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OXYGEN AND WATER VAPOR PERMEABILITY AND REQUIRED LAYER THICKNESS FOR BARRIER PACKAGING

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ABSTRACT

In the packaging industry container applications appear with increased barrier requirements. In order to protect food and medical products against oxygen and water vapor it is necessary to use at least two barrier materials in 2 or 3 layers, whereas one could also be the main packaging material. Materials with low oxygen permeability are tending to absorb water vapor. Studies have shown that the oxygen and vapor permeability strongly depends on its layer thickness. Based on this, the layer structure of multilayer containers can be defined. With measurements of oxygen and water vapor permeability the configuration of the layer can be improved to extend the shelf life of the package and to minimize the use of material. With the knowledge the required layer thicknesses in a container package can be determined. These layer structures can be simulated with the help of the flow sheet analyzes the injection blow molding process.

1 INTRODUCTION

The use of plastics in the manufacture of medical and cosmetic packaging receives an ever increasing importance. Through various manufacturing processes such as injection molding, film extrusion, blow molding and combinations of these, it is possible to produce functional products with a high added value. Packages which are needed in medical and cosmetics packaging have to fulfill requirements for oxygen and hydrogen barrier. Barrier improvement is obtained by multilayer technology that applies a barrier layer to the package, that typically is produced by co-injection molding. A skin and a core component are injected into a cavity. Processing techniques such as multi-layer injection blow molding connect the processes of injection and blow molding. In order to achieve a uniform wall thickness and thus a constand barrier layer thickness along the whole bottle cross section, preforms have to be designed and manufactured accordingly. This paper is discusses the oxygen and hydrogen permeability of particular plastics (COP and PA) and allows the definition of required layer thicknesses in order to obtain defined barrier properties [SIM13].

1.1 Manufacturing Process

At present, various methods for the production of multilayer packages are applied. The most common methods are injection molding blow molding, blown film extrusion and injection blow molding. Blow molded containers can either be processed by a single or two-stage process. In the first step of the two-stage process the preforms are injection molded. There, they are cooled down and transported to the blowing machine. The preform is then re-heated above the glass transition point to then be stretch blow molded into the container for its application to the subsequent filling process. The single-stage process also known as injection blow molding injection molds preforms in one station of the machine and blow the thermally still conditioned preform in the second station as displayed in Fig.1.1. There are different methods to choose the sequence of the process steps, i.e. omitting the preform conditioning after injection and blow molding at 120-130°C subject to the material processed [SIM13] or including an additional stretching of the preform prior to blowing.

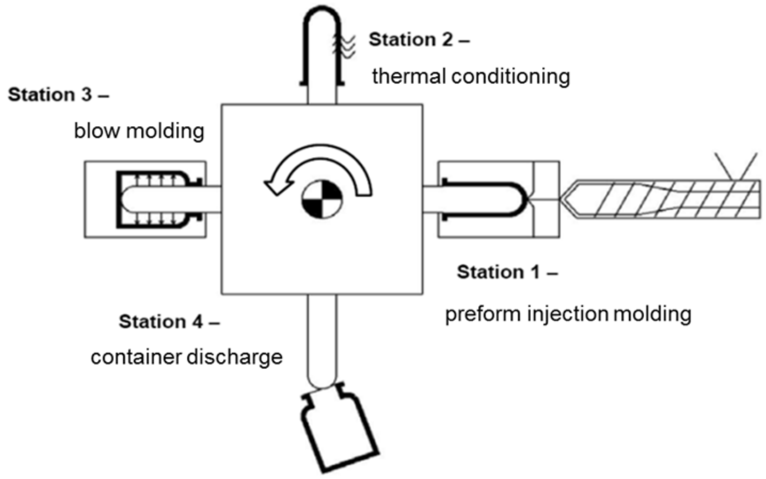

Figure 1.1: Injection Blow Molding Process [TUE12]

In case of multilayer injection technology, two injection units are required. When co-injection is applied the option is to simultaneously or sequentially inject the two materials into the cavity. However, in any case, it is required to control the wall layer thickness distribution along the flow path of the preform wall in a way that will allow to blow the container subsequently towards a uniform barrier layer thickness in order to provide reliable and consistent barrier properties in the container. In most cases, it is unknown as to what layer thickness is required in order to obtain desired barrier properties in an economic way. The objective of this work is, to determine the layer thickness performance of a COP/ PA material combination towards its barrier properties.

