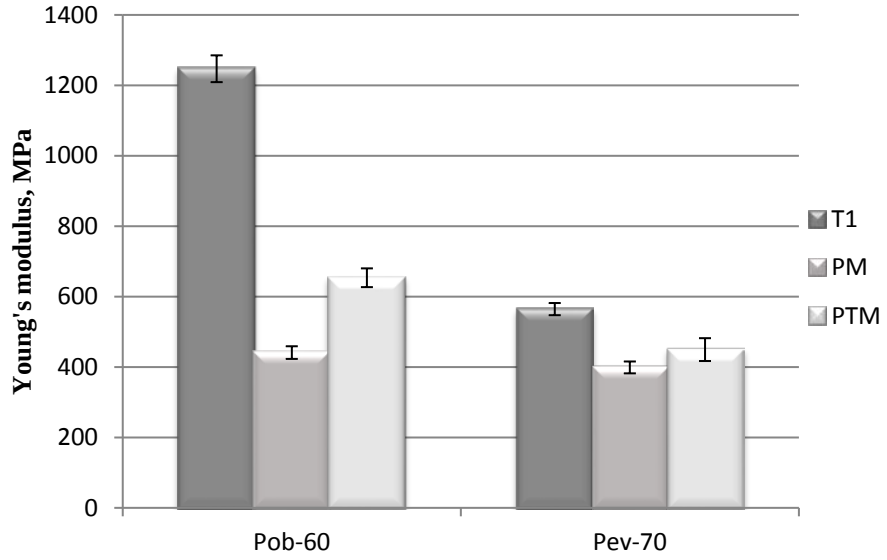


Figure 3. The influence of the treatment on the elasticity modulus of multilayer polymer films

The influence of the treatment on the tensile strength of the multilayer polymeric films is significant ($p < 0.05$), depending on the type of polymeric film used for packaging (Figure 4).

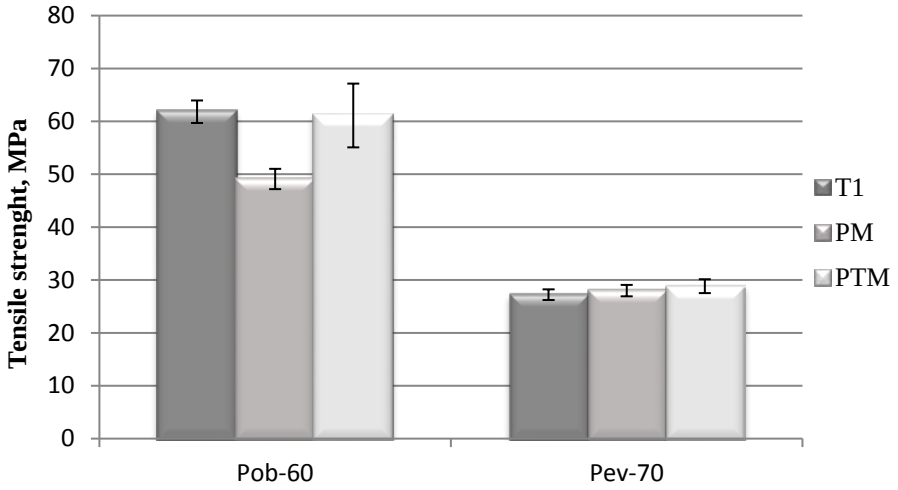


Figure 4. The influence of the treatment on the tensile strength value of multilayer polymer films

In the case of the Pob-60 polymer film, the effect of PATP treatment has a small influence on this parameter, which is characterized by a similar value as the blank sample (T1) and PTM sample. The behaviour of the Pev-70 film shows that the treatment does not cause strong changes in the breaking stress. Thus, the voltage value exhibits a small increase depending on the temperature of the applied treatment, this behavior being observed also by other researchers [10, 11]. This increase demonstrates a slightly rigidity occurrence in the polymeric film structure when a specific treatment is applied. However, the breaking stress value of the treated samples is almost constant compared to the control film (T1). In industry, a variation of up to 25 % is allowed for this parameter [10]. The two polymeric films studied are fitted for this restriction, which demonstrates a low influence of the applied treatments on the breaking stress of these packaging materials.

