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The Production and Characterization of Aluminum Barrier Laminate Tubes and Comparison of Mechanical Properties with Reference Material

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Abstract

This study investigates the characterization of aluminum barrier laminate tubes and how mechanical properties change by difference of polymeric raw materials. In this study, four different prototypes have been produced and compared with themselves plus two different references. References have been obtained from the market with taking into consideration of the most common ones. After the examination of cross section images, it has observed that the main difference of produced prototypes from reference sample is layer distribution. Main layers are thicker in prototypes than reference samples. Prototypes have been produced by different formula and in some cases, different raw materials. Characterization measurements were taken by dynamic scattering calorimetric thermograms. For comparison of mechanical properties, young modulus values were obtained by using tensile meter for measurements of 250µm thickness 25mm wide, 50mm length foil samples. Aim of this study is the discovering possible ways of reaching 600-700 N/mm^2 in young modulus value by different formula like reference samples.

Keywords: Aluminum barrier laminate tubes, flexible packaging, plastics, young modulus.

1. Introduction

Since the discovery of polyethylene (PE) and polypropylene (PP), plastics have easily found their way into every aspect of our lives. Although it is very difficult to build a world without plastics that contains synthetic or organic polymers these days, the emergence of the plastic industry dates back to the recent past ~1950s. The use of the plastic was in the military field at first. Then it started to be used in different sectors such as construction after the World War II. However, the plastic industry market has made its biggest leap in the packaging sector. Currently, the packaging sector without plastics is unthinkable [1,2].

The most basic task of a package is to protect the product to be included in it from environmental factors and help the product to protect its shelf life. In addition, it facilitates the transportation and storage of the product. It informs the consumer about product and has an attractive effect for the consumer with its design. Packaging is divided into three different categories: *Flexible, semi-flexible and rigid*. Paper-plastic bags and pet food packages fall into the flexible category. Paperboard boxes are an example of the semi-flexible category. Rigid packaging involves materials with higher strength such as glass bottles and metal cans [3].

Recently, there has been a transition from rigid to flexible form in PE and PP based plastics. The most important factor in this is to obtain less thick structures with the use of less plastic in flexible packaging. In addition, flexible packaging has many advantages such as versatility, high resistance, light weight, less waste and being suitable for different printing techniques [1]. Thanks to these advantages, it is very easy to come across flexible packaging solutions with different structures in different sector such as food, hygiene and cosmetics. One of these structures is *laminate tubes*, which are a type of packaging where aggressive chemicals such as toothpaste, hair dye and pharmaceutical cream [4,5]. Laminate tubes have a longitudinal back seam along their body as a

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characteristic feature. They can be in different colors and with or without print. Closing the tubes filled with the product to be placed inside can be easily done by thermal processes. These tubes are designed using five layers: a heat sealable layer, a first tie layer, a barrier layer, a second tie layer and an outer layer. Polymeric materials such as low density polyethylene (LDPE) and high density polyethylene (HDPE) are generally used for heat sealable and outer layers, respectively. Ethylene acrylic acid (EAA) or ethleyene methacrylic acid (EMAA) copolymers are often preferred for tie layers [6,7]. One of these layers provides a barrier feature to the packaging, in other words, to the laminate tube, helping it protect the products shelf life. According to the difference in the barrier layer, these tubes are separated into two groups: *Aluminum Barrier Laminate (ABL)* and *Plastic Barrier Laminate (PBL)*. Barrier property in PBL tubes is provided by ethylene vinyl alcohol (EVOH) layer [8]. In the study of Feng et al., it is clearly seen that the oxygen permeability decreases with the increases of the EVOH ratio in the EVOH/LDPE composition [9]. However, ABL tubes include aluminum foil providing barrier properties as shown in Figure 1. This layer protects the product, from environmental factors such as corrosion, diffusion and light, as well as preventing changes in the flavor and odor of the product due to the excellent barrier property provided by aluminum foil [8].