1.2 Materials

1.2.1 Skin Component COP

In the manufacture of multi-layer preforms, COP is used as a skin component. COP stands for cyclic olefins polymer. This plastic is an amorphous COC (cyclic olefin copolymer) which is produced by polymerization and subsequent hydrogenation of dicyclopentadiene. [SAE07]
COP provides high transparency, low birefringence, low moisture absorption, and for the case considered in medical application a good chemical resistance. A comparison with glass and polypropylene (PP) is displayed in Tab. 1.1 and allows to identify particular advantages of COP. Especially, relative to brittleness, malleability and density COP is advantageous.
In order to improve the oxygen barrier in a COP package, it is proposed to apply PA as a barrier layer material. COP is typically processed at melt temperatures of 270 °C to 290 °C, thus being compatible with PA´s processing temperature in the same range. [SIM13]

Table 1.1: Properties of COP, Glass and PP

Properties	***COP***	***Glass***	***Polypropylene***
oxygen barrier	o	+	o
water vapor barrier	+	+	o
transparency after steam sterilization	+	+	-
transparency after EO sterilization	+	+	-
transparency after gamma sterilization	+	+	-
pH shift diluent	+	-	+
brittleness	+	-	+
malleability	+	-	+
disposal	+	-	+
cleanness	+	+	o
density	+	-	+
	favorable = +	average = o	poor = -

1.2.2 Core Component PA

Polyamid provides very good barrier to oxygen and nitrogen. Therefore its use is well-introduced for multi-layer packages in various applications. At a certain wall thickness almost zero oxygen permeability is obtained. In order to assess this point of minimum oxygen permeation, the following work has been conducted with an oxygen permeation measurement device.

2 EXPERIMENTAL STUDIES

In this section of the paper the experimental studies are described and explained. Potential laminate structures of COP and PA film are created with alteration of layer thicknesses and studied. From the information first indications are derived towards injection molding of a preform wall that will provide sufficient barrier material layer thickness for application oriented permeability data in a container.

2.1 Sheet laminates with different material combinations

2.1.1 Laminate Structures

COP and PA film laminates were created whereas the layers were required to be bonded appropriately to one another. The laminate structure was tested for the experiments with different techniques. In the preparation of the laminates it is important to maintain the properties of the sheet as not to impact measurements from undesired damages. [SIM13]
Various layer combinations and thicknesses were examined that are then used for the investigation of oxygen and vapor permeability. The COP layer was first chosen to have a thickness of 60 microns and the PA layer a thickness of 50 microns. Further testing included total layer thickness of up to 390 micron.

2.1.2 Permeability Measurements

The measurement of permeability of oxygen and water vapor is possible with special equipment, available from Mocon Inc.. The tests were made with two special devices, one for water vapor permeation and another one for oxygen permeation. The difference of both devices lies in the used sensor and the testing gas. Both sides of the multilayer film are immersed in different gases. On the water vapor transmission (wvtr) test the H_2 particles permeated thru the film were detected in the carrier gas. In contrast to the wvtr test, the oxygen test detects the parts of oxygen in the carrier gas. The measurement time and the area of the test film at the ratio of the detected gas particels yield the permeability of the multilayer films.

3 EXPERIMENTAL RESULTS AND LEARNINGS

In this section the results of the oxygen and water vapor permeability test are presented discussed. Using this permeability results the layer thicknesses can be determined, which should be achieved in the multi-layer bottles. With these thicknesses the layer of the skin and core components can be found in the preform designed in an A-B-A structure.

3.1 Oxygen Permeability Measurement

The production of multilayer containers, typically, is required to provide the highest possible oxygen barrier capability subject to the application. In many cases, once the oxygen permeability performance is provided, little demand, if any, is remaining for additional vapor transmission reduction. Thus, as oxygen barrier is provided by a PA6 layer to be added into a package container, first measurements were conducted on this material. The measurement of COP film was experienced to be complicated by the fact that in contact with the sealing fats as applied in the measurement set-up, the material tended to display significant stress cracking making it difficult to obtain reproducable results.

