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RESEARCH ARTICLE

Flexible Packaging for High Pressure Treatments: Delamination Onset and Design Criteria of Multilayer Structures

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ABSTRACT

Multi-layer flexible polymeric films employed for high pressure treatments of food packaging for pasteurization and sterilization frequently display delamination phenomena. This problem limits packaging reliability used for this treatment technology. This contribution is aimed at understanding the delamination phenomena of packaging structures under high pressures. Development of interlaminar stress fields, which promote localized delamination events, is here addressed by considering the case of mechanical failure of bi-layer structures. Analytical models and Finite Element based numerical simulations are exploited to this purpose. The theoretical and numerical results, that highlight the crucial role played by the mismatch of Young moduli and Poisson ratios of the laminated film sheets, are in full agreement with experimental findings on high pressure-treated food multilayer packages realized coupling different polymeric materials (i.e. polypropylene-polyethyleneterephthalate, polypropylene-cast polyamide and polypropylene-bioriented polyamide).

1.0 INTRODUCTION

The mechanical behaviour of structures made of polymeric multi-layer thin films has been widely investigated in recent literature works, the main attention being focused on the elastic response of the constituent materials, wrinkling, delamination phenomena and interfacial failure [1-5]. A technological application where these issues are notably relevant is that of Novel Processing (NP) treatments of packaged food, recently introduced to improve safety, quality and shelf-life of foodstuff. In this framework, mechanical performances and structural integrity of multi-layer flexible polymer films used to package food remain a main concern. Among NPs, High Pressure Processing (HPP) is steadily gaining as a food preservation method that also preserves natural sensory and nutritional attributes of food with minimal quality loss [6,7]. High pressure loads are exerted on packaged foodstuff by means of a pressurized confining fluid imprisoned in a vessel. The process consists of a preliminary heating of both confining fluid and packaging, followed by adiabatic pressurization.

In particular, HP pasteurization is a non-thermal treatment in which the food is typically subjected to pressures of 400 to 600 MPa at ambient or cooled temperature for 1 to 15 min. These conditions inactivate vegetative microorganisms, providing safety and prolonged shelf life to chilled or high-acid foods. Bacterial spores, however, are extremely resistant to commercially attainable pressure levels, and therefore low-acid shelf-stable products can be achieved only combining high pressure with elevated temperatures in the so-called HP sterilization treatment. A typical high-pressure commercial system for sterilization purposes uses initial chamber temperatures between 60°C and 90°. Pressures above 600 MPa are applied and actually in-process temperatures can reach 90°C to 130°C due to adiabatic heating associated to compression of packaged food and pressure transmitting fluid. A suitable choice of a multi-layer packaging for HPP has to be performed in such a way the treatment process does not affect package integrity as well as its functional properties. Literature highlights that several types of multilayer films, including bi-oriented polyethyleneterephthalate/polypropylene (PET/PP) bilayer films, aluminium foils and metalized layers, exhibit delamination phenomena [8,9].

From the mechanical standpoint, HPP can actually kindle interfacial stresses between the different elements of multilayer structures with selected thermo-mechanical properties as a result of the high pressure loading exerted by the pressure transmitting fluid, thus inviting delamination and extensive detachment phenomena. In general, the mechanical analysis of multilayer systems under severe pressures requires modelling incorporating large displacements, intrinsic and deformation-induced film anisotropy, non linear stress-strain relationships, visco-elastic and plastic behaviours, as well as selected constitutive assumptions for adhesives and bonding conditions at the layers interfaces. However, if the role of each of these aspects in the delamination onset is at the beginning still unclear and thus preliminary sensitivity analyses are needed, the combination of the above mentioned types of nonlinearities as well as the strong difference between the characteristic (in-plane) size of the sheets (generally of the order of centimetres) and film thicknesses (of the order of tens of microns) could not recommend the recourse to onerous in silico Finite Element Method (FEM)-based simulations [10], that might obscure the actual contribution of the single geometrical and mechanical factors in promoting the failure. For this reason, simpler mechanical models and ad hoc analytical solutions can be helpfully used to gain specific insights and preliminary qualitative information into the key factors causing delamination onset in multilayer structures, this being not a simple task given the limited amount of scientific works dealing with exact solutions to problems involving the mechanical response of thin multilayer structures [11-15].