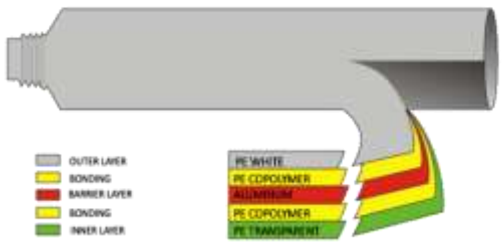

Figure 1. ABL tube layers [10].

Samples are produced as taking into consideration of most common ABL tubes in market and this refers as 12/250. The meaning of 12/250 comes from 12µm for aluminum thickness and 250 µm for total thickness. Inner and outer layers are produced in blown PE film production lines as co-extruded films. Then, these films are laminated via melted polymers with aluminum foil in extrusion lamination lines. ABL tubes should be examined considering many mechanical properties such as coefficient of friction, tear resistance and stiffness value. Stiffness is a very important parameter especially when filling the tube with product. If the tube is not tough enough, problems such as loosening in the tube and flowing of the product occur during filling.

In this study, it is aimed to characterize ABL tubes produced with different formulas by comparing them with reference materials and to compare the stiffness of laminants. Thus, it will be learned how changes in formulas affect stiffness or young modulus values.

2. Materials and Methods

A, B, C and D samples were fabricated using different polymeric raw materials such as HDPE, LDPE, linear low density PE (LLDPE), metallocene low linear density PE (mLLDPE) and cyclic olefin copolymer (COC). Trials were done using different resins with melt flow index (MFI) and density values for the same type of raw materials. The density values of raw materials are 0,95, 0,923, 0,918, 0,918, 1,01 g/cm^3 for HDPE, LDPE, LLDPE, mLLDPE and COC, respectively. The MFI values are 1,5, 0,75, 1, 1 and 2 g/10 min in the same order. Inner and outer PE layers were produced in Windmöller Hölscher (2010) branded blown film line. Then, the PE films were laminated in Erwepa-Davis Standart (2015) branded extrusion maination machine. Dynamic Scattering Calorimetry (DSC) analysis was used for the characterization and verification of the samples. DSC thermograms were taken with Perkin Elmer-DSC 4000 device. Lloyd Insrument's tensilemeter device was used for young modulus values. Olympus-BX53F2 branded microscopy device was used for the thickness distribution of the ABL structures.

2.1 Samples Preparing

Compared to market leaders' products, the product subject to this work has a particular difference in layer distribution. In this project, production has been making with thicker inner and outer layers despite thinner tie layers. This adjustment is mostly relevant to production technologies and limitations. Examined reference sample has been produced in consecutive extrusion lamination lines which are specially designed for ABL productions. These production lines allow applying higher polymer melt weights which mean thicker tie layer in another saying.

In this project, ABL production has been making in a compact extrusion lamination line which is designed for thinner packaging. PE films of inner and outer layers has been produced in Pilenpak PE film production site by 5-layer Windmöller & Hölscher blown film lines. PE film formulation had been designed in the scope of this study. Hereby different versions of 120µm thickness white PE for outer layer and 70µm transparent PE film for inner layer had been produced. Beside that two reference samples had been chosen according the customer's referral and market share of ABL laminates. As the customer's feedbacks, these two references show ideal production efficiency and provide consumer satisfaction. References samples' microtome cross sections have been examined under microscope to determine thickness of each layer. Cross section of sample B is shared in Figure 2 as an example.

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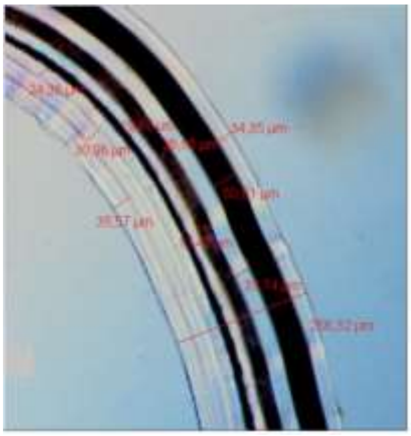

Figure 2. Cross-section of sample B.