In Figure 3.1 the result of the permeability test for PA 6 is displayed for a measuring time of 70 hours, showing that permeability decreases as the test environment increases in relative humidity. An increasing thickness of PA6 specimen results apparently in better barrier performance. The thickness of the specimen was accomplished by adding several layers of 50 micron film segments over one another. The results display an almost minimum level of oxygen permeability at and above 100 micron thickness. The values shown represent the average of 6 measurements.

The PA6 film with a thickness of 50 microns displays an oxygen permeability value of 31.374 $cm^3/(m^2d)$ for 0% RH which corresponds to data found in literature with 30 $cm^3/(m^2d)$ [MCK12].

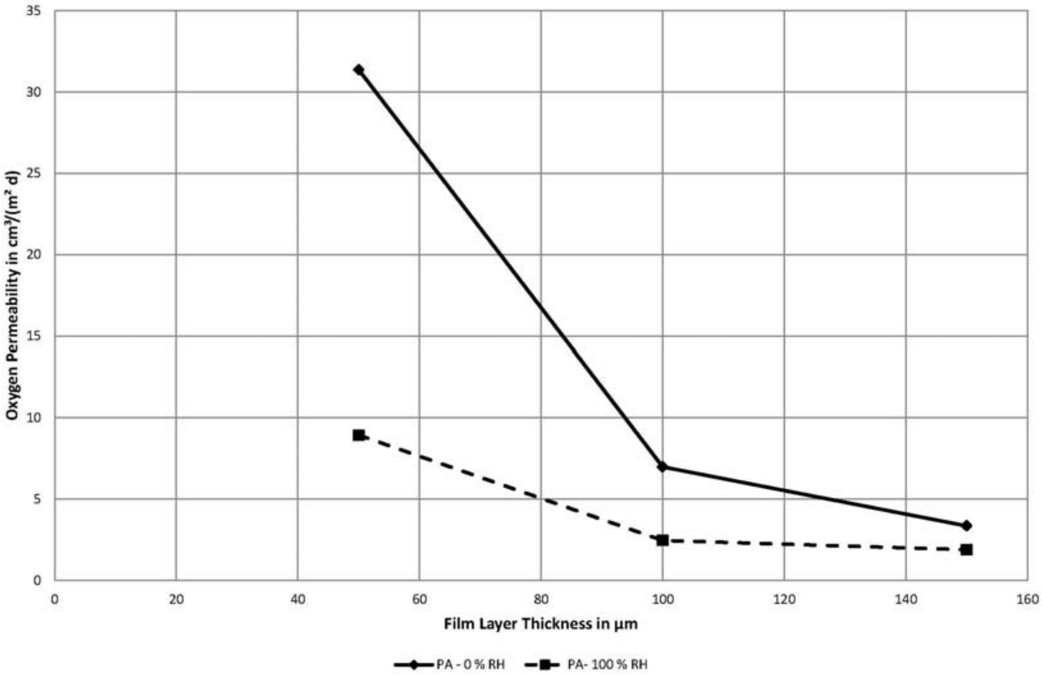

Figure 3.1: Oxygen permeability of PA RH 0 % und RH 100 % [SIM13]

The results of the measurements conducted at 100% and 0% RH on a layer thickness of 100 micron and above show similar results with little difference. At a film thickness of 150 microns, a value of 1.891 cm³/(m²d) could be measured as the minimum value achieved in this test series. This value represents an almost perfect oxygen barrier performance that in most cases is not required to that extent, since barrier loss on the container finish or closure often times yields to much higher values thus making side wall performance data like this unnecessary and purely adding to container cost.