The present paper explores the main mechanisms governing the delamination phenomena experimentally observed in polypropylene based bilayer films during HPP (i.e. PP/PET, PP/OPA and PP/PA, OPA and PA denoting oriented polyamide and cast polyamide, respectively), performing both analytical and Finite Element (FE) analyses of pouches containing tap water.

2.0 MATERIALS AND METHODS

2.1 Polymers films

Capability of multilayer polymer films to withstand high pressure pasteurization and sterilization treatments was assessed by realizing pouches containing a food simulant (tap water and small solid carrots) and submitting them to HP treatment similar to those performed on industrial scale. In particular, bilayer films were obtained by laminating commercial plastic films, i.e. cast PP, bi-oriented PET, bi-oriented PA (OPA) and cast polyamide. Three types of bi-layer films were investigated, that is PP/PET, PP/OPA and PP/PA. In all cases the inner layer of the pouches, in contact with tap water, was PP, to guarantee the sealability of the package. Due to the production process, the four polymer films used to realize the bilayer structures are oriented, thus exhibiting a transversely isotropic thermo-mechanical behavior. As a consequence, in the following, 'machine direction' or 'longitudinal direction' (L) and 'transverse direction' (T) are respectively parallel and orthogonal to the main axis of the film reel, all the polymers used in this study being semicrystalline.

2.2 Realization of Pouches

Pouches were obtained by sealing the three sides of a folded bi-layer film with a custom built heat sealing equipment. Heat sealing was performed by hot-bar welding, at a heat-seal bar temperature of 110-120°C, under an applied pressure of 0.4 MPa (a force of 400N applied on a 150mmx10mm surface) exerted for 1-2s. Before sealing the fourth side of the pouches, they were filled with the selected food simulant (both tap water and solid carrots were used) and air was removed from the head space by vacuum pumping.

2.3 HP Treatments

The filled pouches were subjected to high pressure treatments, performed in a pilot scale high pressure/high temperature unit at Wageningen UR (University and Research centre) - Food & Biobased Research, in Wageningen, The Netherlands. This apparatus was developed by Resato, Solico and Unilever companies in cooperation with Wageningen UR Food & Biobased Research and consists of a single, vertically oriented high pressure vessel of 2.5 litre.

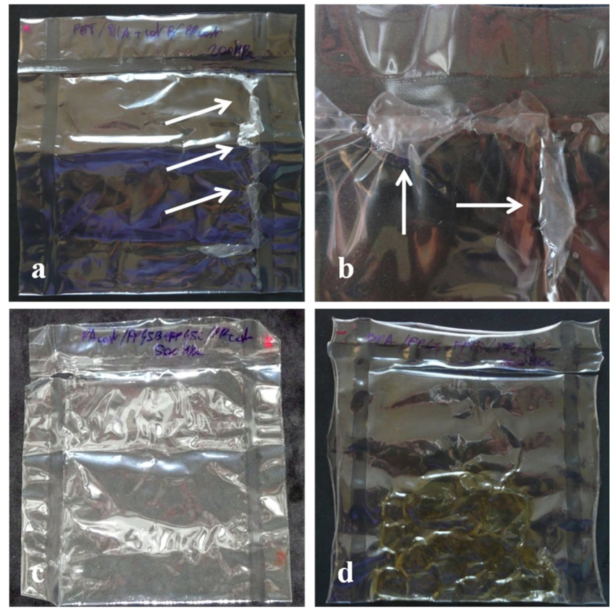


Fig.1. Photographs of pouches after high pressure treatment. a) picture of a PET/PP pouch after HP sterilization treatment @200MPa (food simulant: tap water), arrows indicating regions of delamination; b) detail of a delaminated region in PET/PP pouch with arrows highlighting the delamination zones; c) picture of a PA/PP pouch after HP sterilization treatment @500MPa (food simulant: tap water); d) picture of a OPA/PP pouch after HP sterilization treatment @700MPa (food simulant: solid carrots).