Layer distributions of sample A, B, C, D and reference samples are given into Table 1. Since outer and inner layers constitute almost 70% of finished good by weight, actions to increase stiffness have been made by focusing to edit these layers. Four different samples have been produced by editing formulas of inner and outer layers.

Table 1. Layer distributions of ABL samples.

	A-B-C-D	Ref. 1	Ref. 2
PE White (outer)	120µm	113µm	80µm
Tie layer	21µm	35µm	68µm
Aluminum	12µm	12µm	12µm
Tie layer	27µm	30µm	40µm
PE Transparent (inner)	70µm	60µm	50µm
Total	250µm	250µm	250µm

Table 2. Material dispersions of inner and outer layers of sample A, B, C and D.

	A	B	C	D
LDPE	35-50%	25-40%	40-55%	20-35%
LLDPE	2-15%	2-15%	10-25%	
MDPE	15-30%	15-30%	15-30%	
mLLDPE	10-25%	10-25%	5-20%	25-40%
HDPE (0,3)				20-35%
HDPE (1,5)		5-20%		
COC			5-20%	

3. Results and Discussion
3.1 Characterization

DSC termograms were taken into consideration to crosscheck which materials have been used. DSC analysis has been designed as 5 steps. First, samples have been heated 50°C to 150°C at 50°C/min. After have been held a minute in 150°C as step 2, samples have been cooled back to 0°C at 15°C/min. Then again, held a minute. And last, have been heated 0°C to 150°C at 10.00°C/min which is relatively slower. That's why more clear outcomes are expected from step 5.

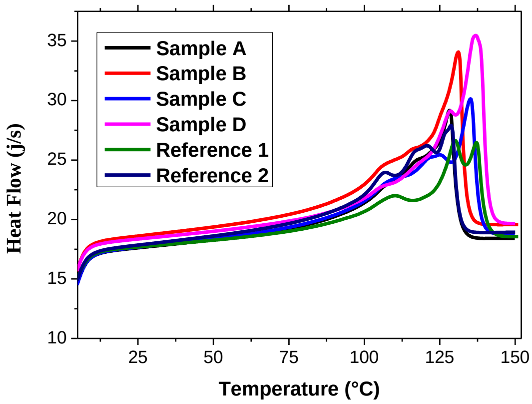

Figure 3. DSC thermograms of samples A,B,C, D, Reference 1 and Reference 2.

In Figure 3, DSC termograms of sample A, B, C, D with reference 1 and 2 based on step 5 outcomes. Especially LDPE, LLDPE, HDPE and COC materials are able to specified on DSC depending their relatively different melting temperatures. On the flipside mLLDPE – LLDPE and MDPE – HDPE have quite close melting temperatures therefore these materials may be confused on DSC termograms [11].

3.2 Mechanical Properties

Young modulus values have been considered to compare samples due to their stiffness. Young modulus or in another saying elastic modulus can be referred as ratio of strain to unit elongation in strength. Unit elongation is ratio of length difference to first length. In tensile tester devices, young modulus is calculated with curve of strain to unit elongation as shown in Figure 4 [12].

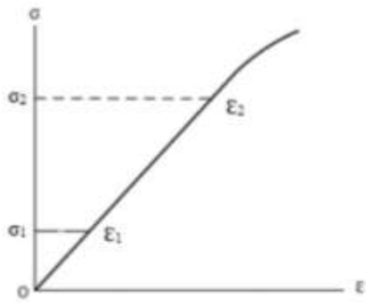

Figure 4. Strain-unit elongation curve [12].

Young modulus (E) is equals to ratio of strain differences (Δσ) to elongation differences (Δε).

$$E = \frac{\Delta\sigma}{\Delta\varepsilon}$$

In this work, samples have been prepared as 25mm width, 10cm length and 250µm thickness and analyzed machine direction (MD) and transverse direction (TD) both. In other saying, MD is the direction which melt flows through and TD is the vertical direction to this.