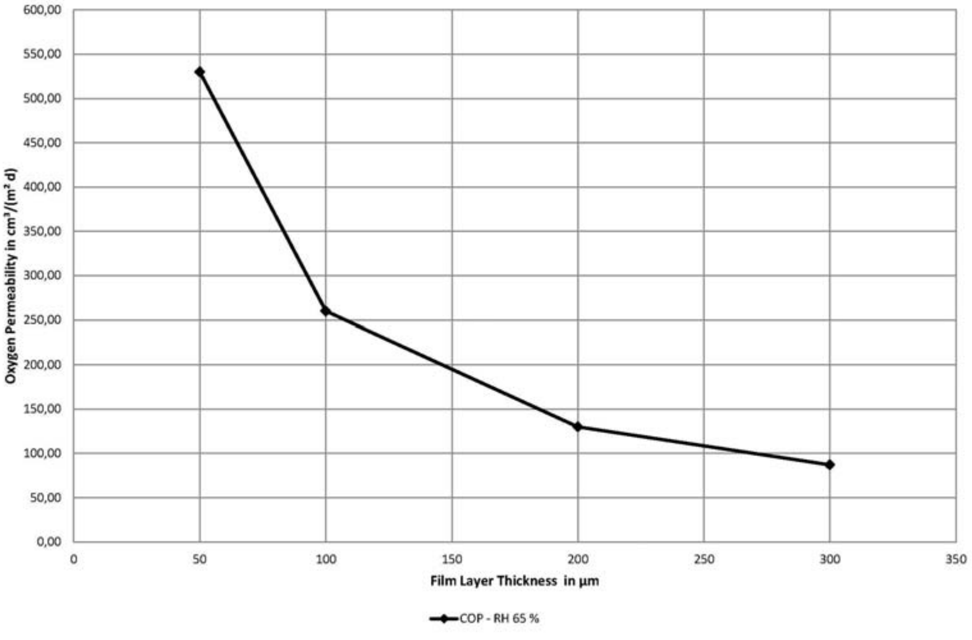

Figure 3.2: Oxygen permeability of COP bei RH 65 %

Figure 3.2 shows the measurement of oxygen permeability data on COP film, conducted like for the PA6 film, however the thickness of the specimen was increased up to 300 micron. A flattening of the curve was observed for a thickness of 300 micron and above. It becomes apparent, that a pure COP layer, even with a thickness of larger than 300 micron, would not suffice an advanced barrier requirement on an oxygen sensitive packaged good as provided easily by a PA6 layer.

The following diagrams in Figure 3.3 and Figure 3.4 show measurements as a function of time in one cell of the device with the three layer thicknesses of 50, 100 and 150 micron again comparing the two extremes of RH values. The graphs plot the oxygen permeability measured in cubic centimeters per square meter per day over time (in hours and minutes).

The first six measured values in Figure 3.3 represent the measurement of the so called Independent Zero. The Individual Zero is measured prior to the current measurement, the points seven to twelve represent the measured values and the proportion of oxygen in the system due to leakage and system-related errors in the measuring chamber paths.

The Custom Zero is assumed in the main measurement as a fundamental value of the existing oxygen permeability. That means the displayed main value of the Individual zero has to be added. The diagrams show the time required for the measurement.

The actual measurement of the oxygen permeability does not begin until about 21 hours after the initiation of the measurement. Equivalent to these results are the results in Figure 3.4. The first six measurement points are Individual zero measuring points, the points seven to twelve represent oxygen vapor permeability data.

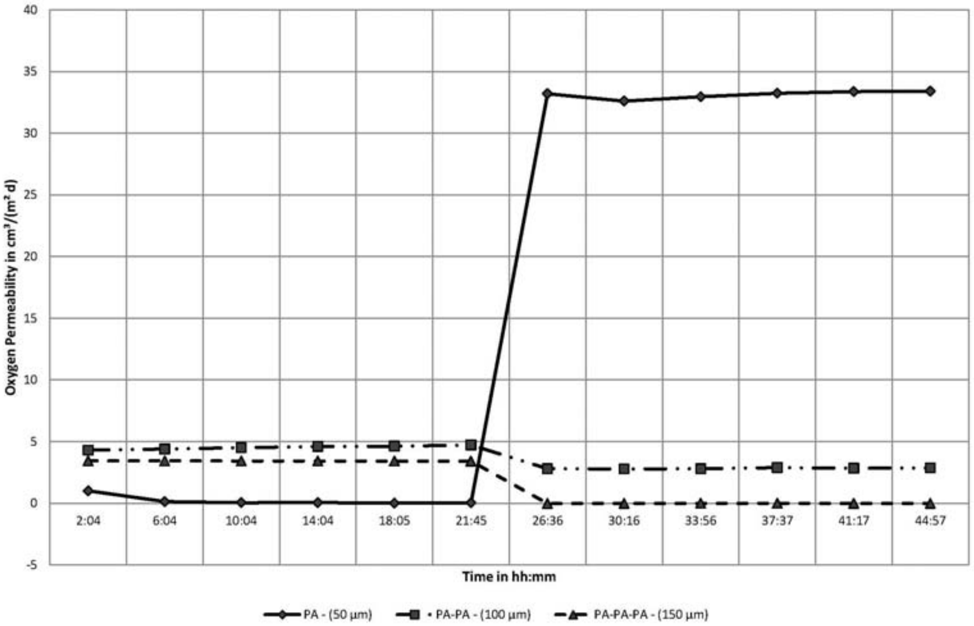

Figure 3.3: Oxygen permeability of PA layer structures (50 µm-150 µm) RH 0 % [SIM13]