In a HP process, pressure is increased up to the treatment value due to volume reduction using a plunger at the vessel top (plunger system). Typically, pressure can be built up to 700 MPa in 24 s. The temperature of the vessel is controlled by an electric heating jacket attached to the outer vessel wall and a bottom heater to heat up the vessel wall to a maximal temperature of 90 °C; however, the actual temperature inside the vessel rises well above the wall temperature due to adiabatic heating. Both low temperature and high temperature HP treatments have been performed on pouches using tap water as pressurizing medium. High temperature treatments were performed by pre-heating pouches at 90°C into a water bath for ten minutes, followed by transfer into the HP vessel where hydrostatic pressure was applied and maintained for five minutes. Treatments were performed at three different pressures, i.e. 200, 500 and 700 MPa (holding the pressure for 5 minutes). Low temperature treatments were instead performed with at the same pressures (holding the pressure for 10 minutes) and with a similar procedure, but with an initial room temperature. During the HP process, temperature inside the vessel rises due to the adiabatic heating associated to compression: typically 3-4 °C increase for 100 MPa pressure increase in the case of water-based food. Temperature is not actually uniform inside the vessel and temperature gradients are indeed present.

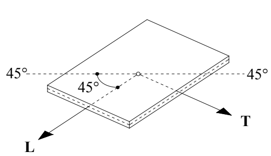
3.0 EXPERIMENTAL

3.1 Effect of HP Treatments on Pouches

The performed tests indicate that all the three bilayer films are able to withstand the pasteurization treatment without displaying any evident mechanical failure. However, PP/PET pouches displayed evidence of localized delamination (see Figures 1a and 1b) after HP sterilization, with both food simulants used, over the whole investigated pressures range. No delamination after HP sterilization was instead observed, even at 700 MPa, in the case of PP/PA (see Figure 1c) and was barely present in the case of PP/OPA (see Figure 1d), for both food simulants.

Several phenomena occurring during sterilization treatment might induce delamination observed in PP/PET structures: difference in the thermal

Table 1. Young moduli [MPa] determined at 25°C for the four films in the three longitudinal (L), transversal (T) and diagonal (45°) main directions. The values reported in bold in the diagonal cells represent the bi-layer homogenized moduli estimated for each film coupling, following the (Voigt) rule of mixtures, the values in parentheses being referred to the corresponding moduli at 100°C. In square brackets are indicated the film thicknesses coherently with those actually chosen for the pouches

			PET [12µm]			OPA [15µm]			PA [20µm]		
			L	T	45	L	T	45	L	T	45
			2936 (2900)	**2755** (2700)	**2637** (1400)	**2243** (1400)	**2001** (520)	**2346** (140)	**664** (200)	**779** (155)	**785** (170)
PP [50µm]	**L**	**376** (170)	**871** (700)			**807** (450)			**458** (180)		
	T	**297** (120)		**773** (620)			**690** (210)			**435** (130)	
	45	**345** (170)			**789** (410)			**807** (165)			**471** (170)

expansion coefficients of the two materials, differences in the mechanical behaviour of the two films making up the multilayer structure (i.e. stiffnesses in the elastic regime) and in their dependence on temperature and pressure, dependence on temperature of the mechanical resistance of the interlayer lamination adhesive and increase of glass transition temperature of the materials determined by pressure increase.

An accurate analysis of such effects leaded us to conclude that the main cause of delamination onset in food packaging structures under HP can be attributed to the discrepancy of mechanical properties of the coupled polymeric films and to highlight the marginality of the other physical phenomena occurring during the sterilization treatment.

The mechanical behaviour of the single films was determined at 25 and 100 °C at atmospheric pressure in the three main directions. Stress-strain curves were obtained for elongation, determining

the values of the Young modulus in the elastic regime, whose measured values are summarized in *Table 1*, in which, at 25°C, the values of the moduli for PP are close to those of PA. Differences are instead significant when comparing PP with OPA to become even more relevant for the case of PET. At 100°C, the largest differences are still found for the PP/PET coupling, while both PA and OPA display values of moduli which are close to those of PP. The analysis of the results reported in *Table 1* suggests that a possible cause for delamination might be related to differences in mechanical behaviour, as discussed in the following sections by means of analytical and numerical simulations.

One could argue that pressurization, inducing a change in the glass transition temperature (Tg), would cause ratios of mechanical moduli that are different with respect to those reported in table 1. Actually, an analysis base on measurement of the change of Tg with pressure leads to conclude that, in the investigated HP processing conditions, moduli ratios are still higher in the case of PP/PET as compared to PP/OPA and PP/PA structures.

4.0 THEORETICAL ANALYSES

4.1 Onset of Belamination and Failure Localization in Bi-layer Pouches

In a general case, interfacial stresses responsible for delamination may result from the combination of both normal and shear stresses at the films interface. Nevertheless, given that high pressure applied on the bi-layer structure imprisoning a fluid determines compressive normal stresses, it is expected that delamination is dominated by shears.