Tensile tester has been drawn until samples elongate 1%. To elongate the samples 1%, ratio of required strength to surface area is based as young modulus which makes the unit N/mm^2. Outcomes are shared in Table 3 and Figure 5.

Table 3. Young Modulus values.

Direction of section	A	B	C	D	Ref 1	Ref 2
MD	589	613	706	758	675	738
TD	457	623	743	685	654	758

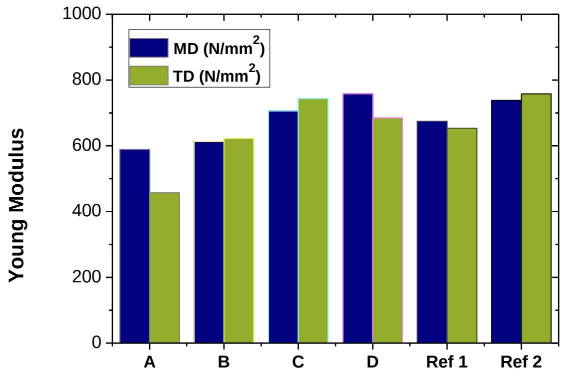

Figure 5. Young Modulus Comparison.

The result has shown that reference samples has at least 650 N/mm^2 young modulus values for MD and TD both. Hereunder 650 N/mm^2 young modulus value has been set as target in this project. Sample A which had been mostly made of LDPE, LLDPE and MDPE has been achieved lowest Young modulus values. Accordingly, LDPE, LLDPE and MDPE combination is insufficient can be deduced to reach target. Especially in TD, there is a huge gap between target. Sample C has quite promising outcomes. COC provides the ending good a significant stiffness and this may be considered as working solution. Yet according to reference termograms, there is no sign to COC is used. Sample B and D are HDPE added prototypes. They also show some promise by increasing young modulus values. As a comparison to each other, using HDPE with lower MFI effects more to increase young modulus. Low MFI HDPE use may be considered as key inference of this work.

4. Conclusion

In this study, ABL tubes have been fabricated by using different polymeric raw materials and formulas. Lower stiffness causes ovalization problem and this leads to loss while filling of ending good. In the examination of Pilenpak's products and reference samples, significant difference between young modulus values had been observed and this had linked to stiffness failure. Target value in young modulus were determined as 600-650 N/mm^2 by reference materials from the market. To increase Young modules, 4 different samples have been produced. Sample A had been produced mainly by LDPE and Sample B is the theoretically 5-20% HDPE included version of A. In sample C, Cyclic Olefin Copolymer (COC) had been used 5-20% and sample D had been designed with lower MFI HDPE (0.3 in 190°C and 2.16 kg). DSC thermograms have showed that reference samples involve HDPE and according to cross section images, main layers are thinner compared to produced prototypes. Using thicker tie layer may provide higher young modulus. Because of the limits of Pilenpak production lines, tie layer can only be this much thicker. That's why different formulas and raw materials had been used to increase young modules.

When the results are examined, Sample A and B show lower young module values than the other samples. It was observed that using COC and HDPE with lower MFI work to increase young modules. Sample C and D looks comparable with references in terms of young modules. The difference of Sample B and C is the using different HDPE especially with different MFI. Results show that lower MFI HDPE provides better young modulus comparing to higher MFI and this supports Abbas-Abadi and friends [13]. Sample D also shows promising results. COC is known for providing stiffness and lower tear resistance on PE films [14]. Especially in MD, Sample D has exceeded target values and made better results. Sample C and D, 706 and 758 N/mm^2 young modulus values in MD and 743 and 685 N/mm^2 in TD which are significantly promising results compared to references..

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Author's Contributions

Mahir Doğan: Drafted and wrote the manuscript, performed the experiment and result analysis.

Keriman Şanlı: Performed the characterization studies and helped in manuscript preparation.

Gizem Güler: Drafted and wrote the manuscript.

Yusuf Över: Performed the evaloution of the results and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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