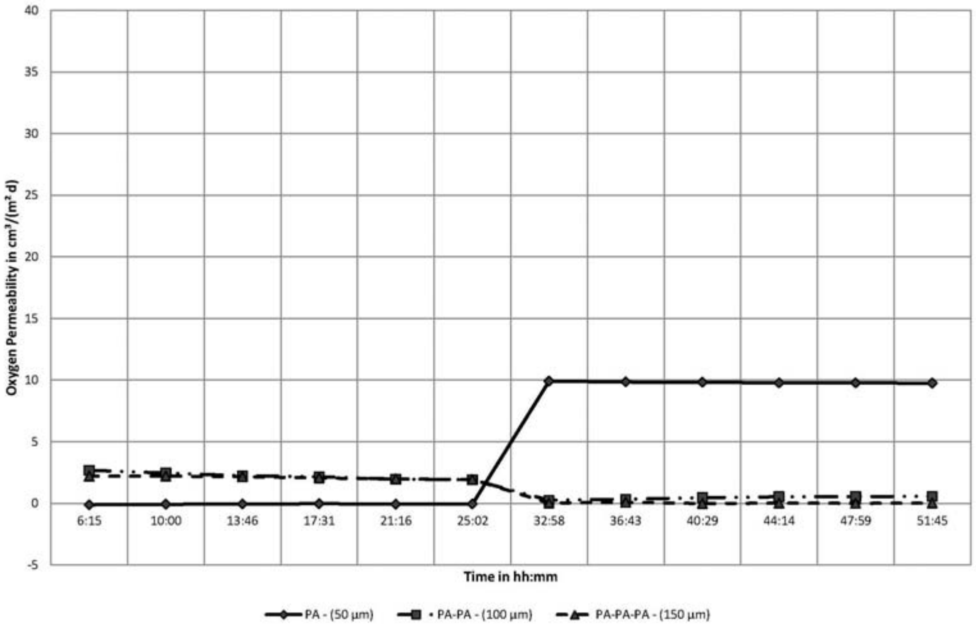

Figure 3.4: Oxygen permeability of PA layer structures RH 100 % [SIM13]

3.2 Water Vapor Permeability Measurement

Equivalent to the oxygen vapor permeability measurement the measurements for water vapor permeability were carried out. The COP film was first studied for the permeability of water vapor. Lab measurements with film layer thicknesses of 60, 120 and 180 microns were performed. Figure 3.5 shows the measured values of water vapor permeability for two different environments of RH. This result shows that with increasing layer thickness, the water vapor permeability is reduced. The measured values in Figure 3.5 indicate an exponential curve, which again allows to establish a layer thickness of now 200 micron and above where there will be little yield in further vapor barrier enhancement.

The application of this information for multi-layer containers lead to a minimum of 200 micron COP layer thickness in order to provide most effective water vapor permeability results. This also takes into consideration the economic aspect of minimum container weight (=wall thickness). This means that with the layer thickness established in these measurements a reasonable optimum is defined for water vapor as well as for oxygen barrier performance.