The complex pouch geometry and the actual loads exerted on the real multi-layer package have been first analysed by considering two simpler ideal problems whose exact solutions are constructed to detect the influence of mechanical and geometrical factors on the occurrence of interfacial shear stresses and to predict the critical regions where delamination might start.

In particular, the Problem A focuses the attention on the pouch welded sides and treats a rectangular bi-layer film under self equilibrated and spatially varying applied pressures. The closed-form elastic solution is obtained to establish the influence of pressure magnitude and spatial gradients – which can locally appear in the transition zone as effect of the difference between external and fluid pressure – on the kindling of interfacial shear stresses. In this framework, supported by classical results from literature [16], it is proved that relevant interlaminar shear stresses actually appear and localize near the flat sealing regions of the bi-layer structure and increase when differences in elastic moduli characterize the coupled films.

In the Problem B it is investigated how stresses develop far from the pouch welded sides by idealizing the folded regions through a bi-layer cylindrical

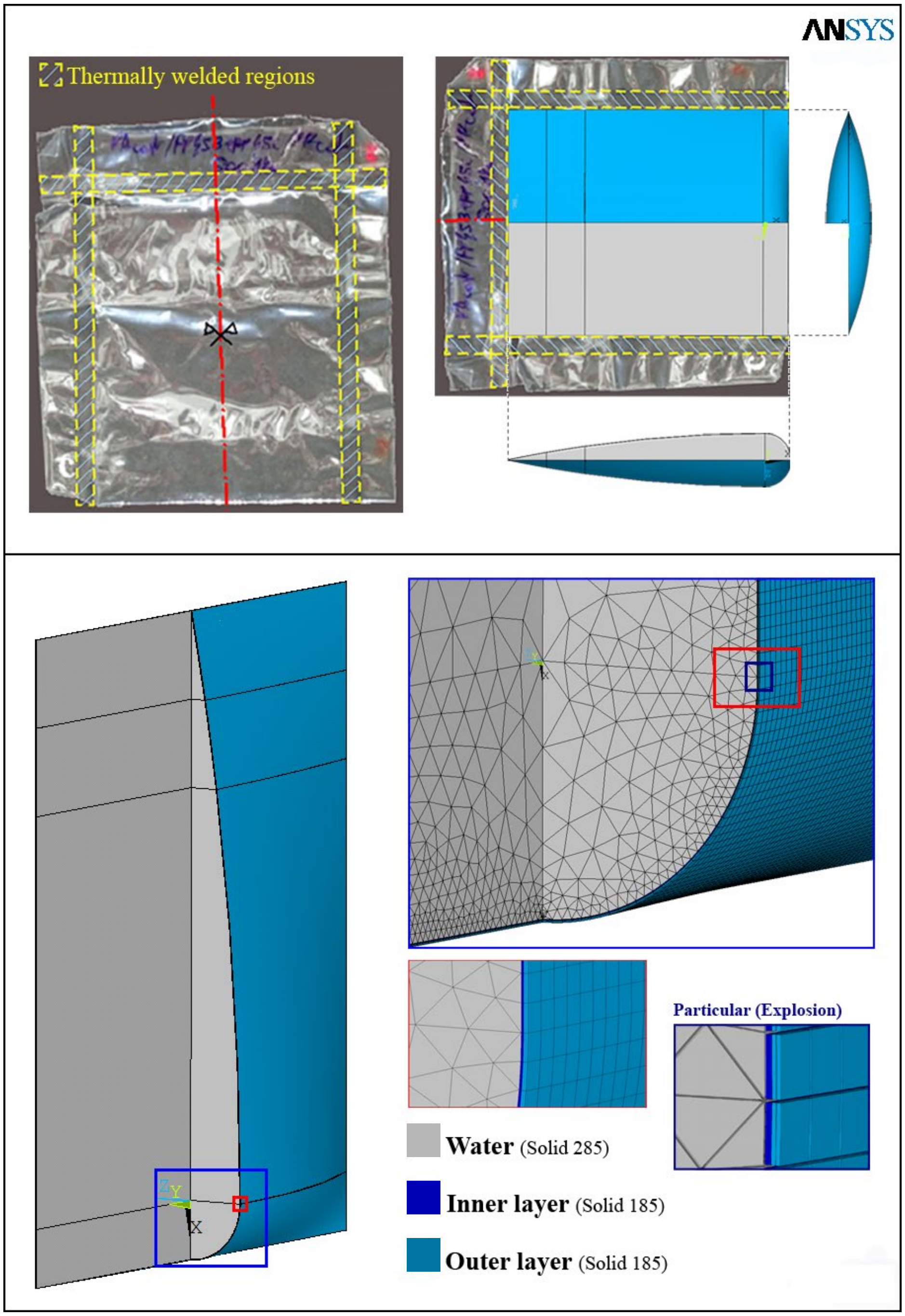


Fig. 2. Typical food package polymeric bi-layer structure and three-dimensional model used in the FE simulations. Geometry and details of the mesh for the food package Finite Element model

envelope containing an incompressible fluid and subjected to high pressure. Sensitivity analyses and outcomes from the proposed analytical solution, which also exploit some literature results [17], show that, for the case of interest, bending-driven deformation modes dislocate elastic energy induced by pressure increases from film interface toward overall buckling or local wrinkling phenomena, which significantly reduce the interlaminar shear stresses and limit the onset of delamination far from the pouch borders.

Finally, Finite Elements, FE, analyses reproducing the three film couplings actually utilized for realizing the polymeric pouches have been performed, by taking into account geometrical and material nonlinearities in the mechanical response of the food packages filled by water, under the action of applied high pressure. The numerical results quantitatively confirm both the qualitative theoretical outcomes highlighted by the analytical solutions in terms of localization of stress peaks and delamination onset and the mechanical failure in PP/PET pouches, also showing very good agreement with the experimental observed findings. In particular, Finite Element (FE)-based simulations have been conducted in order to take into account the real shape of the food-package and the truthful mechanical features of the polymeric bi-layer films. Two simulations have been performed. The first one is aimed at determining the distribution of interlaminar stresses for the three bi-layer polymeric structures, say PP/PET, PP/OPA and PP/PA films, at a treatment pressure up to 200 MPa. The second analysis is instead devoted to catch local deformation modes of the food package due to large strain gradients induced by severe pressures up to 500 MPa, here obtained for the particular case of the PP/PET bi-layer which is the most likely to exhibit wrinkling and delamination.