The melting temperature (Tm) and melting enthalpy (ΔHm) for each polymer were determined from endothermic curves (melting). The results were presented on the thermograms (Figure 5). The Pob-60 multilayer polymer film has PA, PE, EVOH and m-PE polymers in its structure. Figure 5 shows the endothermic curves for the unprocessed Pob-60 multilayer polymer film and the PATP processed Pob-60 multilayer polymeric film, respectively. There is no significant difference between the thermal melting behavior of the processed PATP and unprocessed Pob-60 film, the value of the thermodynamic parameter Tm (melting temperature) remaining almost constant. By integration of the curves, important data on the thermal behavior of this film were obtained.

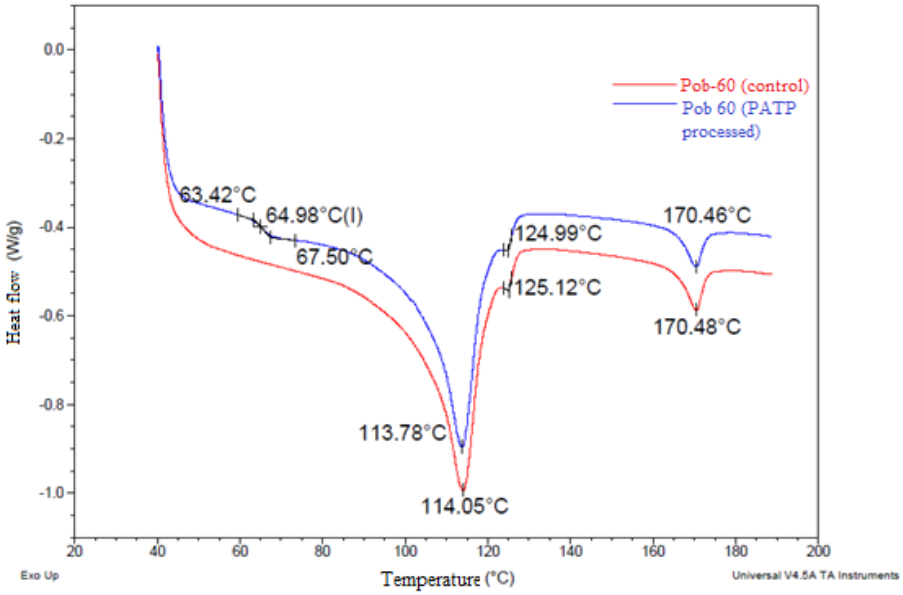


Figure 5. Endothermic DSC curves for Pob-60 multilayer polymer film before and after PATP processing

From the red endothermic DSC curve, no heat related event associated with the vitreous transition was detected for the untreated Pob-60 film. Three distinct melting peaks were recorded. The major (strong) and sharp endothermic peak centered at 114.05 °C can be attributed to the PE polymer, whose melting temperature (Tm) is in the range of 105-115 °C. The second peak with a small area was centered at 125.12 °C corresponding to the melting m-PE. The third peak with an intermediate concentration was recorded between the first two peaks at 170.48°C, indicating the melting temperature of EVOH, whose Tm is in the range of 160-190 °C. The weak peak, centered at 125.12 °C, could also be attributed to the crystallization of PE polymer [12]. From the blue endothermic curve of the Pob-60 multilayer polymer film, four heat events were recorded: a glass transition at 64.98 °C and three endothermic signals. The first signal was shown at 113.78 °C, signifying the PE melting point, the second peak, much weaker, at

124.99 °C, indicating melting m-PE and the third one at 170.46 °C corresponding to the melting point of EVOH.
The following table (Table 1) shows the influence of PATP treatment on the ΔHm (melting enthalpy) value of Pob-60 multilayer polymer film.

Table 1. The influence of PATP treatment on the ΔHm (melting enthalpy) value of Pob-60 multilayer polymer film

Analysed film	ΔHm (J/g) PE	ΔHm (J/g) EVOH
Pob-60 (control)	35.19	3.26
Pob-60 (PATP treated)	43.38	2.53

In case of the Pev-70 film, a heat event associated with the vitreous transition was identified at 70.29 °C (Figure 6). The same Tg can also be seen on the endothermic curve of the PATP-treated Pev-70 film, its value being very close to that of Tg for the control sample (68.33 °C).