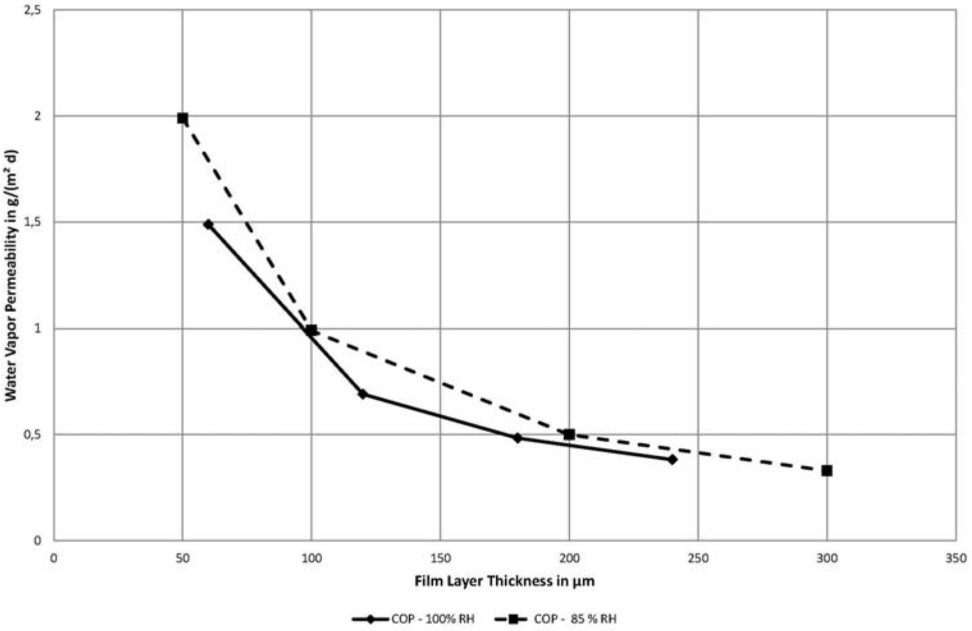

Figure 3.5: Water vapor permeability of COP [SIM13]

4 CONCLUSION

Multi-layer injection blow molding is going to be more widely established in the packaging industry. While processing such containers is one significant requirement where different technology solutions will be applied, it is apparent that in order to obtain sustainable barrier properties, containers must achieve minimum wall thickness for reliable performance. The work conducted shows that for the material combination of COP and PA in an A-B-A structure with PA in the middle layer, there are definite layer thicknesses of the two materials that will provide an optimum in technical (good barrier performance with little further improvement by increased layer thickness) and economic (amount of material/ cost used) relation. In a container, the middle layer thickness of PA should be above 100 micron to provide best oxygen barrier and the outside COP layers will provide best water vapor barrier with a total layer thickness of 200 microns. Assuming that two COP layers are required, the total container wall thickness should not be less than 300 micron in order to obtain a best cost/ performance relationship in terms of barrier performance, i.e. three layers each with a thickness of 100 micron.

A challenge for future work will address to assert that these required layer thicknesses will be achieved in the container side wall. This can only be granted once the preform wall thickness is maintained on a level that considers local stretch ratios from preform to bottle and defines the corresponding layer thickness in a preform, which will have to be examined in detailed blow experiments with different preforms. An indication of the preform layer set-up has been conceived in [SIM13] resulting in a preform cross section as displayed in Fig.4.1. The desired layer thickness in the preform has to be obtained by processing during injection, ideally through a combination of sequential and simultaneous co-injection. A simulation of various process configurations for preform molding shows that only particular processes will assert the required preform wall thickness distribution. Experiments are being conducted to confirm these simulation assessments.

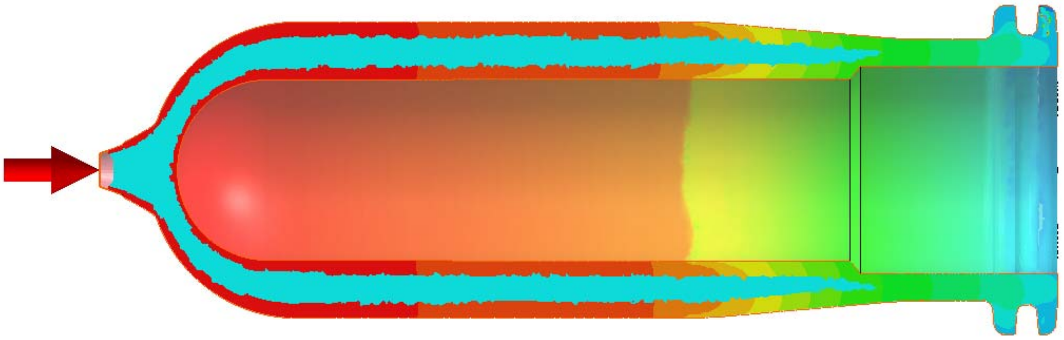

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Figure 4.1: Preform with good wall thickness distribution [SIM13]

5 ILLUSTRATIONS, GRAPHS, AND PHOTOGRAPHS

5.1 List of Figures

5.2 List of Figures

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