With reference to the determination of the distribution of interlaminar stresses, numerical simulations have been carried out by using the commercial code ANSYS® (ANSYS 13, 2009) by constructing a three-dimensional model $110\ mm \times 100\ mm \times 20\ mm$ bi-layer pouch with geometry and sizes replicating the actual food package used in the HP experiments (see *Fig. 2*). Water inside the package has been modelled using the Tait equation for taking into account volume change with pressure. Also, according to the characteristics of the samples used in the experiments, the FE model considers the bi-layer structure made of two perfectly bonded polymeric films, whose thicknesses and material properties are those related to the three above mentioned types of coupling utilized for HP tests.

The analyses have been performed in the static regime, by considering large displacements and finite deformations. By exploiting symmetry of the object, the simulations have been performed with respect to one half of the pouch model, by applying uniform pressure on the outer surfaces up to 200 MPa. The results show that the stress regimes at the interface, in terms of principal, shear and von Mises stresses, attain maximum values in the case of PP/PET coupling, intermediate magnitudes in the case of PP/OPA structures, getting lowest values in the case of PP/PA bi-layer films, these stress peaks being located at the corners as well as along the welded sides. Both these findings confirm the outcomes from the analytical solutions found for detecting what happens near and far from the sealing sides (Problems A and B) and also result in full agreement with the experimental evidences, which highlight that local failure phenomena, essentially observed only in the case of PP/PET structures, prevalently occur close to the welded regions. Additionally, as predicted by the analytical solution determined to analyse what occurs far from the pouch borders (Problem B), the numerical results confirm that no relevant interlaminar stresses take place in the neighbourhood of the folded pouch side, as a consequence of local wrinkling phenomena which drive energy from the films interface towards rippled deformation modes, in the FE analysis highlighted by corrugated strain profiles associated to low magnitude stress fields.

At the end, with respect to the sole case of PP/PET bi-layer structure, a further nonlinear FE analysis has been conducted to evaluate the mechanical response of the pouch up to 500 MPa. The numerical results point out increasing strain gradients and local deformation modes which induce wrinkling and pearling-like patterns in the films, which qualitatively resemble the permanent deformation patterns observed experimentally as a consequence of HP treatment.

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