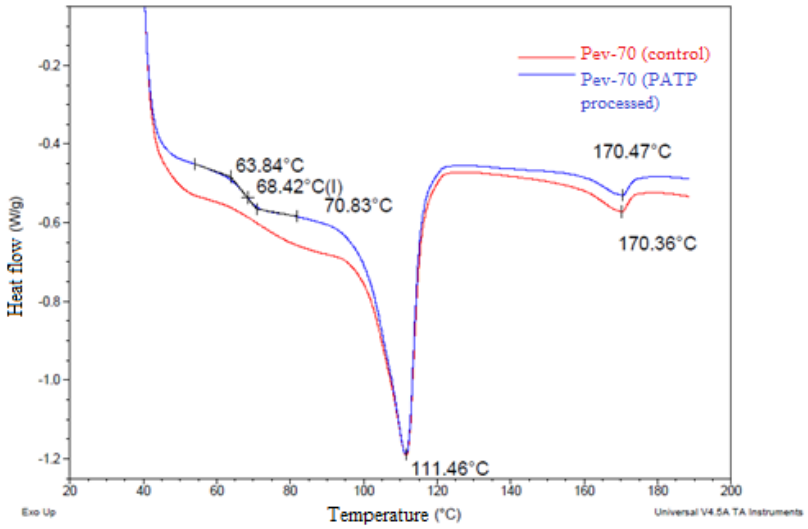


Figure 6. Endothermic DSC curves for the Pev-70 multilayer polymer film before and after PATP processing

Both endothermic curves of the Pev-70 multilayer polymer films exhibit two distinct melting peaks. The major (strong) and sharp endotherm peak, centered at 111.46 ˚C, has the same value for both the blank and PATP treated samples (Figure 6). This value can be attributed to the melting point of PE. The second peak with a lower area, centered at 170.36 °C for the control sample and 170.47 °C for the PATP treated sample, indicates the melting temperature of EVOH.
Table 2 shows the influence of PATP treatment on the value of the ΔHm parameter for the Pev-70 multilayer polymer film.

Table 2. The influence of PATP treatment on the value of the ΔHm parameter for the Pev-70 multilayer polymer film

Analysed film	ΔHm (J/g) PE	ΔHm (J/g) EVOH
Pev-70 (control)	33.02	2.75
Pev-70 (PATP treated)	44.97	2.49

By integration, the value of ΔHm for the polymers identified on the endothermic curve was obtained. The value of ΔHm for PE increases by 27 % in the case of the Pev-70 sample – treated PATP compared to the control sample. This increase of the melting enthalpy in both films after treatments can be explained due to an improvement of the crystallinity of the PE components. So, in this way, an increase of the crystallinity of the PATP polymer film was recorded. Higher values of the melting enthalpy lead to higher values for the breakage resistance and elongation percentage [13].

4. Conclusions

Various structural changes of the two studied materials were found after the PATP treatment. Pob-60 material displayed no delamination or opaque areas and thus the foil-air interface remains clear. The results of DSC analysis showed an increase of the crystallinity of multilayer polymers, which implies the improvement of barrier and mechanical properties. Minor changes were identified in the mechanical properties of both multilayer polymeric materials. The mechanical parameters of the Pob-60 material showed the smallest changes. Thus, from mechanical characteristics standpoint, the Pob-60 multilayer material represents a better option for meat based products packaging, demonstrating a better ability to withstand PATP treatments, and a better stability compared to Pev-70 polymeric material.
In conclusion, PATP treatment induce structural, thermal and mechanical properties changes in the multilayer polymer films used as packaging materials applied in meat industry. The choice of the packaging materials adequate for PATP treatments requires a deep knowledge of the changes that occurs during PATP and the transformations that takes place during food processing and storage.

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Acknowledgments
The work was supported by project SOP HRD – TOP ACADEMIC 107/1.5/S/76822. The authors wish to thank POR RE-Spia (SMIS 11377) project for the infrastructure provided in this study.